TEXT-BOOK OF
ORGANIC CHEMISTRY

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(*FOR B.Sc. STUDENTS*)

by

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ELEVENTH REVISED EDITION

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PREFACE TO ELEVENTH EDITION

Some modern concepts of Organic Chemistry such as the Orbital concept of bonding and the mechanistic principles of Organic reactions were introduced in the previous edition of the book The authors are happy that these new innovations were appreciated and the 10th edition of the text-book of Organic Chemistry had to be reprinted in 1969 and again in 1970. That was the first phase of modernising the subject matter which has been followed up in the eleventh edition of the book. The new edition has been considerably enlarged and improved in all respects. The chief features of the new edition are :

(1) A separate chapter covering the principles of mechanism of organic reactions has been given and these principles have been applied to interpret the mechanism of almost all important reactions in the remaining portions of the text.

(2) A new chapter on 'Classification and Nomenclature' giving details of the latest IUPAC system of naming all classes of organic compounds has been included. The naming of higher organic compounds on the basis of 'seniority of functional groups' is the latest innovation that has also been described.

(3) Some modern topics such as sublimation under vacuum, chromatography, oxygen flask method for estimation of halogens, direct estimation of oxygen have been given.

(4) Spectroscopy of organic compounds especially the ultraviolet and Infrared spectra, their explanation and application to some important substances is a new feature of this edition.

(5) The description of Optical Isomerism has been given modern touches and *R* and *S* conventions have been discussed in detail.

(6) Under the chapter on alkanes the new topic Conformations of ethane and propane' has been included.

(7) The chapter on 'Carbohydrates' has been re-written and enlarged so as to give the latest conventions of writing structural formulae of aldoses.

(8) Numerous new illustrations of industrial processes, mechanism of reactions, molecular models, the geometry of certain organic molecules form a novel feature of this edition.

(9) The latest numerical problems and questions asked in the various universities of India have been included at the end of each chapter.

The authors hope that the eleventh revised edition of the book which has been rewritten and modernised in many respects will be well received by our colleagues and the student community. Any suggestions for further improvement of the book will be acknowledged with thanks.

Jullundur B. S. BAHL
July, 1970 ARUN BAHL

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ALIPHATIC COMPOUNDS

AROMATIC COMPOUNDS

1

Introduction

Friedrich Wohler
(1800—1822)
German chemist. Well-known for the historical synthesis of urea, which gave a death blow to the Vital Force theory.

WHAT IS ORGANIC CHEMISTRY ?

Organic Chemistry owes its name and origin to the study of those substances which had been produced in living organisms, whether vegetable or animal. Such substances were classed as **Organic** in distinction to those which were derived from the mineral world and were known as **Inorganic**. Thus common salt, marble, soda and carbon dioxide were inorganic substances whereas acetic acid (*from vinegar*), alcohol (*from wine*), tartaric acid (*from grapes*), and sugar (*from sugarcane*) were organic.

The Vital Force Theory. It was long believed that organic compounds were produced in plants and animals under the influence of '*Vital force*', *i.e.*, the same force which was responsible for the growth of the plant or the animal. Thus it was considered impossible to synthesise organic substances in the laboratory.

However, in 1828, Wohler accidentally discovered that urea, a typical organic compound, could be obtained by heating together ammonium sulphate and potassium cyanate, both of which are inorganic compounds.

$$\underset{\text{Amm. sulphate}}{(NH_4)_2SO_4} + 2KCNO \longrightarrow \underset{\text{Amm. cyanate}}{2NH_4CNO} + K_2SO_4$$

$$NH_4CNO \longrightarrow \underset{\text{Urea}}{NH_2CONH_2}$$

This simple reaction did much to dispel the absurd idea of vital force in the formation of organic compounds. A few years later Kolbe was able to synthesise acetic acid starting from the elements carbon, hydrogen and oxygen, thus showing clearly that no special life process was needed for the preparation of organic compounds. Thereafter numerous organic compounds were synthesised in the laboratory and by 1850 *The Theory of Vital Force* had been gradually overthrown.

Modern Definition of Organic Chemistry. With the fall of the *Vital force theory,* the term 'organic' lost its original significance. It was, however, established that all the so-called organic compounds contained carbon as an essential constituent. Therefore, the name 'organic' has been retained to describe all carbon compounds irrespective of their origin or the method of preparation. Thus in modern practice the term **Organic Chemistry** is defined as *the study of the compounds of carbon,* the study of the rest of the elements and their compounds falling under the scope of Inorganic Chemistry. However, a few common compounds of carbon like carbon monoxide, carbon dioxide and carbonates are still classed as inorganic substances for obvious reasons.

Thus the modern definition of Organic Chemistry could be given as the study of compounds of carbon other than the oxides, carbonates and bicarbonates, and hydrogen cyanide and its salts.

Since all the organic compounds could be considered as derived from hydrocarbons (containing C and H only), a more precise definition of Organic Chemistry could be given as

"A study of hydrocarbons and their derivatives."

REASONS FOR SEPARATE STUDY

The organic compounds obey the same fundamental laws of Chemistry that hold for Inorganic compounds. However, they are studied as a separate branch of Chemistry as a matter of convenience mainly for two reasons :

(1) The total number of organic compounds known is about 20,00,000, which exceeds several times the total number of inorganic compounds which is hardly 50,000. If the study of twenty lakhs of carbon compounds be included with that of carbon in Inorganic Chemistry, it would throw the subject out of balance.

(2) There are marked differences between the composition, structure and behaviour of the organic and inorganic compounds which make their separate study more fruitful.

The chief differences between organic and inorganic compounds are stated below :—

ORGANIC	INORGANIC
(1) Organic compounds are built mostly from 10 elements *viz.*, C, H, O, N, S, P, Cl, Br, F and I.	(1) Inorganic substances are formed from any of 101 elements known.
(2) Carbon has the wonderful capacity to unite with itself and also with other elements *with the help of covalent bonds.* Carbon atoms joined each to each in straight chains or rings give rise to the formation of a large number of simple as well as complex compounds with huge molecules.	(2) The atoms in the molecules of inorganic substances are joined by electrovalent bonds, forming relatively simple and smaller number of compounds.
(3) Organic compounds with similar 'groups of atoms' display similar chemical behaviour. Thus they form many such classes of compounds *e.g.*, alcohols, ethers, ketones, acids, amines, etc.	(3) Most of the inorganic compounds which have been studied are either *acids, bases*, or *salts.*
(4) They frequently possess pronounced colour and odour which are characteristic of certain classes of compounds.	(4) They are, in general, colourless and odourless. Certain metallic salts possess distinct colours.
(5) They are, in general, insoluble in water but soluble in organic solvents such as ether, alcohol, benzene etc.	(5) They are generally soluble in water but insoluble in organic solvents.
(6) They are volatile compounds having relatively lower melting points and boiling points.	(6) They are generally non-volatile and possess high melting points and boiling points.
(7) Burn readily. Solutions and melts do not conduct electric current.	(7) Hard to burn. Conduct electric current in solutions and melt.
(8) Their reactions being 'molecular' in nature are slow and usually complex.	(8) Their reactions for the most part being ionic in nature are rapid and simple.
(9) Covalent bonds being rigid and directional, give rise to 'Chain isomerism' and different types of 'Space isomerism' in organic compounds.	(9) Electrovalent bonds being non-rigid and non-directional, cannot give rise to isomerism in inorganic substances.
(10) Law of multiple proportions in its rigid form, is not applicable to many organic compounds. In such compounds the weights of an element combining with a fixed weight of the other, bear only an integral ratio and not a simple one.	(10) Law of multiple proportions is universally applicable to inorganic compounds.

SCOPE OF ORGANIC CHEMISTRY

The scope of organic chemistry is vast indeed. There is no art, science or industry in which this branch of chemistry is not applied. It will be of interest to outline here very briefly some of the applications of organic chemistry in everyday life and industry.

(1) **Applications in Everyday life.** No other branch of science has so many contacts with human life as organic chemistry has. In our day-to-day life we find ourselves in a strange panorama of things that are in one way or the other connected with this branch of chemistry. From the basic requirements of life like food, fuel, clothing and health aids, to the obviously luxurious things like perfumes and cosmetics—and in-between these two extremes come the following with varying degrees of importance : leather and wooden products ; pencil, paper and writing inks ; fuels like coal, oil and wood ; dyes of all kinds whether natural or synthetic ; rubber plastics ; oils, fats, paints and varnishes ; photographic films an developers ; medicines, anaesthetics and antiseptics—all things seem to have organic origin and touch. It is no wonder, therefore, organic chemistry is a part and parcel of our daily life. In fact are ourselves nothing but complex structures built of thousan

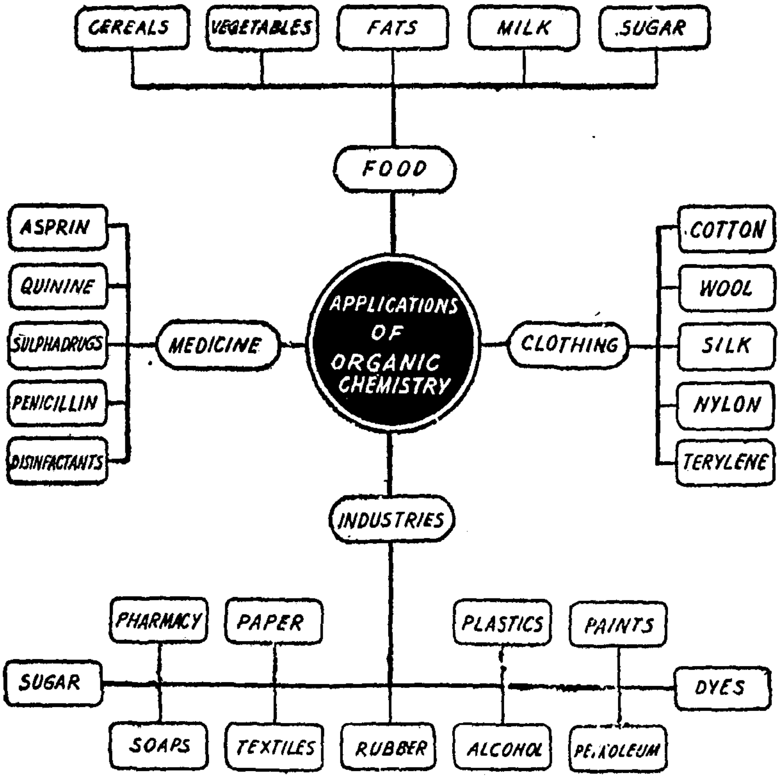


Fig. 1·1.

organic compounds which are derived from the plant and animal foods.

(2) **Applications in Industry.** A knowledge of organic chemistry is necessary in many important chemical industries, *e.g.*, preparation of foods, pharmacy, manufacture of soap and other cosmetics, textile industry, manufacture of dyes and explosives, paper industry, fertilizers, leather industry, sugar industry, fermentation industries, wood-distillation industry, synthetic rubber and transparent wrappings for foods and other commodities, petroleum industry, etc.

(3) **Study of Life processes.** The most important application of organic chemistry is the study of the nature of the material and of the processes of living organisms. The investigation of the tissues, the secretions and other constituents or products of plants and animals is based upon organic chemistry. The understanding of the process of digestion and assimilation of food involves the fundamental principles of organic chemistry. The vitamins and the hormones are organic compounds that are produced in our body and play an important role in its development. The injection of a hormone can turn a male into female and *vice versa*. All such miracles of nature concerned with the life process can be interpreted only by the aid of organic chemistry.

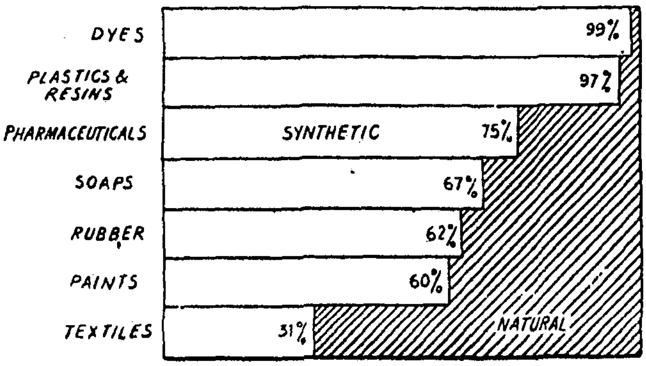
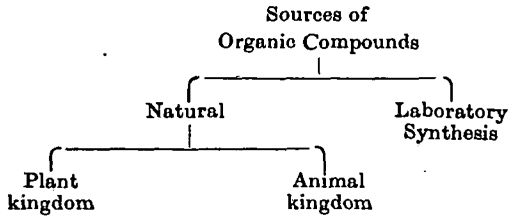


Fig. 2·2. Proportions of synthetic and natural products capturing industry.

There are other fields of organic chemistry at present less developed. Further researches may bring these in the front rank. This naturally means a more thorough study of what we already know. The subject itself is worthy of study from the purely scientific and cultural standpoint. The intellectual beauties of the closely inter-woven relations of organic chemistry will be revealed to the student only when he studies the subject logically, keeping before him the molecular structure of the compounds involved.

SOURCES OF ORGANIC COMPOUNDS

Organic compounds are obtained from natural sources and are prepared by synthesis in the laboratory. The natural sources of these substances may be traced to either the plant or animal kingdom. Thus :



Source	Compounds Obtained
(1) Plants (direct)	Sugars, starches, cellulose, citric acid, oxalic acid, tartaric acid, indigo, oils, vitamins, etc.
(2) Animals	Fats, proteins, urea, uric acid, vitamins, hormones, etc.
(3) Wood distillation	Acetic acid, methanol and acetone.
(4) Coal-tar distillation	Benzene, toluene, naphthalene, carbolic acid, cresols, pyridine, dyes, perfumes, drugs, etc.
(5) Natural Gas and Petroleum distillation	Alkanes and their derivatives such as methyl chloride, chloroform, methyl alcohol, ethyl alcohol, allyl chloride, etc.
(6) Fermentation processes	Ethyl alcohol, amyl alcohol, acetic acid, etc.

About 40 years back, the main sources of organic compounds were the processes of fermentation and wood distillation, while fewer compounds were derived from coal and petroleum. With the recent development of petrochemical industry and low-temperature coking techniques of coal, the number of carbon compounds now derived from petroleum and coal is far greater than from any other source. While the fermentation processes are still in use for the preparation of a large number of organic compounds, wood distillation is almost obsolete and replaced by synthetic methods.

How long the World's Coal and Petroleum Reserves would last ?

Coal and petroleum are undoubtedly the biggest natural sources of organic compounds. For the past 100 years coal dominated the scene but during the last 20 to 30 years, petroleum has assumed comparable importance. To meet the great demand of organic compounds, the world's production of coal increased enormously during the last decade or so. In 1966 the total production of coal was 2,800,000,000 long tons. Although coal is far more sou and widely distributed in nature, petroleum resources

also

equally vast. The total crude oil production of the world in the year 1966 recorded 1,601,000,000 long tons

A chemist is naturally interested to know the extent of world's coal and petroleum reserves as also the probable time of their consumption. Ultimately it is he who has to face the problem of replenishing their consumption by other synthetic means. The world's total coal reserves are estimated to be 5,562,656 million long tons, while oil reserves as estimated on Dec. 31, 1966 amount to 2,886,915 million long tons.

There are many speculations regarding the coal and oil supply of the world. According to some specialists, the reserves are enough to last for a few generations even at the present rate of production. Prof. N.N. Chatterji puts India's total reserves of coal at 20,000 million tons which are sufficient to last for another four centuries. India's oil reserves are estimated to be 6580 tons only.

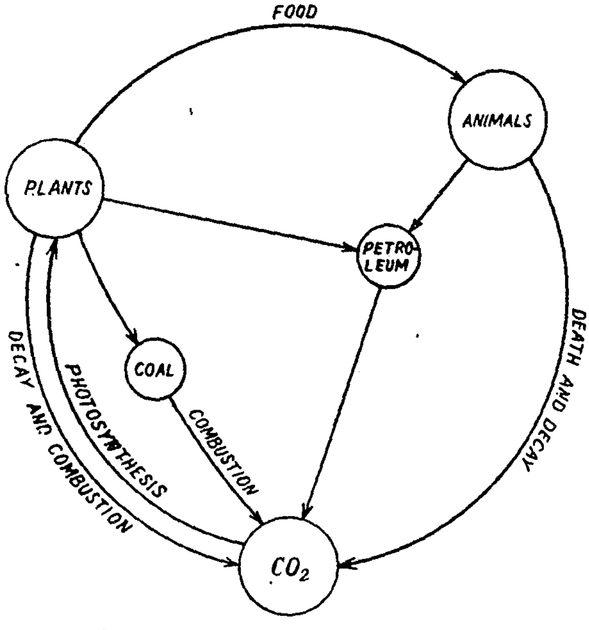


Fig. 1·3. Decay and Formation Cycle of Coal and Petroleum.

At the present rapid rate of depleting the natural resources of coal and petroleum, some economists are raising alarm for their conservation by other sources of energy. In this context, it may be pointed out that due to the external reaction between carbon dioxide and water in presence of sunlight (Photosynthesis), the organic compounds are being produced continuously in plants.

$$CO_2 + H_2O + \textit{Sunlight} \xrightarrow{\text{Photosynthesis}} \text{Organic compds} + O_2$$

The organic compounds whether in the form of coal or petroleum on combustion give back CO_2.

$$\text{Organic Compds.} + O_2 \xrightarrow{\text{Combustion}} CO_2 + H_2O$$

The cycle of formation of plants and animal products and their ultimate decay and combustion to give carbon dioxide is a perpetual one. This indicates that the deposits of carbon compounds will continue to be used up and reformed in the ages to come. However, the location of the deposits may be shifted from place to place.

QUESTIONS

1. State clearly what you understand by an Organic and inorganic substance. Give examples.

2. What was the *Vital Force Theory* ? How was it overthrown ?

3. What was the original meaning of the term organic ? Give the modern definition of this term.

4. What are the reasons usually advanced for a separate study of organic chemistry ?

5. Give a brief survey of the scope and applications of the organic chemistry

6. Trace briefly the development of organic chemistry in the nineteenth century.

7. How would you justify the treatment of organic compounds as a distinct branch of chemistry ?

8. Mention the chief sources of organic compounds. Indicate the development of new sources during the last ten years

9. How long the world's petroleum and coal reserves are likely to last ?

2

Purification of Organic Compounds

Justice F. Von Liebig
(1803—1873)
German. He was the founder of Agricultural Chemistry. Liebig invented many pieces of laboratory apparatus which are still in daily use.

The organic compounds derived from natural sources are seldom pure. They are often mixed with other substances which also occur with them. Similarly, the compounds prepared in the laboratory are generally mixed with the products which may also have been formed during the course of reaction. In order to study its properties and to determine its formula, a given substance must be first of all obtained in a state of purity. The methods employed for purification depend on the nature of the organic compound and the impurities present in it. The processes commonly used for the separation and purification of organic substances are :

(1) *Crystallisation.*
(2) *Sublimation,*
(3) *Distillation,*
(4) *Fractional Distillation,*
(5) *Distillation under Reduced Pressure,*
(6) *Steam Distillation, and*
(7) *Extraction with Solvents.*

CRYSTALLISATION

The most general method for the purification of solid organic substances is crystallisation. In principle it is the same as employed for inorganic salts. The only difference is that here, in addition to water, several other solvents are used. The more common solvents are acetone, alcohol, ether, chloroform, benzene, etc.

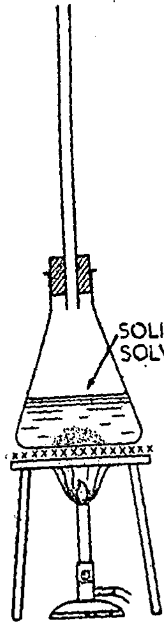


Fig. 2·1. Preparation of solution.

Procedure. A solvent in which the given substance is more soluble at higher temperature than the room temperature is selected. The solvent is heated with excess of the solid substance. The saturated solution thus prepared is filtered while still hot. As the filtrate cools, the pure solid crystals separate which may be removed by filtration.

Preparation of the solution. A suitable quantity of the powdered substance is taken, say, in a conical flask and treated with a small quantity of the solvent. The quantity of the solvent should be just enough to dissolve the whole of the solid on boiling. In case of volatile solvents, it is advisable to fit the vessel with a long glass tube which serves as a condenser and also prevents the inflammable solvent vapours to reach the flame of the burner. The heating may be done on a water-bath or wire gauze according as the solvent is 'low-boiling' or 'high-boiling'.

Filtration of the solution. The hot saturated solution obtained above is then filtered through a fluted filter-paper placed in an ordinary glass funnel. If the quantity of the solution is large, it takes

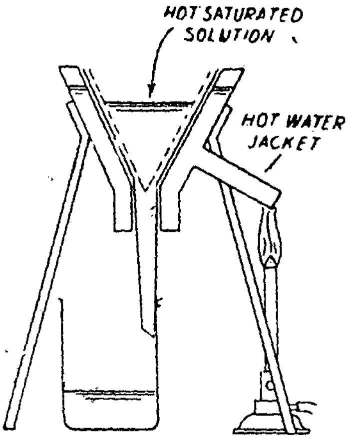


Fig. 2·2. Filtration through fluted filter paper.

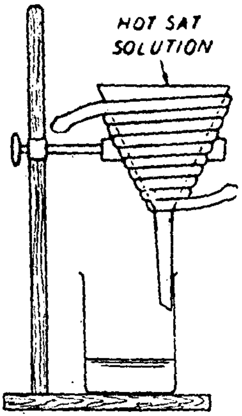


Fig. 2·3. Hot-water funnel.

longer time to filter and the crystals may form in the funnel during filtration. To prevent this, a "*Hot-water funnel*" may be used with advantage.

Crystallisation. The filtrate is allowed to cool undisturbed in a beaker or a "crystallising dish". After some time the solid substance separates in beautiful geometrical forms called crystals. Sometimes the crystals do not appear due to super-cooling of the solution. In such a case the crystallisation is induced either by scratching the sides of the vessel with a glass rod or by sowing a few crystals of the same substance in solution.

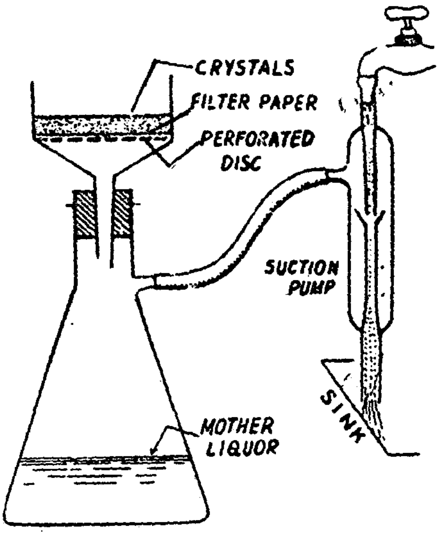


Fig. 2·4. Filtration under suction.

Separation and Drying of Crystals. The crystals are separated from the mother liquor by filtration. This may be done more rapidly with the help of a Buchner funnel and a suction pump as shown in Fig. 2·4. When the whole of the mother liquor has been drained into the filtration-flask, the crystals are washed two o three times with small quantities of the pure solvent. The filte paper carrying the crystals is then placed over a porous plate an dried in a steam or air-oven.

Sometimes, the crystals obtained are coloured owing to th traces of impurities present. In such cases, the crystals are redi solved in a small quantity of the solvent, boiled with a little anim charcoal, filtered and crystallised once again as described abov The process is repeated till the substance is obtained in absolute pure form as indicated by its sharp melting point.

SUBLIMATION

Certain substances when heated, pass directly from the so to the vapour state without melting. The vapours when cooled g back the solid substances.

This process known as **sublimation** is very helpful in se rating volatile from non-volatile solid. It is, however, of limi application as only a few substances like naphthalene, camphor benzoic acid can be purified by this process.

The impure substance is placed in a china dish which is ge heated on a sand-bath. The dish is covered with a perforated fi paper over which is placed an inverted funnel. The vapours r from the solid pass through the holes in the filter-paper an deposited as solid on the walls of the funnel. The filter paper has two functions : (*i*) it does not permit the sublimed substance to drop back into the dish and (*ii*) it keeps the funnel cool by cutting off the direct heat from the dish (Fig. 2·5).

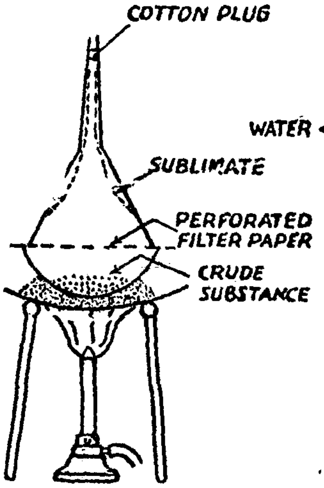


Fig. 2·5. Sublimation.

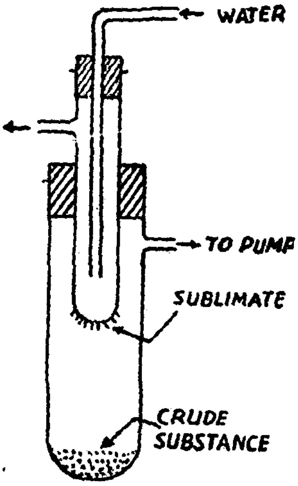


Fig. 2·6. Sublimation under reduced pressure.

Organic substances such as benzoic acid, naphthalene etc. which 'igh vapour pressure at temperatures below their melting can be sublimed relatively quickly. These can be conveni- urified by the laboratory operations described above. Such

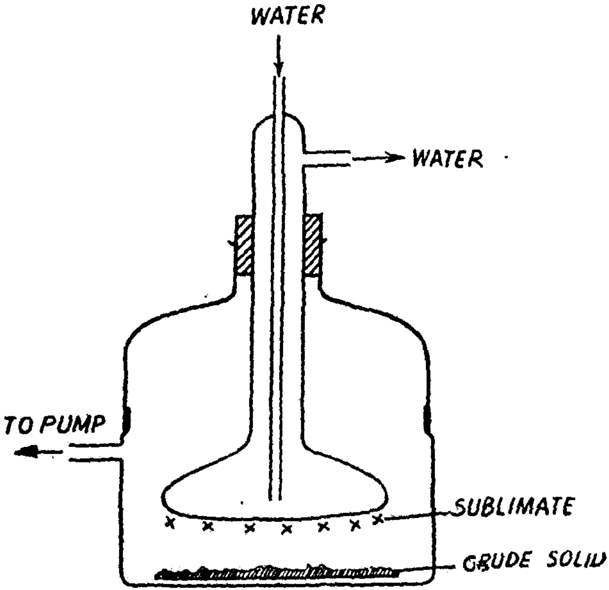


Fig. 2·7. Sublimation under vacuum.

substances which have very small vapour pressure or tend to decompose upon heating, are purified by sublimation under reduced pressure

A simple glass apparatus now used for sublimation under reduced pressure is shown in Fig. 2·7. The chief features of this apparatus are a large heating and a large cooling surface with a small distance in between. This is necessary because the amount of the substance in the vapour phase is much too small in case of a substance with low vapour pressures.

DISTILLATION

The operation of distillation is employed for the purification of liquids from non-volatile impurities. The impure liquid is boiled in a flask and the vapours so formed are collected and condensed to give back the pure liquid in another vessel. The non-volatile impurities are left behind in the flask.

The apparatus used for distillation is shown in Fig. 2·7. It consists of a distillation-flask fitted with a thermometer in its neck and a condenser at the side-tube. The liquid to be purified is placed in the distillation-flask and the thermometer so adjusted that its bulb stands just below the opening of the side-tube. This ensures the correct recording of the temperature of the vapour passing over to the condenser. A suitable vessel is attached to the lower end of the condenser to receive the condensed liquid. On heating the distillation flask the thermometer first records a rise in temperature which soon becomes constant. At this point, which is the boiling temperature of the pure liquid, most of the liquid passes over. Towards the end of the operation the temperature rises once again on account of the superheating of the vapour. The distillation is stopped at this stage and the receiver disconnected.

In case of liquids having boiling points higher than 110° C, the water-condenser is replaced by air condenser. To prevent bumping, it is customary to put a few pieces of unglazed porcelain in the distillation flask.

While distilling a very volatile and inflammable liquid such as ether, the distillation flask is heated on a water-bath and not on a wire gauze. In case of very high-boiling liquids, the flask is heated directly with a naked flame.

FRACTIONAL DISTILLATION

A mixture of two or more volatile liquids can be separated by fractional distillation When their boiling points differ by more than 40°, the operation can be carried with the help of ordinary distillation apparatus described in Fig. 2·8. The more volatile liquid passes over first and is collected in a receiver. When the temperature begins to rise for the second time, the first receiver is disconnected. A new receiver is attached as soon as the temperature becomes constant once again. Thus the distillate is collected in fractions and the process is termed *Fractional Distillation.*

When the liquids present in the mixture have their boiling points close to each other, the separation is best effected by fitting the distillation flask with a *fractionating column* which in turn is connected to the condenser (Fig. 2·9). On heating, the vapours of

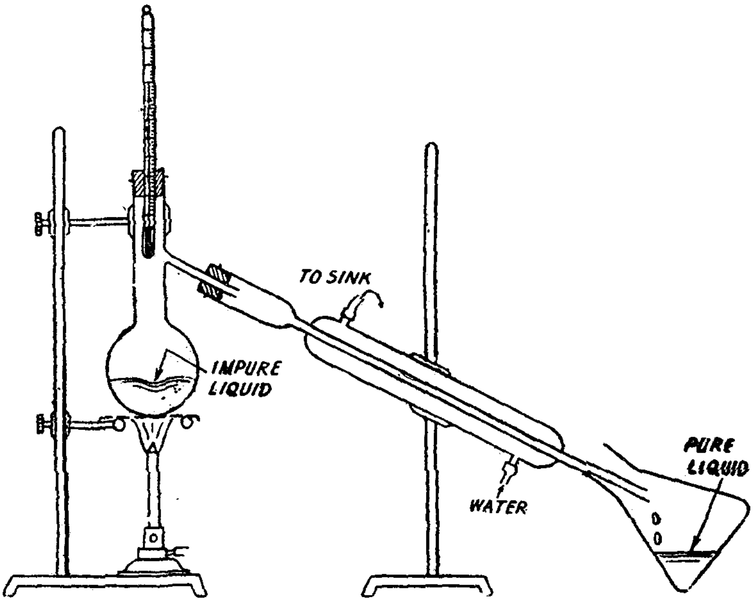


Fig. 2·8. Distillation.

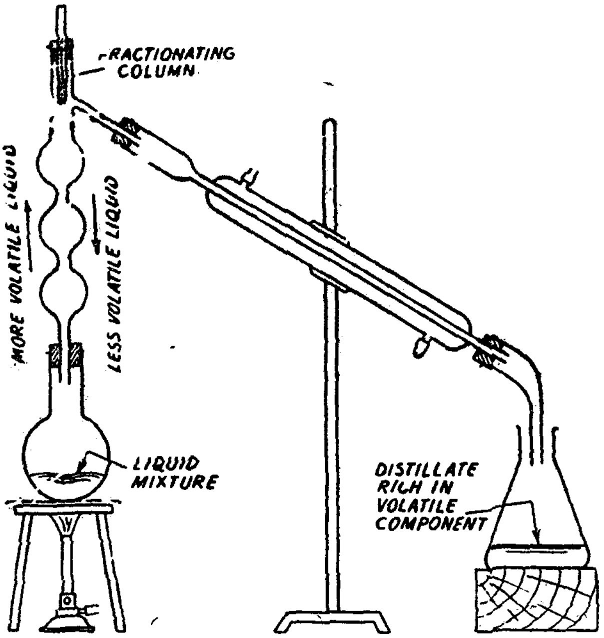


Fig. 2·9. Fractional distillation.

the more volatile liquid A, along with a little of the vapours of less volatile liquid B, rise up and come in contact with the large cooling surface of the fractionating column. The vapours of B condense first and that of A pass on. The condensed liquid flowing down the column meets the fresh hot ascending vapour. It snatches more of B from the vapour mixture and gives up any dissolved vapour of A. This process is repeated at every bulb of the fractionating column, so that the vapour escaping at its top consists almost exclusively of A and the condensed liquid flowing back into the distillation flask is rich in B. If necessary, the process can be repeated with the distillate and the liquid left in the distillation flask.

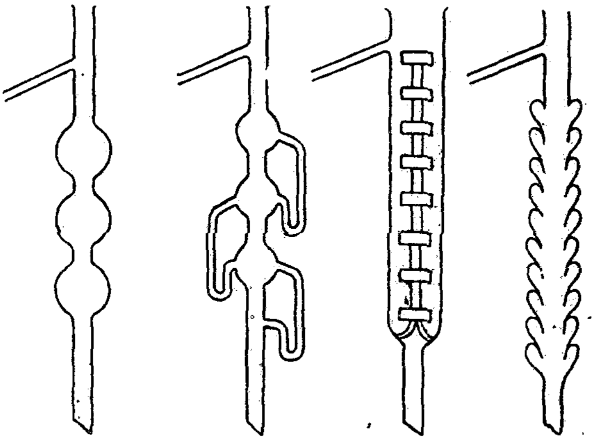


Fig. 2·10. Different types of fractionating columns.

The use of a fractionating column has found a remarkable application in modern industry, especially in the distillation of petroleum, coal-tar and crude alcohol.

DISTILLATION UNDER REDUCED PRESSURE

The 'straight' distillation is suitable only for liquids which boil without decomposition at atmospheric pressure. In case of organic liquids which decompose before their boiling point is reached, the distillation is carried under reduced pressure when the liquid boils at a lower temperature*.

The apparatus used for distillation under reduced pressure is shown in Fig. 2·11.

(*i*) *Claisen Flask*, having two necks. It is fitted with a long drawn jet, dipping in the liquid to be distilled. During the distillation, a stream of bubbles rises through the capillary of this jet and prevents bumping, which is so pronounced here than in ordinary distillation

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**A liquid boils when its vapour pressure is equal to the atmospheric pressure*. When the pressure is reduced by suction, the liquid boils at a lower temperature.

(*ii*) *Condenser*, connected with the Claisen flask on the one hand and a filtration flask, serving as a receiver, on the other.

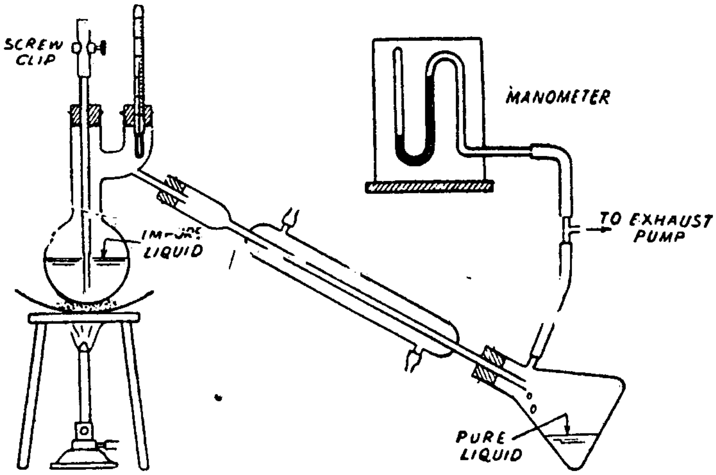


Fig 2·11. Distillation under reduced pressure.

(*iii*) *Manometer*. The receiver flask is connected to an exhaust pump through (*a*) a mercury manometer which tells the pressure under which the distillation is being carried, and (*b*) a trap, to eliminate any condensed liquid.

The pressure in the apparatus is reduced with the help of a water pump. Whenever a lower pressure is desired, the water pump is replaced by a mercury pump.

An important application of this process is the recovery of glycerol from spent-lye in soap industry. Glycerol is decomposed at its boiling point (298°C) but can be distilled unchanged at 12 mm. pressure when it boils at 180°. Another application of 'vacuum distillation' is the concentration of sugar juice under reduced pressure.

STEAM DISTILLATION

Many substances that are insoluble in water are volatile in steam can be purified by distillation in a current of steam (*Steam Distillation*). The non-volatile impurities are left behind in the distillation flask.

The impure mixture together with some water is placed in a round-bottom flask which is then connected to a steam-generator on one side and a water condenser on the other (Fig. 2·12) The flask is adjusted in a slanting position so that no droplets of the mixture splash into the condenser on brisk boiling and bubbling of steam The mixture in the flask is heated and then a current of steam passes into it. Heating of the flask is controlled so as to avoid unnecessary condensation of steam in it. Steam picks up the volatile substance from the mixture and passes into the condenser. The distillate collected in the receiver consists of a mixture of water and the organic substance. The distillation is stopped when the droplets or the solid particles of the organic substance cease to appear in the condenser

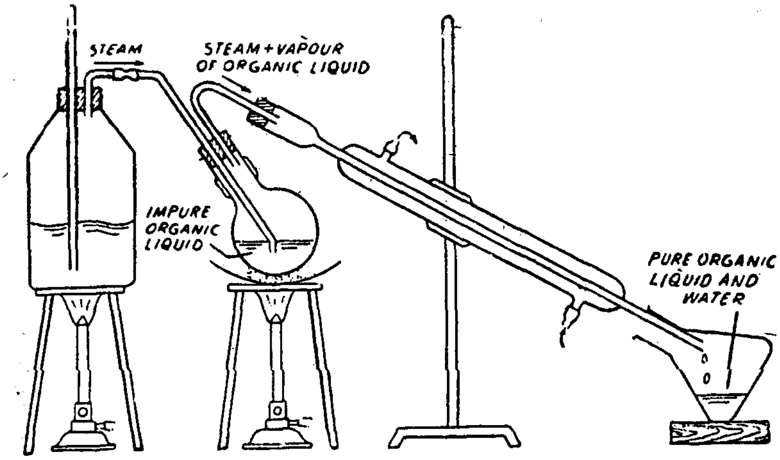


Fig. 2·12. Steam distillation.

The distillate is then treated to recover the organic substance by a suitable method. In case it is a solid, the substance may be separated by simple filtration, and if it is a liquid, it can be removed by means of a separating funnel. The aqueous layer in both cases may be extracted with a solvent.

Steam distillation is employed in industry for the recovery of various essential oils from plants and flowers. It is also used in the manufacture of aniline and turpentine oil.

Principle of Steam Distillation. A liquid boils when its vapour pressure is equal to the atmospheric pressure. In steam distillation, a mixture of water and an organic liquid is heated. The mixture boils when the combined vapour pressure of water (p_1) and that of the organic liquid (p_2) is equal to the atmospheric pressure (P) *i.e.*,

$$P = p_1 + p_2$$

Naturally, the boiling temperature of the mixture would be lower than the boiling temperature of the pure organic liquid when the vapour pressure of this liquid alone would be equal to the atmospheric pressure. Thus, in steam distillation the liquid is distilled at a lower temperature than its boiling point when it might decompose. It serves the same purpose as distillation under reduced pressure.

EXTRACTION WITH A SOLVENT

When an organic substance is present as solution in water, it can be recovered from the solution by the following steps :

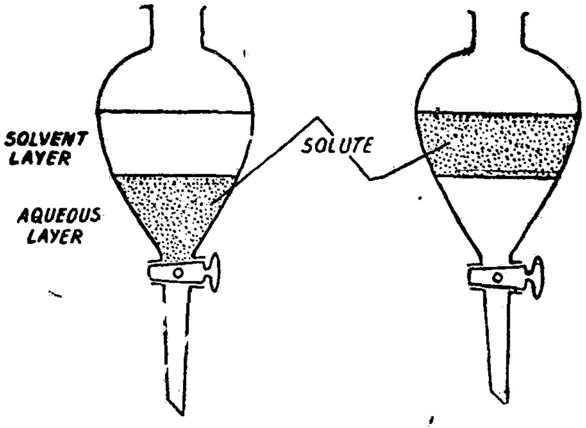
(*i*) *The aqueous solution is shaken with an immiscible organic solvent in which the solute is more soluble.*

(ii) The solvent layer is separated by means of a separating funnel.

(iii) The organic substance is then recovered from it by distilling off the solvent.

The process of removing a substance from its aqueous solution by shaking with a suitable organic solvent is termed EXTRACTION.

Procedure. The aqueous solution is placed in a separating funnel. A small quantity of the organic solvent, say ether or chloroform, is then added to it. The organic solvent being immiscible with water, will form a separate layer. The mouth of the funnel is closed with a stopper or the palm of the hand and the contents shaken gently. The solute being more soluble in the organic solvent is transferred to it. The solvent layer is then separated by opening the tap and running out the lower layer. The organic substance dissolved in it is finally recovered by distilling off the solvent.



Before extraction After extraction

Fig. 2·13. Extraction with a solvent.

Note. It is always better to extract two or three times with smaller quantities of the solvent than once with the whole bulk of the solvent provided.

Soxhlet Extraction. When an organic substance is to be recovered from a solid, it is extracted by means of an organic solvent in which the impurities are insoluble. In actual practice the extraction from solids is often tedious and requires thorough contact and heating with the solvent. This is done in a special apparatus, the *Soxhlet Extractor* (Fig. 2·13). It consists of a glass of cylinder C having a side tube T and syphon S. The cylinder carries a water condenser at the top and is fitted below into the neck of a boiling flask.

The powdered material is placed into the thimble made of stout filter paper and the apparatus is fitted up as shown in Fig. 2·14. The flask containing a suitable solvent is heated on a water-bath or sand bath. As the solvent boils, its vapours rise through the side tube T up into the water condenser. The condensed liquid drops on the solid in the thimble, dissolves the organic substance and filters out into the space between the thimble and the glass cylinder C. As the level of liquid here rises, the solution flows through the syphon back into the boiling flask. The solvent is once again vaporised, leaving behind the extracted substance in the flask. In this way, a continuous stream of pure solvent drops on the solid material, extracts the soluble substance and returns to the flask. At the end of the operation the solvent in the boiling flask is distilled off, leaving the organic substance behind.

Soxhlet Extractor is used with advantage for the extraction of oils and fats from flowers and seeds, and alkaloids from plants. The apparatus ensures maximum extraction with a limited quantity of the solvent.

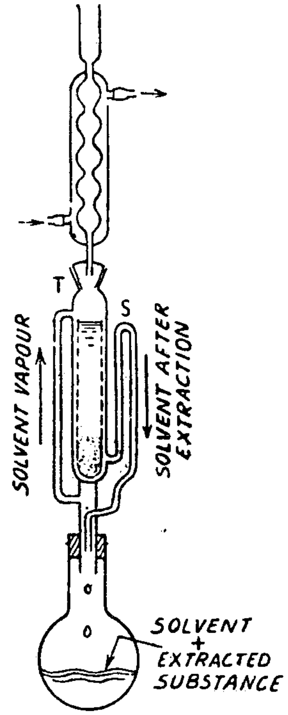


Fig. 2·14. Soxhlet extractor.

CHROMATOGRAPHY

This new technique of purification and separation of organic substances was discovered by a Russian scientist Tswett in 1903. It is now extensively used for separation of small samples of organic mixtures when the routine methods like crystallisation and distillation fail.

The chromatic separation of organic mixtures depends on the selective adsorption of the components from solutions. When solution of the mixture is passed through a column of the adsorbent (say alumina), the different solutes present in the solution will be adsorbed to different extents. The most highly adsorbed solute will be retained at the top of the column while the weakly adsorbed solutes will penetrate various distances down the column depending on their degree of adsorbability. The solutes thus separated in the column can be washed down, one at a time by passing fresh solvent through it and this process is known as *elution.*

This new technique of separation of organic mixtures was first applied to a mixture of leaf pigments (dyes) which separated as coloured bands on the column of white alumina, Hence its name **chromatography**, meaning *'colour writing'*. This process is now widely used for separating organic substances whether coloured or colourless, though the term chromatography still remains.

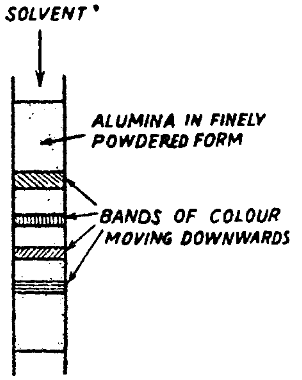


Fig. 2·15. Column Chromatography (*Illustrated*).

In case of coloured substances, the separation can be observed visually. If colourless mixtures are being separated, ultraviolet light may be used to illuminate the column to show up the separation. Sometime it may be necessary to use some chemical on the adsorbent to change the colourless into coloured substances.

The above procedure which makes use of a column of solid adsorbent such as alumina, magnesium oxide or silica gel is termed **column chormatography**. *The solvents commonly used for elution of the column are water, alcohol, acetone, petroleum ether etc.*

Porous paper or filter paper may also be used as the adsorption medium instead of the column of adsorbent, when the technique is known as **Paper Chromatography**.

In another technique the vaporised mixture dissolved in a gas such as nitrogen or helium is separated by passing through a tube packed with, say, fire brick granules and this is termed **Vapour Phase Chromatography** (VPC).

The following experiments will illustrate the techniques of Chromatography.

Experiment 1. *Separation of screened methyl orange into its component dyes by Column Chromatography.*

Set up the apparatus as shown in Fig. 2·16. Fill three-quarters of the tube with alumina suspended in ethyl alcohol. Remove the air bubbles by tapping it and keep the alumina covered with ethyl alcohol throughout the experiment. Add a few drops of screened methyl orange to the top of the column. Go on adding ethyl alcohol until the yellow and

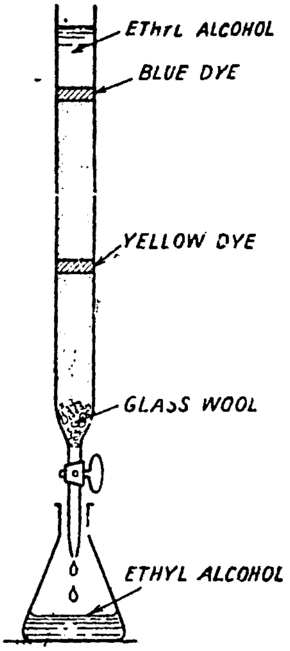


Fig. 2·16. Separation of dye mixture by column chromatography.

the blue dye have separated. The yellow dye moves down leaving behind the blue dye near the top of the column.

Experiment 2. *Separation of a mixture of food dyes by Paper Chromatography.*

Cut a filter paper eight inches square. Roll it up into the shape of a cylinder and fix the two ends with plastic clips. Place a spot of mixed food dyes (green, red and yellow) at one-quarter of an inch from one end of the paper.

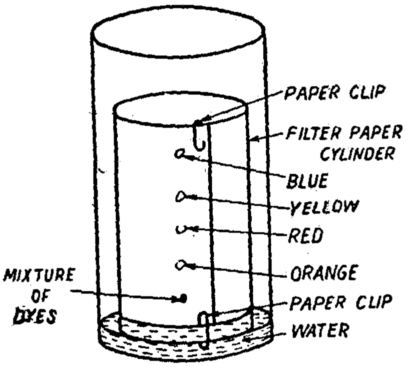


Fig. 2·17. Paper chromatography.

Place the paper cylinder in a large beaker containing water to about one-eighth of an inch. Cover the beaker with a glass plate and leave it undisturbed for about half an hour. Now take out the filter paper and you will see that the mixture is completely separated into blue, yellow, red and orange components.

DRYING OF SUBSTANCES

Organic substances, otherwise pure, often contain a small amount of water. Before it is fit for analysis, a substance must be absolutely dry. Even traces of moisture present may alter the results of analysis and interfere with the study of its reactions.

How to dry a Solid. The preliminary drying of freshly prepared crystals is done by pressing between pads of filter papers or by spreading them over a porous plate. The final removal of moisture is then carried by heating the crystals in an oven below their melting point. In case the substance decomposes on heating it may be dried by placing in a desiccator or better still in a *Vacuum Desiccator* (Fig. 2·18).

How to dry a Liquid. Liquids are dried by allowing them to stand with a dehydrating substance with which they do not react. One of the following substances may be used : calcium chloride, sodium hydroxide, sodium sulphate, lime, sodium metal, or phosphorus pentoxide. In actual practice, the liquid is placed in contact with appropriate dehydrating agent in a stoppered bottle or flask and kept over-night. Next day, the upper clear layer of the liquid is decanted off and distilled in a dry flask.

TESTS OF PURITY

A pure organic substance has characteristic physical properties, crystalline form, refractive index, specific gravity, melting point and boiling point. If a given sample of a substance shows the properties that the pure compound is known to possess, it may be considered pure. The numerical value of these properties changes with the nature of the amount of impurities present. In most laboratory work, the melting point of a solid substance and the boiling point of a liquid substance is considered a sufficient indication of its purity.

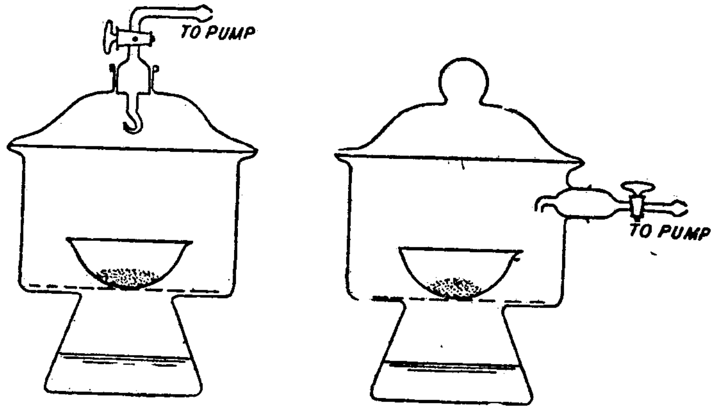


Fig. 2·18. Drying of organic solids.

Melting Point. A pure solid substance melts sharply at a definite temperature, while an impure substance will have a lower and indefinite melting point.

Determination. The apparatus employed for the determination of the melting point of a given solid substance is shown in Fig. 2·19. The crystals are powdered finely and charged into a capillary tube sealed at one end. The capillary tube should be 5 to 6 cms. long and 1 mm. in diameter. The substance should stand in the capillary 3·4 mm. from the bottom when thoroughly packed. The capillary tube is wetted with the liquid in the bath and placed along side a thermometer fixed in an iron stand. The capillary remains sticking to the thermometer by itself and is so adjusted that the solid in it stands just opposite to the middle of the mercury bulb. The thermometer is now lowered in a beaker containing sulphuric acid and the apparatus set up as shown in Fig. 2·19. The beaker is heated slowly and the temperature of the bath kept uniform by gentle but constant stirring with a ring stirrer. When the substance in the capillary just shows signs of melting, the burner is removed and the stirring continued. The temperature at which the substance just melts and becomes transparent is recorded. The experiment is repeated with a new capillary charged with fresh substance and the average of the two melting points thus determined is the correct melting point of the substance under examination.

The sulphuric acid bath can be replaced by a water-bath for melting points below 100°C.

Mixed Melting Point. The method of mixed melting point as a means of establishing the purity of a substance depends upon the fact that *a pure organic compound possesses a sharp melting point while the presence of impurities usually lowers the melting point.* A substance mixed with impurities does not melt sharply at a fixed temperature but does so over a range of temperatures. It will start melting at a certain temperature but will not become entirely liquid until a higher temperature is reached.

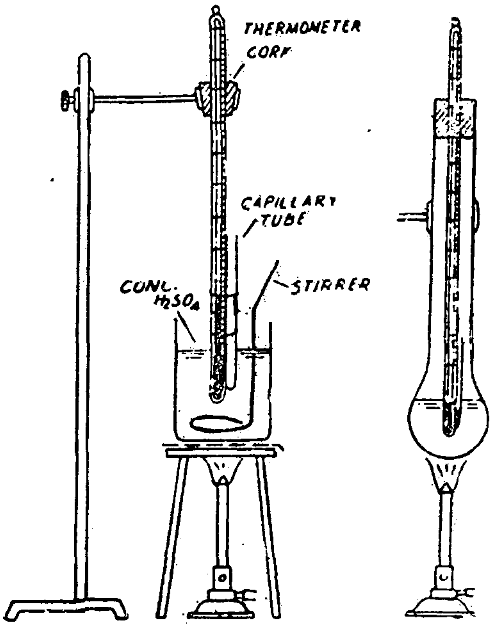


Fig. 2·19. Determination of melting point.

The substance whose purity is to be ascertained is mixed with a sample of the authentically pure substance. The melting point of the mixture is determined as usual. If this mixture melts sharply and the melting point comes out to be the same as that of the sample under experiment taken alone, it is proved that the two are indeed the samples of the same substance. In other words, the substance under trial is proved to be pure beyond doubt.

Boiling Point. A pure organic liquid boils at a fixed temperature which is characteristic of that substance. The presence of impurities raises its boiling point.

(1) *Distillation Method.* If enough liquid is available, its boiling point is determined in an ordinary distillation apparatus (Fig, 2·20). A pure liquid will distil at a constant temperature which is its boiling point. In case the liquid is impure, the boiling point will rise during distillation.

(2) *Capillary-tube Method.* When only a small quantity of the liquid is available, its boiling point is determined by the 'Capillary-tube Method'. A

few drops of the liquid are placed in a thin-walled small test-tube. A capillary tube sealed at about one centimetre from one end, is dropped into it. The glass tube containing the liquid and the capillary, is then tied alongside a thermometer so that the liquid stands just near the bulb. The thermometer is then lowered in a beaker containing water or sulphuric acid (any liquid whose boiling point is higher than that of the substance under investigation).

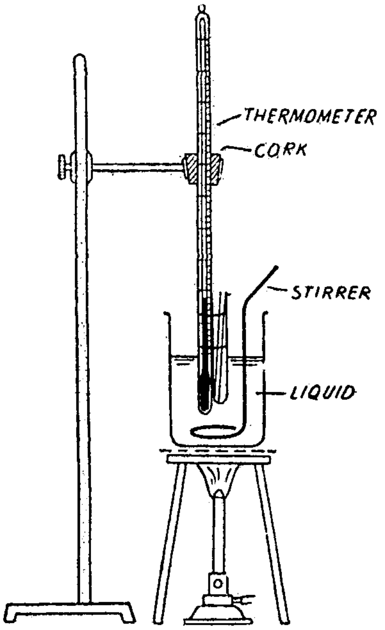


Fig. 2·20. Determination of boiling point.

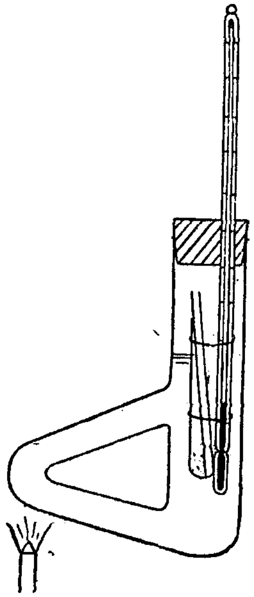


Fig. 2·21. The use of Thiele tube.

The beaker is heated and the bath liquid stirred continuously with a ring stirrer. When the boiling point is reached, bubbles issue in a rapid stream from the lower end of the capillary. The thermometer is read when the evolution of bubbles just stops. The experiment is repeated with a fresh liquid in a new capillary and the boiling point recorded as before. The mean of the two readings is taken to be the correct boiling point of the liquid under examination.

In the above determination of the boiling point the tube containing the liquid and capillary may be heated in a *Thiele Tube* instead of the beaker. It is handy and eliminates the use of a stirrer.

QUESTIONS

1. Write an account of the various methods by which organic compounds are purified

2. The isolation of organic compounds is sometimes effected by distillation in steam, sometimes by extraction with a suitable solvent. Describe how each of these processes is employed, giving an example of each. Write a short account of the physical principles on which they depend for their success.

3. What are the methods generally employed for the purification of organic compounds ? How can you obtain a sample of pure ether from a mixture of alcohol, acetic acid and ether ?

4. Write an essay on methods of purification and criteria of purity of organic compounds.

5. Describe how you would separate in a pure condition each component of a mixture of ethyl alcohol, benzoic acid and acetanilide.

6. You are given an organic liquid ; how would you proceed to test its purity ? If it contains dissolved liquid impurity, describe a simple method for purifying it.

7. Give a brief description of the process of "extraction with solvents" and its use in the purification of organic compounds. Describe the construction and use of Soxhlet apparatus.

8. What is the significance of melting point and boiling point in Organic Chemistry ? How would you proceed to find the boiling point of a liquid, only 0·5 ml. of which is available.

9. Give an organic compound for identification, how would you proceed to determine whether it is a single pure compound or an impure substance or a mixture. *(Banaras B.Sc.,* 1958)

10. With the help of a sketch describe the extraction of oil seeds using Soxhlet's apparatus. *(Bangalore B.Sc.,* 1969)

3

Composition of Organic Compounds

Friedrich K. Beilstein
(1836–1906)
Russian organic chemist. He discovered isomerism of benzyl chloride and chlorotoluene. Students know him through his test of halogens

1. DETECTION OF ELEMENTS

The first step in the analysis of an organic compound is the detection of elements present in it. Most of these compounds contain 2 to 5 different elements. The principal elements present are : carbon, hydrogen and oxygen. Often, in addition to these, they may contain nitrogen, sulphur and halogens. Phosphorus and metals are also present but only rarely. The order of abundance in which these elements are found in organic compounds is indicated below :

ELEMENTS		ORDER OF ABUNDANCE
Carbon	...	Always present
Hydrogen	...	Nearly always present
Oxygen	...	Generally present
Nitrogen, Halogens and Sulphur	...	Less commonly present
Phosphorus and Metals		Rarely present

DETECTION OF CARBON AND HYDROGEN

If the compound under investigation is known to be organic, there is no need to test for carbon. This test is performed only to establish whether a given compound is organic or not. With the exception of few compounds *e.g.*, carbon tetrachloride, all organic compounds also contain hydrogen. The presence of both these elements is confirmed by the following common test :

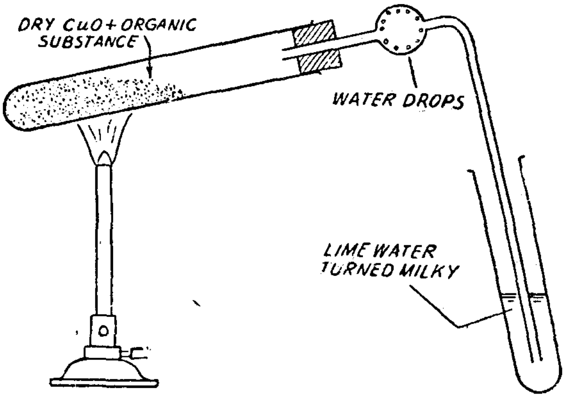


Fig. 3·1. Testing for carbon and hydrogen.

The organic substance is mixed intimately with about three times its weight of *dry* copper oxide. The mixture is then placed in a hard glass test-tube fitted with a bent delivery tube (Fig. 3·1), the other end of which is dipping into lime water in another test-tube. The mixture is heated strongly when the following reactions take place :—

$$C + 2CuO \longrightarrow CO_2 + 2Cu$$
$$2H + CuO \longrightarrow H_2O + Cu$$

Thus if carbon is present, it is oxidised to carbon dioxide which turns lime water milky. If hydrogen is also present, it will be oxidised to water which condenses in small droplets on the cooler wall of the test-tube and inside the bulb. The formation of water is further confirmed by testing the condensed liquid with anhydrous copper sulphate (*white*) that is turned blue.

If the substance under investigation is a gas or a volatile liquid, the above test is modified. The vapours of the substance are passed over heated copper oxide contained in a hard-glass combustion tube. The issuing gases are tested for carbon dioxide and water vapour as described before.

Note. While testing for hydrogen, it is essential that the apparatus and copper oxide used are absolutely dry. Cupric oxide being hygroscopic in nature it is heated strongly just before use.

DETECTION OF OXYGEN

There is no conclusive test for oxygen, through its presence in organic compounds is often inferred by indirect methods.

(1) The substance is heated alone in a dry test-tube, preferably in an atmosphere of nitrogen. Formation of droplets of water on cooler parts of the tube obviously shows the presence of oxygen. A negative result, however, does not necessarily show the absence of oxygen.

(2) The second method is to test for the presence of various

oxygen-containing groups such as *hydroxyl* (OH), *carboxyl* (COOH), *aldehyde* (CHO), *nitro* (NO_2), etc. If any of these is detected, the presence of oxygen is confirmed.

(3) The sure test for oxygen depends on the determination of the percentage of all other elements present in the given compound. If the sum of these percentages falls short of hundred, the remainder gives the percentage of oxygen and thus confirms its presence.

DETECTION OF NITROGEN

(1) The presence of nitrogen in an organic compound is shown by the following tests :

(1) A little of the substance is heated strongly in a test-tube or by directly placing it in the Bunsen flame. A smell of burnt feathers indicates nitrogen.

(2) **Soda-lime Test**. The given substance is mixed with double the amount of soda-lime (NaOH+CaO) and heated in a test tube. The vapours of ammonia evolved show the presence of nitrogen. A negative result, however, is not a proof of the absence of nitrogen. Many classes of nitrogenous compounds including *nitro* and *diazo* derivatives, do not respond to this test.

(3) **Sodium Test** (*Lassaigne's Test*). This is a golden test for the detection of nitrogen in all classes of nitrogenous compounds. **It involves the following steps :**

(*i*) ***The substance is heated strongly with sodium metal.***

$$\mathrm{Na} + \underbrace{\mathrm{C} + \mathrm{N}}_{\text{From Org. Compd.}} \longrightarrow \mathrm{NaCN}$$

(*ii*) *The water extract of the fused mass is boiled with ferrous sulphate solution.*

$$\mathrm{FeSO_4} + \underset{\substack{\text{From excess}\\ \text{of sodium}}}{\mathrm{2NaOH}} \longrightarrow \mathrm{Fe(OH)_2} + \mathrm{Na_2SO_4}$$

$$\mathrm{6NaCN} + \mathrm{Fe(OH)_2} \longrightarrow \underset{\text{Sod. ferrocyanide}}{\mathrm{Na_4[Fe(CN)_6]}} + \mathrm{2NaOH}$$

(*iii*) *To the cooled solution is then added a little ferric chloride solution and excess of concentrated hydrochloric acid.*

$$\underset{\text{Sod. ferrocyanide}}{\mathrm{3Na_4[Fe(CN)_6]}} + \mathrm{4FeCl_3} \longrightarrow \underset{\text{Prussian blue}}{\mathrm{FeCl_4[Fe(CN)_6]_4}} + \mathrm{12NaCl}$$

The formation of Prussian blue or green coloration confirms the presence of nitrogen.

Hydrochloric acid is added in this step to dissolve the greenish precipitate of ferrous hydroxide produced by the excess of sodium hydroxide on ferrous sulphate in step (*ii*), which would otherwise mark the Prussian blue precipitate.

Note. In case sulphur is also present along with nitrogen in the given organic compound, a blood red coloration may appear while performing the above test. This is due to the formation of sodium sulphocyanide which again reacts with ferric chloride to produce blood red coloration :

$$\mathrm{Na} + \mathrm{C} + \mathrm{N} + \mathrm{S} \longrightarrow \underset{\text{Sodium sulphocyanide}}{\mathrm{NaCNS}}$$

$$3NaCNS + FeCl_3 \longrightarrow Fe(CNS)_3 + 3NaCl$$

Ferric sulpho-cyanide
(*Blood red*)

Procedure of Sodium Test. Fix a fusion tube in an iron stand, clamping it just near the upper end (Fig. 3·2). Take a freshly cut piece of sodium of the size of a pea and dry it by pressing between the folds of a filter paper. Place the metal in a fusion tube and heat it from below. When it melts to a shining globule, put a pinch of the organic compound on it. Heat the tube with the tip of the flame till all reaction ceases and it becomes red hot. Now plunge it in about 50 mls. of distilled water taken in a china dish and break the bottom of the tube by striking against the dish. Boil the contents of the dish for about ten minutes and filter. Label the filtrate as 'sodium extract' and proceed with it as follows.

Take a portion of the sodium extract in a test-tube and note if it is alkaline. If it is not, make it so by adding sodium hydroxide. Then add to it freshly prepared ferrous sulphate solution and heat it to boiling. Put 2-3 drops of ferric chloride solution, cool and acidify with conc. hydrochloric acid. A Prussian blue or green precipitate, or even coloration, confirms the presence of nitrogen.

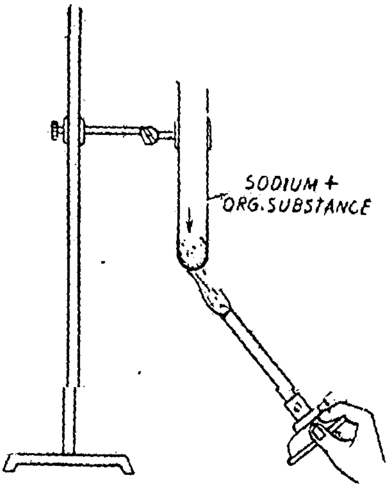


Fig. 3·2. Sodium test for nitrogen.

DETECTION OF SULPHUR

The presence of sulphur in organic substances is shown as described below :

(1) **Sodium Test.** Sulphur, if present, in the given organic compound, upon fusion with sodium reacts to form sodium sulphide.

$$2Na + S \longrightarrow Na_2S$$

Sodium sulphide

Thus, the 'sodium extract' obtained from the fused mass may be tested as :

(*i*) To a portion, add freshly prepared sodium nitroprusside solution. A deep violet coloration indicates sulphur.

(*ii*) Acidify a second portion of the extract with acetic acid and then add lead acetate solution A black precipitate of lead sulphide confirms the presence of sulphur.

$$Pb(CH_3COO)_2 + Na_2S \longrightarrow PbS + 2CH_3COONa$$

Lead acetate — Lead sulphate (*Black*)

(2) **Oxidation Test.** The organic substance is fused with mixture of potassium nitrate and sodium carbonate. The sulphu if present, is oxidised to sulphate.

$$Na_2CO_3 + S + 3O \longrightarrow Na_2SO_4 + CO_2$$

The fused mass is extracted with water, acidified with hydrochloric acid and then barium chloride solution is added to it. A white precipitate indicates the presence of sulphur.

$$\underset{}{BaCl_2+Na_2SO_4} \longrightarrow \underset{\substack{\text{Barium sulphate}\\ \text{(White ppt.)}}}{BaSO_4} + 2NaCl$$

DETECTION OF HALOGENS

(1) **Sodium Test.** Upon fusion with sodium, the halogens in the organic compound are converted to the corresponding sodium halides. Thus,

$$Cl+Na \longrightarrow NaCl$$
$$Br+Na \longrightarrow NaBr$$
$$I+Na \longrightarrow NaI$$

Acidify a portion of 'sodium extract' with dilute nitric acid and add to it silver nitrate solution.

White precipitate soluble in ammonia indicates CHLORINE,

Yellowish precipitate sparingly soluble in ammonia indicates BROMINE,

and Yellow precipitate insoluble in ammonia indicates IODINE.

Note. When nitrogen or sulphur is also present in the compound, the 'sodium extract' before testing for halogens is boiled with strong nitric acid to decompose the cyanide and the sulphide formed during the sodium fusion. If not removed, these radicals will form a white and black precipitate respectively on the addition of silver nitrate.

$$NaCN+HNO_3 \longrightarrow NaNO_3+HCN\uparrow$$
$$Na_2S+2HNO_2 \longrightarrow 2NaNO_2+H_2S\uparrow$$

(2) **Copper Wire Test** (*Beilstein's Test*). The copper wire flattened at one end is heated in an oxidising Bunsen flame till it ceases to impart any green colour to the flame. A small quantity of substance under investigatio is now taken on the flattened end of the wire which is re-inserted in the Bunsen flame. Upon heating for a while, the halogen present in the substance is converted to a volatile copper halide which imparts a blue or green colour to the flame. This test though very sensitive, is not always reliable. A substance like urea which contains no halogen, also colours the flame green.

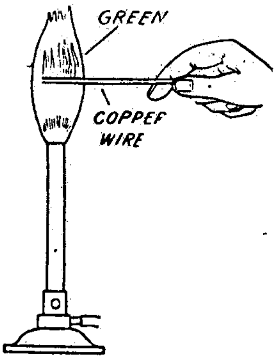


Fig. 3·3. Beilstein's test.

DETECTION OF PHOSPHORUS

The solid substance is heated strongly with an oxidising agent such as conc. nitric acid or a mixture of sodium carbonate and potassium nitrate. The phosphorus present in the substance is thus oxidised to phosphate. The residue is extracted with water, boiled with some nitric acid, and then a hot solution of ammonium molybdate is added to it in excess. A yellow coloration or *precipitate* indicates the presence of phosphorus.

DETECTION OF METALS

The substance is strongly heated in a crucible, preferably of platinum, till all reaction ceases. An incombustible residue indicates the presence of a metal in the substance. The residue is extracted with dilute acid and the solution tested for the presence of metallic radical by the usual scheme employed for inorganic salts.

2. Estimation of Elements

Having known the elements present in a given organic compound, we proceed to determine their composition by weight. The estimation of carbon, hydrogen, nitrogen and other elements can be done accurately by methods described below. No dependable method is, however, available for the determination of oxygen and hence its amount is always determined by difference.

ESTIMATION OF C AND H

Both carbon and hydrogen are estimated together in one operation. A known weight of the organic substance is burnt in excess of oxygen when the carbon and hydrogen present in it are oxidised to carbon dioxide and water respectively.

$$C_xH_y + \underset{\text{(excess)}}{O_2} \longrightarrow xCO_2 + y/2\,H_2O$$

The weights of carbon dioxide and water thus formed are determined and the amounts of *carbon* and *hydrogen* in the original substance calculated.

Apparatus. The apparatus employed for the purpose consists of three units :

(*i*) Oxygen supply,
(*ii*) Combustion tube, and
(*iii*) Absorption apparatus.

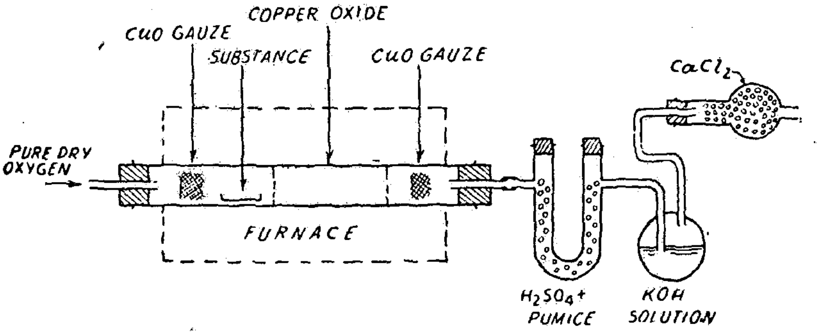


Fig. 3·4. *Apparatus for the estimation of C and H.*

Oxygen Supply. Oxygen from the aspirator is allowed to bubble through sulphuric acid contained in a Drechsel bottle and then passed through U-tubes charged with soda-lime. The oxygen gas thus freed from moisture and carbon dioxide enters the combustion tube.

Combustion tube. A hard-glass tube about 33 inches in length and ½ inch in diameter, and open at both ends is used for the combustion of the organic substance. It is filled as shown in Fig. 3·4, with (*i*) a roll of oxidised copper gauze to prevent the backward diffusion of the products of combustion, (*ii*) a porcelain boat containing a known weight (about 0·2 gm.) of the organic substance, (*iii*) coarse copper oxide packed in about two-thirds of the entire length of the tube, and kept in position by loose asbestos plugs on either side ; and (*iv*) a roll of oxidised copper gauze placed towards the end of the combustion tube to prevent any vapours of the organic substance leaving the tube unoxidised. The combustion tube is enclosed in a furnace, heated by gas burners.

Absorption Apparatus. The products of combustion containing moisture and carbon dioxide are then passed on to the absorption apparatus which consists of : (*i*) a weighed U-tube packed with pumice soaked in concentrated sulphuric acid, to absorb water, (*ii*) a set of bulbs containing strong solution of potassium hydroxide, to absorb carbon dioxide, and finally (*iii*) a guard-tube filled with anhydrous calcium chloride to prevent the entry of moisture from atmosphere.

Procedure. To start with, before loading it with the boat, the combustion tube is detached from the absorption unit. The tube is heated strongly to dry its contents and carbon dioxide present in it is removed by passing a current of pure, dry oxygen through it. It is then cooled slightly and connected to the absorption apparatus. The other end of the combustion tube is opened for a while and the boat containing weighed organic substance introduced. The tube is again heated strongly till the whole of the substance in the boat has burnt away. This takes about two hours. Finally, a strong current of oxygen is passed through the combustion tube to sweep away any traces of carbon dioxide or moisture which may have been left in it. The U-tube and the potash bulbs are then detached and the increase in weight of each of them determined.

Let the weight of the substance taken $= x$ grams

Increase in weight of U-tube (H_2O) $= y$ grams

Increase in weight of potash bulbs (CO_2) $= z$ grams

Since 18 grams of water contain hydrogen $= 2$ grams

y grams of water contain hydrogen $= \frac{2}{18} \times y$ grams

Also, 44 grams of CO_2 contain carbon $= 12$ grams

z „ „ „ „ $= \frac{12}{44} \times z$ grams

Hence the given organic substance contains

$$H = \frac{2y}{18} \times \frac{100}{x}\%$$

and

$$C = \frac{12z}{44} \times \frac{100}{x}\%.$$

Note. (1) If the organic substance under investigation also contains nitrogen, upon combustion it will produce oxides of nitrogen which will also be absorbed in the potash bulbs. Hence a spiral of copper is introduced at the right extreme of the combustion tube, so that the oxides of nitrogen are reduced to free nitrogen which escapes unabsorbed.

(2) If the compound contains halogens as well, a spiral of silver is also introduced in the combustion tube. The free halogens, which would have been otherwise absorbed in the potash bulbs, are converted to silver halides and thus eliminated from the products of combustion.

(3) In case the substance also contains sulphur, the copper oxide in the combustion tube is replaced by lead chromate. The sulphur dioxide formed during combustion is thus converted to lead sulphate and is thus prevented from passing into the absorption unit.

Example 1. *0·2475 gm. of an organic substance gave on combustion 0·4950 gm. of carbon dioxide and 0·2025 gm. of water. Calculate the percentage of carbon and hydrogen in it.*

Weight of the substance taken = 0·2475 gm.

Weight of CO_2 formed = 0·4950 gm.

Weight of H_2O formed = 0·2025 gm.

Now, we know, $\underset{44}{CO_2} \equiv \underset{12}{C}$ and $\underset{18}{H_2O} \equiv \underset{2}{2H}$

Weight of C in 0·4950 gm. of CO_2 $= \frac{0{\cdot}4950 \times 12}{44}$ gm.

Weight of H in 0·2025 gm. of H_2O $= \frac{0{\cdot}2025 \times 2}{18}$ gm.

$$\text{Hence, percentage of C} = \frac{0{\cdot}4950 \times 12}{44} \times \frac{100}{0{\cdot}2475}$$

$$= 54{\cdot}54$$

$$\text{and percentage of H} = \frac{0{\cdot}2025 \times 2}{18} \times \frac{100}{0{\cdot}2475}$$

$$= 9{\cdot}00$$

Example 2. *0·2346 gm. of an organic compound containing carbon, hydrogen and oxygen only was analysed by the combustion method. The increase in weight of the U-tube and the potash bulbs at the end of the operation was found to be 0·2754 gm. and 0·4488 gm. respectively. Determine the percentage composition of the compound.*

Wt. of CO_2 (increase in wt. of potash bulbs) = 0·4488 gm.

Wt. of H_2O (increase in wt. of U-tube) = 0·2754 gm.

Since we know that $\underset{44}{CO_2} \equiv \underset{12}{C}$ and $\underset{18}{H_2O} \equiv \underset{2}{2H}$

Wt. of C in 0·4488 gm. of $CO_2 = \frac{0{\cdot}4488 \times 12}{44}$ gm.

Wt. of H in 0·2754 gm. of $H_2O = \frac{0{\cdot}2754 \times 2}{18}$ gm.

But the wt. of the compound taken for analysis = 0·2346 gm.

$$\therefore \text{ Percentage of C in it } = \frac{0{\cdot}4488 \times 12}{44} \times \frac{100}{0{\cdot}2346} = 52{\cdot}18$$

$$\text{Percentage of H } = \frac{0{\cdot}2754 \times 2}{18} \times \frac{100}{0{\cdot}2346} = 13{\cdot}04$$

Percentage of O (*difference*) = 34·78.

ESTIMATION OF NITROGEN

The two chief methods for the estimation of nitrogen in an organic substance are :

(*i*) *The Dumas' Method*,

and (*ii*) *The Kjeldahl's Method*.

Dumas' Method. This method is based upon the fact that nitrogenous compounds when heated with copper oxide in an atmosphere of carbon dioxide yield free nitrogen. Thus :

$$C_xH_yN_z + (CuO) \longrightarrow xCO_2 + y/2\ H_2O + z/2\ N_2 + (Cu)$$

Traces of oxides of nitrogen, which may be formed in some cases, are reduced to elementary nitrogen by passing over heated, copper spiral.

Apparatus. The apparatus used in the Dumas' method consists of :

(*i*) *CO_2 generator*,
(*ii*) *Combustion tube*,
and (*iii*) *Schiff's nitrometer*.

CO_2 GENERATOR. The carbon dioxide needed in this process is prepared by heating magnesite or sodium bicarbonate contained in a hard-glass test-tube, or by the action of dilute hydrochloric acid on marble in a Kipp's apparatus. The gas is passed into the combustion tube after being dried by bubbling through concentrated sulphuric acid contained in a Drechsel bottle.

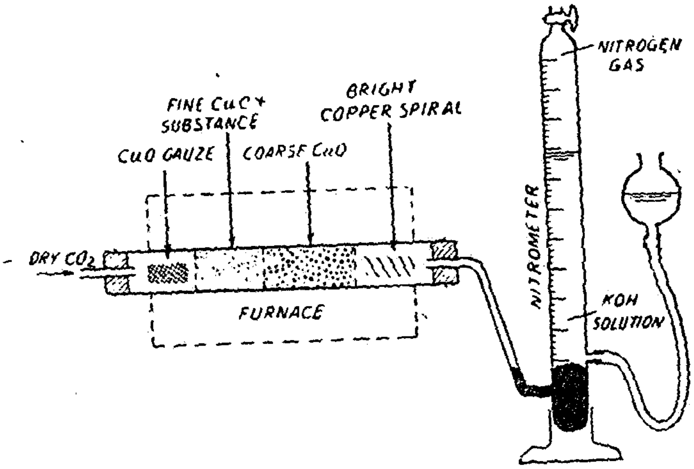


Fig. 3·5. Dumas' method for nitrogen estimation.

COMBUSTION TUBE. The combustion tube of about 90 cms. length, which is heated in a combustion furnace, is charged with :

(*i*) *a roll of oxidised copper gauze* to prevent the back diffusion of the products of combustion and to heat the organic substance mixed with copper oxide by radiation ;

(*ii*) a weighed amount (about 0·2 gm.) of the *organic substance* mixed with excess of copper oxide;

(*iii*) *a layer of coarse copper oxide* packed in about two-thirds of the entire length of the tube, and kept in position by loose asbestos plugs on either side ; this oxidises the organic vapours passing through it ; and

(*iv*) *a reduced copper spiral* which reduces any oxides of nitrogen formed during combustion, to nitrogen.

SCHIFF'S NITROMETER. The nitrogen gas obtained by the decomposition of the substance in the combustion tube is mixed with considerable excess of carbon dioxide. It is estimated by passing into Schiff's nitrometer where carbon dioxide is absorbed by caustic potash solution and the nitrogen collects in the upper part of the graduated tube.

Procedure. The apparatus is fitted up as shown in Fig. 3·5, and to start with, the tap of the nitrometer is left open. Carbon dioxide is passed through the combustion tube to replace the air in it. When the gas bubbles rising through the potash solution fail to reach the top of it and are completely absorbed, it shows that only carbon dioxide is coming and that all the air has been displaced from the combustion tube. The nitrometer is then filled with potassium hydroxide solution by lowering the reservoir and the tap closed. The combustion tube is now heated in the furnace, raising the temperature gradually. The nitrogen set free from the compound collects in the nitrometer. When the combustion is complete, a strong current of carbon dioxide is sent through the apparatus in order to sweep the last traces of nitrogen from it. The volume of the gas collected is noted after adjusting the reservoir so that the level of solution in it and the graduated tube is the same. The atmospheric pressure and the temperature are also recorded.

Calculations :

Let w = weight of the substance in grams

v = volume of moist N_2 in mls.

t = room temperature in °C

B = barometric pressure in mm. of mercury

b = aq. tension at room temperature (t°C)

$$\text{Volume of } N_2 \text{ at N.T.P} = \frac{v\,(B-b)}{t+273} \times \frac{273}{760}$$

$$= V \text{ mls. } (say)$$

Now, 22,400 mls. of N_2 at N.T.P. weigh $=28$ gms.

V mls. „ „ „ $=\frac{28}{22400}\times V$ gms.

$\therefore$ Percentage of N $=\frac{28V}{22400}\times\frac{100}{w}$.

Example 3. *0·1877 gm. of an organic substance when analysed by the Dumas' method yield 31·7 mls. of moist nitrogen measured at 14°C and 758 mm. mercury pressure. Determine the percentage of nitrogen in the substance. (Aqueous tension at 14°C = 12 mm.)*

Volume of N_2 at N.T.P $=\frac{v\,(B-b)}{t+273}\times\frac{273}{760}=V$ mls.

Substituting the various values in the above equation,

$$V=\frac{31\cdot7\,(758-12)}{14+273}=\frac{273}{760}=29\cdot6 \text{ mls}$$

Weight of 29·6 mls. of nitrogen $=\frac{28}{22400}\times29\cdot6$ gms.

$\therefore$ Percentage of nitrogen $=\frac{28\times29\cdot6}{22400}\times\frac{103}{0\cdot1877}$

$=19\cdot72$

Example 4. *In the estimation of nitrogen present in an organic compound by Dumas' method, 0·200 gm. yielded 20·7 mls. of nitrogen at 15°C and 760 mm. pressure. Calculate the percentage of nitrogen in the compound.*

Volume of N_2 at N.T.P. $=\frac{v\times B}{t+273}\times\frac{273}{760}=V$ mls.

Substituting the various values in the above equation,

$$V=\frac{20\cdot7\times7\cdot0}{288}\times\frac{273}{760}=19\cdot63 \text{ mls.}$$

Weight of 19·63 mls. of nitrogen $=\frac{28}{22400}\times19\cdot63$ gms.

$\therefore$ Percentage of nitrogen $=\frac{28}{22400}\times10\cdot63\times\frac{100}{0\cdot2}$

$=12\cdot27$.

Kjeldahl's Method. This method is carriea much more easily than the Dumas' method. It is used largely in the analysis of foods and fertilisers.

Kjeldahl's method is based on the fact that when an organic compound containing nitrogen is heated with concentrated sulphuric acid, the nitrogen in it is quantitatively converted into ammonium sulphate. The resultant liquid is then treated with excess of alkali and the liberated ammonia gas absorbed in excess of standard acid. The amount of ammonia (and hence of nitrogen) is determined by finding the amount of acid neutralised by back titration with some standard alkali.

Procedure. A weighed quantity of the substance (0·3 to 0·5 gm.) is placed in a special long-necked '*Kjeldahl flask*' made of resistant glass About 25 mls. of concentrated sulphuric acid together with a little potassium sulphate and copper sulphate is added to it. Potassium sulphate raises the boiling point and thus ensures complete reaction, while copper sulphate acts as a catalyst. The flask is loosely stoppered by a glass bulb and heated gently in an inclined position. The heating is continued till the brown colour of the liquid first produced, disappears leaving the contents clear as before. At this point all the nitrogen in the substance is converted to ammonium sulphate. The Kjeldahl flask is then cooled and its contents diluted with some distilled water, and then carefully transferred into a one-litre round-bottomed flask. An excess of sodium hydroxide solution is poured down the side of the flask and it is fitted with a Kjeldahl trap and a water condenser, as shown in Fig. 3·7. The lower end of the condenser dips in a measured volume of excess of the N/10 H_2SO_4 solution. The liquid in the round-bottomed flask is then heated and the liberated ammonia distilled into sulphuric acid. The Kjeldahl trap serves to retain any alkali splashed up on vigorous boiling. When no more ammonia passes over (test the distillate with red litmus), the receiver is removed. The excess of acid is then determined by titration with N/10 alkali, using phenolphthalein as the indicator.

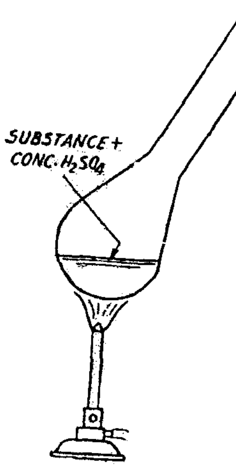


Fig. 3·6. Kjeldahl flask.

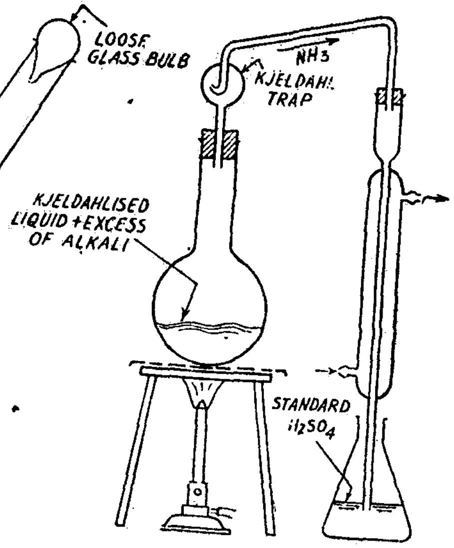


Fig. 3·7. Distillation of ammonia.

Calculations. Let the weight of the organic substance be x gms. and V mls. of N. HCl is required for complete neutralisation of ammonia evolved.

$$V \text{ ml. N. HCl} \equiv V \text{ ml. of N. } NH_3$$

1000 mls. of N.NH_3 contain 17 gms. of ammonia or 14 gms. of nitrogen.

Amount of nitrogen present in V mls. of N. NH_3

$$=\frac{14}{1000}\times V\times N \text{ gm.}$$

$$\text{Percentage of nitrogen} = \text{Wt. of nitrogen} \times \frac{100}{\text{Wt. of substance}}$$

$$= \frac{14}{1000} \times V \times N \times \frac{100}{x}$$

$$= \frac{1 \cdot 4VN}{x}$$

where N stands for normality of the acid used

V stands for volume of the acid used up

and x stands for the substance kjeldahlised.

Example 5. *0·257 gm. of an organic substance was heated with conc. sulphuric acid and then distilled with excess of strong alkali. The ammonia gas evolved was absorbed in 50 mls. of N/10 hydrochloric acid which required 23·2 mls. of N/10 NaOH for neutralisation at the end of the operation. Determine the percentage of nitrogen in the substance.*

Volume of N/10 HCl neutralised by ammonia $= 50 - 23 \cdot 2$

$= 26 \cdot 8$ mls.

Now, 26·8 mls. of N/10 HCl ≡ 26·8 mls. of N/10 NH_3

≡ 26·8 mls. of N/10 N (*combined*)

26·8 mls. of N/10 N solution contains $\frac{14}{10} \times \frac{26 \cdot 8}{1000}$ gms. of nitrogen

This weight of nitrogen was originally present in 0·257 gm. of the organic substance.

$$\therefore \text{ Percentage of nitrogen} = \frac{14 \times 26 \cdot 8}{10 \times 1000} \times \frac{100}{0 \cdot 257} = 14 \cdot 6.$$

Example 6. *0·4 gm. of an organic compound was kjeldahlised and ammonia evolved was absorbed into 50 mls. of semi-normal solution of sulphuric acid. The residual acid solution was diluted with distilled water and the volume was made up to 150 mls. 20 mls. of this diluted solution required 31 mls. of N/20 NaOH solution for complete neutralisation. Calculate the percentage of nitrogen in the compound.*

(*i*) CALCULATION OF ACID USED BY AMMONIA.

Volume of $\frac{N}{2}$ H_2SO_4 taken $= 50$ mls.

Let the volume of N/2 H_2SO_4 left unused by ammonia $= V$ mls.

V mls. of this acid solution was diluted to 150 mls. and titrated against N/20 NaOH.

20 mls. of diluted solution ≡ 31 mls. of N/20 NaOH

$$\therefore \text{ Normality of diluted solution} = 31 \times \frac{N}{20} \times \frac{1}{20} = \frac{31}{400} N$$

$$\text{Normality of 150 mls. of acid solution} = \frac{31}{400} N$$

i.e., V mls. of $\frac{N}{2}$ H_2SO_4 ≡ 150 mls. of $\frac{31}{400}$ N diluted acid

$$V = 150 \times \frac{31}{400} \times \frac{2}{1} = 23\ 25 \text{ mls.}$$

Volume of $\frac{N}{2}H_2SO_4$ left $=23{\cdot}25$ mls.

∴ Volume of acid used up by ammonia$=50-23{\cdot}25=26{\cdot}75$ mls.

(*ii*) CALCULATION OF PERCENTAGE OF N.

26·75 mls. of N/2 H_2SO_4 ≡ 26·75 mls. of N/2 NH_3 solution

≡26·75 mls. of N/2 N (*combined in solution*)

∴ Wt. of nitrogen in 26·75 mls. of N/2 solution

$$=\frac{14}{2}\times\frac{1}{1000}\times 26{\cdot}75 \text{ gms.}$$

This wt. of nitrogen was originally present in 0·4 gm. of the substance.

$$\therefore \text{ Percentage of nitrogen } =\frac{14}{2}\times\frac{1}{1000}\times 26{\cdot}75\times\frac{100}{0{\cdot}4}=46{\cdot}81.$$

ESTIMATION OF HALOGENS

Carius Method. It consists in oxidising the organic substance with fuming nitric acid in the presence of silver nitrate. The halogen of the substance is thus converted to silver halide which is separated and weighed.

The Carius method of estimating halogens involves the use of a stout hard-glass tube (*bomb tube*) of about 50 cms. length and closed at one end. About 5 mls. of fuming nitric acid together with 2 to 2·5 gms. of pure silver nitrate is placed in it. A narrow 'weighing tube, containing an accurately weighed quantity of the substance is then slipped into the bomb tube, taking care to avoid the mixing of the substance with nitric acid. The open end of the tube is then sealed off. It is now heated in an iron jacket of the furnace heated by burners from below. The temperature of the furnace is gradually raised to 300°C. After heating for about six hours, the tube is allowed to cool. The high pressure developed inside the tube is released by softening the sealed end with a small flame, when a hole is blown open through which the gases escape. The end of the tube is now cut off and the contents transferred into a beaker. The halide formed is collected in a Gooch crucible, washed, dried and weighed.

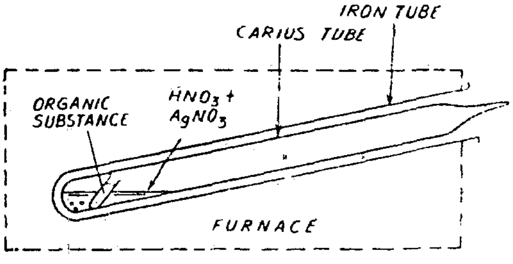


Fig. 3·8. Heating the bomb tube in a furnace (*Carius Method*).

Let w gms. of the organic substance give x gms. of the silver halide.

$$\therefore \text{ Percentage of halogen}=\frac{\text{At. Wt. of halogen}}{\text{M. Wt. of silver halide}}\times\frac{100x}{w}.$$

Example 7. *0·197 gm. of an organic substance when heated with excess of strong nitric acid and silver nitrate gave 0·3525 gm. of silver iodide. Find the percentage of iodine in the compound.*

Since, $\underset{(108+127)}{AgI} \equiv \underset{127}{I}$

In this case 0·197 gm. of the compound gave 0·3525 gm. of AgI

$$\equiv \frac{0\cdot3525\times127}{235}\text{ gm. iodine}$$

$$\therefore \text{ the percentage of iodine} = \frac{0\cdot3525\times127}{235}\times\frac{100}{0\cdot197}$$

$$=96\cdot68.$$

Example 8. *0·2562 gm. of an organic substance when heated with excess of strong nitric acid and silver nitrate gave 0·3066 gm. of silver bromide. Find the percentage of bromine in the compound.*

Since $\underset{(108+80)}{AgBr} \equiv \underset{80}{Br}$

Here, 0·2562 gm. of the substance gave 0·3066 gm. of AgBr

$$=\frac{0\cdot3066\times80}{188}\text{ gm. bromine}$$

∴ the percentage of bromine

$$=\frac{0\cdot3066\times80}{188}\times\frac{100}{0\cdot2562}=50\cdot93$$

Oxygen Flask Method. This method of estimating halogens has been introduced only recently. It is simple in operation and general in application. The organic sample is ignited in an atmosphere of oxygen and the products of combustion are absorbed in aqueous alkaline hydrogen peroxide. The chlorine and bromine of the organic substance are converted into chloride and bromide respectively, whereas iodine if present is changed into molecular iodine with some iodate. These products are then determined by titration method.

Procedure. A known weight of the organic sample is wrapped in a filter paper so that a small tail of paper is left out as a fuse. The wrapped sample is clasped between the folds of a platinum gauze attached to the glass stopper by platinum wire. Dilute sodium hydroxide and a few drops of hydrogen peroxide (H_2O_2) are placed in a conical flask (*see* Fig. 3·9). The flask is briskly flushed with a stream of oxygen from an 'oxygen cylinder'. The paper fuse is ignited and the ground glass stopper carrying the sample replaced rapidly into the flask. The stopper is pressed with hand to make the joint air-tight for the few seconds of combustion. The 'oxygen flask' (from which the method

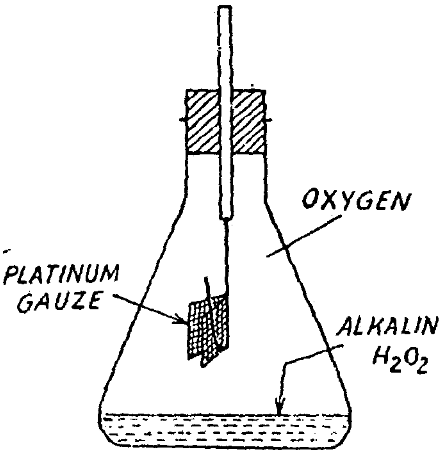


Fig. 3·9. Estimation of halogens by oxygen flask method.

takes its name) is now shaken vigorously to ensure complete absorption of the gaseous products. The stopper and the platinum mounting (gauze and holding wire) are carefully washed into the flask and the contents analysed as follows.

Chlorine and Bromine are estimated by making the contents of the flask slightly acidic with sulphuric acid and then titrating with standard solution of silver nitrate. If the weight of the organic sample taken be x gms. and V mls. of N silver nitrate is required to reach the *end point*, the percentage of chlorine can be calculated.

Since $\quad Cl \equiv AgNO_3$

V mls. of N $AgNO_3 \equiv V$ mls. of N chlorine (Cl)

But 1000 mls. of N chlorine (Cl) solution contains Cl

$$=35{\cdot}5 \text{ gm.}$$

∴ V mls. of N chlorine (Cl) solution contains Cl

$$=\frac{35{\cdot}5}{100}\times N\times V \text{ gm.}$$

Hence percentage of Cl in sample

$$=\frac{35{\cdot}5}{1000}\times N\times V\times\frac{100}{x}$$

Similarly, the percentage of bromine (Br) in the organic sample would be

$$=\frac{80}{100}\times N\times V\times\frac{100}{x}$$

Iodine is determined by first converting it into iodate by adding excess of bromine. Then potassium iodide and sulphuric acid is added to liberate iodine which is titrated with standard thiosulphate.

$$I_2+5Br_2+6H_2O \longrightarrow 2HIO_3+10HBr$$

$$HIO_3+5HI \longrightarrow 3I_2+3H_2O$$

If x gm. of the sample require V mls. of N sodium thiosulphate,

$$\text{Percentage of } I=\frac{127}{1000}\times\frac{N}{6}\times V\times\frac{100}{x}$$

ESTIMATION OF S AND P

Sulphur is estimated by a slight modification of the *Carius method*. The organic substance is heated with fuming nitric acid but no silver nitrate is added. The sulphur of the substance is oxidised to sulphuric acid which is then *precipitated* as barium sulphate by adding excess of barium chloride solution. The precipitate is filtered, washed, dried and weighed. From the weight of the barium sulphate so obtained, the percentage of sulphur can be calculated.

Phosphorus is also estimated like sulphur. The organic substance is heated with fuming nitric acid whereupon its phosphorus is oxidised to phosphoric acid. The phosphoric acid is precipitated as ammonium phosphomolybdate, $(NH_4)_3PO_4.12MoO_3$, by the addition of ammonia and ammonium molybdate solution, which is then separated, dried and weighed.

Example 9. *In an estimation of sulphur by the Carius method 0·2175 gm. of the substance gave 0·5825 gm. of barium sulphate. Calculate the percentage of sulphur in the substance.*

We know, $BaSO_4 \equiv S$

$(137+32+64)$ 32

Or, 233 gms. of $BaSO_4$ contain 32 gms. of sulphur.

0·5825 ,, ,, ,, $\frac{32}{333} \times 0{\cdot}5825$ gm. of sulphur.

This is the weight of sulphur present in 0·2175 gm. of the substance.

Hence, percentage of $S = \frac{32 \times 0{\cdot}5825}{233} \times \frac{100}{0{\cdot}2175} = 36{\cdot}77.$

Example 10. *0·395 gm. of an organic compound by Carius method for the estimation of sulphur gave 0·582 gm. of $BaSO_4$. Find the percentage of sulphur in the compound.*

We know, $BaSO_4 \equiv S$

233 32

i.e., 233 gms. of $BaSO_4$ contains 32 gms. of sulphur.

∴ 0·582 ,, ,, ,, $\frac{32}{233} \times 0{\cdot}582$ gm. of sulphur.

This is the weight of sulphur present in 0·395 gm. of the substance.

Hence, the percentage of sulphur

$$= \frac{32}{233} \times 0{\cdot}582 \times \frac{100}{0{\cdot}395}$$

$$= 20{\cdot}23.$$

ESTIMATION OF OXYGEN

Until recently, the percentage of oxygen in a given organic compound was found by difference. Any percentage of the total composition not accounted for by the foregoing determination was taken to be oxygen. This rather faulty procedure of estimating oxygen has now been replaced by a direct experimental method described below.

Principle. The given organic sample is pyrolysed (decomposed by heating) in a stream of nitrogen gas. The elemental oxygen along with other gaseous products is passed through hot carbon (1100°). All the oxygen is thereby converted to carbon monoxide. This when passed through warm (175°) iodine pentoxide (I_2O_5) is oxidised to carbon dioxide producing iodine.

$$\text{Org. Compound} \xrightarrow{\text{heat}} O_2 + \text{gaseous products}$$

$$O_2 + 2C \xrightarrow{(1100°)} 2CO$$

$$5CO + I_2O_5 \xrightarrow{(175^\circ)} 5CO_2 + I_2$$

By determining the amount of CO_2 (or I_2) produced, the percentage of carbon in the original organic compound can be calculated.

Procedure. The pyrolysis of the given organic compound is carried in a combustion apparatus similar to the one used for the estimation of carbon and hydrogen.

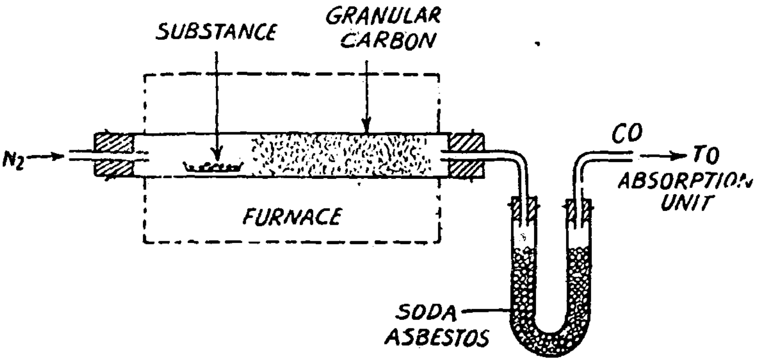


Fig. 3·10. Pyrolysis unit of the apparatus used for the estimation of oxygen.

A weighed quantity of the sample is charged in a porcelain boat which is loaded into the combustion tube. The latter part of the combustion tube is packed with granular carbon. The temperature of the heating furnace jacket is kept at 1100°C. Pure nitrogen from a cylinder enters the tube from the left end and sweeps through it.

The gases emerging from the combustion tube containing carbon monoxide are first passed through a U-tube containing soda-asbestos (asbestos impregnated with dry NaOH). This retains any acidic materials obtained from halogens, nitrogen or sulphur present in the organic sample. The gaseous mixture free from the acidic materials is then passed through a wide glass tube packed with iodine pentoxide kept at 175°C. It converts carbon monoxide to carbon dioxide and generating iodine.

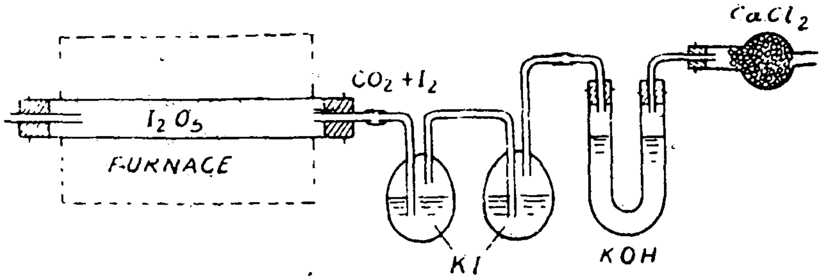


Fig. 3·11. Absorption unit.

The resulting gaseous mixture is now allowed to pass over a bed of potassium iodide (KI) laid in a wide glass tube. This removes iodine. The residual gases containing carbon dioxide are finally passed through a soda-asbestos U-tube where CO_2 is retained. The soda-asbestos tube is weighed before and after pyrolysis. The difference in weight gives the amount of CO_2 obtained from the given sample of the organic compound.

Calculations :

Let the weight of organic substance taken $= x$ gms.

Increase in the weight of KOH tube $= y$ gms.

Since $O \equiv CO \equiv CO_2$

16 gms. of oxygen present in the substance can form 44 grams of CO_2.

$\therefore$ 44 gms of CO_2 are obtained from oxygen

$$= 16 \text{ gms.}$$

y gms. of CO_2 are obtained from oxygen

$$= \frac{16}{44} \times y \text{ gms.}$$

Hence the weight of oxygen in the weight of sample taken

$$= \frac{16}{44} \times y \text{ gms.}$$

$\therefore$ the percentage of oxygen

$$= \frac{16}{44} \times \frac{y}{x} \times 100$$

QUESTIONS

1. Give an account of the methods by which the presence of nitrogen, chlorine and sulphur is tested in organic solids.

2. How would you test for the presence of chlorine in an organic compound ? Describe how it is qualitatively determined.

3. How can you identify halogens and nitrogen when they occur together in an organic compound ?

4. Explain briefly with a diagram of the apparatus employed in the method of determining the percentage of carbon and hydrogen in an organic compound containing carbon, hydrogen and nitrogen only.

5. Describe fully how you would detect the presence of (*a*) nitrogen, (*b*) sulphur, (*c*) phosphorus in an organic substance, explaining as far as possible the reactions involved by means of equations. How would you determine one of these elements quantitatively ?

6. Describe with essential details the various methods available for the quantitative estimation of nitrogen in an organic compound.

0·8 gm. of a substance was digested with sulphuric acid and then dissolved with an excess of caustic soda. The ammonia gas evolved was passed through 100 c.c. of 1 N sulphuric acid. The excess of acid required 80 c.c. of 1 N caustic soda solution for its complete neutralisation. Calculate the percentage of nitrogen in the compound. [**Ans.** 35%] (*Nagpur B.Sc., 1960*)

7. How is nitrogen detected and estimated in an organic compound ? 0·2 gm. of an organic substance on Kjeldahl's analysis gave enough ammonia to just neutralise 20 c.c. of decinormal sulphuric acid. Calculate the percentage of nitrogen in the compound. [**Ans.** 14·0%] (*Annamalai B.Sc., 1961*)

8. Describe the method of estimation of sulphur in an organic compound.

Three isomeric compounds have vapour density 29·5 and contain C =61·02%, H=15·25% and N=23·73%. Assign structural formulae to them and suggest a method to distinguish them.

(Atomic weights : H=1, C=12, N=14)

[Ans. $C_3H_7NH_2$; $CH_3NHC_2H_5$; $(CH_3)_3N$] *(Baroda B.Sc., 1962)*

9. How do you detect the presence of nitrogen, sulphur and halogen in organic compounds ? Explain the chemical reactions involved. How are organic compounds purified ? *(Osmania B.Sc. Part II, 1963)*

10. How would you estimate nitrogen in a nitrogenous organic compound ? Give all details and discuss the reactions involved. *(Nagpur B.Sc. II, 1964*

11. Describe fully Kjeldahl's method for the estimation of nitrogen in an organic compound. What are its limitations ? *(Calcutta B.Sc., 1964)*

12. How can you estimate nitrogen quantitatively in an organic compound ? *(Dibrugarh B.Sc., 1967)*

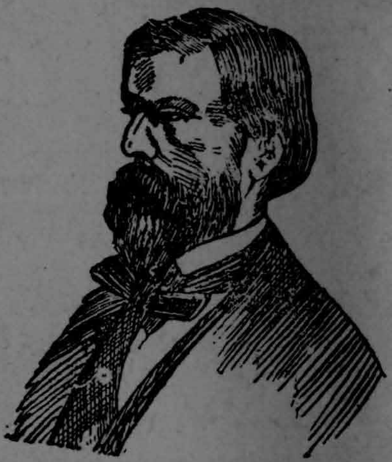
13. Give a brief account of (*a*) the detection and (*b*) a method for the estimation of nitrogen and sulphur in an organic compound. *(Osmania B.Sc., 1968)*

14. How are nitrogen and sulphur detected in an organic compound ? *How is nitrogen estimated ?* *(Madurai B.Sc., 1968)*

15. How can you detect the presence of nitrogen, sulphur and halogens in an organic compound ? *(Dibrugarh B.Sc., 1968)*

4

Empirical and Molecular formulae. Determination of Molecular Weights



Victor Meyer
(1848–1897)
German chemist. He investigated nitroalkanes. He gave a method for the determination of vapcur density which bears his name.

I. EMPIRICAL FORMULA

The **Empirical formula** of a compound is *the simplest formula which expresses its percentage composition.* Such a formula, while it tells us the ratio of the atoms of different elements present in the molecule, does not indicate the actual number of atoms of each element present in it.

CALCULATION OF EMPIRICAL FORMULA

Having determined the percentage of each element present in a compound as described in Chapter 3, its empirical formula is calculated by the following steps :

(1) *The percentage of each element is divided by its atomic weight.* This gives the relative number of different kinds of atoms in the molecule.

(2) *The numbers obtained in step* (1) *are then divided by the smallest of these numbers* (H.C.F.), so as to give simple atomic ratio.

(3) The figures expressing the simple atomic ratio, as obtained

from step (2), give the number of atoms of each element in the molecule, minor fractions being neglected as due to experimental error. *However, if necessary, they are further reduced to whole numbers by multiplying with a suitable factor.*

Example 1. *An orgnnic substance on analysis was found to contain 10·06 per cent carbon, 0·84 per cent hydrogen, and 89·10 per cent chlorine. Calculate its empirical formula.*

Step 1. Divide the percentage composition of each element by its respective atomic weights.

Carbon	*Hydrogen*	*Chlorine*
$\frac{10·06}{12}=0·84$	$\frac{0·84}{1}=0·84$	$\frac{89·10}{35·5}=2·51$

Step 2. Divide these numbers by the smallest number (in this case 0·84).

$$\frac{0·84}{0·84}=1 \qquad \frac{0·84}{0·84}=1 \qquad \frac{2·51}{0·84}=3$$

Hence, the empirical formula is $C_1H_1Cl_3$ or $CHCl_3$.

Example 2. *Percentage composition of an organic substance as determined by analysis was*

Carbon 14·5 ; hydrogen 1·8 ; chlorine 64·46 ; oxygen 19·24.

Calculate its empirical formula.

Element	%age		At. Wt.		Atomic ratio		H.C.F.	Atoms present
C	14·5	÷	12	=	1·21÷1·20	=	1·0	1×2=2
H	1·8	÷	1	=	1·8 ÷1·20	=	1·5	1·5×2=3
Cl	64·46	÷	35·5	=	1·81÷1·20	=	1·5	1·5×2=3
O	19·24	÷	16	=	1·20÷1·20	=	1·0	1×2=2

In this case, the final figures representing the number of atoms of each element are multiplied by 2 so as to get whole numbers. Hence, the empirical formula of the compound is $C_2H_3Cl_3O_2$.

Example 3. *When analysed by the combustion method, 0·20 gram of an organic substance yielded : (i) 0·147 gram of carbon dioxide and 0·12 gm. water and (ii) 74·6 mls. of nitrogen gas at S.T.P. Find the simplest formula of the substance.*

CALCULATION OF PERCENTAGE OF ELEMENTS

Since $CO_2 \equiv C$; $H_2O \equiv 2H$, 22,400 mls. $N_2 = 28$ gms

$$\text{Percentage of carbon} = \frac{0·147 \times 12}{44} \times \frac{100}{0·2} = 20·04$$

$$\text{,, \quad ,, hydrogen} = \frac{0·12 \times 2}{18} \times \frac{100}{0·2} = 6·66$$

$$\text{,, \quad ,, nitrogen} = \frac{74·6 \times 28}{22400} \times \frac{100}{0·2} = 46·63$$

$$\text{,, \quad ,, oxygen (by difference)} = 26·77$$

CALCULATION OF EMPIRICAL FORMULA

	%age		At. Wt.		Atomic Ratio		H.C.F.		Atoms present
C	20·04	÷	12	=	1·67	÷	1·66	=	1
H	6·66	÷	1	=	6·66	÷	1·66	=	4
N	46·63	÷	14	=	3·33	÷	1·66	=	2
O	26·77	÷	16	=	1·66	÷	1·66	=	1

Hence the empirical formula of the substance is CH_4N_2O.

Example 4. *0·21 gram of an organic substance containing C, H, O and N only, gave on combustion 0·462 gram carbon dioxide and 0·1215 gram water. 0·104 gram of it when distilled with caustic soda evolved ammonia which was neutralised by 15 mls. of N/20 H_2SO_4. Calculate the empirical formula.*

CALCULATION OF PERCENTAGE COMPOSITION:

Percentage of nitrogen :—

15 mls. of $\frac{N}{20}$ $H_2SO_4 \equiv$ 15 mls. of $\frac{N}{20}$ $NH_3 \equiv$ 15 mls. of $\frac{N}{20}$N (combined)

∴ wt. of nitrogen in 0·104 gm. substance $= 15 \times \frac{14}{20} \times \frac{1}{1000}$ gm.

$= 0{\cdot}0105$ gm.

%age of the nitrogen $= \frac{0{\cdot}0105}{0{\cdot}104} \times 100 = 10{\cdot}09$

Percentage of C and H :—

Since $CO_2 \equiv C$; $H_2O \equiv 2H$

$$\%\text{age of C} = \frac{0{\cdot}462 \times 12}{44} \times \frac{100}{0{\cdot}21} = 60{\cdot}0$$

$$\text{,,} \quad H = \frac{0{\cdot}1215 \times 2}{18} \times \frac{100}{0{\cdot}21} = 6{\cdot}43$$

Percentage of oxygen (by difference) = 23·48

CALCULATION OF EMPIRICAL FORMULA

	%age		At. Wt.		Atomic Ratio		H.C.F.		Atoms present
C	60	÷	12	=	5·00	÷	0·72	=	7
H	6·43	÷	1	=	6·43	÷	0·72	=	9
N	10·09	÷	14	=	0·72	÷	0·72	=	1
O	23·48	÷	16	=	1·46	÷	0·72	=	2

Hence, Empirical formula is $C_7H_9NO_2$.

II. MOLECULAR FORMULA

The **Molecular formula** of a substance expresses *the actual number of atoms of each element present in its molecule.* It may be the same as the empirical formula of the substance or an exact multiple of it.

Substance	*Empirical Formula*	*Molecular Formula*
Methane	CH_4	CH_4 or $(CH_4)_1$
Ethylene	CH_2	C_2H_4 or $(CH_2)_2$
Acetic acid	CH_2O	$C_2H_4O_2$ or $(CH_2O)_2$
Glucose	CH_2O	$C_6H_{12}O_6$ or $(CH_2O)_6$

Thus we can write :

$$\textit{Molecular Formula} = (\textit{Empirical Formula})_n$$

when $n = 1, 2, 3$ etc. When $n = 1$, the molecular formula coincides with the empirical formula. It follows from the above relation that

$$M.\ Wt. = Emp.\ formula\ Wt. \times n$$

whence $$n = \frac{M.\ Wt.}{Emp.\ Formula\ Wt.}$$

If the molecular weight is known, the value of n can be found with the help of this relation.

Example 5. *An organic compound has been found to possess the empirical formula CH_2O and the molecular weight$=90$. Give its molecular formula, ($C=12$; $H=1$; $O=16$).*

Molecular formula $=$ (Empirical formula)$_n$

But $$n = \frac{\text{M. Wt.}}{\text{Emp. F. Wt.}}$$

In this case, M. Wt. $=90$

Emp. F. Wt. $=12+2+16=30$

$$n = \frac{90}{30} = 3$$

Hence, the molecular formula$=(CH_2O)_3$ or $C_3H_6O_3$.

Example 6. *An organic liquid contains 12·8 per cent carbon, 2·1 per cent hydrogen and 85·1 per cent bromine. 0·188 gram of it in a Victor Meyer experiment, displaced 24·2 mls. of moist air measured at 14°C and 752 mm. pressure. Find the molecular formula of the substance. (Aq. tension at 14°C = 12 mm.)*

CALCULATION OF MOLECULAR WEIGHT :

Volume of dry air replaced at N.T.P. $= \frac{24{\cdot}2(752-12)}{287} \times \frac{273}{760}$

$= 22{\cdot}42$ mls.

Now, the wt. of 22·42 mls. of vapour of substance$=0{\cdot}188$ gm.

„ „ 22400 „ „ „ $= \frac{0{\cdot}188}{22{\cdot}42} \times 22400$

$= 187{\cdot}9$ gms.

Molecular weight of the substance$=187{\cdot}9$.

CALCULATION OF EMPIRICAL FORMULA :

	%age		*At. Wt.*		*Atomic ratio*		*H.C.F.*		*Atoms present*
C	12·8	÷	12	=	1·066	÷	1·064	=	1
H	2·1	÷	1	=	2·10	÷	1·064	=	2
Br	85·1	÷	80	=	1·064	÷	1·064	=	1

∴ Empirical formula is CH_2Br.

CALCULATION OF MOLECULAR FORMULA :

Let the molecular formula be $(CH_2Br)_n$

But $$n = \frac{\text{M. Wt.}}{\text{Emp. F. Wt.}} = \frac{187{\cdot}9}{12+2+80} = 2$$

∴ Molecular formula $= C_2H_4Br_2$.

Example 7. *An organic dibasic acid contains C=17·39 ; H=1·45, and Br=57·97 per cent. The vapour density of its ethyl ester is 166. Determine the molecular formula of the acid.*

CALCULATION OF MOLECULAR WEIGHT OF ACID :

Let the dibasic acid be RH_2 and its ethyl ester $R(C_2H_5)_2$.
Molecular weight of ethyl ester $=2\times V.D.=2\times 166=332$
Thus $R(C_2H_5)_2=R+2\ (24+5)=332$
Whence $R=274$
$\therefore$ Molecular weight of the acid $RH_2=274+2=276$.

CALCULATION OF EMPIRICAL FORMULA :

Percentage of oxygen $=100-(17·39+1·45+57·97)=23·19$

	%age		At. wt.		Atomic Ratio		H.C.F.		Atoms present
C	17·39	÷	12	=	1·45	÷	0·72	=	2
H	1·45	÷	1	=	1·45	÷	0·72	=	2
Br	57·97	÷	80	=	0·72	÷	0·72	=	1
O	23·19	÷	16	=	1·45	÷	0·72	=	2

Hence, the empirical formula is $C_2H_2BrO_2$.
Let the molecular formula of the acid be $(C_2H_2BrO_2)_n$.

$$\text{But}\quad n=\frac{\text{M. Wt.}}{\text{Emp. F. Wt}}=\frac{276}{24+2+80+32}=\frac{276}{138}=2$$

$\therefore$ Molecular formula is $C_4H_4Br_2O_4$.

Example 8. *0·20 gm. of anhydrous organic acid gave on combustion 0·040 gm. water and 0·195 gm. carbon dioxide. The acid is found to be dibasic and 0·5 gm. of its silver salt leaves on ignition 0·355 gm. silver. What is the molecular formula of the acid ?*

CALCULATION OF MOLECULAR WEIGHT :

$$\frac{\text{M. Wt. of silver salt}}{2\times 108}=\frac{0·5}{0·355}$$

$$\text{M. Wt. of silver salt}=\frac{0·5}{0·355}\times 2\times 108=304·2$$

If RH_2 be the dibasic acid, its silver salt is RAg_2.
But $RH_2=RAg_2-2Ag+2H$
$=304·2-216+2=90·2.$

CALCULATION OF EMPIRICAL FORMULA :

$$\text{Percentage of C}=\frac{0·195\times 12}{44}\times\frac{100}{0·2}=26·59$$

$$\text{,, ,, H}=\frac{0·040\times 12}{18}\times\frac{100}{0·2}=2·22$$

,, ,, O (by difference) $=71·19$.

	%age		At. Wt.		Atomic ratio		H.C.F.		Atoms present
C	26·59	÷	12	=	2·22	÷	2·22	=	1
H	2·22	÷	1	=	2·22	÷	2·22	=	1
O	71·19	÷	16	=	4·45	÷	2·22	=	2

$\therefore$ Empirical formula is CHO_2.

CALCULATION OF MOLECULAR FORMULA

Let it be $(CHO_2)_n$; $n=\dfrac{\text{M. Wt.}}{\text{Emp. F. Wt.}}=\dfrac{90·2}{12+1+32}=2$

Hence, Molecular formula of the acid is $C_2H_2O_4$.

Example 9. *An organic monobasic acid gave the following percentage composition : C=70·59 ; H=5·88 ; O=23·53.*

0·272 gm. of the acid required 20 mls. of N/10 NaOH for complete neutralisation.

Deduce the empirical and the molecular formulae of the acid.

CALCULATION OF MOLECULAR WEIGHT :

$$20 \text{ mls. } \frac{N}{10} \text{ NaOH} \equiv 20 \text{ ml. } \frac{N}{10} \text{ acid} \equiv \frac{20}{100} \times \frac{N}{10} \text{ gm. acid}$$

Thus: $\frac{20}{1000} \times \frac{N}{10} = 0{\cdot}272$

Whence $N = 500 \times 0{\cdot}272 = 136$

Molecular weight of acid $= N \times \text{Basicity}$

$= 136 \times 1 = 136$

CALCULATION OF EMPIRICAL FORMULA :

	At. Wt.		Atomic ratio		H.C.F.		Atoms present
C 7·059 ÷	12	=	5·88	÷	1·47	=	4
H 5·88 ÷	1	=	5·88	÷	1·47	=	4
O 23·53 ÷	16	=	1·47	÷	1·47	=	1

Hence, empirical formula is C_4H_4O.

CALCULATION OF MOLECULAR FORMULA :

Let molecular formula be $(C_4H_4O)_n$

But $$n = \frac{\text{M. Wt.}}{\text{Emp. F. Wt.}} = \frac{136}{48+4+16} = \frac{136}{68} = 2.$$

Hence, molecular formula is $C_8H_8O_2$.

Example 10. *A mono-acid organic base gave the following results on analysis :—*

(*i*) *0·100 gm. gave 0·2882 gm. CO_2 and 0·0756 gm. H_2O.*

(*ii*) *0·200 gm. gave 21·8 mls. nitrogen at 15°C and 750 mm.*

(*iii*) *0·400 gm. of the platinichloride, left on ignition, 0·125 gm. of Pt.*

What is the molecular formula of the base ?

CALCULATION OF MOLECULAR WEIGHT :

M. Wt. of platinichloride $= 195 \times \frac{\text{Wt. of salt taken}}{\text{Wt. of Pt left}}$

$$= 195 \times \frac{0{\cdot}4}{0{\cdot}125} = 624$$

$$B = \frac{B_2H_2PtCl_6 - H_2PtCl_6}{2}$$

$$= \frac{624 - 410}{2} = 107$$

∴ Molecular weight of the base is 107.

CALCULATION OF EMPIRICAL FORMULA :

Volume of nitrogen at N.T.P. $= 21{\cdot}8 \times \frac{273}{288} = 20{\cdot}66$ mls.

$$\text{Percentage of C} = \frac{0{\cdot}2882 \times 12}{44} \times \frac{100}{0{\cdot}1} = 78{\cdot}6$$

$$\text{,, \quad ,, \quad H} = \frac{0{\cdot}0756 \times 2}{18} \times \frac{100}{0{\cdot}1} = 8{\cdot}4$$

$$\text{,, \quad ,, \quad N} = \frac{20{\cdot}66 \times 28}{22400} \times \frac{100}{0{\cdot}2} = 12{\cdot}91$$

Element	*% age*		*At. weight*		*At. ratio*		*H.C.F.*		*Atoms present*
C	78·6	÷	12	=	6·25	÷	0·92	=	7
H	8·4	÷	1	=	8·40	÷	0·92	=	9
N	12·95	÷	14	=	0·92	÷	0·92	=	1

∴ Empirical formula is C_7R_9N.

CALCULATION OF MOLECULAR FORMULA :

Let the molecular formula be $(C_7H_9N)_n$

$$\text{But} \quad n = \frac{\text{M. Wt.}}{\text{Emp. F. Wt.}} = \frac{107}{84+9+14} = \frac{107}{107} = 1$$

∴ Molecular formula is $(C_7H_9N)_1$ or C_7H_9N.

MOLECULAR FORMULA OF GASEOUS HYDROCARBONS

The molecular formula of a gaseous hydrocarbon may be determined directly without a previous knowledge of its percentage composition. A known volume of the hydrocarbon is mixed with a measured excess of oxygen and the mixture exploded in a eudiometer tube. The carbon and hydrogen of the substance is oxidised to form carbon dioxide and water respectively. The equation of explosion reaction can be written as

$$C_xH_y + (x + y/4)O_2 = xCO_2 + y/2H_2O$$

The following observations are recorded :—

(1) *The volume of the gaseous products after explosion and cooling* (V_1). This corresponds to the volume of carbon dioxide and unreacted oxygen, the water vapour being condensed to liquid which occupies negligible volume.

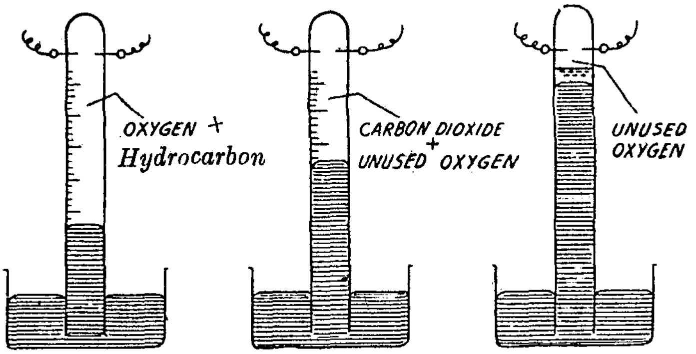


Fig. 4·1. Explosion of gaseous hydrocarbons in eudiometer tube.

(2) *The volume of the residual oxygen after introducing alkali* (V_2). When a little alkali is introduced in the eudiometer tube, it absorbs carbon dioxide, leaving behind unreacted oxygen. The volume of carbon dioxide alone would thus be equal to $(V_1 - V_2)$.

The molecular formula of the hydrocarbon is then found by the application of Avogadro Law.

Example 10. *10 mls. of a gaseous hydrocarbon was mixed with 100 mls. of oxygen and the mixture exploded in a eudiometer tube. The volume of the mixture after cooling was reduced to 90 mls. which upon treatment with potash solution was further reduced to 70 mls. Determine the molecular formula of the hydrogen.*

Volume of oxygen used $= 100 - 70 = 30$ mls.

,, ,, carbon dioxide formed $= 90 - 70 = 20$ mls.

If C_xH_y be the formula of the hydrocarbon,

$$C_xH_y + (x + y/4)O_2 = xCO_2 + y/2\ H_2O$$

Applying the converse of Avogadro Law,

$$1 \text{ ml. } C_xH_y + (x + y/4) \text{ mls. } O_2 = x \text{ mls. } CO_2 + y/2 \text{ mls. } H_2O$$

or $$10 \text{ mls. } C_xH_y + 10(x + y/4) \text{ mls. } O_2 = 10x \text{ mls. } CO_2 + 10y/2 \text{ mls. } H_2O$$

Thus $10(x + y/4) = 30$ and $10x = 20$

whence $x = 2$ and $y = 4$

Therefore, the molecular formula of the hydrocarbon is C_2H_4.

Alternative Solution :

Total oxygen used (for CO_2 and H_2O) $= 30$ mls.

$C + O_2 = CO_2$ $\quad \therefore$ 1 vol. $CO_2 = 1$ vol. O_2

Hence for 20 mls. CO_2 formed, volume of oxygen used $= 20$ mls.

$\therefore$ Volume of oxygen used for water alone $= 30 - 20 = 10$ mls.

$2H_2 + O_2 = 2H_2O$; $\quad$ 1 vol. $O_2 \equiv 2$ vol. H_2O

Hence for 10 mls. oxygen used, volume of water formed $= 20$ mls.

Now, 10 mls. hydrocarbon $+ 30$ mls. $O_2 + 20$ mls. $CO_2 + 20$ mls. H_2O

or 1 ml. ,, $+ 3$ mls. $O_2 = 2$ mls. $CO_2 + 2$ mls. H_2O

Applying Avogadro's Law, 1 molecule of hydrocarbon yields two molecules of CO_2 (containing two C atoms) and two molecules of H_2O (containing four H atoms). Hence the molecular formula of the hydrocarbon is C_2H_4.

III. DETERMINATION OF MOLECULAR WEIGHT

The **Molecular weight** of a compound is *the weight of one molecule of it as compared to the weight of an atom of hydrogen as 1.*

The methods commonly employed for the determination of molecular weights of organic substances are :

PHYSICAL	CHEMICAL
1. Victor Meyer method	1. Silver salt method for acids
2. Dumas method	2. Platinichloride method for bases
3. Hofmann method	3. Volumetric method for Acids and Bases
4. Freezing point and Boiling point method	

1. Physical Methods

VICTOR MEYER METHOD FOR VOLATILE SUBSTANCES

In this methode, a known weight of the substance is converted into vapour by dropping in a hot tube. The vapour displaces its own volume of air which is collected over water and its volume measured at the observed temperature and pressure.

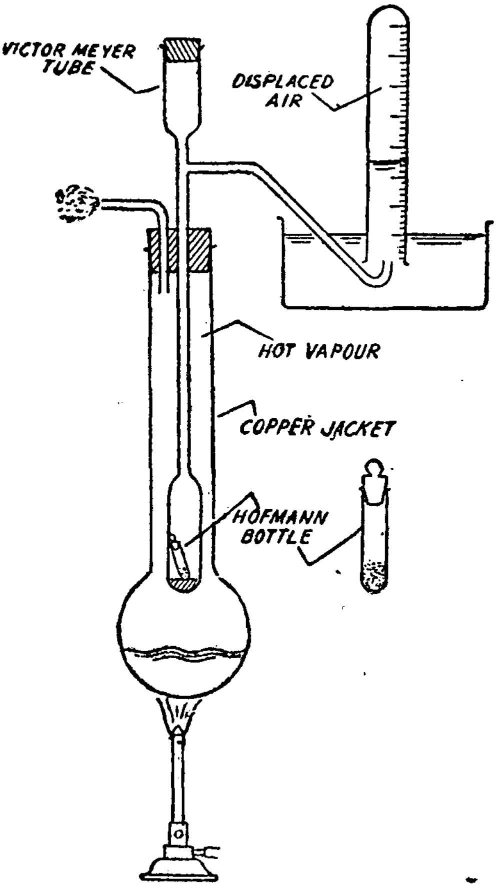
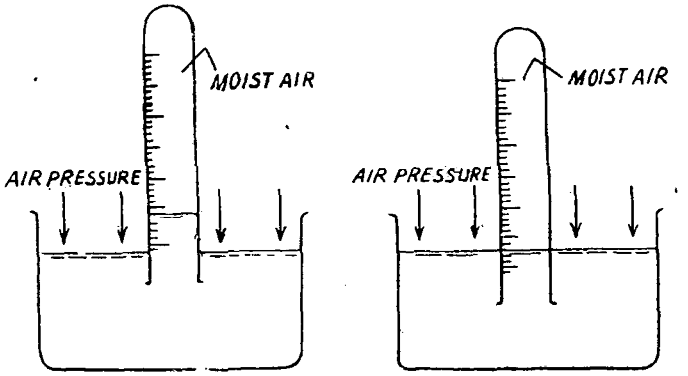


Fig. 4·2. Victor Meyer method for Mol. Wt. determination.

The apparatus used in this method consists of: (*i*) a *'Victor Meyer Tube'* of hard glass, having a side-tube leading to the arrangement for collection of displaced air over water, (*ii*) an *Outer Jacket* of copper, containing a liquid boiling about 30° higher than the substance whose molecular weight is to be determined, and (*iii*) a *'Tiny Stoppered Bottle'* (Hofmann bottle), in which the substance is weighed and introduced into the heated Victor Meyer tube.

Procedure. The apparatus is fitted up as shown in Fig. 4·2. The liquid in the copper jacket is boiled by heating it with a Bunsen burner, when the hot vapours of the liquid in turn heat the Victor Meyer tube. When no more air bubbles escape from the side-tube, a graduated tube filled with water is inverted over its end dipping in water. The Hofmann bottle containing a weighed quantity (0·1—0·2 gm.) of the substance and loosely stoppered, is then dropped into Victor Meyer tube opening its cork for a while. The substance at once converts into vapours which blow out the stopper and displace on equal volume of air from the upper part of the Victor Meyer tube. The volume of air collected in the graduated tube is read off after carefully levelling in a cylinder of water, and the atmospheric pressure and temperature recorded. The volume is reduced to

S.T.P. and the weight of 22·4 litres of vapour calculated. This is numerically equal to the molecular weight of the substance.



Before levelling *After levelling*

Fig. 4·3. After levelling the pressure of moist air collected is equal to the atmospheric pressure.

Example 1. *In a Victor Meyer determination of molecular weight 0·1 gm. of the substance displaced 27 mls. of moist air measured at 15°C and 745 mm. pressure. What is the molecular weight of the substance ? (Vapour tension of water at 15°C = 12·7 mm.)*

Volume of displaced air, $V_{15} = 27$ mls.

Atmospheric temperature $= 15°C$ or on absolute scale

$$T_{15} = 273 + 15 = 288°$$

Pressure of dry air, $P_{15} = 745 - 12·7 = 732·3$ mm.

$$\frac{P_N \times V_N}{T_N} = \frac{P_{15} \times V_{15}}{T_{15}} \quad \text{or} \quad V_N = \frac{P_{15} \times V_{15} \times T_N}{T_{15} \times P_N}$$

Hence, volume of displaced air at N.T.P. $= \dfrac{732·3 \times 27 \times 273}{288 \times 760}$

$= 24·67$ mls.

Thus the weight of 24·67 mls. of vapour of the substance = 0·1 gm.

" " 22400 " " " $= \dfrac{0·1 \times 22400}{24·67}$

$= 90·80$ (mol. wt.)

Example 2. *0·22 gm. of a substance when vaporised by Victor Meyer's method displaced 45·0 mls. of air measured over water at 20°C and 755 mm. pressure. Calculate the molecular weight of the substance. (Vapour pressure of water at 20°C is 17·4 mm.)*

(*i*) CALCULATION OF VOLUME AT N.T.P.

Initial Conditions		*Final Conditions*	
Volume	$(V_1) = 45$ mls.	Volume	$= V_2$
Pressure	$(P_1) = 755 - 17·4$ $= 737·6$ mm.	Pressure	$= 760$ mm.
Temperature	$(T_1) = 20 + 273$ $= 293°$A.	Temperature	$= 273°$A

Applying the General Gas Equation

$$\frac{760 \times V_2}{273} = \frac{45 \times 737 \cdot 6}{293}$$

$$\therefore \quad V_2 = \frac{45 \times 737 \cdot 6}{293} \times \frac{273}{760}$$

$$= 40 \cdot 70 \text{ mls.}$$

(*ii*) CALCULATION OF M. WT.

Wt. of 40·7 mls. of vapours at N.T.P. = 0·22 gm.

$\therefore$ Wt. of 22400 mls. of vapours at N.T.P.

$$= \frac{0 \cdot 22}{40 \cdot 7} \times 22400 = 121 \cdot 1$$

Thus the molecular weight of the substance

$$= 121 \cdot 1.$$

Dumas Method. This is based on the principle of weighing a known volume of the vapour of the substance in a glass bulb at an elevated temperature. The calculation of the molecular weight is done as in Victor Meyer method.

Hofmann Method. This method is suitable for determining molecular weight of substances at their boiling point under atmospheric pressure.

A known weight of the substance is vaporised above a mercury column in a barometric tube and the volume of the vapour formed noted. The molecular weight of substance is then calculated as described under Victor Meyer method.

CRYOSCOPIC METHOD OR FREEZING POINT METHOD

The molecular weight of a non-volatile organic compound can be easily determined by noting the depression of freezing point of a solvent produced by dissolving a definite weight of the substance in a known weight of solvent.

$$m = \frac{100Kw}{\Delta TW}$$

m = molecular weight of the dissolved compound,
K = molecular depression constant,
w = weight of dissolved compound, and
ΔT = depression of freezing point.

The **Molecular depression constant** or the **Freezing point constant** is defined as the depression of freezing point which would be produced by dissolving one gram-molecule of the solute in 100 grams of the solvent. Its value is usually given in ready-reference tables.

VALUES OF K FOR SOME SOLVENTS

Water	18·6°C	Acetic acid	38·2°C
Benzene	51·2°C	Phenol	73°C

Determination of Depression of Freezing point. The apparatus which is almost exclusively employed for the determination of the lowering of freezing point was designed by Beckmann (Fig. 4·4). It consists of (*i*) the *inner freezing point tube* provided with a side-tube for introducing the solute and fitted with Beckmann thermometer reading up to ·01°C and a platinum stirrer ; (*ii*) the *outer air-jacket* surrounding the inner tube which ensures a slower and more uniform rate of cooling of the liquid ; (*iii*) a stout *glass cylinder* which contains freezing mixture and is also provided with a stirrer.

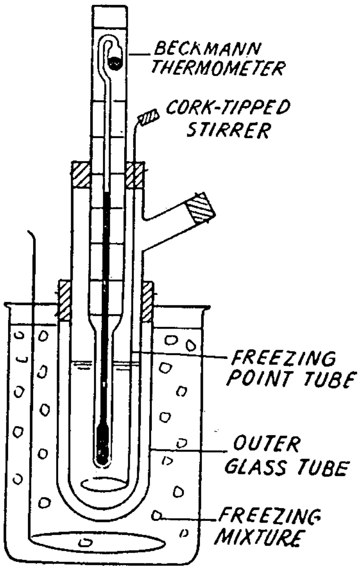


Fig. 4·4. Determination of depression of freezing point.

In an actual determination 15·20 grams of the solvent is taken in the inner freezing point tube and the apparatus set up as shown in the diagram. The solvent is gently stirred and the mercury thread of the thermometer watched carefully. The temperature first falls below the freezing point of the solvent but later as it begins to solidify, it rises rapidly owing to the latent heat set free, and finally remains steady at the true freezing point.

The freezing point of the solvent having been accurately determined, the solvent is remelted by removing the tube from the bath, and a weighed amount (0·1–0·2 gm.) of the solute is introduced through the side-tube. Now the freezing point of the solution is determined in the same way as that of the solvent alone. A further quantity of the solute may then be added and another reading taken. Knowing the depression of the freezing point produced, the molecular weight of the solute can be calculated.

Example 1. *0·512 gram of an organic substance when dissolved in 25 grams of water lowered its freezing point by 0·19°C. Calculate the molecular weight of substance. (Molecular depression constant for water is 18·5).*

Substituting the values in the expression

$$m=\frac{100\mathrm{K}w}{\Delta \mathrm{TW}}$$

$$=\frac{100\times 18{\cdot}5\times 0{\cdot}512}{0{\cdot}19\times 25}={}'99{\cdot}5$$

Example 2. *1·355 gms. of a substance dissolved in 55 gms. of acetic acid produced depression of 0·618°C in the freezing point. Calculate the molecular weight of the dissolved substance. The molecular depression of the freezing point of acetic acid (100 gms.) is 38·5°C.*

Depression of freezing point = 0·618°
Weight of solute = 1·355 gms.
Weight of solvent = 55 gms.

Substituting the values in the expression

$$m=\frac{100Kw}{\triangle TW}$$

$$=\frac{100\times 38{\cdot}5\times 1{\cdot}355}{0{\cdot}618\times 55}=153{\cdot}5.$$

EBULLIOSCOPIC METHOD OR BOILING POINT METHOD

The molecular weight of a non-volatile organic compound can also be determined by noting the elevation of boiling point produced by dissolving a definite weight of it in a known weight of the solvent.

$$m=\frac{100Kw}{\triangle TW}$$

m=Molecular weight of the dissolved compound,
K=Molecular elevation constant,
w=Weight of dissolved substance,
W=Weight of solvent,
T=Elevation of boiling point.

The **Molecular elevation constant** or the **Boiling point constant** is defined as the elevation of the boiling point which would be produced by dissolving one gram-molecule of the solute in 100 grams of the solvent. Its value is generally given in ready-reference tables.

VALUES OF K FOR SOME SOLVENTS

Water	5·2°C	Benzene	26·7°C
Ethyl alcohol	11·5°C	Ether	21·0°C
Acetone	16·7°C	Acetic acid	25·3°C

Determination of Elevation of boiling point. The apparatus now commonly used for the determination of the elevation of boiling point was designed by Landsberger. It consists of : (*i*) *a boiling flask* which sends vapours of the solvent into the inner tube ; (*ii*) an *inner boiling tube* which has a bulb with a hole in the side, and is graduated in mls. It is fitted with a thermometer reading up to ·01°C and a glass tube having a rose-head at the lower end. The rose-head ensures uniform distribution of the vapours through the solvent. The bulb reflects back any particles of the solvent which happen to fly about when the boiling becomes brisk ; (*iii*) *an outer covering tube* which receives hot vapours from the inner tube through the hole H. This forms a

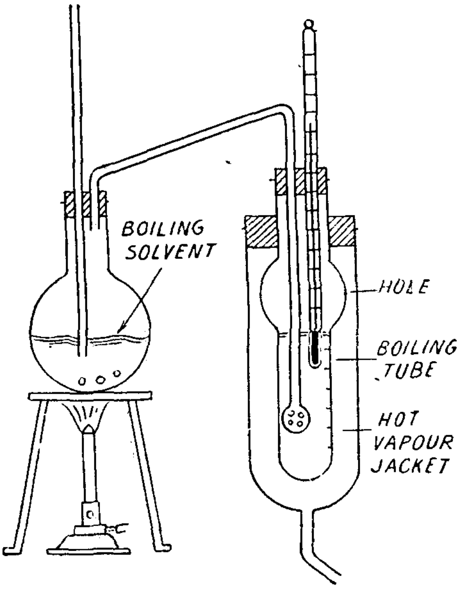


Fig. 4·5. Determination of elevation of boiling point by Landsberger's method.

protecting jacket round the boiling-tube and prevents the loss of heat due to radiation.

In an actual determination 5·7 mls. of solvent are placed in the inner tube and the vapours of the solvent passed through it. At the start the solvent vapours condense and as more vapours are passed the liquid begins to boil. As soon as the temperature has become steady, the temperature is read on the thermometer This is the boiling point of the pure solvent. Now the supply of solvent vapours is cut off for a while and a weighed quantity (0·2—0·5 gram) of the substance whose molecular weight is to be determined is dropped into the solvent in the boiling tube. The boiling point of the solution is then determined as before. Immediately after reading the temperature, the thermometer and the rose-head are carefully raised out of the solution and the volume of the solution noted. The weight of the solvent can be found by multiplying its volume with density.

Example 1. *The boiling point of pure acetone is 56·38°C at normal pressure. A solution of 0·717 gram of a compound in 10 grams of acetone boiled at 56·88°C. What is the molecular weight of the compound ? The molecular elevation constant for acetone is 16·7°.*

Elevation in boiling point$=56{\cdot}88-56{\cdot}38$

$=0{\cdot}50°$.

Substituting the given values in the expression

$$m=\frac{100Kw}{\Delta TW}$$

we have

$$m=\frac{100\times16{\cdot}7\times0{\cdot}717}{0{\cdot}50\times10}$$

$$=239{\cdot}4$$

Example 2. *A solution made by dissolving 1·5126 gms. of a substance in 21·01 gms. of benzene has a boiling point 1·05°C higher than the boiling point of pure benzene. Find the molecular weight of the substance.*

Molecular elevation of boiling point of 100 gms. benzene is 25·70.

Elevation of boiling point$=1{\cdot}05°C$

Substituting the given values in the expression

$$m=\frac{100Kw}{\Delta TW}$$

$$=\frac{100\times25{\cdot}7\times1{\cdot}5126}{1{\cdot}05\times21{\cdot}01}$$

$$=176{\cdot}2.$$

II. CHEMICAL METHODS

SILVER SALT METHOD FOR ACIDS

This method of determining molecular weights of organic acids is based on the fact that they form insoluble silver salts which upon heating decompose to leave a residue of metallic silver.

Procedure. A small quantity of the unknown acid is dissolved in water and treated with a slight excess of ammonium hydroxide.

The excess of ammonia is then boiled off, To this is added sufficient quantity of silver nitrate, when a white precipitate of silver salt is obtained. The precipitate is separated by filtration, washed successively with water, alcohol and ether and dried in the steam oven. About 0·2 gm. of the dry silver salt is weighed into a crucible and ignited until all decomposition is complete. Ignition is repeated till the crucible with the residue of silver has attained constant weight. The molecular weight of the acid is then calculated from the weight of the silver salt taken and the weight of the residue of metallic silver obtained from it.

Calculations. Let the weight of the silver salt taken be x gms. and the weight of the residue of metallic silver be a gms.

The weight of silver salt that would leave 108 gms. (equivalent weight of the silver) of residue $= \frac{x}{a} \times 108$ and this is the equivalent weight of the silver salt of the acid.

But Eq. Wt. of acid = Eq. Wt. of the silver salt — Eq. Wt. of silver + Eq. Wt. of Hydrogen

$$= \frac{x}{a} \times 108 - 108 + 1$$

$$= \frac{x}{a} \times 108 - 107$$

Molecular weight of the acid

$$= \text{Eq. Wt.} \times \text{Basicity}$$

$$= \left(\frac{x}{a} \times 108 - 107\right) \times n.$$

Example 3. *0·759 gm. of the silver salt of a dibasic organic acid was ignited, when a residue of 0·463 gm. of metallic silver was left. Calculate the molecular weight of the acid.*

Weight of silver salt taken = 0·759 gm.

Weight of silver left as residue = 0·463 gm.

∴ The weight of silver salt that would leave 108 gms. of silver

$$= \frac{0·759}{0·463} \times 108 = 177·05$$

and this is the equivalent weight of silver salt.

Now, the equivalent weight of the acid

$$= 177·05 - 108 + 1 = 70·05$$

∴ Molecular weight of the acid

$$= 70·05 \times 2 \text{ (basicity)}$$

$$= 140·1.$$

Example 4. *When heated cautiously in a crucible, 0·3652 gram of silver benzoate gave 0·1720 gram silver. Find the molecular weight of benzoic acid.*

The weight of silver benzoate that would leave 108 gms. of silver

$$= \frac{0·3652}{0·1720} \times 108$$

$$= 229·2 \text{ gms.}$$

∴ Equivalent weight of benzoic acid

$$= 229·2 - 108 + 1 = 122·2$$

Since benzoic acid is a monobasic acid, its molecular weight

$$=122{\cdot}2\times1=122{\cdot}2$$

PLATINICHLORIDE METHOD FOR BASES

Most organic bases (amines) combine with hydrochloro-platinic acid, H_2PtCl_6, to form insoluble salts known as *platinichlorides.* These double salts may be represented by the general formula $B_2H_2PtCl_6$, where B stands for one equivalent of the base. Platinichlorides on ignition decomposes to leave a residue of platinum.

$$B_2H_2PtCl_6 \longrightarrow Pt$$

Knowing the weights of the platinichloride taken and the platinum left behind, the molecular weight of the base can be calculated.

Let x gms. be the weight of the platinichloride taken and a gms. of the platinum residue after ignition.

(1) Since one molecule of the platinichloride of the base, $B_2H_2PtCl_6$, contains one atom of platinum (atomic weight = 195), 195 gms. of platinum will be left by 1 gm. molecular weight of the platinichloride.

But a gms. of platinum is left by x gms. platinichloride

$\therefore$ 195 gms. „ „ „ $\frac{x}{a}\times195$ gms. „

Hence Mol. Wt. of platinichloride

$$=\frac{x}{a}\times195$$

(2) The equivalent weight of the base, B

$$=\frac{B_2H_2PtCl_6-H_2PtCl_6}{2}$$

$$=\frac{\text{M.Wt. of platinichloride}-410}{2}$$

$$=\frac{\frac{x}{a}\times195-410}{2}$$

(3) If the acidity of the base is n, the Mol. Wt. of the base

$$=\left(\frac{x}{a}\times195-410\right)\frac{n}{2}.$$

Example 5. *0·6387 gm. of the platinichloride of a monoacid base on ignition gave 0·209 gm. of platinum. Find the molecular weight of the base. (Pt=195).*

(i) 0·209 gm. platinum is left by 0·6387 gm. of platinichloride

$\therefore$ 195 gms. „ „ „ $\frac{0{\cdot}6387}{0{\cdot}209}\times195$ gms. „

Hence Mol. Wt. of the platinichloride $=\frac{0{\cdot}6387}{0{\cdot}209}\times195=596{\cdot}0$

(*i*) $\text{Eq. Wt. of base} = \dfrac{\text{Mt. Wt. of platinichloride} - 410}{2}$

$$= \frac{596 - 410}{2} = 93{\cdot}0$$

(*ii*) $\text{Mol. Wt. of base} = \text{Eq. Wt.} \times \text{Acidity}$

$$= 93{\cdot}0 \times 1 = 93{\cdot}0$$

Example 6. *0·98 gm. of the platinichloride of a diacid base left on ignition 0·3585 gm. of platinum. Find the molecular weight of the base.*

(*i*) 0·3585 gm. Pt is left by 0·98 gm. platinichloride

195 gms. „ „ „ $\dfrac{0{\cdot}98}{0{\cdot}3585} \times 195$ gms. „

$\therefore$ M. Wt. of platinichloride $= \dfrac{0{\cdot}98}{0{\cdot}3585} \times 195 = 533$

(*ii*) $\text{Eq. Wt. of base} = \dfrac{\text{M. Wt. of platinichloride} - 410}{2}$

$$= \frac{533 - 410}{2} = \frac{123}{2}.$$

(*iii*) $\text{M. Wt. of base} = \text{Eq. Wt.} \times \text{Acidity}$

$$= 123/2 \times 2 = 123.$$

VOLUMETRIC METHOD FOR ACIDS AND BASES

The molecular weight of an acid can be determined by dissolving a known weight of it (x gms.) in water and titrating the solution against standard alkali solution (say N/10) using phenolphthalein as indicator.

Suppose V mls. of N/10 alkali neutralise x gms. acid

$\therefore$ 1000 mls. „ 1N „ „ $\dfrac{x}{\text{V}} \times 1000 \times 10$ gms. acid

Since acids and bases neutralise each other in equivalent proportions, and 1000 mls. of 1 N alkali contain one gram equivalent of it.

the $\text{Eq. Wt. of acid} = \dfrac{a}{\text{V}} \times 1000 \times 10$

and $\text{Mol. Wt. of acid} = \text{Eq. Wt.} \times \text{Basicity}$.

The molecular weight of a base may also be determined exactly as above by titrating a known weight of it against a standard acid and applying the relationship :

$$\text{Mol. Wt.} = \text{Eq. Wt.} \times \text{Acidity}$$

Example 7 *0·183 gm. of an aromatic monobasic acid required 15 mls. of N/10 sodium hydroxide solution for exact neutralisation. Calculate the molecular weight of the acid.*

15 mls. N/10 NaOH solution $\equiv 0{\cdot}183$ gm. acid

1000 mls. 1 N NaOH solution $\equiv 0{\cdot}183 \times \dfrac{1000}{15} \times 10$ gms. acid.

But 1000 mls. of 1 N sodium hydroxide contain 1 gm. equivalent of it and will neutralise 1 gm. equivalent weight of acid.

$\therefore$ Eq. Wt. of acid $= 0{\cdot}183 \times \dfrac{1000}{15} \times 10$

$$= 122.$$

Mol. Wt. of solid $=$ Eq. Wt. $\times$ Basicity
$=122 \times 1=122$.

Example 8. *0·25 gm. of a dibasic organic acid were dissolved in water and the volume made to 100 mls. 10 mls. of this solution required 12·3 mls. of N/30 sodium hydroxide solution for complex neutralisation. Find the molecular weight of the acid.*

12·3 mls. N/30 NaOH solution $\equiv$ 10 mls. of acid
123 mls. N/30 NaOH solution $\equiv$ 100 mls. of acid
$\equiv$ 0·25 gm. acid
1000 mls. 1 N NaOH solution $\equiv \frac{0·25}{123} \times 1000 \times 30$ gms.
∴ Eq. Wt. of acid $= \frac{0·25}{123} \times 1000 \times 30 = 61·0$
Mol. Wt. of acid $=$ Eq. Wt. $\times$ Basicity
$= 60·96 \times 2 \times 121·92$.

Example 9. *0·20 gm. of a diacid base required 25 mls. of N/8 HCl for exact neutralisation. What is the molecular weight of the base ?*

25 mls. of N/8 HCl $\equiv$ 0·20 gm. of the base
1000 mls. of N HCl $\equiv \frac{0·20}{25} \times 1000 \times 8$ gms. of base

But 1000 mls. of N HCl contain 1 gm. equivalent of acid and will neutralise 1 gm. equivalent of the base.

∴ Eq. Wt. of base $= \frac{0·20}{25} \times 1000 \times 8$
$=64$
Mol. Wt. of base $=$ Eq. Wt, $\times$ Acidity
$=64 \times 2=128$.

QUESTIONS

1. On analysis an organic compound was found to contain C=43·98%, Cl=37·18%, H=2·09%. Calculate the empirical formula. Given that the compound is a monobasic acid, write the molecular formula.

2. The organic liquids each containing 54·5 per cent carbon and 9·0 per cent hydrogen and having vapour density 44 gives different results on hydrolysis. One of them yields methyl alcohol and the other ethyl alcohol ; while the saline residue in the former case on acidification yields propionic acid and in the latter acetic acid. Establish the identity of the two.

3. An organic substance *A* gave the following analysis : 0·123 gm. gave 0·234 gm. of carbon dioxide and 0·045 gm. of water.

0·1845 gm. of it gave 16·8 c.c. of nitrogen at N.T.P.

When it was treated with tin and hydrochloric acid it gave a substance *B* containing 77·41% carbon, 7·63% hydrogen and 15·05% nitrogen.

The substance *B* when diazotised and heated in presence of water gave a compound *C* which on distillation with zinc dust gave benzene.

Assign structural formulae to *A*, *B* and *C*.

4. An organic compound contains 81·55 per cent carbon, 4·8 per cent hydrogen and 13·6 per cent nitrogen and has the vapour density 51·5. It evolves ammonia when heated with caustic potash and on reduction with sodium and

alcohol forms a base which reacts with nitrous acid giving off nitrogen and yielding alcohol. The alcohol can be oxidised to benzoic acid. What is the original substance and how is it prepared ? Explain the above changes.

5. An aromatic dibasic acid gave the following results on analysis : —

(*i*) 0·249 gm. of the dibasic acid gave on combustion 0·528 gm. carbon dioxide and 0·081 gm. water.

(*ii*) 1·9 gms. of the silver salt of the dibasic acid gave 1·08 gms. of silver on ignition.

(*iii*) On nitration, the acid gave only one mono-nitro derivative. Assign structural formula to the acid and describe one method of preparing it.

(H=1 ; C=12 ; O=16 ; Ag=108).

6. An organic compound X gave the following results on analysis : C, 16·27% ; H, 0·68% ; O, 10·83% and Cl, 72·20%. It reduced Fehling's solution and the vapour density was found to be 73·8. On heating with alkali it gave a pleasant smelling liquid Y.

X could also be prepared by the action of chlorine on ethyl alcohol.

What is the nature of the compound X and what is the liquid Y ?

7. An organic compound (A) has the molecular formula $C_7H_5NO_4$. Tin and HCl reduce it to a compound (B) having the formula $C_7H_7NO_2$. The compound (B) on boiling with $NaNO_2$ and HCl gives a compound (C) with molecular formula $C_7H_6O_3$. The compound (C) gives the following reactions :

(*a*) It is acidic and evolves CO_2 with $NaHCO_3$. (*b*) Ferric chloride gives a deep violet colour. (*c*) On heating with soda lime, it loses CO_2 and gives phenol.

Assign structures to A, B and C, and explain all the reactions.

(*Agra B.Sc. II, 1967*)

8. An organic compound (A) containing 76·6% C and 6·38% H, gave a mixture of two isomers (B) and (C) ; when an alkaline solution of (A) was refluxed with chloroform at 60°C. B, being steam volatile, was separated by steam distillation. B, on oxidation gave an acid (D) containing 60·87% C and 4·34% H. The (D) acid was also obtained by heating sodium salt of (A) with CO_2 at 120—140°C under pressure. Assign structures to A, B, C and D and explain the reaction involved. (*Banaras B.Sc. II, 1967*)

9. An organic compound (A), containing 40% of C, 6·67% of hydrogen and vapour density 15, restored the colour of Schiff's reagent. On treatment with caustic potash, it gave an alcohol (B) that could be obtained by the reduction of (A) and an acid (C) which could be obtained by the oxidation of (A). What was the compound (A) ? Explain these reactions.

(*Gorakhpur B.Sc., 1967*)

10. A neutral organic compound (X) contains C=65·3%, H=3·4% and N=9·5%. On heating with sodalime, it evolved ammonia but does not undergo diazotisation or react with acetyl chloride. On reaction with sodium hypobromite it gave an acid (Y) $C_7H_7O_2N$ which dissolves in acids as well as in alkalies. What are compounds (X) and (Y) and explain the reactions involved ? Give one method for the preparation of the compound (X).

(*Allahabad B.Sc. II, 1967*)

11. An organic compound containing 58·53% carbon, 4·065% hydrogen and 11·39% nitrogen, gave on reduction a product which on subsequent acetylation formed acetamide. Assign the structural formula to the compound and explain the reactions involved. (*Agra B.Sc. III, 1967*)

12. (*i*) 0·2905 gm. of a solid organic acid on combustion gave 0·6160 gm. of CO_2 and 0·0945 gm. of H_2O. (*ii*) On heating with sodalime, its sodium salt gave benzene. (*iii*) It forms two series of salts and two series of esters and (*iv*) It furnishes an anhydride on simple heating. From the above facts about the acid, find out its structural formula and explain the reactions.

(*Agra B.Sc. III, 1967*)

13. An aromatic organic compound containing 58·53% of carbon, 4·07% of hydrogen, 11·39% of nitrogen and 26·01% of oxygen was found to have a molecular weight 123. On reduction it gave a monoacid organic base. What structural formula would you assign to it ? *(Indore B.Sc. III, 1967)*

14. An organic compound A on analysis was found to contain C=16·271%, H=0·677% and Cl=72·203%. It reduced Fehling's solution and on oxidation gave a monocarboxylic acid B having C=14·679, H=0·612 and Cl=65·137. On distillation with sodalime, B gave a sweet smelling liquid C containing 89·12% chlorine and which can also be obtained by heating A with alkali. What structural formulae would you assign to A, B and C ? Explain the above reactions. *(Udaipur B.Sc., 1968)*

15. An aromatic substance A contains 77·8% carbon and 7·4% hydrogen and forms an ester 'B' with acetyl chloride. 'A' on treatment with phosphorus pentachloride gives a product 'C' containing 28·0% chlorine. On oxidation with nitric acid 'A' gives a monocarboxylic acid 'D'. Explain the above reactions and suggest suitable structures for A, B, C and D. *(Osmania B.Sc., 1960)*

16. A compound, $C_6H_{12}O$ (A), reacted with hydroxylamine but not with Fehling's solution. On catalytic hydrogenation A gave $C_6H_{14}O$ (B). The compound B when passed over hot alumina, yielded C_6H_{12} (C). The compound C on ozonolysis furnished two compounds. One of which gave a negative Tollen's test and a positive Iodoform test. The other gave a positive Tollen's test and a negative Iodoform reaction. Suggest structures for the compounds A, B and C. *(Jadavpur B.Sc., 1968)*

17. A compound on analysis, is found to possess the following percentage composition :

C=66·4, H=5·53 and Cl=28·06

When the compound is oxidised with potassium permanganate an acid is obtained which contains 68·8% carbon and 4·9% hydrogen. In another experiment when the compound is treated with sodium hydroxide a new compound is produced which contains 77·8% carbon and 7·4% hydrogen.

Explain these reactions and determine the structural formula of the compound. *(Ujjain B.Sc., 1968)*

18. 0·106 gm. of an aromatic hydrocarbon of mol. wt. 106 gave on combustion 0·352 gm. CO_2 and 0·090 gm. H_2O. Calculate the molecular formula and write all the possible structures. Discuss how you would distinguish between them. *(Kurukshetra B.Sc., 1968)*

19. An organic compound containing 65·45 per cent of carbon, 9·09 per cent of hydrogen and the rest nitrogen was found to have vapour density 27·5. On boiling with dilute sulphuric acid it gave a monobasic organic acid which on distillation with soda lime gave ethane. But on treatment with tin and hydrochloric acid it gave a monoacid base which gave propyl alcohol with nitrous acid. What is the formula of the compound ? Explain these reactions.

20. How is chlorine in an organic compound detected and estimated ?

Two different volatile substances gave the following identical results on analysis C=52·2%, H=13·0% and the rest is oxygen. The vapour density of both the compounds was the same and found to be 23. Assign the structural formulae to the two substances and describe the action of boiling HI on each of them. *(Bangalore B.Sc., 1969)*

21. How is nitrogen detected in an organic compound ? 2·0 gm. of an organic compound containing C, H and O gave on combustion 2·93 gm. of CO_2 and 1·2 gm. of water ? Its molecular weight is 180. What is its molecular formula ? *(Bangalore B.Sc., 1969)*

22. A hydrocarbon (A) of formula $C_{15}H_{14}$ takes up readily one mole of hydrogen or one mole of Bromine. Oxidation converts it into benzoic acid and other acid (B) of molecular formula $C_8H_8O_2$ More vigorous oxidation of hydrocarbon (A) gives benzoic acid and phthalic acid. What is the structure of hydrocarbon (A) and the acid (B) ? Write their names. *(Udaipur B.Sc., 1969)*

23. The organic compounds A and B contain C=40% and hydrogen=6·66%. The vapour density of A was 15 and that of B was 30. A reduced

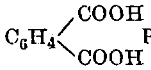
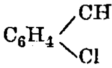
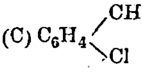
Fehling's solution but did not react with sodium carbonate, while B did not reduce Fehling solution but produced effervescence with sodium carbonate. Deduce the structural formulae of A and B and explain the above reactions. (*Udaipur B.Sc., 1969*)

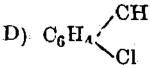
24. An organic compound gave the following results on analysis. 0·2115 gm. on combustion gave 0·4655 gm. CO_2 and 0·2533 gm. water. The vapour density of the substance was 29·7. When treated with potassium dichromate and dilute H_2SO_4 it produced a substance which gave the Iodoform test. What was the original compound. (*Panjab B.Sc., 1969*)

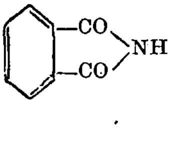
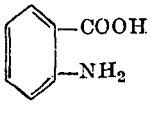
25. A dibasic organic acid (A) contains C=41·38% and H=3·45%. It reacts with bromine and gives a bromoacid (B) containing Bromine=57·9%. Suggest structural formulae for the acids (A) and (B). (*Kurukshetra B.Sc., 1969*)

26. A primary alcohol with a vapour density 29 contained C=62·1%, H=10·3% and reacted with bromine to give a derivative which contained carbon=16·5, H=2·7 and Br=73·4%. Determine the structural formula of the compound and its derivative. (*Meerut B.Sc., 1969*)

ANSWERS

1. $C_6H_3Cl_2COOH$.
2. $C_2H_5COOCH_3$, methyl propionate ; $CH_3COOC_2H_5$, ethyl acetate.
3. A=$C_6H_5NO_2$, B=$C_6H_5NH_2$, C=C_6H_5OH.
4. C_6H_5CN.
5.  $C_6H_4(COOH)_2$ Phthalic acid
7. (A) $C_6H_5CH_3$; (B)  $C_6H_4(CH_3)(Cl)$ ortho ; (C)  $C_6H_4(CH_3)(Cl)$ meta ;

(D)  $C_6H_4(CH_3)(Cl)$ para.

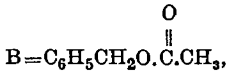
8 C_3H_5N ; $C_3H_6O_2$.
9. HOOCHC=CHCOOH ; A=maleic acid and B=fumaric acid.
10. $C_6H_4(CH_3).COOH$ ortho-toluic acid.
11. (A) HCHO ; (B) CH_3COOH_4.
12. C_2H_5COOH.
13. (A) CCl_3CHO ; (B) CCl_3COOH ; CCl_3H.
14. $C_3H_5COONH_4$.
15. C_3H_6O.
16. A=C_8H_6 ; B=$C_7H_6O_2$; C=$C_8H_6Cl_2$
17. $CH_3CH_2CONH_2$.
18. $C_6H_4Cl_2$.
19. $C_6H_4(CH_3)_2$.
20. $C_2H_4Cl_2$.
21. CH_3CONH_2.
22. (A) $C_6H_4(COOH)_2$ Phthalic acid ;
 (B) $C_6H_4(CO)_2O$ Phthalic anhydride ;
 (C) $C_6H_4(CO)_2NH$ Phthalimide ;
 (D) $C_6H_4(NH_2)COONa$ sod. o-aminobenzoate.
23. 93·07 ; aniline.
24. $CH_3CH_2NH_2$.
7. (A) $C_6H_4(NO_2)COOH$; (B) $C_6H_4(NH_2)COOH$;
 (C) $C_6H_4(OH)COOH$.
8 (A) C_6H_5OH ; (B) $C_6H_4(OH)$ CHO, ortho ;
 (C) $C_6H_4(OH)CHO$, para ; (D) $C_6H_4(OH)COOH$, ortho ;
9 (A) HCHO ; (B) CH_3OH ; (C) HCOOH.
10. (*x*)  ; (*y*) 

11. $C_6H_5NO_2$ and $C_6H_5NH_2$.

12. $C_5H_6O_2$. 13. $C_6H_5NO_2$.

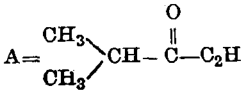
14. A=CCl_3CHO, B=CCl_3COOH and C=$CHCl_3$.

15. A=$C_6H_5CH_2OH$, B=

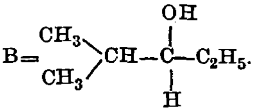


$C_6H_5CH_2O.\overset{\overset{O}{\|}}{C}.CH_3$, C=$C_6H_5CH_2Cl$ and D=C_6H_5COOH

16. A=

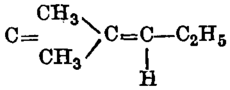


$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!CH-\overset{\overset{O}{\|}}{C}-C_2H_5$, B=



$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!CH-\underset{\underset{H}{|}}{\overset{\overset{OH}{|}}{C}}-C_2H_5$.

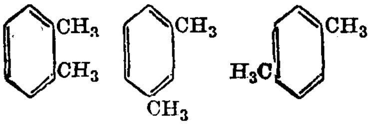
and C=



$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!C=\underset{\underset{H}{|}}{C}-C_2H_5$

17. $C_6H_5CH_2Cl$.

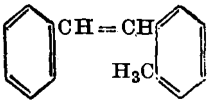
18. C_8H_{10} ;



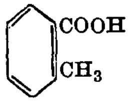
19. C_2H_5CN.

20. C_2H_5OH ; CH_3OCH_3. 21. $C_6H_{12}O_6$.

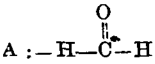
22. A :—



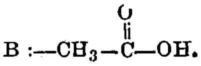
; B :—



23. A :—



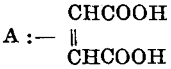
$H-\overset{\overset{O}{\|}}{C}-H$; B :—



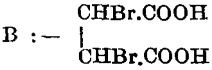
$CH_3-\overset{\overset{O}{\|}}{C}-OH$.

24. $C_2H_5OCH_3$.

25. A :—



$\begin{matrix}CHCOOH\\\|\\CHCOOH\end{matrix}$; B :—



$\begin{matrix}CHBr.COOH\\|\\CHBr.COOH\end{matrix}$

26. $CH_2=CH-CH_2OH$; $CH_2Br.CHBr.CH_2OH$.

5

Structure of Organic Molecules. Classical Concept

Joseph A. Le Bel

ATOMIC STRUCTURE AND VALENCY

The views on the atomic structure which are accepted today have developed from the classical Rutherford Bohr Theory. According to this theory, the atom is made of a central positively charged **nucleus** containing positively charged particles called **protons**, and neutral particles called **neutrons**, both having unit mass. The nucleus is surrounded by negatively charged particles called **electrons** which carry one unit negative charge and negligible weight. The number of potons and electrons in an atom being equal, it is electrically neutral.

The extra nuclear electrons are said to revolve round the nucleus in fixed orbits or 'energy levels'. While the electron moves in such a level, it possesses a definite quantity of energy and it neither emits nor absorbs energy. The electrons are arranged in the outer orbits so that the maximum number of electrons in the various orbits starting from the first one is 2, 8, 18, 32, 18, 8. The outermost orbit of electrons in different atoms (except those of inert gases) is incomplete and the electrons in it are known as **valency electrons.**

HOW ATOMS JOIN TO FORM MOLECULES ?

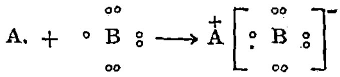
The classical concept of formation of molecules, proposed by **Lewis and Kossel**, is based upon the electronic structure of atoms. The atoms of inert gases have either *two* (*helium*) or *eight electrons* in the outermost orbit. These gases do not enter into chemical combination and, therefore, they are assumed to have complete or stable orbits. The atoms of all other elements have incomplete last orbits and tend to complete them by chemical combination with other atoms. G.N. Lewis proposed that *it is the urge of atoms to complete their outermost orbits of electrons as in the inert gases, which is responsible for chemical combination.* In other words, chemical union between two atoms results from the redistribution of electrons between them so that both the atoms complete their last orbits or acquire stable configuration possessed by the inert gases. The chemical linkages are of three types :

(*i*) *Electrovalent Linkage ;*

(*ii*) *Covalent Linkage , and*

(*iii*) *Co-ordinate Linkage.*

Electrovalent Linkage. The type of linkage unites two atoms one of which has excess electrons than the stable number (2 or 8), and the other is short of electrons. Thus :

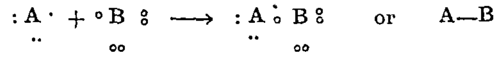


$$\mathrm{A}\cdot + \circ\overset{\circ\circ}{\underset{\circ\circ}{\mathrm{B}}}\,\overset{\circ}{\circ} \longrightarrow \overset{+}{\mathrm{A}}\left[\overset{\circ}{\cdot}\,\overset{\circ\circ}{\underset{\circ\circ}{\mathrm{B}}}\,\overset{\circ}{\circ}\right]^{-}$$

Here, the atom A transfers its excess electron to B, and thus both complete their last orbit of electrons. The atoms A and B become positive and negative respectively, and are thus bound by electrostatic lines of force. This type of linkage occurs commonly in inorganic compounds.

Electrovalent compounds are non-volatile, soluble in water and possess high melting points. Their aqueous solutions conduct electric current.

Covalent Linkage. This type of linkage binds two atoms, both of which are short of electrons. The two atoms contribute one electron each and then share the resulting pair of electrons.

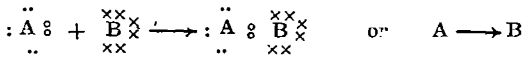


$$:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{A}}}\cdot + \circ\overset{\circ\circ}{\underset{\circ\circ}{\mathrm{B}}}\,\overset{\circ}{\circ} \longrightarrow\ :\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{A}}}\overset{\cdot}{\circ}\overset{\circ\circ}{\underset{\circ\circ}{\mathrm{B}}}\,\overset{\circ}{\circ} \quad \text{or} \quad \mathrm{A{—}B}$$

This linkage, signified by a single line, is termed **Covalent Linkage** (*Co-joint*). It is commonly found in organic compounds.

Covalent compounds are volatile, generally insoluble in water but soluble in organic solvents, and possess low melting and boiling points. Their solutions do not conduct electric current.

Co-ordinate Linkage. A co-ordinate linkage connects two atoms, one of which has a spare pair of electrons and the other is short of a pair of electrons. The first atom (*donor atom*) contributes its pair (*lone pair*) of electrons and the second atom (*acceptor atom*) accepts.



$$:\overset{\cdot\cdot}{\underset{\cdot\cdot}{A}}\overset{\circ}{\circ} + \overset{\times\times}{\underset{\times\times}{B}}\overset{\times}{\times} \longrightarrow :\overset{\cdot\cdot}{\underset{\cdot\cdot}{A}}\overset{\circ}{\circ}\overset{\times\times}{\underset{\times\times}{B}}\overset{\times}{\times} \quad \text{or} \quad A \longrightarrow B$$

After the formation of the linkage, the lone pair of electrons is held in common and fills the last orbit of A as well as B. The linkage is represented by an arrow, pointing away from the donor atom.

Co-ordinate compounds resemble covalent compounds in respect of their physical properties.

VALENCY OF CARBON ATOM

The atomic number of carbon is 6 and its atomic weight 12. Its electronic structure can be represented as shown in Fig. 5·1. It has four electrons in the last orbit and tends to gain four more electrons by forming four covalent bonds with other H atoms. Thus, the structural formula of the simplest hydrocarbon methane (CH_4) can be written as :

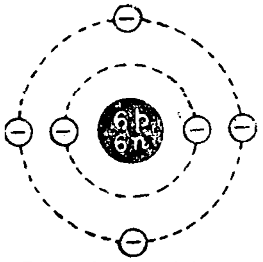
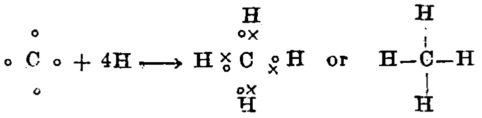


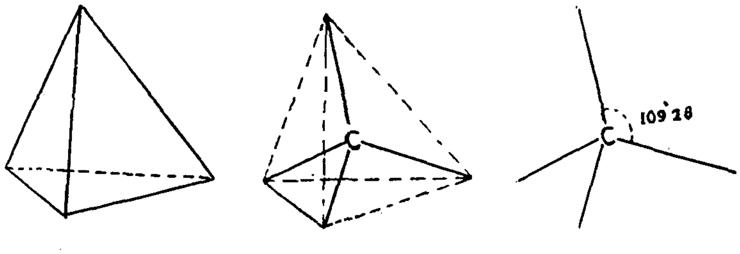
Fig. 5·1. Atomic structure of carbon.



$$\overset{\circ}{\underset{\circ}{\circ\,C\,\circ}} + 4H \longrightarrow H\overset{\times}{\underset{\circ}{}}\overset{\overset{H}{\circ\times}}{\underset{\underset{H}{\circ\times}}{C}}\overset{\circ}{\underset{\times}{}}H \quad \text{or} \quad H-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-H$$

Similarly in all organic molecules carbon atom is tetracovalent.

According to Le Bel and van't Hoff, the four valencies of the carbon atom are not lying in one plane but instead these are symmetrically distributed in space so that the angle contained between any two valency bonds is 109° 28′.



A regular tetrahedron with 4 similar faces

Space model of carbon atom

The normal direction of valencies

Fig. 5·2.

It will be instructive for the student to construct model of a tetrahedron from a sheet of paper as follows :

Cut out the paper along the solid lines around the edges. Then fold the other solid lines over a foot-rule, and glue the faces of the tetrahedron together with the aid of the three glue flaps. If the centre of this tetrahedron is taken to represent a carbon atom, the vertices will show the direction of the four valencies.

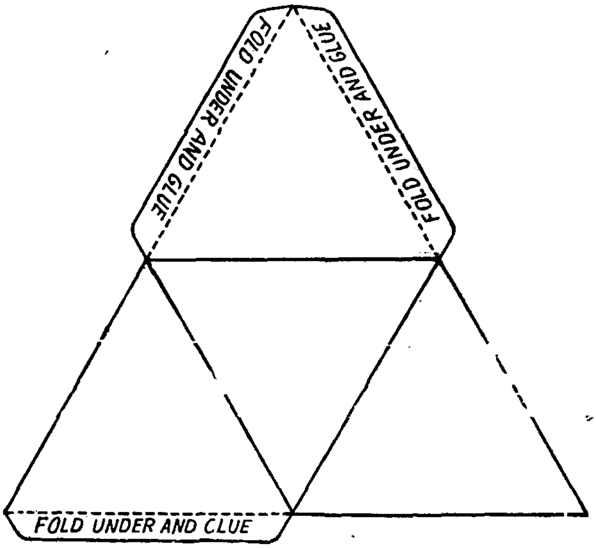
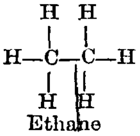


Fig. 5·3. How to make a paper tetrahedron.

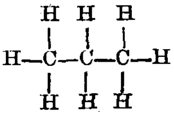
SINGLE CARBON-TO-CARBON BOND

A carbon atom has the wonderful instinct of uniting with other carbon atoms through covalent bonds. This serves to construct the carbon structure of organic molecules. Thus the molecules of hydrocarbons, ethane and propane contain two and three carbon atoms respectively linked by covalent bonds.



$$\begin{array}{ccccccc} & & H & & H & & \\ & & | & & | & & \\ H & - & C & - & C & - & H \\ & & | & & | & & \\ & & H & & H & & \end{array}$$

Ethane



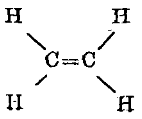
$$\begin{array}{ccccccccc} & & H & & H & & H & & \\ & & | & & | & & | & & \\ H & - & C & - & C & - & C & - & H \\ & & | & & | & & | & & \\ & & H & & H & & H & & \end{array}$$

Propane

Single carbon-to-carbon bond is usually strong and is not easily broken during chemical changes.

DOUBLE BOND OR ETHYLENIC LINKAGE

In certain compounds, two of the valencies of a carbon atom may be satisfied by union with the two valencies of another carbon atom. Thus in ethylene molecule the two carbon atoms are linked by two covalent bonds.



Such a union involving two covalent bonds between the adjacent carbon atoms is spoken of as **Double Bond** or *Ethylenic Linkage*, since it occurs in ethylene molecule. The two valency bonds of each of the carbon atoms while they join to form a double bond have been much distorted from their normal direction and are consequently under strain. Therefore, a **double bond is weak** and is easily ruptured by oxidation, or is reduced to a stable single bond during chemical reaction.

TRIPLE BOND OR ACETYLENIC LINKAGE

Sometimes, two adjacent carbon atoms are linked together by three covalent bonds. Thus, acetylene molecule is represented as

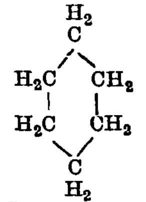
$$H—C \equiv C—H$$

Such a linkage involving triple union between adjacent carbon atoms is called a **Triple Bond** or *Acetylenic Linkage* as it occurs in acetylene molecule.

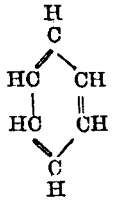
Like a double bond, a triple bond also signifies a great strain in the molecule. In fact, *a triple bond is weaker than even the double bond.* It is readily ruptured by oxidation, or reduced to a double bond and then to a single bond during chemical reactions.

RING STRUCTURES

We have given above some examples of substances where the molecules consist of carbon atoms joined together in chains that are free at both ends. There are also numerous compounds known where carbon atoms join to form closed rings. These are termed **Ring Compounds** or **Cyclic Compounds**. Thus we have :



Cyclohexane



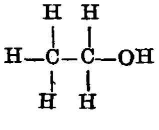
Benzene

STRUCTURAL FORMULA

We have seen that a molecular formula states the number and kind of atoms in the molecule. Thus ethyl alcohol has molecular formula C_2H_6O which implies that a molecule of the compound is made of two carbon atoms, six hydrogen atoms and one oxygen atom. A molecular formula remains silent as to how these atoms of various elements are joined in the molecule.

A formula showing a complete picture as to how the various atoms are linked to each other in the molecule, is known as a **Structural formula**.

For example ethyl alcohol having molecular formula C_2H_6O has structural formula



$$H—\overset{\displaystyle H}{\underset{\displaystyle H}{\overset{|}{\underset{|}{C}}}}—\overset{\displaystyle H}{\underset{\displaystyle H}{\overset{|}{\underset{|}{C}}}}—OH$$

Thus a structural formula shows clearly as to which atom is bonded to which atom in the molecule. It may be recalled here that the valency bonds of carbon atoms are distributed symmetrically in space. Therefore, a structural formula written in the plane of the paper is not an exact picture of the molecular structure.

A model of the molecule is often useful to facilitate our thinking about the structure of a molecule. One simple kind of a model to represent structure of a molecule consists of coloured balls and sticks or pegs of metal wire. This is called **ball-and-stick model** or **ball-and-peg model.** The following model of methane (CH_4) shows that it has a three dimensional structure.

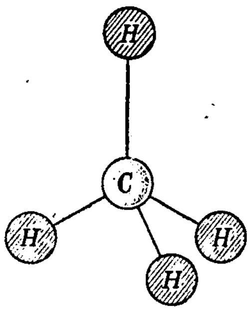


Fig. 5·4. Model of methane.

The model shows the exact angle between the bonds. Hence models are very helpful in telling us as to how the various atoms of the molecule are arranged in space.

It is true that the beginning student finds it useful to construct models of organic compounds. In this way he can visualise their shapes better. But it is inconvenient to draw a three dimensional sketch each time. Since we must write on a flat surface for convenience, we should always keep in mind that the actual molecule is really three-dimensional and that the formula we have written is simply a projection of the former. This is illustrated by the following models of methylene chloride (CH_2Cl_2). We should not forget despite the appearance of the projection formulae that the carbon bond angles are not 90° and the molecules are not flat. Or, that the formulae really do not represent the models.

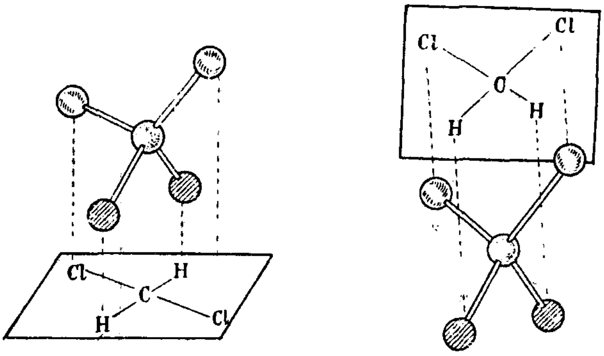


Fig. 5·5. Projections of CH_2Cl_2 molecular models give formulae on the plane paper.

We have discussed above the ball-and-stick models of organic substances. These models consist of coloured wooden balls of the same size connected by sticks or pegs While they give an adequate method of indicating which atoms are bonded to which atoms and also give an idea of bond angles, the size of individual atoms is ignored. This defect has been overcome in the **Stuart models.**

In these models the ball representing the various atoms are made of a size proportional to the effective atomic radii. The model is undoubtedly more compact but there is a certain loss of visual clarity with the bond angles.

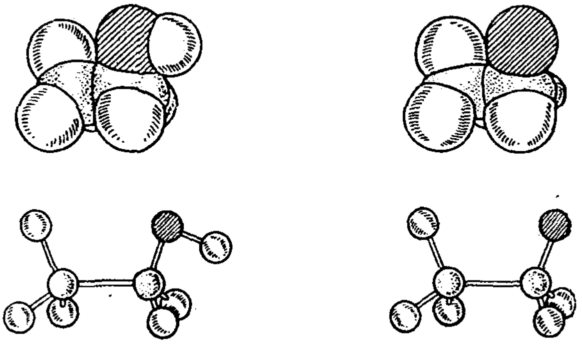


Fig. 5·6. Stuart and ball-and-stick models of ethyl alcohol and chloroethane.

In the space-filling or Stuart models, the spheres representing atoms in the molecule are designed so as to indicate sharing of electron clouds.

Writing structural formulae. We have seen that real molecules are three dimensional as shown by the models. Usually the chemists write formulae in the plane of the paper and indicate the angles between valencies of carbon atoms as right angles. This is only for convenience, otherwise valency bonds of carbon lie in a *zig-zag* way. Thus the structural formulae written on paper simply indicate the order in which the various atoms are joined and do not give any idea of their disposition in space. In other words, they only depict the structural representation of a molecule and the valency bonds may be put in any direction. Thus ethyl chloride may be written as

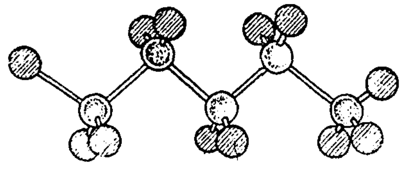
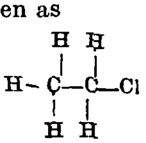
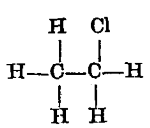


Fig. 5·7. Valency bonds of carbon atoms in pentance lie in a zig-zag way.



$$\begin{array}{ccccc} & H & & H & \\ & | & & | & \\ H- & C & - & C & -Cl \\ & | & & | & \\ & H & & H & \end{array}$$

or

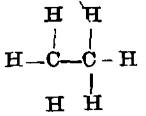


$$\begin{array}{ccccc} & H & & Cl & \\ & | & & | & \\ H- & C & - & C & -H \\ & | & & | & \\ & H & & H & \end{array}$$

Condensed structural formulae. The detailed structural formulae of the type given above use a great deal of space and are often not necessary. For this reason chemists often write what we call *'condensed structural formulae'*. These can be written more rapidly and in less space.

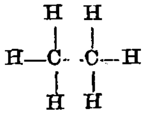
In a condensed formula all atoms linked to a given carbon atom are given after the 'C' and in the same line but their bonds are not shown.

Structural formula *Condensed formula*



$$H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-H$$

CH_3CH_3
Ethane



$$H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-H$$

CH_3CH_2Cl
Ethyl chloride

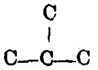
It may be noted that atoms other than hydrogen are written after the hydrogen atom in the condensed structural formulae.

Skeletal formulae. Sometime skeletal formulae are used for brevity or to make the differences in the carbon chains more apparent. *A skeletal formula shows all atoms in a molecule except hydrogen.* Thus skeletal formula of ethane and propane would be

C—C C—C—C

It is assumed that all the remaining valencies of carbon atom are filled by hydrogen atoms. The skeletal formulae of the two butanes may be written as

C—C—C—C
Normal butane



$$C-\overset{C}{C}-C$$

Isobutane

BOND LENGTHS

When two atoms are linked by a covalent bond, the distance between the centre of the two atomic nuclei is called the **Bond Length**. There are several methods available for the measurement of bond lengths (or bond distances) which include X-ray diffraction, electron diffraction and molecular spectroscopy but the description of these belongs to Physical Chemistry. The concept of bond lengths and their measurement is of considerable interest in Organic Chemistry. The unit length here is an Angstrom (symbol Å) which is equal to 10^{-8} cm.

Bond lengths of certain pairs of atoms involved in organic molecules are given in the table below :

Bond	Bond Length (Å)	Bond	Bond Length Å
C—H (Alkanes)	1·07	C—Br (Bromoalkane)	1·94
N—H (Amines)	1·00	C—I (Iodoalkane)	2·14
O—H (Alcohols)	0·96	C=C (Alkenes)	1·35
C—C (Alkanes)	1·54	C=O (Ketones)	1·22
C—N (Amines)	1·47	C≡C (Alkynes)	1·20
C—O (Alcohols)	1·48	C≡N (Nitriles)	1·16
C—Cl (Chloroalkanes)	1·76	C=C (Benzene)	1·39

BOND ENERGIES

The bond C—H, or any other chemical bond is characterised by a **bond energy** *which is the energy needed to break that bond in any compound in which it exists.* The value of bond energy can be calculated from the bond spectrum of the molecule concerned.

For molecules containing three or more atoms. *i.e.*, two or more bonds, the heat of formation of the molecule from the atoms can be regarded as the sum of all the bond energies. Thus the heat of formation of the water molecule from hydrogen and oxygen atoms is twice the bond energy of O- H bond. This can be easily calculated from the heat of formation of steam (from molecular hydrogen and oxygen) and the known dissociation energies of the O_2 and H_2 molecules by application of Hess's law of Constant Heat Summation (*see a Text-book of Physical Chemistry*).

The bond energies of C—H, C—C, C=C and C≡C bonds can be calculated in a similar manner, using known heats of combustion of hydrocarbons and the heats of combustion of carbon and hydrogen.

Example. *Find the bond energy of the C—H bond from the following data :*

$$CH_4+2O_2 \longrightarrow 2H_2O\ (\text{gas}) + CO_2 + 191\ \text{Kcals}$$

$$\underset{(\text{graphite})}{C} \xrightarrow{\text{Sublimes}} C\ (\text{gas}) - 170\ \text{Kcals.}$$

$$2H_2 \longrightarrow 4H - 207\ \text{Kcals.}$$

$$2H_2O \longrightarrow 2H_2 + O_2 - 116\ \text{Kcals.}$$

$$CO_2 \longrightarrow \underset{(\text{graphite})}{C} + O_2 - 94\ \text{Kcals.}$$

Solution. By Hess's law, thermochemical equations can be added and subtracted like algebraic equations.

$$CH_4 \longrightarrow 4H + C\ (\text{gas}) - 395\ \text{K calories}$$

This naturally involves the breaking of four C—H bonds.

∴ The average value for the C—H bond energy is 99 Kilocalories.

A list of bond energies of important bonds is given below :

BOND	BOND ENERGY (KCAL/MOLE)	BOND	BOND ENERGY (KCAL/MOLE)
C—H	98·7	C—C	82·6
C—Cl	80·0	C=C	145·8
C—Br	69·0	C≡C	199·6
C—I	55·0	C—O	85·0
		C=O	178·0
		O—H	110·6

Bond energies provide a very useful indication of the strengths of the various chemical bonds. The bond energies of carbon-to carbon single, double and triple bonds show that the order of their strength is $- > = > \equiv$.

SPECTROSCOPY OF ORGANIC COMPOUNDS

The structural formulae of organic compounds were for long derived from a study of the chemical reactions of these compounds and then confirmed by their synthesis by proven steps from known starting materials. The last two decades have witnessed a virtual revolution in this field and now sufficient information regarding the chemical structure of an unknown compound can be obtained directly by purely physical methods. One such modern method is the examination of 'spectra' of organic compounds or **spectroscopy**. This is based on the fact that when light is made to pass through a sample of a given organic substance, certain portions of it are absorbed while others are transmitted. The wavelength (or frequency of the portion absorbed depends on the chemical structure of the substance. Thus a study of its absorption spectrum can provide us valuable clues to its structure.

How is absorption Spectrum caused by Radiant energy ? We know that light consists of electromagnetic waves which travel in a straight line (velocity$=3\times10^{10}$ cm. in vacuum) away from the source, the direction of vibrations being perpendicular to the direction of propagation. While ordinary light is made of components having wavelength range $7{\cdot}5\times10^{-5}$ cm. to 4×10^{-5} cm., a monochromatic source gives a single wavelength component.

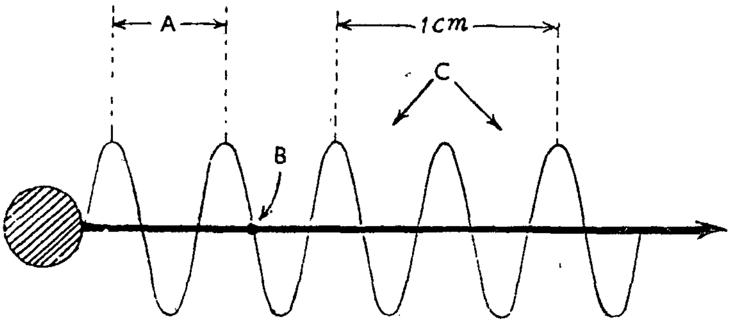


Fig. 5·8.

A : Wavelength, λ (cm.).

B : Number of waves passing per second=frequency, ν (sec.$^{-1}$)

C : Number of waves per cm.=Wave Number, $1/\lambda$ (cm.$^{-1}$).

Quantum theory tells us that in addition to its wave nature, light also consists of discrete quanta ('packets' of energy) and that a particular wavelength is associated with a quantum of energy (ergs). This is given by the following simple relation

$$E=h\nu=\frac{hc}{\lambda}$$

where E=energy of light ; λ its wavelength or ν its frequency ; c= velocity of light ; and h, the Planck's constant. From the above relation it is evident that shorter the wavelength, greater the energ,

For the study of absorption spectra we generally consider three kinds of light :

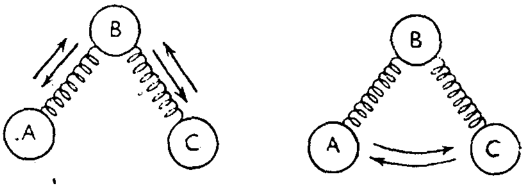
(*i*) *Visible*, those wavelengths (4 to $7{\cdot}5\times10^{-5}$ cm.) which human eye can see unaided ;

(*ii*) *Ultraviolet*, having shorter wavelength (1 to 4×10^{-5} cm.) than the visible light : and

(*iii*) *Infrared*, having longer wavelength (3×10^{-2} to 7×10^{-5} cm.) than the visible light.

RADIATION	WAVELENGTH (*cm*)	WAVE NUMBER (*cm^{-1}*)	ENERGY (*ergs*)
1. Infrared	3×10^{-2} to 7×10^{-5}	33 to $1{\cdot}4\times10^{4}$	66 to $2{\cdot}8\times10^{-12}$
2. Visible	$7{\cdot}5\times10^{-5}$ to 4×10^{-5}	$1{\cdot}0\times10^{4}$ to $2{\cdot}5\times10^{4}$	$2{\cdot}7\times10^{-12}$ to 5×10^{-12}
3. Ultraviolet	4×10^{-5} to 10^{-5}	$2{\cdot}5\times10^{4}$ to 10^{5}	5×10^{-12} to $2{\cdot}8\times10^{-12}$

In addition to energy of electrons, a molecule has kinetic energy due to the rotational and vibrational motions of the atoms in each chemical bond. For example, a non-linear molecule made of three atoms A, B and C with bonds represented by springs could be visualised to be executing vibrations as shown in Fig. 5·9.



Stretching vibrations Bending vibrations

Fig. 5·9. Vibratory motion in a molecule.

The total energy *E* of the molecule (leaving aside the nuclear energy) may be taken as the sum of the three energy terms :

$$E = E_{\text{electronic}} + E_{\text{vibrational}} + E_{\text{rotational}}$$

When light radiations are made to pass through an organic substance (or its solution), not only the electrons of the component atoms are excited but the vibrational and rotational energies are also increased.

According to Quantum theory, both vibrations and rotations are quantised and the kinetic energy due to these is also increased by certain definite levels. Hence any wavelengths (or frequencies) of light that a particular molecule will absorb, will be determined by the changes in the electronic, vibrational or rotational energy levels permissible for its atoms. The wavelengths or radiations absorbed are measured with the help of a *spectrometer* and are said to constitute a *spectrum*. The spectrum of a compound is generally presented in the form of a continuous graph indicating the absorption of light at all wavelengths (or frequencies) over a particular range. The shape of such a plot is highly characteristic of the compound's structure and provides an excellent diagnostic technique to ascertain the molecular structure of unknown substances.

Ultraviolet and visible absorption spectra. It is one of the earliest physical methods of elucidating the structure of organic molecules. Absorption of visible and ultraviolet light produces changes in the energy of electrons, in atoms of the molecule from a stable to an unstable orbital. The significant feature of these spectra are the positions of maximum absorption, λ_{max} and the intensity of absorption at these maxima.

In general, carbon compounds having an alternate single and multiple bonds are apt to absorption in this region of wavelength. A system having only a few *conjugated multiple bonds absorbs the radiation in this region less strongly than those possessing an extended series of conjugated multiple bonds. For example, butadiene (having two conjugated double bonds) gives λ_{max} as $2{\cdot}17 \times 10^{-5}$ cm while β carotene (having 11 conjugated double bonds) absorbs strongly at $4{\cdot}5 \times 10^{-5}$ cm. The following table bears out the statement that value of λ_{max} increases with increased conjugation.

COMPOUND	$\lambda_{max}.\ \times 10^{-5}$ *cm*
Ethylene ($H_2C{=}CH_2$)	1·65
1 : 3—Butadiene ($H_2C{=}CH-CH{=}CH_2$)	2·17
1 : 3 : 5—Hexatriene ($H_2C{=}CH-CH{=}CH-CH{=}CH_2$)	2·58
Acetone ($CH_3.CO.CH_3$)	1·88 and 2·79

Since structural environments also influence the value of λ_{max} in ultraviolet and visible spectra, the technique in general reveals fewer structural features than infrared spectra. However in many cases ultraviolet spectra are useful to confirm structural features derived by other means.

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*A conjugated system of multiple bonds may be as

$$-C{=}C-C{=}C-C{=}C-$$

—the one which contains (here) a double bond and single bond alternately in the carbon chain.

Infrared spectra. Unlike the situation obtaining in visible and ultraviolet absorption spectra, all organic molecules absorb light in the infra-red region. In this region, the absorbed radiation brings about predominant changes in vibrational energy which depends upon (or is a function of) the masses of the atoms, as also the strengths of bonds between atoms and their spatial arrangements in the molecule. Thus it stands to reason that no two compounds except optical enantiomers, can have similar Infrared (I.R.) absorption spectra. Just as fingerprints are taken as a characteristic of identity of every individual, the bands in I.R. spectra are also characteristic of a compound. In other words, the bands in the spectra of a molecule can be regarded as its 'molecular fingerprints' leading to its recognition.

The I.R. spectra of an organic compound helps in—

(*a*) proving its identity by comparison ; and

(*b*) showing the presence of certain groups or atoms in its molecule.

In order to clinch the proof of identity of an organic molecule, its I.R. spectra are compared with I.R. spectra of a previously reported compound of known structure. If the two are found resembling, we can conclude without least hesitation that the two compounds are identical.

A particular functional group gives rise to characteristic absorption bands in the infrared spectra. In other words a particular group strongly absorbs light of certain wavelength no matter to which compound it belongs to. From example a carbonyl group ($>C{=}O$) strongly absorbs the radiation in the region 6×10^{-4} cm. while a carbon hydrogen bond absorbs near $3{\cdot}4 \times 10^{-4}$ cm. The maximum absorption bands in the accompanying plot of I.R. spectrum of acetone show absorptions at $5{\cdot}9 \times 10^{-4}$ cm. and $3{\cdot}45 \times 10^{-4}$ cm. indicating the presence of a carbonyl group and carbon hydrogen bonds of the methyl group.

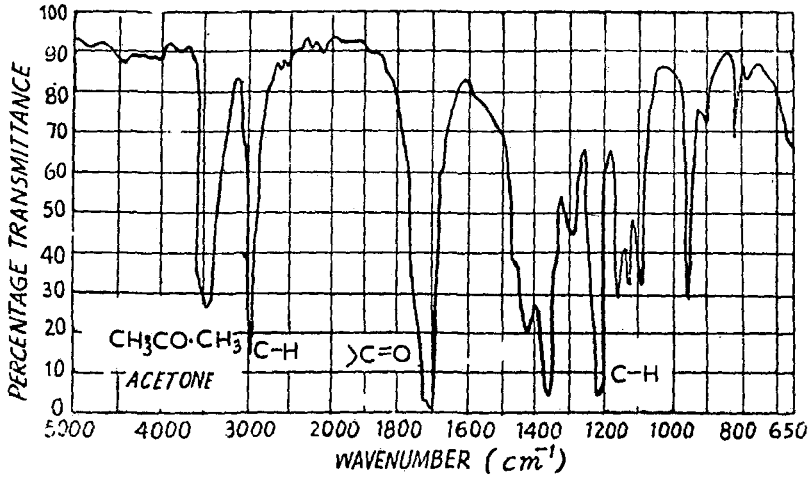


Fig. 5·10. Infrared spectrum of acetone.

Sufficient information can be derived from I.R. spectra of molecules and their determination is now a routine operation in establishing the structure of an unknown compound. This ingenious technique of establishing the identity or analysis of organic compounds has the distinctive advantage that it can be carried out with a very small amount of the sample (1—2 mgms.) which too can be recovered unchanged after the required measurements have been made.

TABLE : **Some Characteristic Infrared Absorption Frequencies**

BOND	TYPE OF COMPOUND	WAVELENGTH cm^{-1}
$-\overset{\mid}{\underset{\mid}{C}}-H$	Alkanes	2850 -2960
$=\overset{\mid}{C}-H$	Alkenes	3010 -3100
$\equiv C-H$	Alkynes	3300
$-\overset{\mid}{\underset{\mid}{C}}-\overset{\mid}{\underset{\mid}{C}}-$	Alkanes	600 —1500
$>C=C<$	Alkenes	1620—1680
$-C\equiv C-$	Alkynes	2100—2260
$>C=O$	Aldehydes	1720—1740
$>C=O$	Ketones	1705—1725
$>C=O$	Acids	1700 —1750
$-OH$	Alcohols	3590—3650
$-NH_2$	Amines	3300—3500

QUESTIONS

1. How do you explain the urge of the atoms for chemical union ? Name the three types of linkages and give examples to illustrate their mode of formation between atoms.

2. Write the structure of carbon atom and show that carbon is tetra-covalent in organic molecules.

3. What is meant by covalent and electrovalent linkages, and which of these linkages generally occur in organic compounds ? Give the electronic formula of methane.

4. On what conception regarding the structure of carbon atom, is the graphic formula of an organic compound based ? Point out its limitations. Describe the electronic structure of a carbon atom and write down the electronic formulae of the following :

Methane, Ethane, Choloform and Carbon tetrachloride.

5. Write notes on : Single carbon-to-carbon linkage, double bond, triple bond. How is it that a single bond is the strongest of all ?

6. What do you understand by the structural formula of a compound ? Mention its significance.

7. (*a*) Explain the terms 'electrovalency' and 'covalency'.

(*b*) Discuss the following statement :

> 'The existence of the organic compounds is consequent on the tendency of carbon atoms to form covalent linkages with one another and with atoms of other elements.'

Illustrate your answer by referring to simple organic substances.

8. What do you understand by the expression 'Tetra-covalency of Carbon' ? Explain the significance of a 'single bond', 'double bond' and a 'triple bond'. Arrange them in the order of their strengths giving reasons for your answer. Give at least one example of the substances containing (*i*) 'single' bonds only, (*ii*) at least one 'double' bond and (*iii*) at least one 'triple' bond.

9. How will you make a paper tetrahedron? Also construct ball-and-peg model of methane.

10. Define a structural formula. Write structural formulae of propane, ethyl alcohol and dichloroethane.

11. How ball-and-stick models are helpful in understanding the structure of organic molecules. What are the limitations of such models and in what way Stuart models are an improvement over ball-and-stick models.

12. How do you write the structural formulae of organic compounds in the plane of the paper ?

13. What is a 'Condensed structural formula' and a 'Skeletal formula' ? Give examples and say why these are commonly used in organic chemistry ?

14. What do you understand by absorption spectra of organic compound? How is infrared spectrum utilized for ascertaining the structure of an organic compound ?

15. Write an essay on spectroscopy of organic compounds.

16. How is infrared spectrum caused ? What changes are brought about as a result of absorption of infrared radiations ?

6

Structure of Organic Molecules. Modern Concepts

Niels Bohr

The classical theory given by Lewis and Kossel proved very profitable in interpreting the nature of chemical bonds. The electronic formulas of organic compounds explained in a satisfactory way the reactions and behaviour of a large number of them.

The orbital theory of chemical bonding based on the modern concepts of atomic structure is more sound and has stood the test of time. It has proved to be much more useful in interpreting and predicting the behaviour of most of the organic compounds. These concepts undoubtedly have their origin in the wave-mechanical treatment of atoms and molecules ; it would be perfectly alright for the present to dispense with any mathematical treatment, and to discuss the theory in a general way.

THE STRUCTURE OF ATOMS

The views on atomic structure which are accepted today have developed from the classical Rutherford-Bohr theory. Thus an atom is made of a positively charged nucleus surrounded by one or more electrons. The stability of such an atom is due to the electrostatic attraction between the positive nucleus and the negative electrons.

The nucleus of an atom consists of protons and neutrons. A *proton* carries one positive charge and has unit mass, while a *neutron* has the same mass but carries no charge. Thus the positive charge of the nucleus of an atom is equal to the number of protons present in the nucleus and is called its **Atomic Number**. An electron carries a unit negative charge and has negligible mass. Since atom is electrically neutral, the atomic number of an atom is also equal to the number of extra-nuclear electrons.

Let us consider the simplest atom, hydrogen. It consists of the nucleus made of one proton and a single outer electron. Next comes helium with atomic number two and, therefore, having two outer electrons. Carbon, the most important element in organic chemistry, has the atomic number of six, and hence possesses six extra-nuclear electrons.

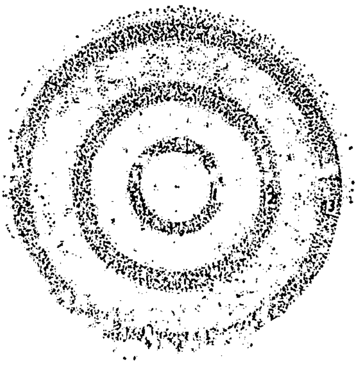


Fig. 6·1. How shells would appear if probability of finding electrons is represented by shading.

Although nearly the entire mass of the atom is concentrated in the nucleus, the formation of chemical bonds is concerned with extra-nuclear electrons only. According to the theory of quantum mechanics, the electron is executing a back and forth motion about the nucleus rather than moving around it in closed orbits as was originally believed. By moving rapidly towards the nucleus and away from it in all possible directions, the electron virtually occupies all space around it and thus offers the appearance of a spherical *cloud*. While the extra-nuclear electrons are free to move about in the cloud, on mathematical calculations it has been noted that they have a greater tendency to align themselves in concentric spherical **shells** placed one above the other around the nucleus, thus giving a structure something like that of an onion. Since the electron when present in a certain shell is associated with a definite amount of energy, the shells are also termed **Energy levels**. Starting from the shell or energy level nearest the nucleus, these are designated as 1, 2, 3, 4, 5, 6, 7. The maximum number of electrons which the various shells can hold is 2, 8, 18, 32, 18, 8 respectively. The increasing number of shells or energy levels implies higher energy of the electrons present in these.

The electrons present in each principal shell or energy level are divided into **subshells** or **sublevels**, as many as the number of the shell. The four subshells are denoted by the letters *s*, *p*, *d* and *f* whose energies increase in the order named. Thus the first shell has single subshell designated as 1*s* ; the second shell has two subshells designated as 2*s* and 2*p*, the third shell has three subshells designated as 3*s*, 3*p*, 3*d* and the fourth shell has four subshells—4*s*, 4*p*, 4*d* and 4*f*.

The subshells are further divided into smaller units called the **orbitals** which the electrons occupy. An *s* subshell is made of one orbital, a *p* subshell, three orbitals ; a *d* subshell, 5 orbitals ; and *f* subshell, 7 orbitals. Since each orbital can hold two electrons, the maximum number of electrons in the subshells *s*, *p*, *d* and *f* is 2, 6, 10 and 14 respectively. Some time the principal shell numbers are also designated by the letters K, L, M, N etc. but the numbers are used in preference. The following diagram (Fig. 6·2) depicts beautifully the concept of shells, subshells, as also the maximum number of electrons which could fill these.

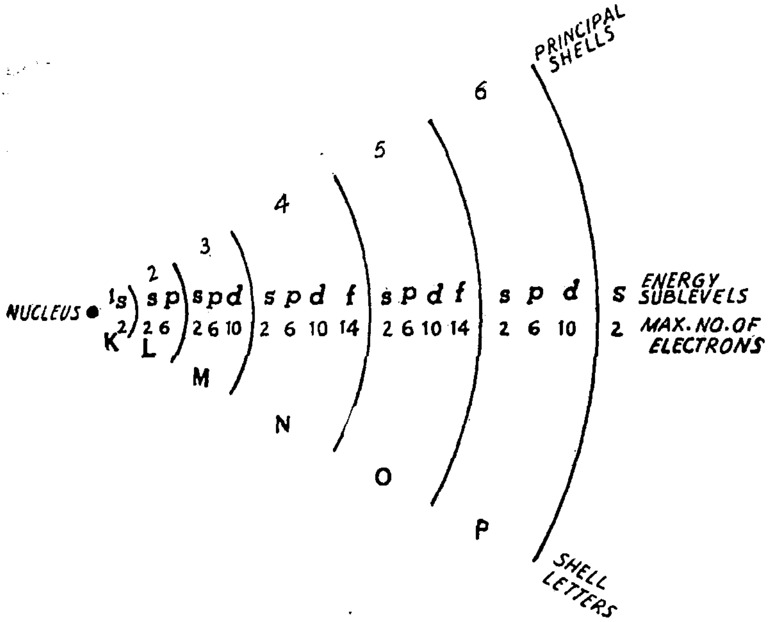


Fig. 6·2. Electron shells of an atom, indicating the number of electrons that can be accommodated in various energy levels.

The maximum number of electrons which occupy the various shells is also being given in the table below. It may be noted that in case of subshells, the number in front indicates the principal shell number and the superscripts give the number of electrons in that particular subshell.

TABLE : **Distribution of electrons in shells and sub-shells**

PRINCIPAL SHELL No.	MAX. NO. OF ELECTRONS	SUBSHELL AND THE MAX. NO. OF ELECTRONS IN EACH			
1 (K)	2	$1s^2$			
2 (L)	8	$2s^2$	$2p^6$		
3 (M)	18	$3s^2$	$3p^6$	$3d^{10}$	
4 (N)	32	$4s^2$	$4p^6$	$4d^{10}$	$4f^{14}$
5 (O)	32	$5s^2$	$5p^6$	$5d^{10}$	$5f^{14}$
6 (P)	18	$6s^2$	$6p^6$		
7 (Q)	8	$7s^2$	$7p^6$		

THE NATURE OF ATOMIC ORBITALS

As already discussed, electrons in each energy level are visualised as tiny particles executing rapid back and forth motion. By and large this movement takes place in a certain region in space. *This region in the atom to which an electron is confined and which has a geometrical shape*, is termed the **Atomic Orbital** or **Orbital**. It may be clearly understood that the term orbital has no association with the term 'orbit' which defines a particular path of movement. It only implies that the electron at any moment is found at any place of the orbital, although it may spend more time in certain parts than in others. Furthermore, not more than two electrons can occupy one orbital. All electrons in orbitals spin clockwise or anticlockwise, and the two 'coupled' electrons of a given orbital must have opposite spins in order to be accommodated in the same orbital. By the same argument, two electrons with the same spin will go to different orbitals.

THE GOEMETRICAL FORM OF THE *s* AND *p* ORBITALS

The first ten elements (At. Nos. 1 to 10) of the periodic table include Hydrogen, Carbon and Oxygen which occur most often in organic compounds. The maximum number of extra-nuclear electrons in the atoms of these elements is 10 (Ne, At. No. 10). Two of these could be present in the first shell and eight in the second. Thus, the first shell is made of one subshell (1*s*) or one orbital called the '*s* orbital'. The second principal shell consists of two subshells—2*s* subshell which has two electrons or one *s* orbital, and the 2*p* subshell which may have six electrons or three '*p* orbitals'. Thus for study of organic compounds, we will confine our discussion to the discussion of the shapes of *s* and *p* orbitals.

According to mathematical derivations, the *s* **Orbital** *has a spherical shape* with the atomic nucleus lying at its centre which is indicated by a plus (+) charge. As discussed earlier, we have one *s* orbital at each principal shell, its size being larger with the higher shell number. Hence the 1*s* orbital lies completely within the 2*s* orbital which is surrounded by the 3s orbital, and so on. It may be noted that there is no bar against two or more orbitals occupying the same space.

The *p* **orbitals** are considerably different from the *s* orbitals. They are not spherical but have dumb-bell shape.

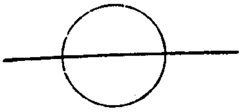


Fig. 6·3. *s* orbital has spherical shape.

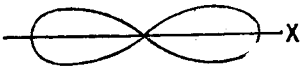
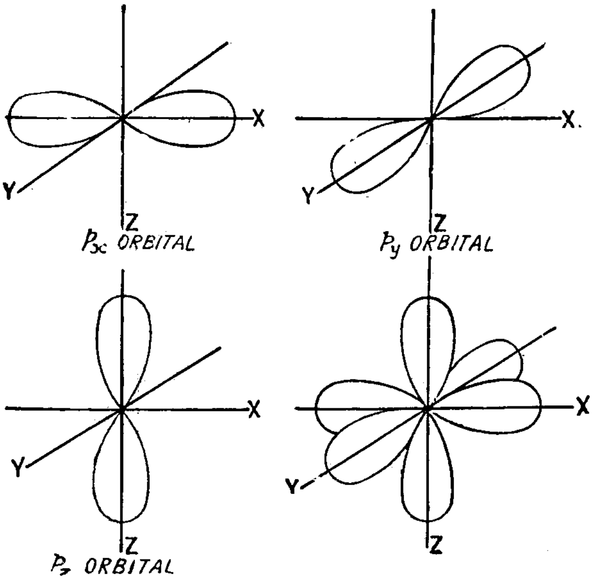


Fig. 6·4. *p* orbital has dumb-bell shape and direction along the central axis.

The two lobes of the orbital have a position concentric with the nucleus, termed a *node*, where the probability of finding an electron becomes zero and the plane passing through this point is termed a *nodal plane*. This type of orbital has a shape as well as direction about the nucleus.

As we have already observed, the possible number of electron in a shell is six and since not more than two electrons can occup an orbital, there are three *p* orbitals. These exist perpendicular t each other along the three axes (named x, y, z) and are designate as p_x, p_y, p_z.

The subscripts do not imply any different energy, but simply indicate the direction of the orbital. The principal shell number to



p_x ORBITAL p_y ORBITAL p_z ORBITAL

Fig. 3·5. The three *p* orbitals are dumb-bell shaped and arranged at right angles to each other, the nucleus of the atom lying at the intersection of the axes.

which a p electron belongs is generally prefixed and thus the three p electrons in the second shell are written as $2p_x$, $2p_y$, $2p_z$.

Electronic Configuration. We have already stated that extranuclear electrons are distributed in shells or energy levels around the nucleus which are divided into subshells (or energy sub-levels) and these are made of orbitals.

(1) The principal shells are numbered as 1, 2, 3, etc. which is also the order of their increasing energy.

(2) The number of sub-shells in a particular shell is given by its number. Thus shell (1) has one sub-shell (s), the shell (2) has two sub-shells (s, p), and so on.

(3) The square of the number of a principal shell gives the number of orbitals in that shell. Thus shell (1) has ($1^2 = 1$) one orbital ; the shell (2) has ($2^2 = 4$) four orbitals.

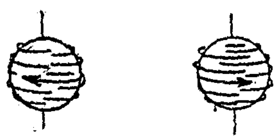


Fig. 6·6. Electrons with opposite spin.

(4) No more than two electrons can occupy the same orbital and these must have opposite spins which are indicated by arrows in opposite directions.

According to the above principles, the first principal shell has one sub-shell s and one orbital (s orbital). The second principal shell has two sub-shells—s and p, the s sub-shell being made of one orbital only, while p sub-shell of three orbitals (p-orbitals). The atom of neon (At. No. 10) has ten electrons arranged in two shells ; the first shell having two electrons and the second shell eight. It stands to reason that neon atom has all the orbitals in the two shells completely filled. The configuration of neon in 'short hand' notation could be written as

$$1s^2, 2s^2, 2p_x^2, 2p_y^2, 2p_z^2.$$

Here, letters indicate the type of orbital, the prefix stands for the principal shell number and the superscripts show the number of electrons in the orbital. The beryllium atom (At. No. 4) has four electrons, two of these occupy the 1s orbital and remaining two will go to the 2s orbital. The remaining elements B, C, N, O, F, Ne (At. Nos. 5 to 10) each have two 1s electrons, two 2s electrons, and the rest of the electrons go into the p-orbitals.

The boron atom (At. No. 5) has five electrons which are placed—two in 1s orbital, two in 2s orbital, and one in $2p_x$ orbital. Carbon (At. No. 6) has six electrons, and the sixth electron goes into $2p_y$ orbital. Proceeding similarly, the seventh electron in Nitrogen will go into $2p_z$ orbital. Now since each p orbital has one electron, the eighth, ninth and tenth electron of Oxygen, Fluorine and Nitrogen will go to fill the p_x, p_y, and p_z orbitals respectively. The complete configurations of the first ten elements are summarized below.

ELEMENT	AT. NO.	ELECTRONIC CONFIGURATION
H	1	$1s^1$
He	2	$1s^2$
Li	3	$1s^2, 2s^1$
Be	4	$1s^2, 2s^2$
B	5	$1s^2, 2s^2, 2p_x^1$
C	6	$1s^2, 2s^2, 2p_x^1, 2p_y^1$
N	7	$1s^2, 2s^2, 2p_x^1, 2p_y^1, 2p_z^1$
O	8	$1s^2, 2s^2, 2p_x^2, 2p_y^1, 2p_z^1$
F	9	$1s^2, 2s^2, 2p_x^2, 2p_y^2, 2p_z^1$
Ne	10	$1s^2. 2s^2, 2p_x^2, 2p_y^2, 2p_z^2$

CHEMICAL BONDING

After this brief review of the atomic orbital theory, let us now extend this concept to interpret chemical bonding.

In the table given above, it may be noted that He and Ne have all available orbitals filled and are chemically stable. The rest of the atoms H, Li, Be, B, C, N, O and F have partially filled orbitals and are chemically active or unstable. The inert gases He and Ne being stable possess lowest energy, while the rest of the atoms mentioned above tend to become stable by combination with other atoms which results in a lowering of their energy. Thus in general, *atoms tend to combine with other atoms to form molecules and in this process there is a lowering of their energy, for the most stable condition is that with the lowest energy.*

It may also be noted that He and Ne have completely filled orbitals (two electrons to each), while the other atoms like H, Li, Be etc. have certain half-filled oribtals (one electron each). Hence it stands to reason that orbitals containing one electron only can cause chemical combination so that the atoms in the resulting molecule come to possess orbitals which are completely filled. This is accompanied by a lowering of energy.

Electrovalent Bond. The formation of an electrovalent bond takes place by the transfer of an electron from the partially filled orbital of an electropositive atom to the partially filled orbital of an electronegative atom which now will have a pair of electrons. Thus Li transfers its lone electron from the $2s$ orbital to the $2p_z$ orbital of F, to form Li^+ and F^- ions.

Li^+ $1s^2$.
F^- $1s^2$ $2s^2$ $2p_x^2$ $2p_y^2$ $2p_z^2$

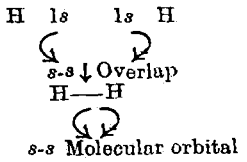
The Li^+ and F^- ions due to electrostatic attraction are bonded to give Li^+F^- molecule, It may be seen that all orbitals in Li^+ and F^- ions possess two electrons each and thus acquire stability (lowest energy).

Covalent Bond. A covalent bond is formed when two half-filled orbitals belonging to different atoms overlap in space and merge to form a new bigger orbital which is known as **molecular orbital.** The molecular orbital surrounds the atomic nuclei of both atoms and marks the region in which the pair of electrons will be found. The new orbital provides a greater freedom of movement to the 'paired' electrons which now belong to both the nuclei. It might be expected, from logical reasoning, that larger the region of movement allowed to an electron lower will be its energy. Thus the greater freedom enjoyed by the electrons in the molecular orbital, results in a decrease of energy (increase in stability). The molecule formed in this way is more stable than the isolated atoms.

Molecular Orbitals (*M.O. s*).

As already stated, a molecular orbital is formed when two atomic orbitals overlap so that the electrons come to occupy the common orbital which surrounds two nuclei. This may involve *s* and *s* orbitals ; *s* and *p* orbitals ; or *p* and *p* orbitals.

***s-s* Molecular Orbitals.** A molecular orbital formed by the overlap of *s* orbitals of two atoms are called *s-s* molecular orbitals. Let us consider the bond formation in hydrogen molecule from two individual hydrogen atoms. As the atoms are brought together, their 1*s* orbitals overlap and merge to form an *s-s* molecular orbital.



This may be pictorially represented as follows :

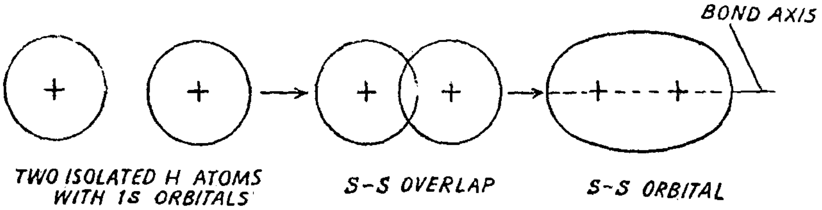
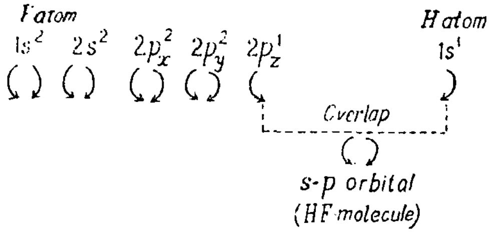


Fig. 6·7. Formation of *s-s* orbital in Hydrogen molecule.

The boundary of the *s-s* orbital in space, which in this case is ovoid, defines the region which the two electrons now occupy jointly. We call this orbital a **Sigma Orbital** (from the Greek letter σ corresponding to *s*) since it is completely symmetrical about the bond axis passing through the two nuclei. Although electrons may be present anywhere in this orbital, the probability of finding electrons is maximum between the two nuclei, for they are attracted equally by both the nuclei.

The bond established by the overlap of two *s* orbitals, is called a **Sigma bond** or **σ-bond.** Since an *s* orbital is spherically symmetrical, the overlap may take place equally well in any direction and hence there is no direction to such a bond.

s-p **Orbitals.** An *s* orbital and *p* orbital may overlap, even though the atomic orbitals in the two atoms lie in different principal shells. The molecular orbital thus formed is known as ***s-p*** **Orbital.** The combination of Hydrogen atom and Fluorine atom giving a molecule of hydrogen fluoride affords an example of this type. There is one 1*s* bonding orbital on hydrogen and one such half-filled 2*p* orbital on Fluorine atom, while the rest of the Fluorine orbitals are completely filled and not available for overlap and entering into bond formation.



Here the orbital overlap consists in an attack of 1*s* orbital on hydrogen atom at a dumbell shaped half-empty 2*p* orbital of fluorine. The resulting molecular orbital (σ orbital) may be depicted to have been formed as in Fig. 6·8.

The *s-p* overlap of orbitals between H and F forms a *sigma bond*, yielding HF molecule. It is noteworthy that in the σ orbital here, the nodal plane stands at right angles to the nuclear axis.

p-p **Orbitals.** We have already studied that the three dumbell shaped *p* orbitals are directed along the three axes *x*, *y* and *z* which are at right angles to each other. For each of the three orbitals

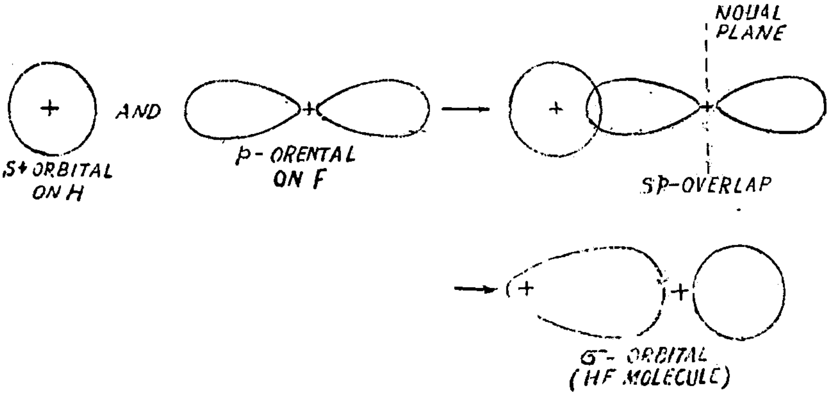


Fig. 6·8. Formation of HF molecule.

p_x, p_y, p_z there is a nodal plane dividing the p orbitals into two lobes.

The overlap of p orbital of one atom with p orbital of another atom may take place to form a p-p molecular orbital in two ways.

(*a*) *Head-on Overlap* : Let us consider two p_x orbitals approaching for an overlap by pointing directly 'heads' towards one another. This head-on overlap, as we call it, ensures so much lowering of energy that the new orbital is very stable and has a direction in relation to other p orbitals in the atom. The orbital thus generated being symmetrical about the nuclear axis, is designated a **Sigma orbital** and the bond so established a **Sigma bond.**

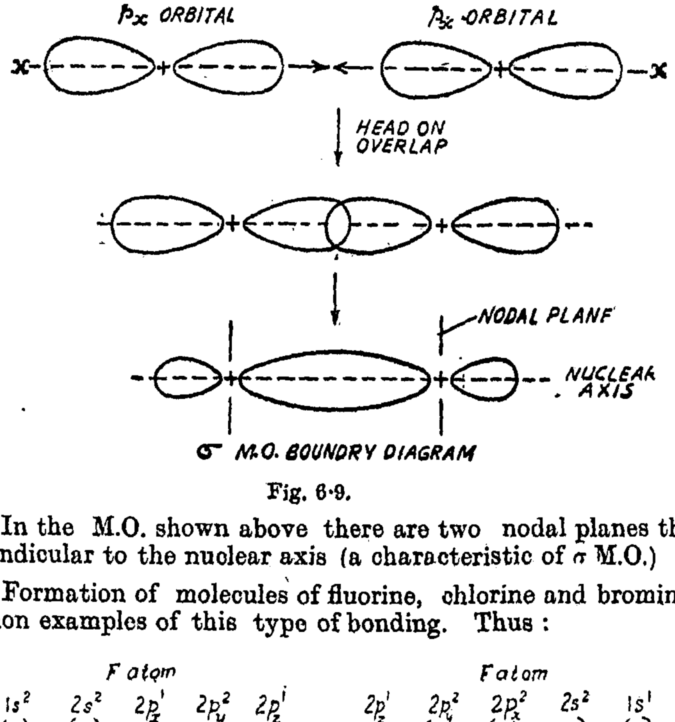
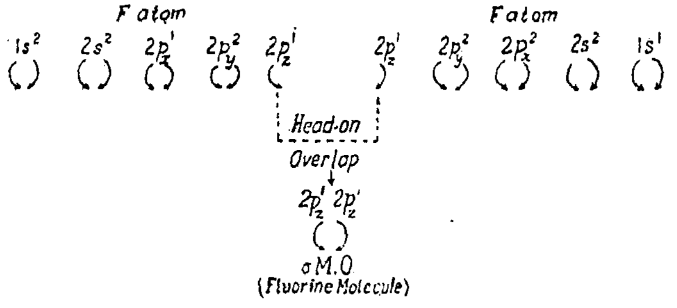


Fig. 6·9.

In the M.O. shown above there are two nodal planes that are perpendicular to the nuclear axis (a characteristic of σ M.O.)

Formation of molecules of fluorine, chlorine and bromine offer common examples of this type of bonding. Thus :



(*b*) *Side-wise Overlap.* When two p orbitals approach each other side-wise as shown below, the overlap takes place at both their lobes simultaneously. The extent of overlap in this case is relatively small (compared to head-on overlap) and the molecular orbital thus formed is oriented above and below the nodal plane which contains the nuclear axis. As indicated by the boundary diagram, this molecular orbital has sausage-like regions parallel to the nodal plane passing through the two nuclei.

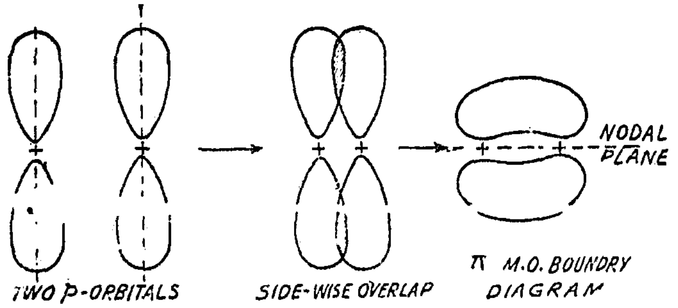


Fig. 6·10. Formation of π M.O. orbital.

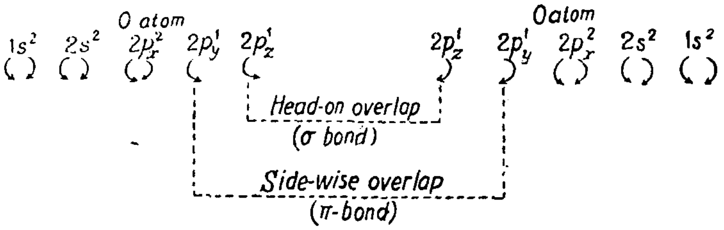
Such a molecular orbital generated by the side-wise overlap of the two half-filled p orbitals and having only one nodal plane containing the nuclear axis is called a π M.O. or **Pi Molecular Orbital.**

For recapitulation it may be re-stated that unlike π M.O., σ M.O. has a nodal plane which is perpendicular to the nuclear axis.

A covalent bond established as a result of π M.O. formation is called a π **(Pi) bond**. There are two important characteristics of a π bond. Firstly, it is weaker than a σ bond since the extent of overlap is relatively smaller and hence there is a lesser decrease in energy of the system. Secondly, it is not possible to rotate the atoms constituting a π bond relative to one another. If an attempt is made to do so, the *p* orbital lobes of the two atoms will no longer be coplanar, their overlap will be decreased and the energy of the system increased. In other words, the rotation around the bond axis of a π bond will be restricted because work will have to be done for the same. This property of a π bond is very useful in explaining the phenomenon of Geometrical isomerism.

Formation of Oxygen molecule – Double bond. We have seen that a single covalent bond results from the overlap of two *s* orbitals, one *s* orbital and one *p* orbital, or two *p* orbitals. All these bonds called σ bonds possess symmetry about the bond axis. In general, all single bonds are σ bonds.

Now let us proceed to discuss the formation of oxygen molecule (O=O) which is known to contain a double bond. In this case the oxygen atoms happen to possess two bonding *p* orbitals on each atom. The $2p_y$ and $2p_z$ half-filled orbitals oriented at right angles, on each of the oxygen atoms experience a head-on and a side-wise overlap respectively resulting in a σ and a π orbital simultaneously.



Thus the two atoms in oxygen molecule are linked by one σ and one π bond.

The following diagram depicts the formation of molecular orbitals in oxygen molecule.

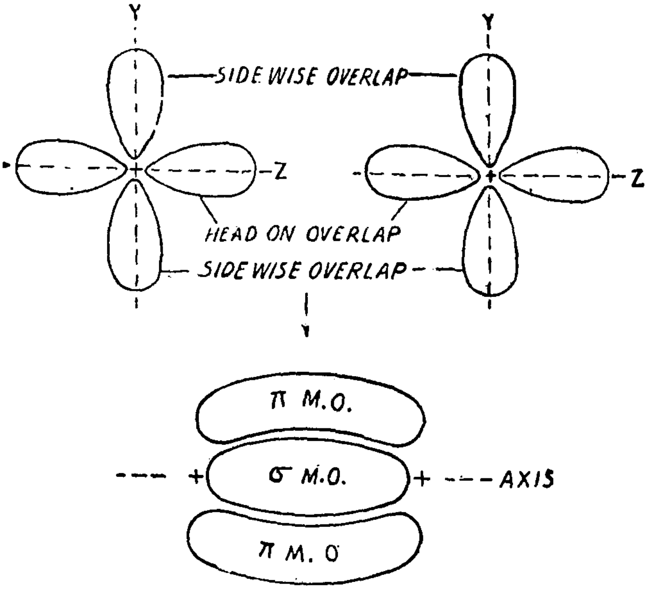
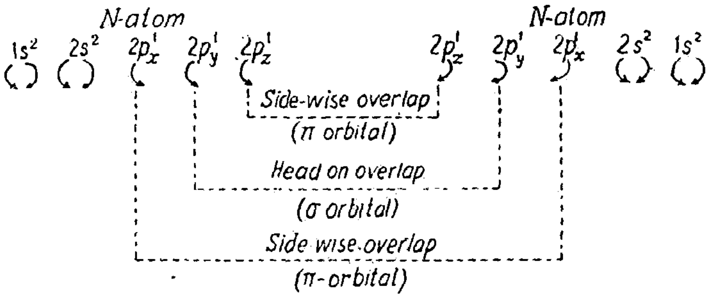


Fig. 6·11. M.O. boundary diagram for σ and π bonds in oxygen molecule.

As is clear from the above considerations the double bond in oxygen is made of one *sigma* bond and one *pi* bond.

Formation of Nitrogen molecule—Triple bond. Here the nitrogen atoms forming the N_2 molecule possess three bonding p orbitals each. The $2p_x$, $2p_y$, $2p_z$ half-filled orbitals are oriented along *the three axes at right angles.* $2p_y$ *orbitals of two nitrogen atoms* form a σ M.O. by head-on overlap, while $2p_x$ and $2p_z$ orbitals form two π M.O's by side-wise overlap.



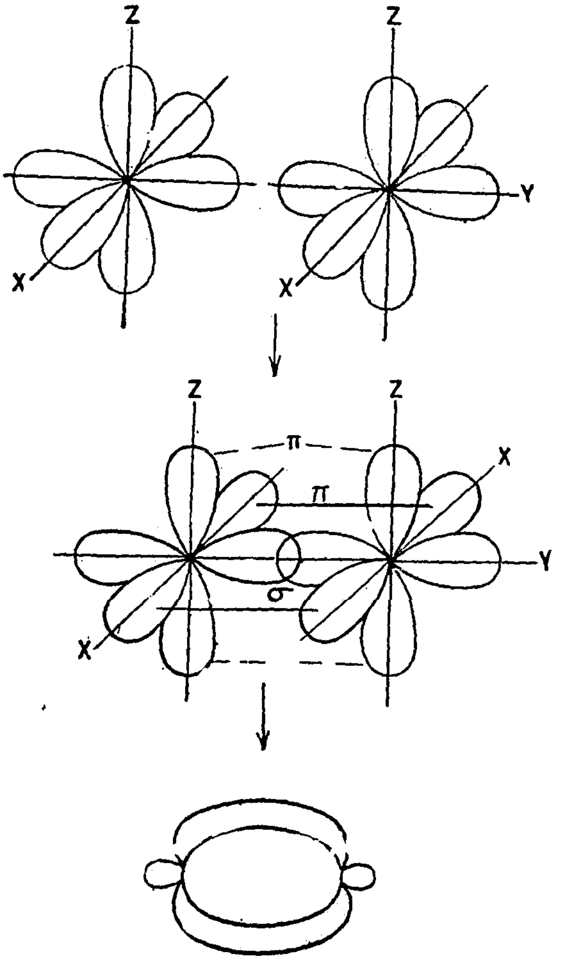


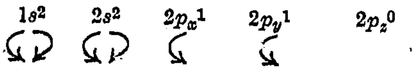
Fig. 6·12. The two "sausage clouds" of two Molecular orbitals.

The preceding diagram (Fig. 6·12) depicts the formation of Nitrogen molecule.

Thus in the classical line structure of nitrogen molecule ($N\equiv N$), one line represents a σ bond and the other two π bonds

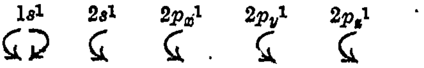
HYBRIDIZATION AND TETRACOVALENCY OF CARBON

Experiment tells us that carbon atom forms four covalent bonds. But when we examine the electronic structure of carbon



we find that it has only two unpaired $2p$ orbitals which can presumably form two σ bonds.

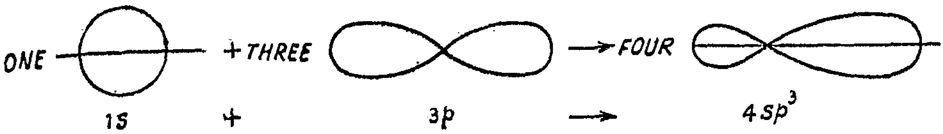
To provide an explanation for the tetra-covalency of carbon in methane (CH_4) and its relatives, it may be assumed that the two $2s$ electrons uncouple themselves and one of these is 'promoted' to the vacant $2p_z$ orbital which will now have higher energy and less stability. The electronic configuration of the 'excited' carbon atom could be written as



Now we have four half-filled orbitals which could possibly overlap with the four $1s$ orbitals of hydrogen atoms to form four σ bonds which would result in the lowering of energy. It stands to reason that the lowering of energy thus caused by the formation of two additional σ bonds of carbon is more than that necessary to promote an electron from a $2s$ orbital to a $2p$ orbital. It follows that although the isolated carbon atom is most stable with $2s$ and $2p$ electrons, the stabler compounds of carbon result when all four electrons in second energy level are in separate orbitals and form four covalent bonds.

We have seen that an excited carbon atom has four available orbitals in the second energy level—one s and three p orbitals. On overlapping with $1s$ orbitals of hydrogen atoms to form methane molecule. there would result one s—s orbital and three s—p orbitals. But we know that the s—s orbital will be different from each of the three s—p orbitals in respect of directional character as well as energy. But this would be contrary to actual facts since experiment shows that the four covalent bonds in methane are equivalent.

To account for the above situation, the concept of hybrid orbitals has been introduced. According to the theory of wave mechanics, *orbitals on the same atom which lie close to one another in energy, tend to combine or 'mix' and then redistribute to form equivalent number of new orbitals* which are called **hybridised orbitals** and the phenomenon is termed **hybridisation**, Thus in an excited carbon atom, it is assumed that one $2s$ and three $2p$ orbitals combine or mix together and redistribute as four new equivalent *hybrid* orbitals which are designated as sp^3 orbitals (spoken as "*sp* three"). Each of the four hybrid orbitals possess three-fourths characteristics of p orbital and one-fourth of s orbital.



The hybridisation of the orbitals of carbon may be pictorially represented as below :

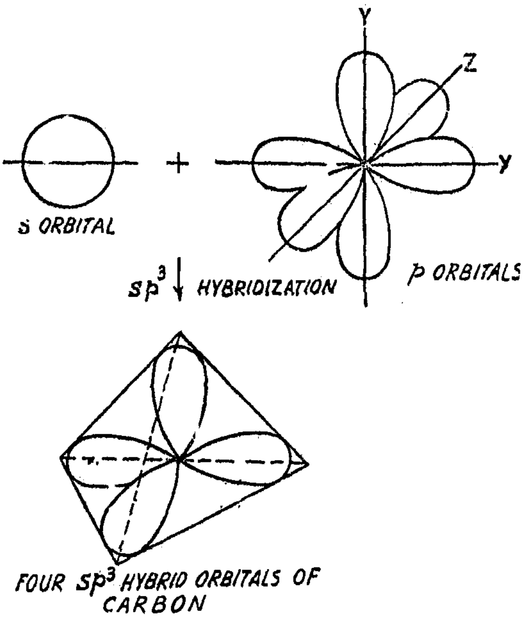


Fig. 6·13. Four sp^3 hybrid orbitals of carbon.

It is noteworthy that the hybrid sp^3 orbital has a new shape which differs somewhat from that of a p orbital, in that the lobe on one side of the node is larger than the lobe on the other side. Overlap with another orbital to form a bond naturally occurs with the larger lobe and for simplifying the molecular orbitals, very often the smaller lobe is not indicated. The most important characteristic of the sp^3 orbitals is that these four are distributed symmetrically in space on account of electronic repulsions keeping them farthest from each other. If the valencies are regarded as radiating from the nucleus of the carbon atom, their directions are towards the corners of a regular tetrahedron and the angles between them are 109° 28′.

The type of hybridisation involving the mixing of four 'pure' orbitals as described above to give four equivalent sp^3 hybrid orbitals, is called **tetrahedral hybridization**. It is met with in saturated carbon compounds.

Let us now proceed to consider the formation of methane molecule. The four sp^3 hybrid orbitals of the carbon atom are directed in space towards the four corners of a regular tetrahedron and the 1*s* orbital of four hydrogen atoms should approach its four apexes for the overlap. This would establish four equivalent σ bonds with the carbon atom resulting in the formation of a symmetrical methane molecule. Thus :

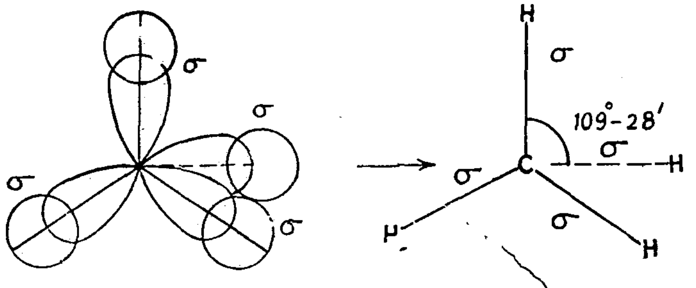


Fig. 6·14. Structure of Methane molecule.

In ethane molecule—the two carbon atoms, each having a set of four sp^3 hybrid orbitals, combine such that one sp^3 orbital of each carbon overlaps in a head-on fashion forming a σ bond. The remaining three orbitals on each carbon get bonded to three hydrogen atoms forming σ bonds as in methane molecule. Thus :

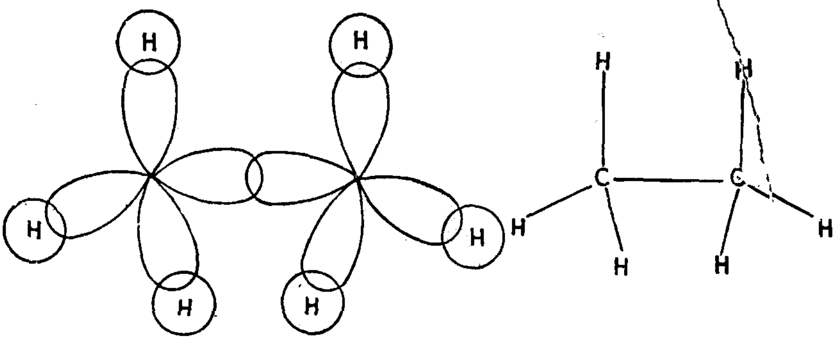
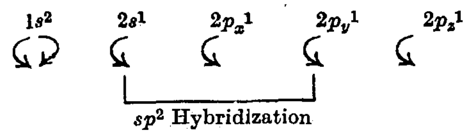


Fig. 6·15. Structure of Ethane molecule.

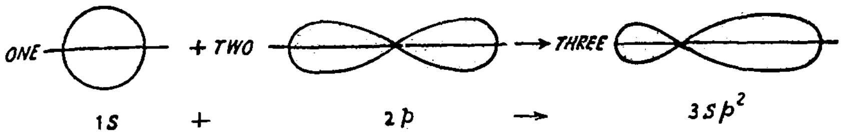
It may be noted how beautifully the sp^3 hybridization of orbitals as illustrated above has theoretically substantiated the Le Bel and van't Hoff's theory of the tetrahedral arrangement of carbon valency bonds in saturated organic molecules.

HYBRIDISATION AND MULTIPLE BONDS

In the classical representation of an ethylenic linkage, $>C=C<$, no difference can be made out between the two bonds which unite the carbon atoms. Huckel's model of hybridization in doubly bonded carbon atoms demonstrates that the two linkages constituting a double bond are not identical. He assumes that in the case of ethylenic compounds of the four 'pure' ,atomic orbitals of excited carbon atom only $2s$, and $2p_x$ and $2p_y$ orbitals are hybridised



to give *three equivalent orbitals.* These orbitals formed by the hybridization of one *s* and two *p* orbitals, are called sp^2 **Orbitals** (spoken as "*sp* two").



The three sp^2 orbitals are very much similar in shape to sp^3 orbitals and lie in one plane (XY plane) and are disposed symmetrically at an angle of 120° to one another. This type of hybridization is termed **Trigonal hybridization** and is visualised to take place as follows :

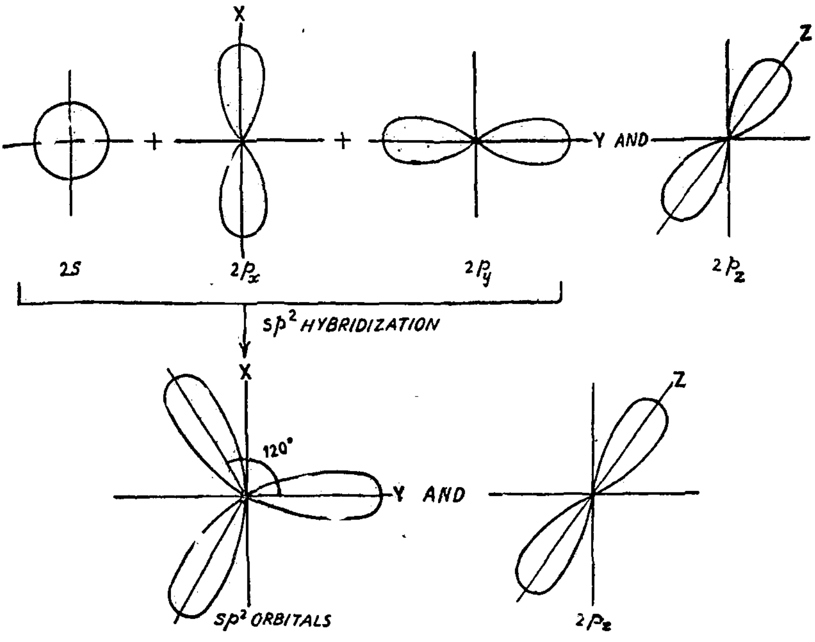


Fig. 6·16. Trigonal Hybridization.

As indicated above, the carbon atoms undergoing trigonal hybridization, undoubtedly possess the third free p_z orbital which has its lobes disposed above and below the plane of hybrid orbitals at right angles to this plane (Fig. 6·17).

Structure of Ethylene molecule. In the formation of ethylene molecule, the two carbon atoms (in sp^2 hybridization state) form σ bond by the head-on overlap of the two sp^2 orbitals contributed one each by the two carbons. The remaining two sp^2 orbitals of

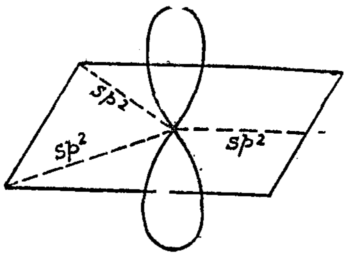


Fig. 6·17.

each carbon form σ bonds with hydrogen atoms. The unhybridized $2p_z$ orbitals of the two carbon atoms undergo a sidewise overlap forming a π bond. Thus the carbon-to-carbon double bond in ethylene is made of one σ and one π bond. Since the energy of a π bond is less than that of a σ bond, the two bonds constituting the ethylenic linkage, are not identical in strength. The π bond being weaker is easily ruptured in addition reactions of ethylene.

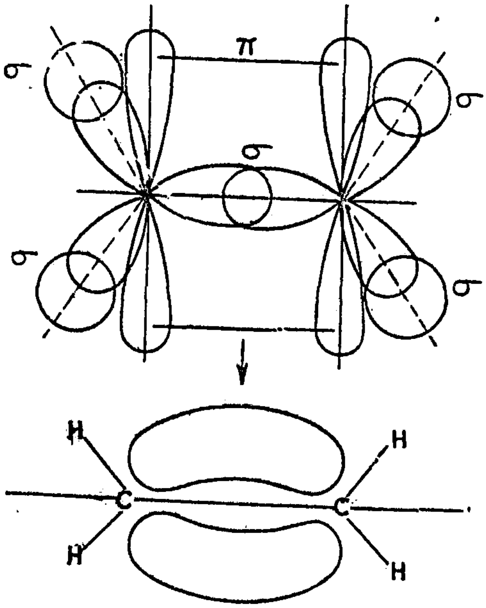
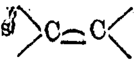
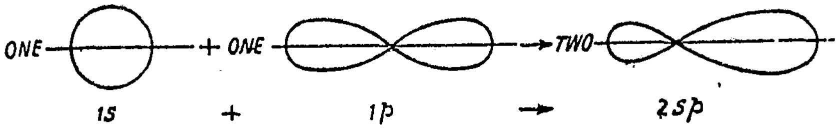


Fig. 6·18. Orbital model for Ethylene.

For the above reason, ethylenic linkage is sometimes represented as



Structure of Acetylene. To interpret the structure of acetylene molecule we visualise another kind of hybrid orbitals of the carbon atom. Here one s orbital and only one p orbital hybridise to form two equivalent collinear orbitals ; the other two p orbitals remaining undisturbed.



This is known as *sp* **hybridization** and the new orbitals are termed *sp* **orbitals.**

The electronic configuration of each carbon atom in acetylene molecule may be written as

$$1s^2\ \underbrace{2s^1\ \ 2p_x^1}_{\text{Hybridisation}}\ \ 2p_y^1\ \ 2p_z^1$$

The $2s$ and $2p_x$ orbitals hybridise to give two sp orbitals. One of the two sp hybrid orbitals on each carbon is then used in forming a σ bond with the other carbon, and the remaining sp orbitals get bonded with a hydrogen atom. This leaves two unhybridised p orbitals ($2p_y$ and $2p_z$) on each carbon atom, both of which are mutually perpendicular to the line of H—C—C—H nuclei. These orbitals are capable of forming two π bonds by the edge-on overlap. Thus :

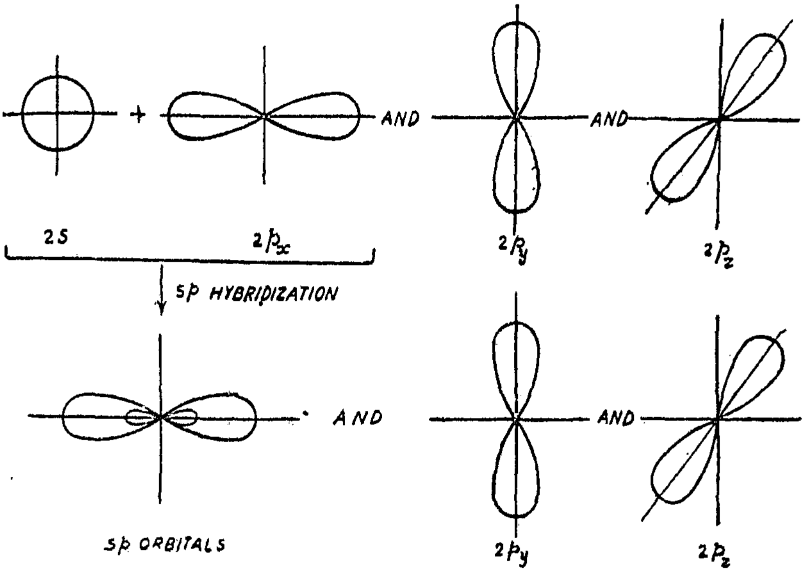


Fig. 6·19.

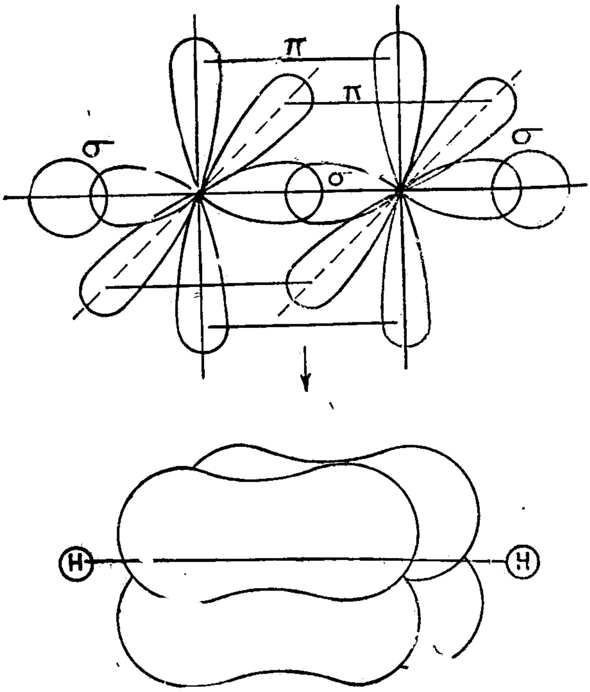


Fig. 6·20. Orbital model for acetylene showing σ and π bonds.

ELECTRONEGATIVITY

An element that tends to acquire rather than lose electrons in its chemical interactions is said to be *electronegative.* Atoms of different electronegative elements differ in their tendency to attract electrons. *A measure of the tendency of an atom of an electronegative element in a molecule to attract electrons to itself (and away from its bond partner) is called its* **Electronegativity.**

Thus in a molecule AB joined by a pair of electrons we may have

$$\underset{\text{I}}{\text{A : B}} \quad \text{or} \quad \underset{\text{II}}{\text{A :\ B}}$$

In formula I, the two electrons are half-way between the nuclei of atoms A and B which naturally exert equal attraction on electrons and hence electronegativities of A and B are equal. In formula II, the two electrons are nearer A which implies that they are attracted more by A than by B, and the electronegativity of A is somewhat greater than that of B.

Based on the methods proposed by Pauling, Mullikan, and others, numerical values of electronegativities have been assigned to almost all elements of the periodic table.

TABLE : ECTRONEGATIVITIES OF SOME ELEMENTS

H 2·1						
Li 0·97	Be 1·5	B 2·0	C 2·5	N 3·1	O 3·5	F 4·1
Na 1·0	Mg 1·2	Al 1·5	Si 1·7	P 2·1	S 2·4	Cl 2·8
K 0·90	Ca 1·0	Ga 1·5	Ge 2·0	As 2·2	Se 2·5	Br 2·7
Rb 0·89	Sr 1·0	In 1·5	Sn 1·72	Sb 1·82	Te 2·0	I 2·2
Cs 0·86	Ba 0·97	Tl 1·4	Pb 1·5	Bi 1·7	Po 1·8	At 1·9

The tendency of an atom to acquire electrons depends on two factors : (*i*) its nuclear charge (at. no.) ; and (*ii*) the distance of the valency shell (atomic radius). Atoms possessing more nuclear charge, *i.e.*, higher atomic number, and less atomic radii, will have higher electronegativities. This leads to the predicition that electronegativities of the elements will be higher in the upper right of the periodic table than in the lower left. It may also be noted that, in general, electronegativities of elements increase from left to right in 'periods' and from bottom to top in 'groups' of the periodic table Exceptions to this statement occur when the factor of 'atomic size' overweighs that of 'nuclear charge'.

The concept of electronegativity has proved very useful in predicting the nature of chemical bonds as also the properties of compounds.

POLARITY IN COVALENT BONDS

We have seen that a covalent bond between two atoms is formed as a result of overlap of two atomic orbitals. The overlapping orbitals, each having one electron, then merge to form a new molecular orbital containing a pair of electrons. When the atoms joined by a covalent bond are similar, say as in H—H molecule the two hydrogen atoms possessing some electronegativity) exert equal attractive force on the two electrons which are, therefore, symmetrically disposed in the molecular orbital. Thus :

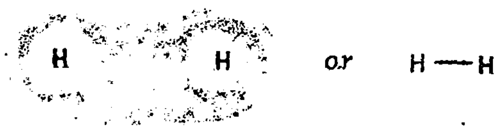


Fig. 6·21. Uniform electron cloud in H_2 molecule.

The covalent bond in hydrogen molecule is, therefore, non-polar.

In a molecule having two different atoms joined by a covalent bond, the atom having higher electronegativity will exert a greater attractive pull on the shared pair of electrons. Thus the two electrons will spend more time near this than the other atom, making it slightly negative. Thus in hydrogen fluoride molecule, H—F, the electronegativity of H atom and F atom is 2·1 and 4·1 respectively. Hence the fluorine atom will exert greater attraction on the shared electrons in comparison to hydrogen atom. The electron population in the molecular orbital would be more around the F-atom as indicated by the density of the cloud in the following diagram.

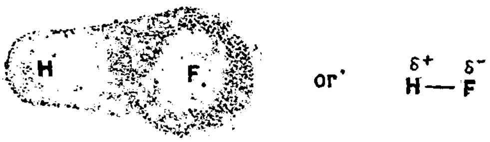
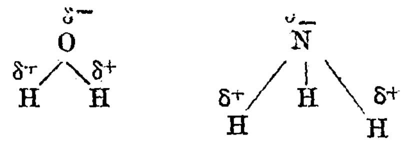


Fig. 6·22.

Thus the covalent bond joining H and F atoms develops polarity and is called a **Polar bond.** By and large the covalent bond between different atoms are polar (ionic). The per cent of polar character in a covalent bond depends upon the relative electronegativity of the atoms joined by the bond; the greater the difference in electronegativity, the greater the polar character of the bond.

Water and ammonia offer important examples of polar molecules.



The polar molecules behave like small magnets and have a greater attraction for each other as also for ions, and thus acquire characteristic physical and chemical properties.

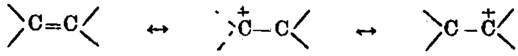
RESONANCE

The concept of resonance was forwarded on purely chemical grounds when Kekule structure of benzene was found unsatisfactory to explain its properties in full. Later it was discovered that there are, in fact, numerous substances which like benzene could be assigned two or more structural formulas differing only in the placement of bonds or electrons, and the actual behaviour of the substance was not represented by any of these structures but by a new structure which is a 'blend' or 'hybrid' of the various possible structures.

The [illegible] of hybridisation of two or more conventional val[illegible] bond structures to yield a new stable hybrid form with less energy is termed **Resonance.**

It may be clearly understood that the old concept that two or more structural formulas oscillate between themselves and each of them contribute to the properties of the substance, -is incorrect. Resonance really involves the delocalisation of electrons in the molecule so as to give a new stable form which explains adequately its behaviour.

Thus carbon-to-carbon double bond in benzene and several other organic compounds behaves as stronger than a normal ethylene linkage and slightly weaker than a single carbon-to-carbon bond. This is explained by the fact that one of the electron pairs between the two carbons is delocalised or displaced to give a stable resonance hybrid form as follows :



(Resonance structures)

It may be noted that as one electron pair shifts to one or the other carbon atom, the double bond becomes a single bond with polarity developed on it. Therefore, the resonance hybrid form of the double bond in such a case becomes stable as in benzene and possesses a character intermediate between that of a double and a single bond.

Sulphur dioxide could be represented by the following two possible structures which differ only in the disposition of a pair of electrons.

$$:\underset{..}{\overset{..}{O}}:\underset{..}{S}::\underset{..}{O}: \qquad :\underset{..}{O}::S:\underset{..}{\overset{..}{O}}:$$

Or $\qquad O\leftarrow S=O \qquad O \quad S\rightarrow O$

(*a*) (*b*)

None of these formulas can properly account for the properties of sulphur dioxide. These postulate two different [illegible] linkages (one double and one covalent) in the molecule, while it has been established by experiment that both S—to—O linkages in sulphur dioxide are equivalent in all respects. Thus none of the structures (A or B) represents the structure of SO_2 molecule but a new 'hybrid' structure having 'equivalent' S—O bond explains its behaviour This new hybrid is stable and has independent existence.

$$O\leftarrow S=O \quad \leftarrow \quad O-\overset{+}{S}-\overset{-}{O}$$

(*a*) (Hybrid)

$$O=S\rightarrow O \quad \leftrightarrow \quad \overset{-}{O}-\overset{+}{S}-\overset{-}{O}$$

(*b*) (Hybrid)

Quantum mechanics reveals that the resonace hybrid possesses less energy than those calculated for any one of the canonical structures. If A and B correspond to the calculated energies of the structures (*a*) and (*b*), and (*c*) stands for the energy state of the actual structure, the energy diagram assumes the following shape.

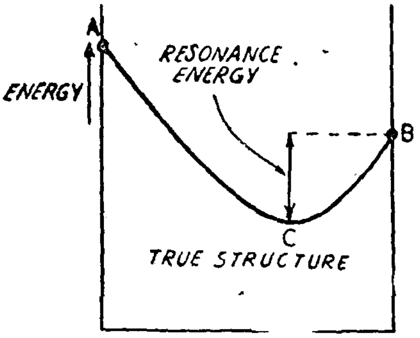
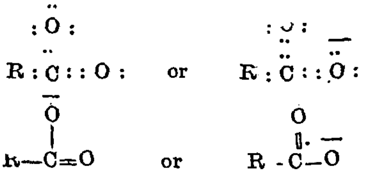


Fig. 6·23.

The amount by which the energy of the resonance structure is less than that of the canonical structure, is termed the ***Resonance Energy*** and this difference of energy is a measure of the added stability conferred by resonance.

Another typical example of resonance is offered by the carboxylate ion. It is capable of being represented by the structures.

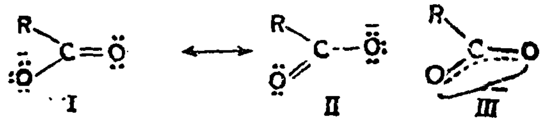
Thus.



$$R:\overset{:\overset{-}{\ddot{O}}:}{\ddot{C}}::O: \quad \text{or} \quad R:\overset{:O:}{\ddot{C}}::\overset{-}{\ddot{O}}:$$

$$R-\overset{\overset{\bar{O}}{|}}{C}=O \quad \text{or} \quad R-\overset{\overset{O}{\|}}{C}-\bar{O}$$

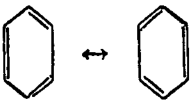
These forms, while they have the same arrangement of atoms, differ only in that the double bond is possessed by alternate oxygen atoms. None of these actually represents the behaviour of carboxylic acids. Each of these forms resonates to give a new stable hybrid' form (III) which explains fully the behaviour of this class of compounds.



The above 'hybrid' form warrants 'equivalence' of the tw

C—O bonds which is confirmed by the measurement of 'bond lengths'. It has been found that the two carbon-oxygen bonds in carboxylate group are equal in length (1·27Å). On the other hand the carbon-oxygen bond length for a double bond is 1·24Å and for a single bond 1·43Å. Hence, it stands to reason that the hybrid carboxyl ion is symmetrical and possibly half the negative charge on the oxygen atom of the original structure now resides on each oxygen of the hybrid as indicated in the above diagram.

Similarly, the benzene molecule which is a resonance hybrid of the structures



has carbon-carbon bond lengths midway between those of C—C and C=C bonds. The C—C distance in ethane molecule has been determined to be 1·54Å, while C=C bond length in ethylene is 1·33Å. For all carbon-carbon bonds in benzene molecule, the value is 1·39Å, indicating clearly their hybrid nature.

The concept of resonance has proved very useful in explaining the unexpected stability and chemical behaviour of many organic molecules. We have seen how the stability of benzene molecule could be explained by resonance, while ordinarily it could have been expected to behave like ethylene, since it contains three double bonds. Also, while aldehydes and ketones can be reduced easily to yield alcohols, the carboxyl group in fatty acids is stable and difficult to reduce.

Resonance and tautomerism must be carefully distinguished from each other

(*a*) Resonance involves only a shift of electrons while tautomerism requires the transference of a hydrogen atom or proton.

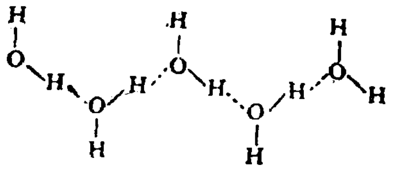
(*b*) Tautomerism implies the simultaneous existence of two molecular forms in equilibrium. In case of resonance, only one molecular form exists which is an intermediate arrangement between the two possible forms.

HYDROGEN BONDING

When a hydrogen atom is linked with a very strongly electronegative atom (as with O in water), it forms positive end of the dipole.

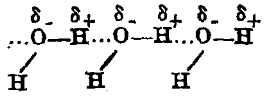
$$\overset{\delta+}{H}-\overset{\delta-}{O}-\overset{\delta+}{H} \quad \text{or} \quad \overset{\delta+}{H}-\underset{\cdot\cdot}{\overset{\delta-}{\ddot{O}}}-\overset{\delta+}{H}$$

Here, the hydrogen atom has an extraordinary urge to become associated with atoms of other molecules which have unshared electrons possessing a negative charge (O in water). There is a strong evidence in support of the fact that hydrogen, though univalent, behaves as a bivalent element under certain conditions. It is noticed those molecules which contain O—H or N—H bonds (*e.g.*, in water, alcohols, carboxylic acids, phenols, amines and amides) have a great tendency to 'associate' or to link up to form larger molecules. Investigation of the crystal structure of ice reveals that the molecules in it are linked in the following fashion.



As indicated above, the hydrogen atom seems to form a linkage between two oxygen atoms *i.e.*, hydrogen bridges them. This mode of linking is called **Hydrogen bonding** or 'hydrogen bridging'. As it is impossible for the H atom to participate in a second covalent bond, the additional bond is shown with the help of dotted lines.

In general, hydrogen bonds may be represented as —A—H...A'— where A and A' may be atoms possessing very high electronegativity (O, N, F, Cl and rarely C also). The A—H bond will be polar with H atom as the positive end. Similarly —A' being highly electronegative, will bear a negative charge. So, the hydrogen bonding between H and A' is more or less due to electrostatic attractive force. Thus in water molecule, association by hydrogen bonding may be represented as

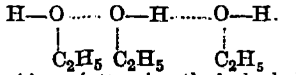


It is the attractive force between every positive H atom and negative O atom which holds them together. Greater the electronegativity of A and A' atoms (which may be the same as O in water crystals), stronger will be the H-bond (H...O). Hydrogen bond energie lie in the range 2 to 8 Kcal/mole, as compared with O—H bond energy 110 Kcal/mole. The H bonds are rather weak but are widespread and have a very significant effect on the physical properties (boiling point, solubility, ionisation) of organic compounds.

(*a*) *Boiling Points*. It is understandable that substances having nearly the same molecular weights, have the same boiling points. The boiling points of ethers and alkanes of comparable molecular weights are not far apart, but the boiling points of alcohols having almost equal molecular weights are considerably higher.

$CH_3—CH_2—CH_3$	$CH_3—O—CH_3$	$CH_3—CH_2—OH$
b.p. —45°C	b.p. —25°C	b.p. 78°C
(m. wt.=44)	(m. wt.=46)	(m. wt.=46)

This could be explained in light of hydrogen bonding, Alcohol molecules are held together by hydrogen bonds and, therefore, more energy is required to separate the molecules for vaporisation.

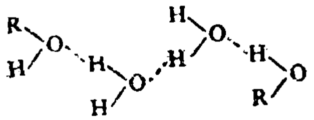


$$\underset{C_2H_5}{H-\underset{|}{O}} \cdots \underset{C_2H_5}{\underset{|}{O}}-H \cdots \underset{C_2H_5}{\underset{|}{O}}-H.$$

(Association in ethyl alcohol)

Such an association is entirely absent in propane and ethane and hence their low boiling points.

(b) *Water solubility*. Organic substances owe their solubility in water to a hydrogen bonding effect between the solute and solvent molecules which are polar in nature. This may be illustrated in the case of alcohols as follows :



As the molecular weight (or the molecular size) of the alcohol increases, the degree of hydrogen bonding with water decreases and there will be a corresponding decrease in the solubility of alcohol in water. However, the high solubility of sugars and starches in water is attributed by a large number of $-OH$ groups, making more hydrogen bonding possible.

The organic compounds containing (*i*) C and H ; (*ii*) C, H, S ; (*iii*) C, H, X, do not dissolve in water appreciably since they are not capable of forming hydrogen bridges with water molecules Alcohols and acids have a marked tendency to form hydrogen bridges with water and hence are very soluble.

QUESTIONS

1. Give a concise account of the atomic structure with a special reference to the number and arrangement of electrons in different shells and subshells.

2. Define 'atomic orbital'. Discuss the shape of '*s*' and '*p*' orbitals.

3. Give the broad principles of 'electronic configuration' in atoms, illustrating taking example of the first ten elements of the Periodic Table.

4. Interpret the formation of electrovalent and covalent bonds in terms of the 'Orbital theory'. Give examples.

5. What do you understand by a 'Molecular Orbital' ? Describe the formation of *s-s* and *s-p* orbital taking examples of H_2 and HF molecules.

6. What do you understand by a σ bond and a π bond ? Give one example of each type of bond.

7. What are Hybridised orbitals ? Explain the tetravalency of carbon using this concept.

8. What do you understand by Hybridisation ? Explain the mechanism of double and triple bonds in ethylene and acetylene molecules.

9. Write an essay on 'The important reaction intermediates.'

10. Write a short not on the concept of resonance.

11. What do you understand by resonance hybrid and resonance energy ? Explain how the concept of resonance has proved useful in explaining the unexpected stability and chemical behaviour of many organic compounds.

12. Explain the concept of resonance in the light of the structures of benzene and carboxylate ion.

13. What do you understand by hydrogen bonding ? What is the nature of such bonds ?

14. Give conditions conducive for hydrogen bonding. How does it affect the physical properties of organic compounds ?

7

Isomerism

Gilbert N. Lewis
(1875—1946, American)
Physical Chemist. Organic chemists are indebted to him for the concepts of valency and atomic structure given by him. His book on valency has given great impetus to research and teaching of Organic Chemistry.

In the study of Organic chemistry we come across many cases when two or more compounds are made of equal number of like atoms. These compounds possess the same molecular formula but differ from each other in physical or chemical properties, and are called **Isomers** and the phenomenon is termed **Isomerism** (Greek, *isos* = equal ; *meros* = parts). Since isomers have the same molecular formula, the difference in their properties must be due to different modes of combination or arrangement of atoms within the molecule. Broadly speaking isomerism is of two types :

(*i*) *Structural Isomerism* ; and

(*ii*) *Stereoisomerism.*

Structural Isomerism. When the isomerism is simply due to difference in the arrangement of atoms within the molecule, without any reference to space, the phenomenon is termed **Structural Isomerism.** In other words, the structural isomers while they have the same molecular formulas, possess different structural formulas. This type of isomerism which arises from difference in the structure of molecules, includes :

(*a*) *Chain or Nuclear Isomerism* :

(*b*) *Positional Isomerism* ; and

(*c*) *Functional Isomerism.*

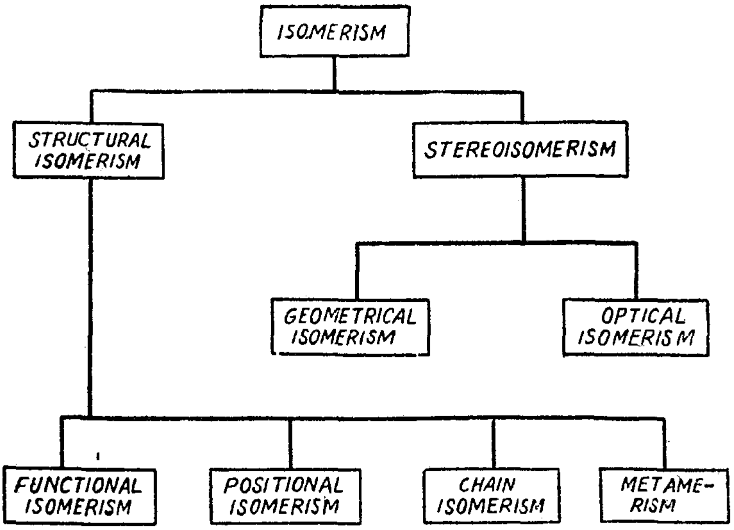
Stereoisomerism. When isomerism is caused by the different arrangements of atoms or groups in space, the phenomenon is called **Stereoisomerism** (Greek, *Stereos*=occupying space). The stereoisomers have the same structural formulas but differ in the spatial arrangement of atoms or groups in the molecule. In other words, stereoisomerism is exhibited by such compounds which have identical molecular structure but different *configuration.*

Stereoisomerism is of two types :

(*a*) *Geometrical or Cis-Trans isomerism* ;

and (*b*) *Optical Isomerism.*

Thus various types of isomerism could be summarised as follows :

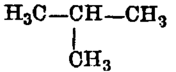


CHAIN OR NUCLEAR ISOMERISM

This type of isomerism arises from the difference in the structure of carbon chain which forms the nucleus of the molecule. It is, therefore, named as **Chain** or **Nuclear Isomerism**. For example, there are known two butanes which have the same molecular formula (C_4H_{10}) but differ in the structure of the carbon chains in their molecules.

$CH_3—CH_2—CH_2—CH_3$

n-Butane

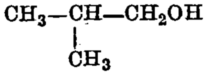


$H_3C—\underset{\displaystyle CH_3}{\underset{|}{CH}}—CH_3$

Isobutane

while *n*-butane has a continuous chain of four carbon atoms, isobutane has a branched chain. These chain isomers have somewhat different physical and chemical properties, *n*-butane boiling at $-0{\cdot}5^\circ$ and isobutane at $-10{\cdot}2^\circ$. This kind of isomerism is also shown by other classes of compounds. Thus, *n*-butyl alcohol and isobutyl alcohol having the same molecular formula C_4H_9OH are chain isomers.

$CH_3{-}CH_2{-}CH_2{-}CH_2OH$
n-butyl alcohol



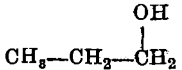
$$CH_3{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}CH_2OH$$

Isobutyl alcohol

It may be understood clearly that the molecules of chain isomers differ only in respect of the linking of the carbon atoms in the alkanes or in the alkyl radicals present in other compounds.

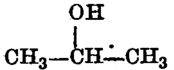
POSITIONAL ISOMERISM

When two or more compounds have structural formulas which differ only in the position of the substituent atom or group on the carbon chain, these are called **Position Isomers** and the phenomenon is termed **Positional Isomerism**. Thus *n*-propyl alcohol and isopropyl alcohol offer an example of positional isomerism. They possess the same molecular formula (C_3H_7OH) and their molecules are made of a chain of three carbon atoms. In *n*-propyl alcohol, the OH group is on the end carbon atom while in isopropyl alcohol it is on the middle carbon atom.



$$CH_3{-}CH_2{-}\overset{\displaystyle OH}{\overset{|}{CH_2}}$$

n-Propyl alcohol



$$CH_3{-}\overset{\displaystyle OH}{\overset{|}{CH}}{-}CH_3$$

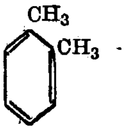
Isopropyl alcohol

The positional isomerism may also be extended to alkanes and alkynes which differ only in the position of the double or triple bond in their molecules. Thus, the molecular formula C_4H_8 stands for two butenes.

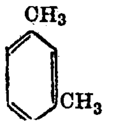
$CH_2{=}CH{-}CH_2{-}CH_3$ 1-Butene
$CH_3{-}CH{=}CH{-}CH_3$ 2-Butene

in which the position of the double bond is different.

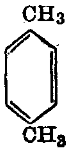
In the aromatic series, the disubstitution products of benzene also exhibit positional isomerism due to different relative positions occupied by the two substituents on the benzene ring. Thus xylene $C_6H_4(CH_3)_2$, exists in the following three forms which are positional isomers.



o-xylene
(*Ortho*)



m-xylene
(*Meta*)



p-xylene
(*Para*)

FUNCTIONAL ISOMERISM

When any two compounds have the same molecular formula but possess different functional groups, they are called **Functional Isomers** and the phenomenon is termed **Functional Isomerism.**

In other words substances with the same molecular formula but belonging to different classes of compounds exhibit functional isomerism. Thus :

(1) Diethyl ether and butyl alcohol both have the molecular formula $C_4H_{10}O$ but contain different functional groups.

$C_2H_5—O—C_2H_5$ Diethyl ether $\qquad$ $C_4H_9—OH$ Butyl alcohol

The functional group in diethyl ether is (—O—), while in butyl alcohol it is (—OH).

(2) Acetone and Propionaldehyde both with the molecular formula C_3H_6O are functional isomers.

$CH_3—CO—CH_3$ Acetone $\qquad$ $CH_3—CH_2—CHO$ Acetaldehyde

In acetone the functional group is (—CO—), while in acetaldehyde it is (—CHO).

METAMERISM

This type of isomerism is due to the unequal distribution of carbon atoms on either side of the functional group in the molecule of compounds belonging to the same class. For example, Methyl propyl ether and Diethyl ether both have the molecular formula $C_4H_{10}O$. The number of carbon atoms attached to the ethereal group —O—,

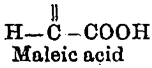
$CH_3—O—C_3H_7$ Methyl propyl ether $\qquad$ $C_2H_5—O—C_2H_5$ Diethyl ether

in methyl propyl ether is 1 and 3, while in dimethyl ether it is 2 and 2. This isomerism known as **Metamerism** is shown by members of classes such as ethers, ketones and amines where the central functional group is flanked by two chains.

GEOMETRICAL ISOMERISM

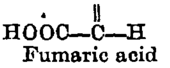
We have discussed above the various types of isomerism arising from difference in the structure of compounds having the same molecular formula. Now we will study a new type of isomerism where the isomers possess the same structural formula containing a double bond and differ only in respect of the arrangement of atoms or groups about the double bond. The simple examples of this kind of isomerism are :

(*i*)



$$\begin{array}{c}\text{H—C—COOH}\\ \|\\ \text{H—C—COOH}\end{array}$$

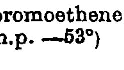
Maleic acid
(m.p. 130°)



$$\begin{array}{r}\text{H—C—COOH}\\ \|\\ \text{HOOC—C—H}\end{array}$$

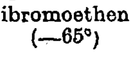
Fumaric acid
(m.p. 286°)

(*ii*)



$$\begin{array}{c}\text{H—C—Br}\\ \|\\ \text{H—C—Br}\end{array}$$

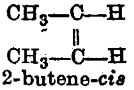
1, 2-dibromoethene-*cis*
(m.p. —53°)



$$\begin{array}{c}\text{H—C—Br}\\ \|\\ \text{Br—C—H}\end{array}$$

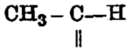
1, 2-dibromoethene-*trans*
(—65°)

(*iii*)



$$\begin{array}{c}\mathrm{CH_3{-}C{-}H}\\ \|\\ \mathrm{CH_3{-}C{-}H}\end{array}$$

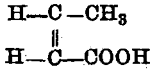
2-butene-*cis*
(b.p. +4°)



$$\begin{array}{c}\mathrm{CH_3{-}C{-}H}\\ \|\\ \mathrm{H{-}C{-}CH_3}\end{array}$$

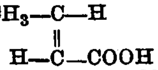
2-butene-*trans*
(b.p. +1°)

(*iv*)



$$\begin{array}{c}\mathrm{H{-}C{-}CH_3}\\ \|\\ \mathrm{H{-}C{-}COOH}\end{array}$$

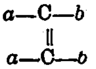
Crotonic acid
(m.p. 72°)



$$\begin{array}{c}\mathrm{CH_3{-}C{-}H}\\ \|\\ \mathrm{H{-}C{-}COOH}\end{array}$$

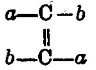
Isocrotonic acid
(m.p. 15°)

It may be noticed that in all the above examples, the doubly bound carbon atoms are linked to two different groups, so that in general we could say that *geometrical isomerism is shown by alkenes or their derivatives in which two different atoms or groups are attached to each carbon containing the double bond.* Thus the compounds having the formula *abC*=*Cxy* or the simple structure *abC*=*Cab* occur in two forms and exhibit geometrical isomerism.



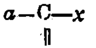
$$\begin{array}{c}a{-}C{-}b\\ \|\\ a{-}C{-}b\end{array}$$

(*cis*-form)



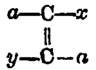
$$\begin{array}{c}a{-}C{-}b\\ \|\\ b{-}C{-}a\end{array}$$

(*trans*-form)



$$\begin{array}{c}a{-}C{-}x\\ \|\\ a{-}C{-}y\end{array}$$

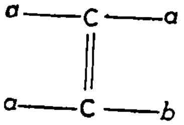
(*cis*-form)



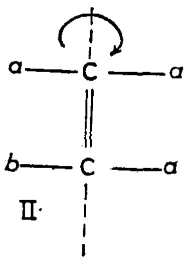
$$\begin{array}{c}a{-}C{-}x\\ \|\\ y{-}C{-}a\end{array}$$

(*trans*-form)

If the two atoms or groups linked to the same doubly linked carbon are similar as in the molecule *aaC*=*Cab*, the compound does not show geometrical isomerism. Here the two possible configurations are, in fact, the same.



I



II

The structure II when rotated through 180° through the axis of the double bond, can be superimposed over structure I.

The geometrical isomerism is also shown by compounds containing C=N or a cyclic ring structure in their molecules.

Explanation and Definition of Geometrical Isomerism. To understand the cause of geometrical isomerism we must return to the fundamental conception of the tetrahedral nature of the carbon atom.

According to Le Bel and van't Hoff (1874), the valencies of the carbon atom are distributed symmetrically in space. They may be pictured as directed towards the four corners of a regular tetrahedron constructed round the carbon atom as the centre. According to this theory, a derivative of ethane, say succinic acid, containing two carbon atoms united by a single bond could be represented by two *tetrahedra joined corner to corner.*

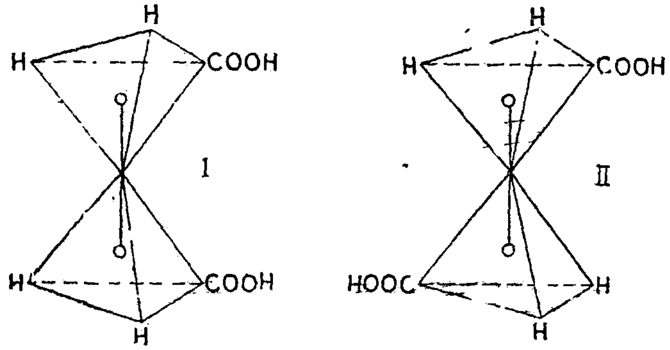


Fig. 7·1. Identical molecules

If the two tetrahedra were fixed rigidly to each other, the two compounds having the models I and II should be possible. Actually there is only one succinic acid known. The natural conclusion is that the two carbon atoms are able to rotate about the axis formed by the bond between them and can, therefore, assume form I or II. Thus, the possibility of different spatial arrangements in ethane derivatives is ruled out.

If, however, the two carbon atoms are united by a double bond, the two tetrahedra representing them must necessarily be in contact at two corners. In such a case all free rotation of the tetrahedra ceases and the groups attached to the two carbon atoms are fixed relative to each other. Thus, different spatial arrangements of the groups about the doubly bound carbon atoms now become possible. For example, the two tetrahedral models representing maleic acid and fumaric acid will be as shown in Fig 7:2.

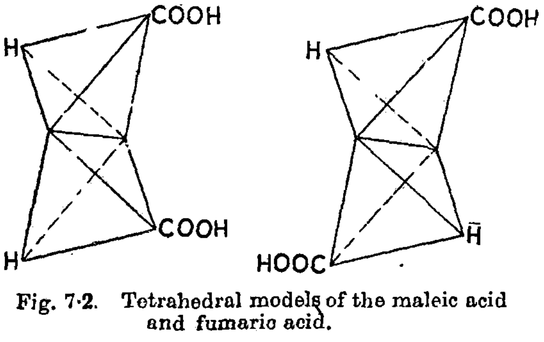
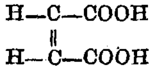


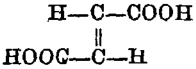
Fig. 7·2. Tetrahedral models of the maleic acid and fumaric acid.

For the sake of convenience the above models are represented in a plane as follows :—



$$\begin{matrix} H-C-COOH \\ \| \\ H-C-COOH \end{matrix}$$

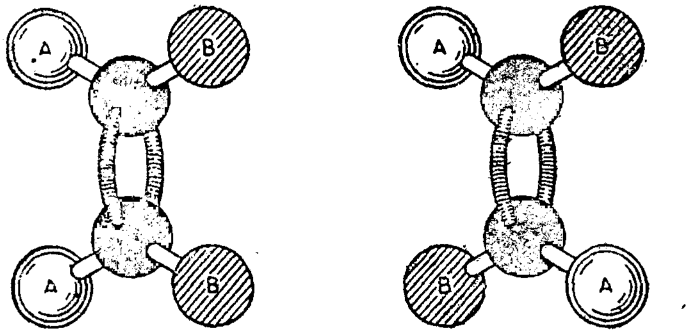
Maleic acid (*cis*)



$$\begin{matrix} H-C-COOH \\ \| \\ HOOC-C-H \end{matrix}$$

Fumaric acid (*trans*)

It may be noted clearly that maleic acid and fumaric acid have quite different arrangements of groups about the double bond. While in one case similar groups are on the same side, in the other they lie on opposite sides. *This type of isomerism due to the different geometrical arrangements of the groups about the doubly bound carbon atoms* is known as **Geometrical isomerism.** When the similar groups lie on the same side as in maleic acid, it is called the **Cis**



(*Cis*) (*Trans*)

Fig. 7·3. Ball and stick models of Geometrical isomers.

isomer (Latin, *cis*=on same side). When similar groups are on the opposite sides as in the fumaric acid, it is called the **Trans isomer** (Latin, *trans*=across). Consequently this type of isomerism is often spoken of as **Cis-Trans isomerism.**

The ball and stick models of geometrical isomers of an organic compound are given below. Here the two black balls (carbon atoms), in each model are joined by two spring-rods and are thus 'fixed' and are incapable of free rotation. The balls A and B (representing different atoms or groups) could be arranged in two ways about the doubly bound black balls. The first model having similar balls on the same side represents the *cis* isomer, while the second one with similar balls on opposite sides represents the *trans* isomer.

A beautiful illustration of geometrical isomerism becoming possible by a double union between the carbon atoms is given in Fig. 7·4.

In (I) two boards are shown joined by a single nail. Since the boards can rotate independently, the marked ends of the boards

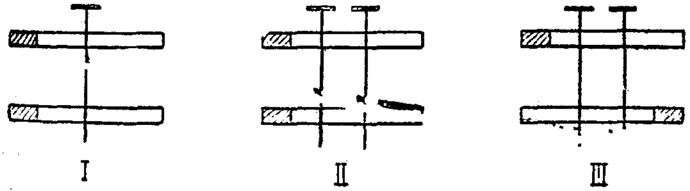


Fig. 7·4 Illustration of geometrical isomerism.

cannot be arranged relative to each other. If, however, the boards are fastened by two nails, they are fixed and hence two arrangements (II and III) of the marked ends are possible.

EXPLANATION BASED ON ORBITAL THEORY

The modern orbital theory offers a more sophisticated explanation of geometrical isomerism. We have already discussed in the previous chapter that the doubly bonded carbon atoms in ethylene exhibit a trioganol type of hybridization ($2s$, $2p_x$, $2p_y$ hybridized). The three new sp^2 orbitals lie in one plane. Thus the three σ bonds formed by each of these two carbon atoms are coplanar. The unhybridized third p_z orbitals of the doubly bonded carbon atoms which stand at right angles to the trioganol bonds, overlap at two positions to form π orbital. The two types of overlapping results in the formation of *Cis* and *Trans* isomers.

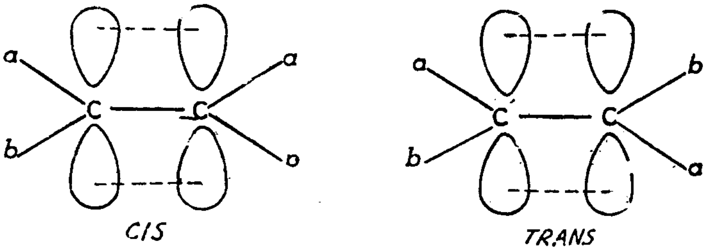


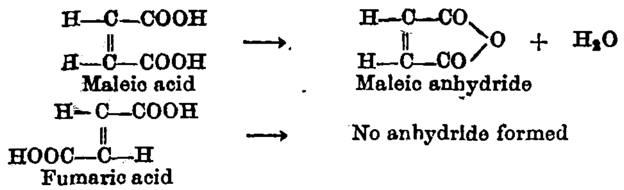
Fig. 7·5.

Determination of Configuration of Isomers. There is no absolute method for the determination of the configuration of *cis-trans* isomers. Several elementary relationships are, however, helpful to the beginner.

(1) From a study of the Physical Properties. The difference in the structure of molecule of *cis-trans* isomers is reflected in their physical properties. Thus it has been observed that in general the *cis* isomer has a lower melting point, a higher boiling point, a higher density, a greater solubility in inert organic solvents, a higher heat of combination and a higher ionisation constant as an acid.

(2) By Formation of a Cyclic Compound. The formation of a cyclic molecule from an open chain molecule takes place easily only when the reacting groups are close to each other. This fact has been most useful in assigning configuration to *cis-trans* isomers in which the doubly bound carbon atoms carry groups that are capable of reacting with each other. The configuration of maleic and fumaric acids is established on this basis.

Maleic acid readily forms cyclic anhydride whereas fumaric acid does not. This means that in maleic acid the two groups are nearer to each other than they are in fumaric acid. That is



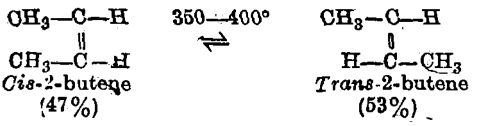
$$\begin{matrix}\mathrm{H-C-COOH}\\ \|\\ \mathrm{H-C-COOH}\\ \text{Maleic acid}\end{matrix} \longrightarrow \begin{matrix}\mathrm{H-C-CO}\diagdown\\ \|\qquad\quad >\mathrm{O}\\ \mathrm{H-C-CO}\diagup\\ \text{Maleic anhydride}\end{matrix} + \mathrm{H_2O}$$

$$\begin{matrix}\mathrm{H-C-COOH}\\ \|\\ \mathrm{HOOC-C-H}\\ \text{Fumaric acid}\end{matrix} \longrightarrow \text{No anhydride formed}$$

Obviously maleic acid is the *cis* form and fumaric acid the *trans*-form.

In addition to the methods given above, other physical measurements such as the measurement of the distances between certain atoms by means of X-rays, measurement of absorption spectra, etc., may be of help for deciding upon the configuration in some cases.

Interconversion of Geometrical Isomers. Although geometrical isomers are stable at ordinary temperatures, one can be converted into the other or to an equilibrium mixture of both by heat, by exposure to ultraviolet light, or by use of catalysts. Thus :



$$\begin{matrix}\mathrm{CH_3-C-H}\\ \|\\ \mathrm{CH_3-C-H}\\ \textit{Cis}\text{-2-butene}\\ (47\%)\end{matrix} \xrightleftharpoons{350-400^\circ} \begin{matrix}\mathrm{CH_3-C-H}\\ \|\\ \mathrm{H-C-CH_3}\\ \textit{Trans}\text{-2-butene}\\ (53\%)\end{matrix}$$

Obviously at the high temperature, one of the bonds of the double linkage breaks sufficiently to permit rotation about the remaining bond.

GEOMETRICAL ISOMERISM OF OXIMES

From the dipole moment and the examination of its infrared spectrum, ammonia molecule has been shown to possess a pyramidal shape. The N-atom is occupying the top position of the pyramid and the H-atoms the corners of the base. Thus the valency bonds of N-atom, like those of C-atom, are distributed in space, the angle contained by any two bonds being 107°

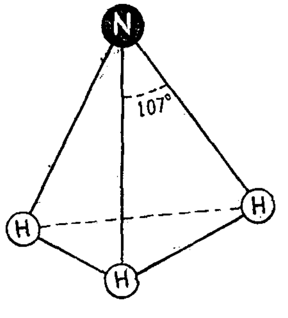


Fig. 7·6. Shape of ammonia molecule.

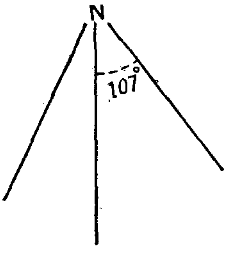
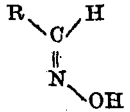
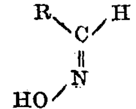


Fig. 7·7. Direction of valency bonds of nitrogen atom.

Therefore, the compounds such as the oximes of aldehydes, R.CH : N.OH, in which the C-atom is joined to a N-atom by a double bond, are capable of exhibiting geometrical isomerism, since the H and OH groups may be arranged on the same side or the opposite sides of the double bond. The two stereoisomers thus obtained are designated as *syn* (equivalent to *cis*) and *anti* (equivalent to *trans*) respectively. The two geometrical isomers of an aldoxime may be written as :

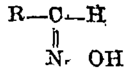


Syn-aldoxime



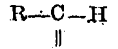
Anti-aldoxime

Or simply as :



$$\begin{array}{l} R-C-H \\ \;\| \\ N\cdot OH \end{array}$$

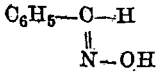
Syn-aldoxime



$$\begin{array}{r} R-C-H \\ \| \;\; \\ HO-N \;\; \end{array}$$

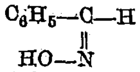
Anti-aldoxime

Two benzaldoximes have been actually isolated : (1) α-benzaldoxime, m.p. 35° ; and (2) β-benzaldoxime, m.p. 130°. The two isomers have been assigned the configurations :



$$\begin{array}{l} C_6H_5-C-H \\ \qquad\;\; \| \\ \qquad\;\; N-OH \end{array}$$

α-benzaldoxime (*Syn*-form)



$$\begin{array}{r} C_6H_5-C-H \\ \| \;\; \\ HO-N \;\; \end{array}$$

β-benzaldoxime (*Anti*-form)

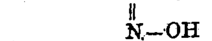
The ketoximes of mixed ketones, R.CO.R′, also show geometrical isomerism. Thus :

$$\begin{array}{l} R-C-R' \\ \quad\;\| \\ \quad\;N-OH \end{array} \qquad \begin{array}{r} R-C-R' \\ \| \;\;\; \\ HO-N \;\;\; \end{array}$$

(Two stereoisomers of ketoximes)

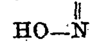
No such geometrical isomerism is possible in ketoximes derived from simple ketones in which R and R′ are same.

Phenyl tolyl ketoxime is known to exist in two forms, while benzophenone oxime, $(C_6H_5)_2C:N.OH$, does not exhibit geometrical isomerism.



$$\begin{array}{l} H_3C.C_6H_4-C-C_6H_5 \\ \qquad\qquad\quad\;\; \| \\ \qquad\qquad\quad\;\; N-OH \end{array}$$

Syn-phenyl tolyl oxime

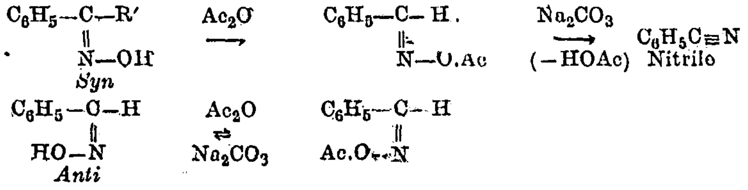


$$\begin{array}{l} CH_3.C_6H_4-C-C_6H_5 \\ \qquad\qquad\quad\; \| \\ \qquad\quad\;\; HO-N \end{array}$$

Anti-phenyl tolyl oxime

Here the prefixes *syn* and *anti* refer to the relative positions of the OH group and the hydrocarbon radical (attached to doubly bound C atom) first named.

Determination of Configuration : The behaviour of the pair of geometrical isomers on treatment with acetic anhydride followed by sodium carbonate forms the basis of determining their configuration. Thus :

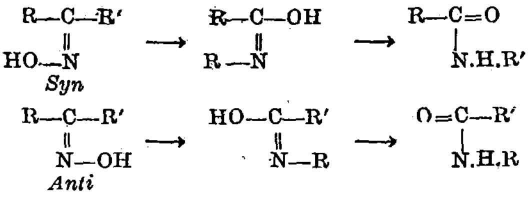


$$\begin{array}{l} C_6H_5-C-R' \\ \qquad\quad \| \\ \qquad\quad N-OH \\ \qquad\quad Syn \end{array} \xrightarrow{Ac_2O} \begin{array}{l} C_6H_5-C-H. \\ \qquad\quad \| \\ \qquad\quad N-O.Ac \end{array} \xrightarrow[(-HOAc)]{Na_2CO_3} \begin{array}{l} C_6H_5C\equiv N \\ \text{Nitrile} \end{array}$$

$$\begin{array}{l} C_6H_5-C-H \\ \qquad\quad \| \\ \qquad HO-N \\ \qquad\;\; Anti \end{array} \underset{Na_2CO_3}{\overset{Ac_2O}{\rightleftharpoons}} \begin{array}{l} C_6H_5-C-H \\ \qquad\quad \| \\ \qquad Ac.O-N \end{array}$$

The form which gives nitrile has the *anti* and the one which is regenerated the *syn* configuration.

Since the oximes of ketones cannot be converted to nitriles as above, their configuration cannot be determined by this method. Here we make use of the fact that when a ketoxime is treated with certain reagents such as phosphorus pentachloride, sulphuric acid, etc., it undergoes molecular rearrangement to form an acid amide. This phenomenon is known as the **Beckmann rearrangement** or **transformation** (1886).



$$\begin{array}{c}R-C-R'\\ \|\\ HO-N\end{array} \longrightarrow \begin{array}{c}R-C-OH\\ \|\\ R-N\end{array} \longrightarrow \begin{array}{c}R-C=O\\ |\\ N.H.R'\end{array}$$

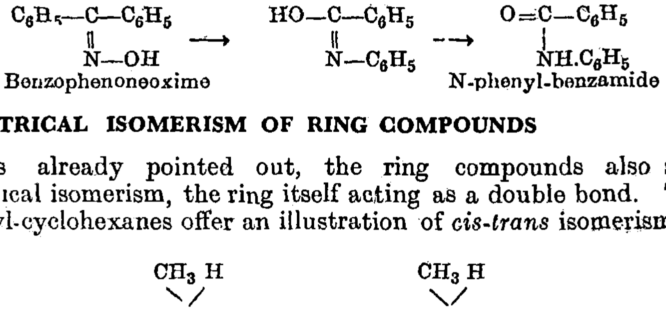
Syn

$$\begin{array}{c}R-C-R'\\ \|\\ N-OH\end{array} \longrightarrow \begin{array}{c}HO-C-R'\\ \|\\ N-R\end{array} \longrightarrow \begin{array}{c}O=C-R'\\ |\\ N.H.R\end{array}$$

Anti

The net result of the above rearrangement is the interchange of the hydrocarbon radical with the OH group in *anti* position. Thus by identifying the acid amide (hydrolysis to parent acid and amine), produced after the Beckmann rearrangement, the configuration of the given ketoxime can be determined.

A simple ketoxime like the benzophenone oxime upon Beckmann transformation would give the corresponding amide.

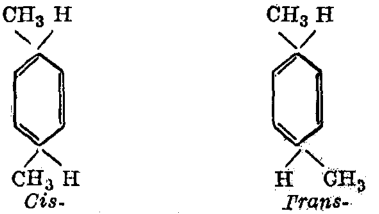


$$\begin{array}{c}C_6H_5-C-C_6H_5\\ \|\\ N-OH\end{array} \longrightarrow \begin{array}{c}HO-C-C_6H_5\\ \|\\ N-C_6H_5\end{array} \longrightarrow \begin{array}{c}O=C-C_6H_5\\ |\\ NH.C_6H_5\end{array}$$

Benzophenoneoxime N-phenyl-benzamide

GEOMETRICAL ISOMERISM OF RING COMPOUNDS

As already pointed out, the ring compounds also show geometrical isomerism, the ring itself acting as a double bond. Thus dimethyl-cyclohexanes offer an illustration of *cis-trans* isomerism.



Cis- *Trans-*

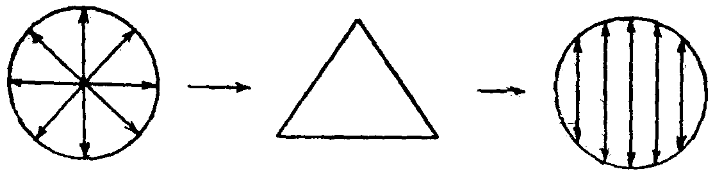
1 4-dimethyl-cyclohexane

The *cis* variety boils at 124·3° and the *trans* variety boils at 119·3°.

OPTICAL ISOMERISM

In optical isomerism we have a much more subtle phenomenon even the geometrical isomerism. While the geometrical isomers differ in physical properties such as melting point, boiling point, density etc., and also in certain chemical properties, the optical isomers will have the same chemical reactions and will be alike in all physical properties mentioned above. They can only be distinguished by their *'action on plane-polarised light'*. This property which is often referred to as the **optical activity** requires a brief discussion.

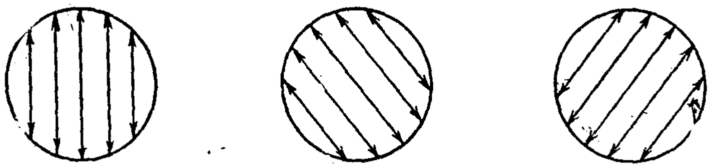
What is Optical Activity ? Light is propagated by a vibratory motion of the 'ether' particles present in the atmosphere. Thus in ordinary light vibrations occur in all planes at right angles to the line of propagation. In plane polarised light the vibrations take place only in one plane, vibrations in other planes being cut off. Plane polarised light can be obtained by passing ordinary light through a *Nicol prism.**



Ordinary light waves vibrating in all directions

Nicol prism

Plane polarised light waves vibrating in one direction only



Plane polarised light

Plane rotated to the left

Plane rotated to the right

Fig. 7·8.

Certain organic compounds, when their solutions are placed in the path of a plane polarised light, have the remarkable property of rotating its plane through a certain angle which may be either to the left or to the right. If the polarised light has its vibrations in the plane XY before entering such a solution, the direction on leaving it will be changed to say X'Y', the plane having been rotated through the angle α (Fig. 7·8). *This property of a*

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*__Nicol Prism__: A Nicol prism is constructed of iceland spar, a substance which is doubly refracting. It is so made that light waves vibrating in all directions except one is cut off by refraction to one side of the prism.

substance of rotating the plane of polarised light is called **optical activity** and the substance possessing it is said to be **optically active**.

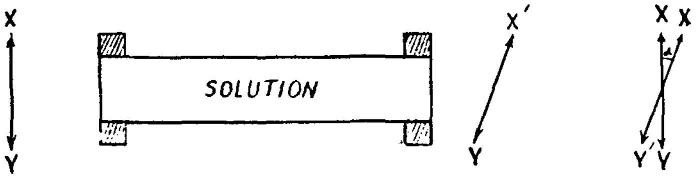


Fig. 7·9. Rotation of the plane of polarised light by a solution. (*Diagrammatic*)

The observed rotation of the plane of polarised light (determined with the help of polarimeter) produced by a solution depends on : (*a*) the amount of the substance in tube ; (*b*) on the length of the solution examined ; (*c*) the temperature of the experiment and (*d*) the wavelength of the light used.

For the measurement of optical rotations, a term **Specific Rotation** is introduced. This is a physical constant characteristic of a substance as much as the melting point, boiling point, density or its refractive index. It is defined as *the number of degrees of rotation observed when light is passed through 1 decimetre (10 centimetres) of its solution having concentration 1 gram per millilitre.* The specific rotation of a given substance can be calculated by using the following expression :

$$\left[\alpha\right]_{D}^{t^\circ} = \frac{\alpha_{obs}}{l \times c}$$

where $\left[\alpha\right]_{D}^{t^\circ}$ stands for specific rotation determined at t°C and using D-line of sodium light ; α_{obs} is the observed angle of rotation ; l is the length of the solution in decimetres ; and c is the concentration of the active compound in grams per millilitre. For example, the specific rotation of amyl alcohol (2-methyl-1-butanol) at 20°C for D-line of sodium light is given by

$$\left[\alpha\right]_{D}^{20^\circ} = -5{\cdot}756^\circ$$

The sign attached with the angle of rotation signifies the direction of rotation. Negative sign (—) indicates that the rotation is towards the left, while positive (+) or no sign means that the direction of rotation is towards right.

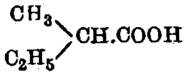
The rotation may be different in different solvents and this needs to be mentioned while reporting the specific rotation. Thus :

$$\left[\alpha\right]_{D}^{25^\circ} \simeq +24{\cdot}7^\circ \text{ (in chloroform)}$$

Definition and Examples of Optical Isomerism. The simple organic compounds which show optical activity are

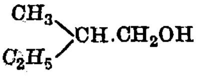
Lactic acid $CH_3.CH(OH).COOH$

Valeric acid



$\begin{matrix}CH_3\\ C_2H_5\end{matrix}\!\!\!>CH.COOH$

Amyl alcohol



$\begin{matrix}CH_3\\ C_2H_5\end{matrix}\!\!\!>CH.CH_2OH$

All these substances are known to exist in three forms

(1) *One rotating the plane of polarised light to the left.* This form is named **Laevo-rotatory** (Latin, *laevous*=left) or simply **l-form.**

(2) *One rotating the plane of polarised light exactly to the same extent but to the right.* This form is named **Dextro-rotatory** (Latin, *dexter*=right) or simply **d-form.**

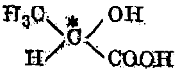
(3) *An inactive form which does not rotate the plane of polarised light at all.* This is a mixture of equal amounts of *d*- and *l*-forms and hence its optical inactivity. It is named **dl-mixture** or **Racemic mixture** (Latin, *racemic*=mixture of equal components).

Thus, three lactic acids are known. They are : (*a*) *d*-lactic acid, (*b*) *l*-lactic acid, and (*c*) *dl*-mixture. Since the *dl*- acid is only a mixture of *d*- and *l*-forms, in reality lactic acid exists in two forms, the *d*-lactic acid and the *l*-lactic acid. These two acids are exactly identical in physical and chemical properties but differ in their action on the plane polarised light. They have different *specific rotation.* Such forms of the same compound which differ only in their optical properties are called **Optical Isomers** and the phenomenon is termed **Optical Isomerism.**

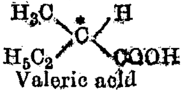
TABLE : *Physical Properties of Lactic Acids*

NAME	M. PT.	DENSITY	$[\alpha]_D$
d-Lactic acid	26°	1·248	+2·24°
l-Lactic acid	26°	1·248	−2·24°
dl-Lactic acid	26°	1·248	0·00°

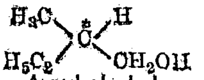
Optically active compounds contain asymmetric carbon atoms. A study of the structural formulas of the optically active substances reveals the fact that they all contain a carbon atom attached to four different groups.



Lactic acid



Valeric acid



Amyl alcohol

The central carbon atom in the above molecules which is linked to four different groups is called an **asymmetric carbon atom.** The asymmetric carbon atom is customarily marked with an asterisk as shown in the formulas mentioned above.

Explanation of Optical Isomerism. Optical isomerism is also a type of stereo-isomerism. Therefore, to understand it we have to revert again to the Le Bel and Van't Hoff's Theory of the tetrahedral carbon atom. According to this theory, the *valencies of a carbon atom are directed towards the four corners of a regular tetrahedron constructed round the carbon atom as the centre.* Thus if the carbon atom is pictured as a tetrahedron and the four different groups *a*, *b*, *c* and *d* are attached at the four corners, two arrangements of the groups about the central carbon atom are possible (Fig. 7·10). Although the two arrangements shown have the same

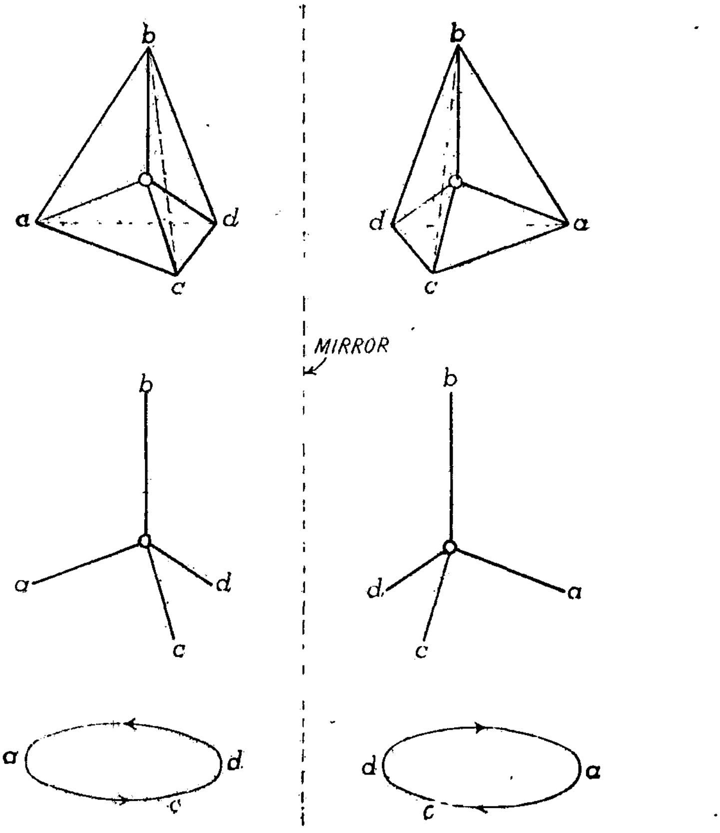


Fig. 7·10. The asymmetric carbon atom offers two space models.

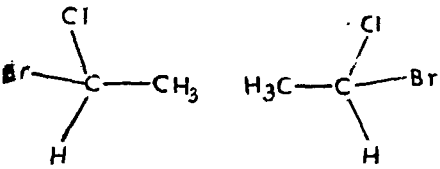
structure, they are not congruent. If you try to superimpose one structure over the other so that the four groups *a*, *b*, *c*, *d* of the first fall over the similar groups of the second, to coincide the groups *a* and c of the two models, group *d* will go on the opposite sides. Hence the two models represent clearly two different spatial arrangements. The space models possibly stand for the *dextro* and *laevo* isomers. They are related as object to its image in the mirror and, therefore, the isomeric substances which they represent are spoken of as **Enantiomorphs** (*mirror images*) or as the shorter equivalent

Enantiomers or **antimers**. We cannot say exactly as to which model represents the *d*-form and which represents the *l*-form, as the mechanism by which the plane of polarised light is rotated is not clearly understood. One thing, however, is clear that leaving out *b*, the arrangement of groups in the lower part of the molecules is different (*see* Fig. 7·10). If in one case they are arranged clockwise, in the other they are anti-clockwise. This offers a satisfactory explanation of the opposite rotatory powers of the *d*- and *l*-isomers.

A large number of compounds are capable of existing in enantiomorphic forms, and the naming of the optically active forms is done in a simple way by placing (+) or (—) before the usual name. For example, lactic acid in the dextro and laevo forms would be (+)lactic acid and (—)lactic acid respectively.

R AND S CONVENTIONS

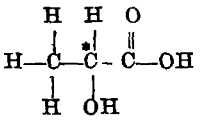
Quite recently a new convention has been introduced by Cahn, Ingold and Prelog to specify the configuration of an asymmetric carbon. According to this convention the name R or S is assigned to an enantiomer by taking into consideration the order of the atoms or groups linked to the asymmetric carbon atom. The order of priority of atoms or groups is decided on the basis of the atomic number of the atoms directly linked to the carbon atom ; the atom of higher atomic number getting higher priority. Thus the priority order of the groups of 1, 1-Bromochloroethane $CH_3.CH.Cl\ Br$, will be $Br > Cl > CH_3 > H$.



(At. Nos. Br=80 ; Cl=35·5 ; C=12; H=1)

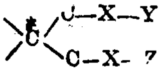
Fig. 7·11. Enantiomers of 1, 1-Bromochloroethane.

But in Lactic acid, two of the atoms linked with asymmetric carbon atom are carbon atoms themselves.



$$H-\underset{H}{\overset{H}{C}}-\underset{OH}{\overset{H}{C^*}}-\overset{O}{\overset{\|}{C}}-OH$$

In this case, the simple rule of determining priority in order of atomic number of atoms directly joining asymmetric carbon atom, will not hold. Here, a comparison of atomic number of atoms next to carbon in the groups decides the issue. In CH_3 group the next atoms are H, H, H and in COOH group they are O, O, H. Since O atom has a higher atomic number (16) as against H (1), the COOH group gets higher priority over CH_3 group. Thus the priority order in Lactic acid will be $OH > COOH > CH_3 > H$. However, in complicated molecules of the type



where the atoms (X) next to carbon of the two groups attached to asymmetric carbon is the same, the comparison of atomic number of further next atoms (Y and Z) will determine their priority. The group containing Y will claim higher priority than the other, if the atomic number of Y is more than that of Z.

After determining the priority order of the attached groups, the molecule as a whole is viewed in the tetrahedral perspective in such a fashion that the group of *lowest* priority is directed away when the arrangement of the remaining groups is being observed. If on viewing from a group of highest priority to the second priority and then the third priority, the eye travels in a clockwise or right-hand direction, the enantiomer is called **R** (Latin, *Rectus*= right) while if the eye moves in the anticlockwise or left-hand direction, the configuration is specified as **S** (Latin, *Sinister*=left).

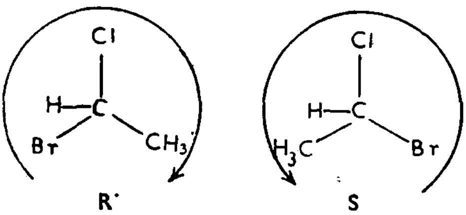
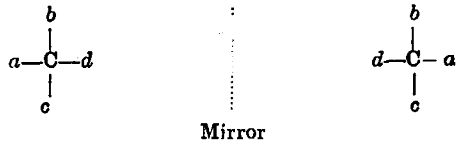


Fig. 7·12. R and S names of the enantiomers of 1, 1-Bromochloroethane. Circular line indicates the direction of vision.

Plane Formulas of Optical Isomers. As we have studied above, plane formulas representing the optically active compounds would be incorrect. But it is more convenient to represent them by plane formulas rather than by sketches of models. It can be done provided that there be no departure from the plane representation. Thus, the plane formulas



$$\begin{array}{c} b \\ | \\ a\text{—}C\text{—}d \\ | \\ c \end{array} \qquad \vdots \qquad \begin{array}{c} b \\ | \\ d\text{—}C\text{—}a \\ | \\ c \end{array}$$

cannot be superimposed and one formula is the mirror-image of the other. This is, however, true *only so long as they are kept in the plane of the paper*. Hence they can conveniently be used to represent *d*- and *l*-isomers of optically active compounds. Thus *d*- and *l*-lactic acids can be represented as

$$\begin{array}{c} CH_3 \\ | \\ H\text{—}C\text{—}OH \\ | \\ COOH \end{array} \qquad \begin{array}{c} CH_3 \\ | \\ HO\text{—}C\text{—}H \\ | \\ COOH \end{array}$$

Fig. 7·13. Plane formulas of *d*- and *l*-lactic acids.

Meaning of Asymmetric object. (1) IT HAS NO PLANE OF SYMMETRY. A plane that divides the object into identical halves, is termed a **plane of symmetry**. If you can interpose such a plane through the given structure, it is symmetrical. In the absence of a plane of symmetry, the structure is asymmetric. Thus while a hand is asymmetric, a ball is symmetrical.

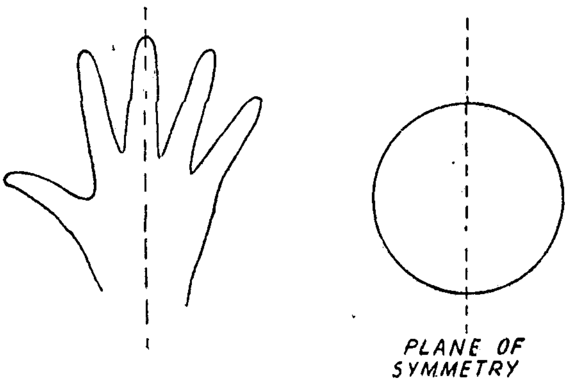


Fig. 7·14. Asymmetric and symmetrical objects.

(2) ASYMMETRIC OBJECT DOES NOT COINCIDE WITH ITS MIRROR IMAGE. An asymmetric object does not coincide with its mirror image in all particulars. For example, left hand is the mirror image of the right hand and the two can never be superimposed. Obviously, a symmetrical object like a ball can be made to coincide with its mirror-image which will be another exactly similar ball.

Optical Activity is a property of Asymmetric molecules. Having learnt the meaning of an asymmetric object, we can now understand easily how optical activity is a property of asymmetric molecules. The tetrahedral models (Fig. 7·15) of *d*- and *l*-isomers are asymmetric since (*i*) one isomer is the mirror image of the other and the two cannot be made to coincide, and (*ii*) they have no plane of symmetry. Thus they represent asymmetric molecules. If, however, any two groups attached to the central carbon atom become similar, the molecules become symmetrical and consequently optical activity vanishes. Thus while lactic acid is optically active, propionic acid is not. These observations can be followed clearly from the plane formulas given in Fig. 7·15.

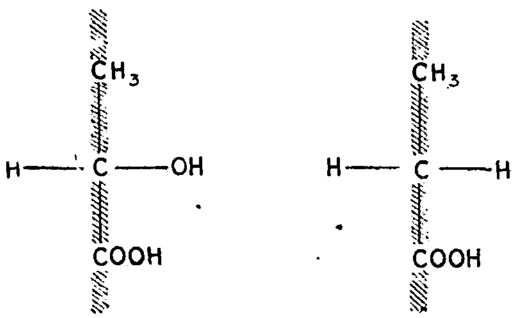


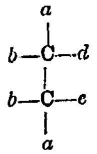
Fig. 7·15. The hatched plane divides the propionic acid molecule into two similar halves, while plane of symmetry is absent in lactic acid molecules.

OPTICAL ISOMERISM IN COMPOUNDS CONTAINING MORE THAN ONE ASYMMETRIC CARBON

We have seen that a substance like lactic acid $CH_3{*}CH(OH)COOH$ which has one asymmetric carbon atom in its molecule, exists in two optically active forms : (1) *d*-lactic acid or

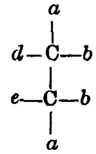
(+) lactic acid ; and (2) *l*-lactic acid or (−) lactic acid, depending on whether it rotates the plane of polarised light to the right or to the left. The third isomeric variety *dl*-lactic acid or (±) lactic acid which is optically inactive, is a mixture of equal molecular quantities of the two enantiomers.

When an organic compound contains two dissimilar asymmetric carbons, it can give four possible isomers. Thus the substance *abdC—Cabe* will exist in the following four forms.



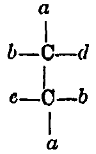
$$\begin{array}{c} a \\ | \\ b—\text{C}—d \\ | \\ b—\text{C}—e \\ | \\ a \end{array}$$

I



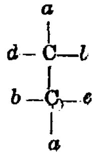
$$\begin{array}{c} a \\ | \\ d—\text{C}—b \\ | \\ e—\text{C}—b \\ | \\ a \end{array}$$

II



$$\begin{array}{c} a \\ | \\ b—\text{C}—d \\ | \\ e—\text{C}—b \\ | \\ a \end{array}$$

III



$$\begin{array}{c} a \\ | \\ d—\text{C}—b \\ | \\ b—\text{C}—e \\ | \\ a \end{array}$$

IV

The forms I and II are enantiomorphs (mirror images) and so are the forms III and IV. These two pairs of enantiomorphs will give rise to two racemic modifications.

It is clear from above that a compound containing two dissimilar asymmetric carbon atoms, exists in four optically active forms. Reasoning in the same fashion, we will find that a compound containing three dissimilar asymmetric carbon atoms can form eight different configurations. Thus, in general, the number of optical isomers is given by 2^n where n is the number of dissimilar asymmetric carbon atoms in the molecule.

The forms I and III are not mirror images (enantiomorphs) ; yet they are optically active isomers. Same is the case with II and IV. *Such compounds which are optically active isomers but not mirror images* are called **Diastereoisomers** or **Diastereomers** (shortened name). Unlike enantiomorphs, they have different physical properties such as melting point and solubility. They rotate the plane of polarised light in the same direction but to different extents.

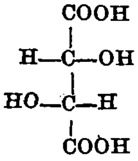
When an organic compound contains two similar asymmetric carbon atoms in its molecule, *abd*—C—C—*abd*, the number of optically active isomers decreases. Thus tartaric acid has two similar asymmetric carbon atoms but exists in three active forms only.

Isomerism of Tartaric acid. Let us now proceed to discuss the optical isomerism of tartaric acid which contains two asymmetric carbon atoms, in detail.

The two asymmetric carbon atoms in tartaric acid,

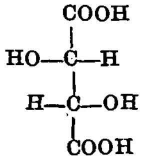
$$\begin{array}{l} {}^{*}\text{CH(OH)COOH} \\ {}^{*}\text{CH(OH)COOH} \end{array}$$

are attached to the groups H, OH, COOH, and CH(OH)COOH. Its molecule can be represented by space models of two tetrahedra joined corner to corner but for the sake of convenience we will use the plane formulas. The end groups being identical, in all four arrangements are possible according as one or both H groups and OH groups are on the left or on the right.



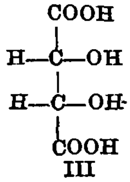
$$\begin{array}{c}COOH\\ |\\ H—C—OH\\ |\\ HO—C—H\\ |\\ COOH\end{array}$$

I



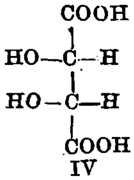
$$\begin{array}{c}COOH\\ |\\ HO—C—H\\ |\\ H—C—OH\\ |\\ COOH\end{array}$$

II



$$\begin{array}{c}COOH\\ |\\ H—C—OH\\ |\\ H—C—OH\\ |\\ COOH\end{array}$$

III



$$\begin{array}{c}COOH\\ |\\ HO—C—H\\ |\\ HO—C—H\\ |\\ COOH\end{array}$$

IV

Of these, formula IV when rotated through 180° in the plane of the paper becomes identical with formula III. Therefore, for tartaric acid we can have only three different arrangements, *viz* I, II and III.

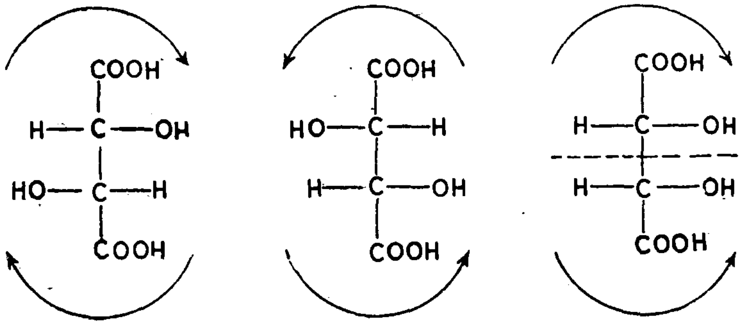


Fig. 7·16. Three forms of tartaric acid.

Now, if the force which rotates the plane of polarised light be directed from H to OH,

(*i*) structure I will rotate the plane of polarised light to the right and will represent *d*-tartaric acid ;

(*ii*) structure II will rotate the plane of polarised light to the left and will represent *l*-tartaric acid ; and

(*iii*) structure III will represent optically inactive tartaric acid, since the rotatory power of the upper half of the molecules is balanced by that of the lower half.

It may also be noted that formulas I and II are mirror images of each other and hence represent *d*- and *l*-isomers. Formula III, however, has a plane of symmetry (dotted line) and hence represents an inactive isomer of tartaric acid.

In actual practice, four tartaric acids are known :

(*i*) *d*-Tartaric acid or (+) Tartaric acid ;

(*ii*) *l*-Tartaric acid or (–) Tartaric acid ;

(*iii*) Inactive or *i*-Tartaric acid ; this is also known as *Meso*-Tartaric acid or *m*-Tartaric acid ; and

(*iv*) *dl*-Tartaric acid or (±)Tartaric acid ; this form of tartaric acid being a mixture of equal amounts of *d*- and *l*-isomers.

The physical properties of the four tartaric acids are tabulated below :

TABLE : *Physical properties of Tartaric Acids*

NAME	M. PT.	DENSITY	$[\alpha]_D$
d-Tartaric acid	170°	1·760	+ 12°
l-Tartaric acid	170°	1·760	−12°
dl-Tartaric acid	206°	1·697	0°
m-Tartaric acid	140°	1·666	0°

The three tartaric acids (*d*-, *l*-, *m*-) are all space-isomers but *m*-tartaric acid is not a mirror image of either of the active forms. Hence it differs from them in melting point, density and other physical properties.

External and Internal Compensation. If equimolecular amounts of *d*- and *l*-isomers are mixed in a solvent, the solution is inactive. The rotation of each isomer is balanced or compensated by the equal but opposite rotation of the other. Optical inactivity having this origin is described as due to **External compensation.** Such mixtures of *d*- and *l*-isomers (*Racemic mixtures*) can be separated into the active components.

In *meso* tartaric acid the inactivity is due to effects within the molecule and not external. The force of rotation due to one half of the molecule is balanced by the opposite and equal force due to the other half. The optical inactivity so produced is said to be due to **Internal Compensation.** It occurs whenever a compound containing two or more asymmetric carbon atoms has a plane or point of symmetry. Since the optical inactivity of such a compound arises within the molecule, the question of separating it into active components does not arise.

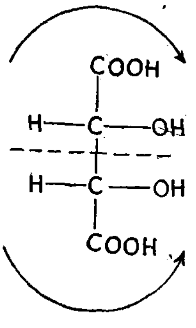
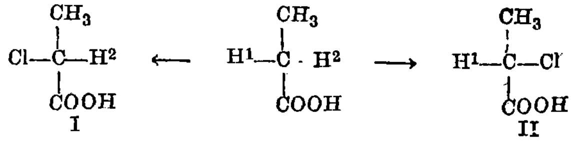


Fig. 7·17. Inactivity of Meso Tartaric acid by Internal Compensation.

Laboratory Synthesis yields Racemic Mixture. When a compound containing an asymmetric carbon atom is synthesised in the laboratory from a compound that has none, the product is always a racemic mixture. Thus if α-chloropropionic acid, $CH_3.CHCl.COOH$, be prepared from propionic acid, racemic mixture results. As shown by the formula below, the two hydrogen atoms H^1 and H^2, in propionic acid are identical. There is equal chance of either hydrogen atom being replaced by chlorine atom.



$$\mathrm{Cl{-}\overset{CH_3}{\underset{COOH}{C}}{-}H^2} \longleftarrow \mathrm{H^1{-}\overset{CH_3}{\underset{COOH}{C}}{\cdot}H^2} \longrightarrow \mathrm{H^1{-}\overset{CH_3}{\underset{COOH}{C}}{-}Cl}$$

I II

Hence, there result equal number of molecules of *laevo* and *dextro* isomers and the product is a racemic mixture. It may be noted that structures I and II are related as mirror images of each other and if I is *laevo* II will be *dextro*.

Resolution of Racemic Mixtures. *The separation of a racemic mixture into its d- and l-components* is termed its **Resolution.** Since the optical isomers have identical physical properties, they cannot be separated by ordinary methods such as fractional crystallisation or fractional distillation.

(1) *Mechanical Separation* (*Pasteur, 1848*). This method is applicable only to solid substances which form well defined crystals. Frequently the racemic mixtures consist of two types of crystals which have different shapes, being the mirror images of each other.

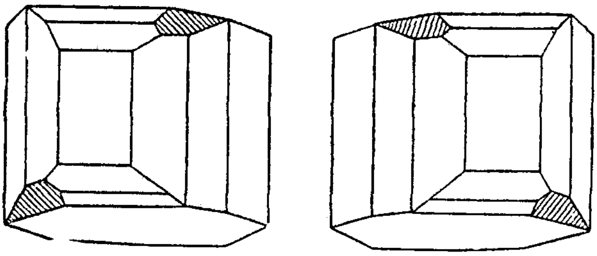


Fig. 7·18. *Two forms of tartaric acid.*

The two varieties of crystals can be separated with the aid of a magnifying lens and a small forceps. Since the crystals of one type are all *d*-isomer and the crystals of the other types are *l*-isomer, their separation leads to the resolution of the racemic mixture. This method is too tedious for practical purposes and is now of historical interest only because it was the first method which Pasteur employed for the separation of the tartaric acids.

(2) *Biochemical Method* (*Pasteur, 1858*). In this method the resolution is effected by destroying one form (*d*- or *l*-) by a biochemical process. When certain micro-organisms such as yeast, moulds and bacteria are allowed to grow in the solution of a racemic mixture, they assimilate one form selectively leaving the other in solution. The separation is almost complete so that the form left in solution can be isolated by fractional crystallisation. For example, if ordinary mould, *Pinicillium glaucum*, is added to a solution of *dl*-tartaric acid, the solution becomes laevo-rotatory due to the destruction of *dextro* form. The selective consumption of one isomer is believed to be due to the asymmetry and optical activity of the enzyme present in the micro-organism.

The method is, no doubt, much more practical than the mechanical separation but it suffers from the following disadvantages :

(*i*) One-half of the material is sacrificed.

(*ii*) It cannot be applied to *dl*-mixtures of poisonous substances which are incapable of acting as food for organisms.

(3) *Chemical Method* (*Pasteur*, *1858*). This is the most general method of resolution. In this method, the *dl*-mixture is united with another suitable optically active isomer when the products are no longer mirror image isomers and may be separated by crystallisation.

For example, a solution of racemic lactic acid may be treated with an optically active base such as the alkaloid *l*-Brucine The resulting product will consist of two salts :

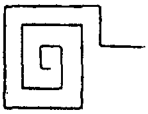
(*i*) *d*-Acid. *l*-Base ;
and (*ii*) *l*-Acid. *l*-Base.

The relation of the configurations of the two salts may be explained by the following illustration. Suppose the two enantiomorphic forms of lactic acid are represented by the symbols

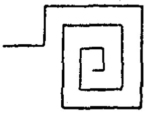
d-lactic acid

l-lactic acid

and the two enantiomorphic forms of brucine by the symbols.

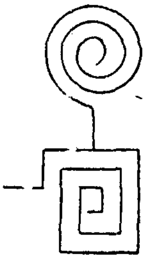


d-brucine

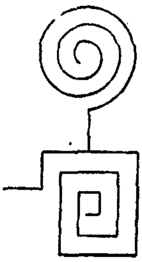


l-brucine

Now the two compounds *l*-brucine.*d*-lactate and *l*-brucine.*l*-lactate may be represented as shown below.



l-brucine.*d*-lactate



l-brucine.*l*-lactate

Inspection of the configurations of the two salts shows that they are not enantiomorphic. Therefore, they have different solubility in water and can be separated by fractional crystallisation. The isolated salts are then treated with dilute sulphuric acid when the optically active acids are regenerated.

Similarly, a racemic mixture of a base can be resolved by combination with an optically active acid such as *d*-tartaric acid. A racemic mixture of alcohols may be resolved by esterification with an optically active acid.

(4) *Kinetic Method* (*Markwald, McKenzie,* 1899). The fact that enantiomers react with an optically active substance at different rates, is used for the separation of racemic mixtures. Thus *l*-menthol (an alcohol) reacts faster with *d*-mandelic acid ($C_6H_5\overset{*}{C}HOHCOOH$) than *l*-mandelic acid to form ester. Therefore, when racemic mandelic acid is esterified with a limited quantity of *l*-menthol, the product is richer in *dl'*-ester than *ll'*-ester which upon hydrolysis gives partially resolved mandelic acid.

(5) *Selective Adsorption.* Sometimes 'resolution' may be achieved by passing a solution of the recemate over a column of a finely powdered, optically active adsorbent such as starch, sugar or quartz. The surface of the adsorbent, adsorbs selectively one enantiomer and thus the solution emerging at the bottom is richer in the other enantiomer In this way partial resolution is effected.

Racemization. An optical isomer (*d*- or *l*-) may lose its optical activity yielding the racemic mixture by the application of heat or light to solution in a solvent, or in the presence of a suitable catalyst.

The conversion of a d- or l-isomer into its racemic mixture is termed **Racemization.**

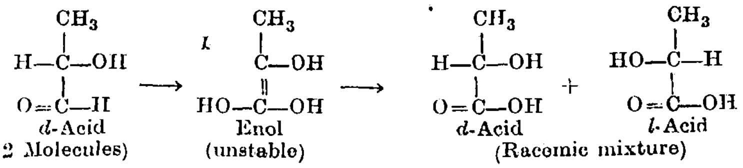
This involves the change of half of the active compound to the isomer of the opposite rotation, resulting in the racemic mixture. Thus :

$$2\,dA \longrightarrow \underset{\text{(Racemic mixture)}}{dA + lA}$$

Or

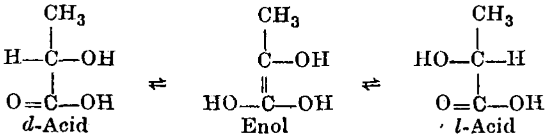
$$2\,lA \longrightarrow dA + lA$$

Racemization takes place readily in the case of optically active hydroxy acids like lactic, malic and tartaric acids in the presence of a base. All these compounds have a carboxyl group adjacent to an asymmetric carbon atom carrying a hydrogen. Thus racemization has been interpreted to take place through the formation of an *enol* which at once changes to the other enantiomer. In case of lactic acid we have :



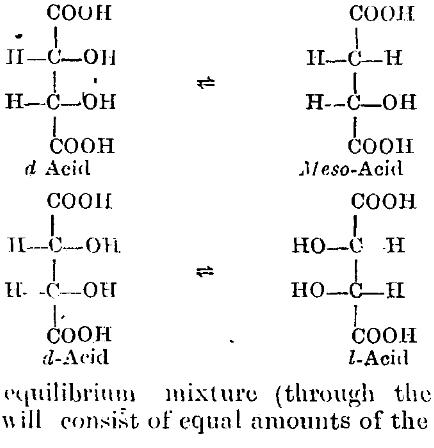
The H-atom linked to d-carbon in d-Acid migrates to O-atom of the carbonyl group to form the enol. Now, the shift of the H-atom of the enol back to d-carbon involves opening of either linkage of the double bond, providing equal opportunity for the H-atom to attach to the left or the right. This leads to the formation of one molecule of d-Acid and one of l-Acid.

But the changes shown above are reversible and in actual practice we get an equilibrium mixture since one molecule of d-Acid remains as if it were unchanged.



The equilibrium mixture thus obtained contains one molecule of d-Acid and one molecule of l-Acid *i.e.*, the racemic mixture of the acid.

Pasteur found that if a solution of d-tartaric acid is heated for some time at 165°C, it loses its optical activity forming the racemic mixture and *meso*-acid. This is due to the fact that tartaric acid having two asymmetric carbon atoms may undergo inversion of H and OH only about one carbon or both, yielding *meso*- or racemic form respectively.



The equilibrium mixture (through the enolic form) in the above case will consist of equal amounts of the d- and l-isomers.

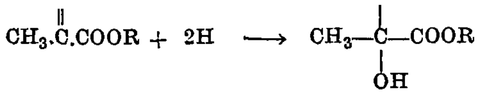
Optically active substances which cannot enolize because they have no hydrogen atom α to a carbonyl group, do not in general racemize except under conditions which bring about other chemical changes as well.

Asymmetric Synthesis. We have already seen that when a compound containing an asymmetric carbon atom is synthesised by ordinary laboratory methods from a symmetric compound, the product is a racemic mixture. If, however, such a synthesis is carried under the "Asymmetric influence" of a suitable optically active reagent, one of the optically active isomers (*d*- or *l*-), is produced in preference. *This kind of process in which an asymmetric compound is synthesised from a symmetric compound to yield the d- or l-isomer directly,* is termed **Asymmetric Synthesis**.

In such asymmetric synthesis, both the active isomers (*d*- and *l*-) are invariably produced simultaneously but one of these is obtained in excess and often (but not always) it has the same sign of rotation as the active reagent employed. An illustration of asymmetric synthesis is offered by the following early example (Mackenzie, 1905)—

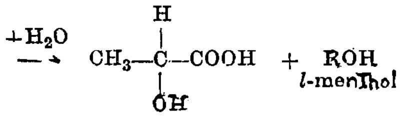
When pyruvic acid is reduced as such, it yields *dl*-lactic acid. However, when pyruvic acid is first combined with an optically active alcohol, ROH, such as *l*-menthol,[*] to form an ester which is then reduced, the product upon hydrolysis yields *l*-lactic acid in excess

$$CH_3.CO.COOH + \underset{l\text{-menthol}}{ROH} \longrightarrow \underset{l\text{-menthyl pyruvate}}{CH_3.CO.COOR} + H_2O$$



$$CH_3.\overset{\overset{\displaystyle O}{\|}}{C}.COOR + 2H \longrightarrow CH_3—\underset{\underset{\displaystyle OH}{|}}{\overset{\overset{\displaystyle H}{|}}{C}}—COOR$$

l-menthyl-*l*-lactate (excess)
+*l*-menthyl-*d*-lactate



$$\xrightarrow{+H_2O} CH_3—\underset{\underset{\displaystyle OH}{|}}{\overset{\overset{\displaystyle H}{|}}{C}}—COOH + \underset{l\text{-menthol}}{ROH}$$

l-lactic acid (excess)
+ *d*-lactic acid

In nature, numerous optically active substances such as terpenes, alkaloids and proteins are produced by asymmetric synthesis, under the influence of optically active enzymes. These enzymes unite with the substance available in plants and when the synthesis

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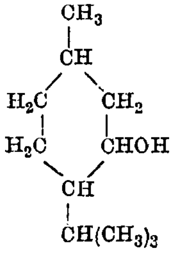
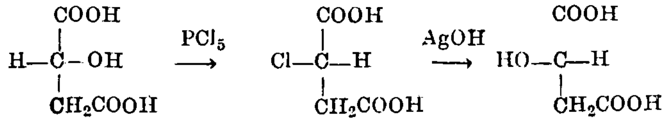
[*] Menthol has the structure



is complete, they separate from the product and are thus again free to combine with more of the parent inactive substance and the endless process continues.

As the things stand today, very little is known about asymmetric synthesis and its mechanism is still a matter of speculation.

Walden Inversion. When an atom or group directly linked to an asymmetric carbon atom is replaced, the configuration of the new compounds may be opposite to that of the original. Thus *d*-malic acid can be converted into *l*-malic acid as follows :



$$\begin{array}{c}COOH\\|\\H-C-OH\\|\\CH_2COOH\end{array} \xrightarrow{PCl_5} \begin{array}{c}COOH\\|\\Cl-C-H\\|\\CH_2COOH\end{array} \xrightarrow{AgOH} \begin{array}{c}COOH\\|\\HO-C-H\\|\\CH_2COOH\end{array}$$

d-Malic acid *l*-Chlorosuccinic acid *l*-Malic acid

This curious phenomenon of the 'inversion' of groups about the asymmetric carbon atom first studied by Walden (1895) is called *Walden Inversion.* The mechanism of this change is not yet clearly understood

QUESTIONS

1. Discuss the electronic structure of the carbon atom. How are its valency bonds distributed in space ?

2. What are the chief types of valency bonds involved in organic molecules ? Comment on the statement : "the double and triple bonds represent weak spots in a molecule."

3. Discuss the ordinary method of representing a double bond and point out its defects. How does Baeyer's strain theory attempt to explain unsaturation in organic compounds ?

4. What do you understand by the structural formula of a compound ? Point out clearly the utility of such a formula.

5. Explain what is meant by isomerism. What is its importance in Organic Chemistry ? Describe and illustrate the different types of isomerism known to you.

6. Give an account of Pasteur's work on the tartaric acid. Describe the method that can be employed for the resolution of recemic organic compounds.

7. Explain van't Hoff and Le Bel's theory of molecular configuration and show how it accounts for the existence of the different varieties of tartaric acid.

8. Explain and illustrate :—

(*a*) Enantiomorphs,

(*b*) Meso compound,

(*c*) Racemisation.

What methods are available for the resolution of racemic compounds ?

9. Give examples of different types of Isomerism known to you in organic chemistry. Discuss the isomerism of maleic and fumaric acids in detail. *(Udaipur B.Sc., 1968)*

10. Discuss fully the isomerism in lactic acid and tartaric acid. *(Sambalpur B.Sc., 1960)*

11. Explain Le Bel and van't Hoff's theory of molecular configuration Show how it explains the existence of observed varieties of tartaric acid. *(Utkal B.Sc., 1962)*

12. Discuss briefly the isomerism existing in (*a*) the butanes (C_4H_{10}), (*b*) lactic acid ($CH_3.CHOH.COOH$), (*c*) the oxime of benzaldehyde ($C_6H_5.CH{=}N.OH$). *(Ceylon B.Sc., 1967)*

13. Mention the names of different isomeric forms of tartaric acid with structural formulae. How are they obtained ? Give an account of the isomerism of tartaric acids. *(Bangalore B.Sc., 1969)*

14. Describe the preparation of tartaric acid and discuss briefly the isomerism exhibited by this acid. *(Udaipur B.Sc., 1968)*

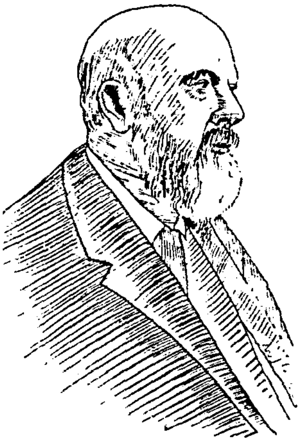
15. Give an account of the stereoisomerism of the tartaric acid. *(Kurukshetra B. Sc., 1969)*

16. What is stereoisomerism. Write what you know about the stereoisomerism of cyclohexane derivatives. *(Berhampur B.Sc., 1969)*

17. Write notes on : (*a*) Optical Isomerism ; and (*b*) Geometrical Isomerism. *(Delhi B.Sc., 1969)*

8

Organic Reactions and their Mechanisms



Adolph von Baeyer
(1835–1917)
German. Best known for the structural theory named after him, Baeyer's Strain Theory.

While inorganic reactions take place between ions, organic reactions are essentially molecular in nature. They may involve a single molecule or may take place between two or more molecules. The organic reactions are generally represented by means of equations in which the formulae of the reacting molecules and those of the products are separated by an arrow in between. The arrow points away from the reactants and toward the products. The conditions of the experiment (catalyst, temperature, pressure, etc.) are mentioned above or below the arrow.

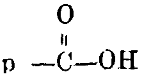
$$\text{REACTANTS} \xrightarrow{\text{conditions}} \text{PRODUCTS}$$

THE CLASSICAL STRUCTURAL THEORY

Till recently the reactions of organic compounds were explained on the basis of their structural formulae. The classical structural theory' visualised that the chemical behaviour of an organic compound was determined by the functional groups present in its molecule. Thus the course of an organic reaction could be easily interpreted by indicating the interaction between the functional groups of the reacting molecules. The incompetence of the classical structural theory became evident when it was established that compounds having the same functional group behaved differently under similar experimental conditions. Thus :

(*i*) The carbon-carbon double bond in ethylene formed addition compounds readily while the double bonds in benzene did so under forced conditions

(*ii*) The Br atom in ethyl bromide (C_2H_5Br) could be easily replaced by OH group upon reaction with aqueous alkalies but the Br in phenyl bromide (C_6H_5Br) could not be exchanged for OH under similar conditions.

(*iii*) The carbonyl group $>C=O$ in aldehydes ($R\text{-}HC=O$) readily formed addition compounds (the cyanohydrins) with HCN, while the carbonyl group present in carboxyl group  $-\overset{\overset{\displaystyle O}{\|}}{C}-OH$ did not.

The above and scores of such other examples proved beyond doubt that the structural theory of organic reactions was inadequate to offer satisfactory interpretation of the course of reactions, and that factors other than functional groups played a significant role in determining the chemical behaviour of organic compounds.

In this chapter we will acquaint ourselves with some fundamental modern aspects of organic reactions and their mechanisms. The amplification of these concepts will be done while discussing specific reactions encountered throughout the remainder of the book.

TYPES OF ORGANIC REACTIONS

From a mechanistic approach, an organic reaction is believed to take place by the attack of a reagent (Cl_2,HBr, etc.) on a compound containing carbon, designated as a *substrate*—literally meaning a substance lying below. Thus an organic reaction may be represented as

ATTACKING REAGENT + SUBSTRATE ⟶ PRODUCTS

A **substrate** may be defined as the reactant that contains carbon atoms some of whose bonds with other atoms are broken and some new ones formed as a result of reaction with the attacking reagent.

In light of the changes that occur in carbon bondings of the substrate, the large variety of organic reactions known may be classified as belonging to one of the relatively small number of types listed below :

(*a*) *Substitution reactions* ;

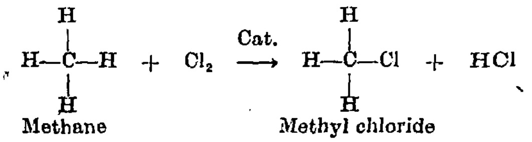
(*b*) *Addition reactions* ;

(*c*) *Elimination reactions* ;

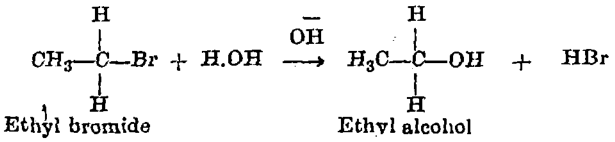
(*d*) *Rearrangement reactions.*

Substitution or Displacement Reactions

As the name implies, *substitution reactions are those in which an atom or group directly attached to a carbon in the substrate molecule is displaced by another incoming atom or group of the same bonding capacity*. In such reactions bonds are both broken and formed at one and the same carbon atom of the substrate. For example,



$$\underset{\text{Methane}}{\mathrm{H{-}\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}{-}H}} + \mathrm{Cl_2} \xrightarrow{\text{Cat.}} \underset{\text{Methyl chloride}}{\mathrm{H{-}\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}{-}Cl}} + \mathrm{HCl}$$



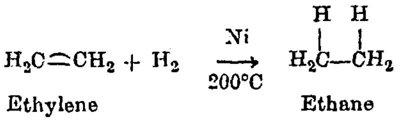
$$\underset{\text{Ethyl bromide}}{\mathrm{CH_3{-}\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}{-}Br}} + \mathrm{H.OH} \xrightarrow{\overline{\mathrm{OH}}} \underset{\text{Ethyl alcohol}}{\mathrm{H_3C{-}\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}{-}OH}} + \mathrm{HBr}$$

In the first reaction, a hydrogen atom of methane is substituted or displaced by a monovalent chlorine atom. In the second reaction, the bromine atom of ethyl bromide is displaced by monovalent hydroxy group.

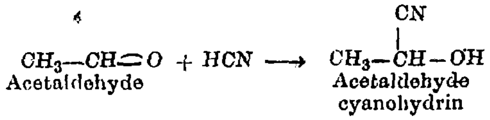
Addition Reactions

Addition reactions are those in which atoms or groups are added to a double or triple bond without the elimination of any atom or other molecules. In this process of addition, at least one π bond is lost while two σ bonds are created.

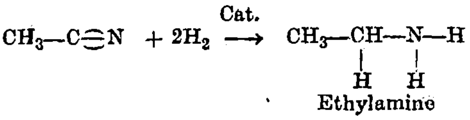
In an addition reaction, two or four atoms/groups are newly attached to a multiple bond. For example,



$$\underset{\text{Ethylene}}{\mathrm{H_2C{=}CH_2}} + \mathrm{H_2} \xrightarrow[200°\mathrm{C}]{\mathrm{Ni}} \underset{\text{Ethane}}{\mathrm{H_2\overset{\overset{H}{|}}{C}{-}\overset{\overset{H}{|}}{C}H_2}}$$



$$\underset{\text{Acetaldehyde}}{\mathrm{CH_3{-}CH{=}O}} + \mathrm{HCN} \longrightarrow \underset{\text{Acetaldehyde cyanohydrin}}{\mathrm{CH_3{-}\overset{\overset{CN}{|}}{C}H{-}OH}}$$



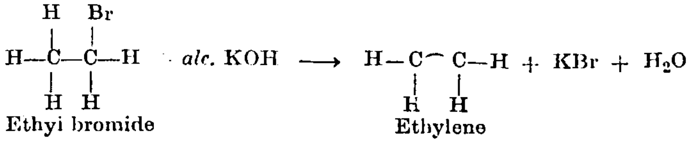
$$\mathrm{CH_3{-}C{\equiv}N} + 2\mathrm{H_2} \xrightarrow{\text{Cat.}} \underset{\text{Ethylamine}}{\mathrm{CH_3{-}\underset{\underset{H}{|}}{C}H{-}\underset{\underset{H}{|}}{N}{-}H}}$$

In the first two cases, a π bond breaks and two bonds are generated. In the third case, two π bonds are broken and four new σ-bonds are produced.

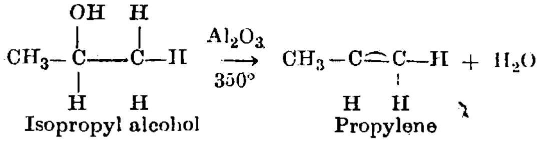
Elimination Reactions

The elimination reactions are the reverse of addition reactions. Here, *two or four atoms/groups attached to the adjacent carbon atoms in the substrate molecule are eliminated to form a multiple bond*

Thus in a simple elimination type reaction, two σ bonds, one each of the two adjacent carbon atoms, are lost and a new π bond is established between this pair of carbon atoms. The formation of an alkene from an alkyl halide or an alcohol offer examples of such a reaction.

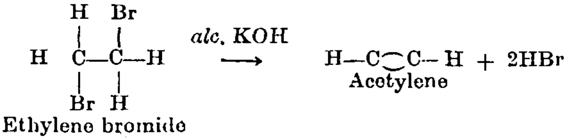


$$\underset{\text{Ethyl bromide}}{H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{Br}{C}}-H} \xrightarrow{alc.\ KOH} \underset{\text{Ethylene}}{H-\underset{H}{C}=\underset{H}{C}-H} + KBr + H_2O$$



$$\underset{\text{Isopropyl alcohol}}{CH_3-\underset{H}{\overset{OH}{C}}-\overset{H}{\underset{H}{C}}-H} \xrightarrow[350°]{Al_2O_3} \underset{\text{Propylene}}{CH_3-\underset{H}{C}=\underset{H}{C}-H} + H_2O$$

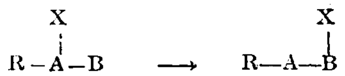
In case four atoms/groups are eliminated from an adjacent pair of carbon atoms, the reaction involves the breaking of two σ bonds of each carbon atom (in all four) resulting in the formation of two new π bonds. Thus :



$$\underset{\text{Ethylene bromide}}{H-\underset{Br}{\overset{H}{C}}-\underset{H}{\overset{Br}{C}}-H} \xrightarrow{alc.\ KOH} \underset{\text{Acetylene}}{H-C\equiv C-H} + 2HBr$$

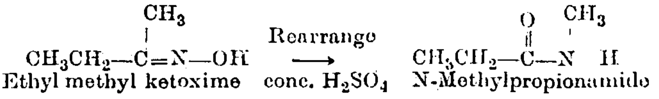
Rearrangement Reactions

It this type of reactions, some atoms/groups shift from one position to another within the substrate molecule itself giving a product having a new structure. *The reactions which proceed by a rearrangement or reshuffling of the atoms/groups in the molecule to produce a structural isomer of the original substance*, are called REARRANGEMENT REACTIONS. Thus,



$$R-\overset{X}{A}-B \longrightarrow R-A-\overset{X}{B}$$

An oxime on treatment with conc. H_2SO_4 undergoes rearrangement reaction to form an amide. For example,



$$\underset{\text{Ethyl methyl ketoxime}}{CH_3CH_2-\overset{CH_3}{C}=N-OH} \xrightarrow[\text{conc. } H_2SO_4]{\text{Rearrange}} \underset{\text{N-Methylpropionamide}}{CH_3CH_2-\overset{O}{\overset{\|}{C}}-\overset{CH_3}{N}-H}$$

Hofmann bromamide reaction offers another example of such a reaction.

REACTION MECHANISMS—FUNDAMENTAL ASPECTS

We have already studied that an organic reaction takes place by the attack of reagent on a compound containing carbon, the substrate.

ATTACKING REAGENT + SUBSTRATE ⟶ PRODUCTS

The carbon bonds in the substrate molecule are broken (or cleaved) to give fragments which are very reactive and constitute *transitory intermediates*. At once they may react with other similar spieces or with molecules present in their environments, thus establishing new bonds to give the products.

The steps of an organic reaction depicting the breaking and making of new bonds of carbon atoms in the substrate leading to the formation of the final product through transitory intermediates, are often referred to as its **mechanism.**

$$\text{SUBSTRATE} \longrightarrow \underset{(\textit{Transitory})}{\text{INTERMEDIATE}} \longrightarrow \text{PRODUCTS}$$

Therefore, to understand the reaction mechanisms it is necessary to know as to how do the processes of bond-breaking (fission) and bond-making in the substrate take place.

How Bond Fission Occurs ?

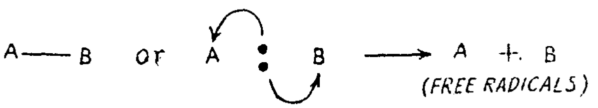
A covalent bond (σ bond) joining two atoms exists because of the shared pair of electrons. When the two atoms are separated from each other, bond fission (or cleavage) is said to have taken place. The fission process can occur in two ways. The separating atoms may take away one electron each of the bonding pair, or one of atoms may get away with both the electrons.

$$A \,\dot{|}\!\cdot\, B \longrightarrow A^{\bullet} + {}^{\bullet}B \quad (\textit{Homolytic fission})$$

$$A : | \, B \longrightarrow A\colon + \; B \quad (\textit{Heterolytic fission})$$

In the first case when one electron of the bonding pair goes with each of the departing atoms the fission is symmetrical or homogeneous and is called HOMOLYTIC FISSION or HOMOLYSIS. In the second case since both the electrons are taken over by one atom and the other atom goes without an electron, the fission is unsymmetrical or heterogeneous and is called HETEROLYTIC FISSION or HETEROLYSIS.

Homolytic bond fission. As described above, *a covalent bond undergoes homolytic fission when each of the two departing atoms makes away with one of the bonding pair of electrons.*



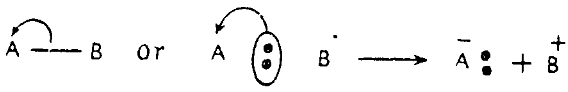
The two fragments produced as a result of homolytic fission carry an odd electron each and are called **free radicals**. These are transitory and at once react with other radicals or molecules by gaining one more electron to restore the stable bonding pair. It may be noted that the association of the odd electron with the free radicals does not make them charged because this electron belonged to the electrically neutral atom itself before the covalent bond came into existence. So, the free radicals are not at all ionic in character and their high reactivity as reaction intermediates is entirely due to the tendency of the odd electron to 'pair up' with another available electron.

Homolytic fission proceeds to produce free radicals by the application of energy — may be heat or light. This process is prevalent in gaseous reactions and adequately explains the substitution reactions of alkanes. The cleavage of chlorine molecule takes place in the presence of ultraviolet light or by heat resulting in free chlorine radicals which are highly reactive.

$$Cl \overset{\times}{\underset{\times}{}} Cl \xrightarrow{\text{Light/Heat}} Cl^{\times} + {}_{\times}Cl$$

(Chlorine free radicals)

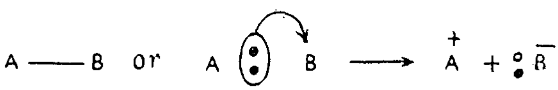
Heterolytic bond fission. When a covalent bond breaks in a fashion that both the bonding electrons are appropriated by one of the two departing fragments (atoms or groups), it is said to have undergone heterolytic fission. This type of fission in a symmetrical molecule A—B may be represented as



...(1)

The curved arrow head points towards the atom (or group) that makes away with both the shared electrons and, therefore, becomes negative leaving behind its partner with a positive charge. In the above example, it may be noticed that the atom B loses its original share of electron in the bonding pair and thus gives the positive ion (B^+), while the atom A which gains one more electron in addition to its own gives the negative ion $\bar{A}$: . Thus speaking in general, the heterolytic bond fission yields one positive and one negative ion.

As a result of the heterolytic fission of the molecule A—B, which of the two atoms (A or B) takes away the bonding electron pair, is a pertinent question since the change could as well have followed the course



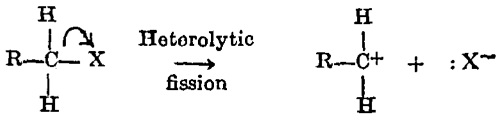
...(2)

giving (A^+) and ($:B^-$) ions. In fact, the course of heterolytic fission is determined by the electronegativities or 'power to attract electrons' of the covalently joined atoms or groups. If A has greater electronegativity than B, the former atom will take away the bonding electron pair and the fission will adopt the course (1). On the other hand if B has higher electronegativity than A, the course of fission will be as shown in (2)

Heterolytic fission is most common in organic reactions taking place in solutions since the energy required to break the bond can be partly drawn from the energy of solvation of the ions produced. Thus the progress of a heterolytic reaction such as $A—B \rightarrow A^+ + B^-$ depends significantly on the nature of the solvent. These reactions take place more readily in polar solvents like water and are catalysed by the presence of ionic catalysts (*e.g.*, acidic or basic).

CARBONIUM IONS

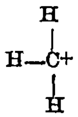
Let us consider the heterolytic fission of the bond C—X present in an organic molecule. If the atom X has greater electronegativity than the carbon atom, the former takes away the bonding electron pair and becomes negatively charged while an ion bearing a positive charge is produced. For illustration,



$$R-\overset{H}{\underset{H}{C}}-X \xrightarrow[\text{fission}]{\text{Heterolytic}} R-\overset{H}{\underset{H}{C^{+}}} + :X^{-}$$

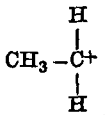
Carbonium ion

An ion containing a positively charged carbon centre is called a CARBONIUM ION as analogy with positive ammon*ium* ion. In general, the carbonium ions are named by adding the suffix *-ium* to the name of the parent alkyl group *i.e.*, Alkylium. For example,



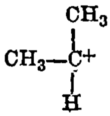
$$H-\overset{H}{\underset{H}{C^{+}}}$$

Methylium, or
Methyl carbonium ion
(Primary)



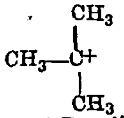
$$CH_3-\overset{H}{\underset{H}{C^{+}}}$$

Ethylium, or
Ethyl carbonium ion
(Primary)



$$CH_3-\overset{CH_3}{\underset{H}{C^{+}}}$$

Isopropylium, or
Isopropyl carbonium ion
(Secondary)



$$CH_3-\overset{CH_3}{\underset{CH_3}{C^{+}}}$$

tert-Butylium or
tert-Butyl carbonium ion
(Tertiary)

The carbonium ions which are produced as reaction intermediates, are very reactive. This is due to the fact that the central positively charged carbon in them has only six electrons (two to a covalent bond) in the outer shell and has a marked tendency to complete the octet. Hence a carbonium ion combines readily with any substance that can donate a pair of electrons to form the fourth covalent bond.

Carbonium ion being deficient in electrons is ordinarily very unstable. However, if an electron repelling group (such as alkyl group) is present adjacent to the positive charge bearing carbon, the former makes the carbonium ion stable by pumping electrons through the connecting bond in an attempt to annul the positive charge.

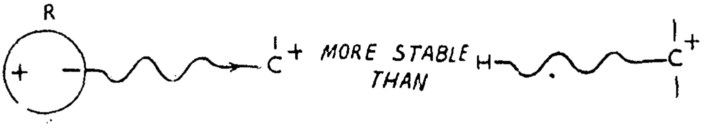
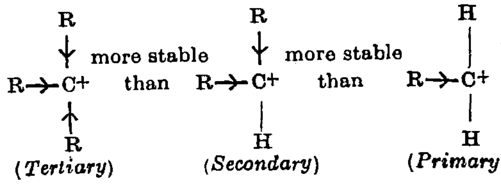


Fig. 8·1. The group R pumps electrons through the connecting bond (shown wavy) to the positive charge bearing carbon of the carbonium ion.

That is why a tertiary carbonium ion is more stable than a secondary carbonium ion ; and a secondary carbonium ion is more stable than a primary ion. That is,



$$\underset{(Tertiary)}{R \rightarrow \overset{R\downarrow}{\underset{R\uparrow}{C^+}}} \text{ more stable than } \underset{(Secondary)}{R \rightarrow \overset{R\downarrow}{\underset{H}{C^+}}} \text{ more stable than } \underset{(Primary)}{R \rightarrow \overset{H}{\underset{H}{C^+}}}$$

The stability of the carbonium ion is reduced by electron-attracting groups ($-NO_2$; $>C=O$) linked to the central positive carbon atom.

Here the groups like 'nitro' or 'carbonyl' withdraw electrons through the connecting bond. Thus rendering the carbonium ion less stable.

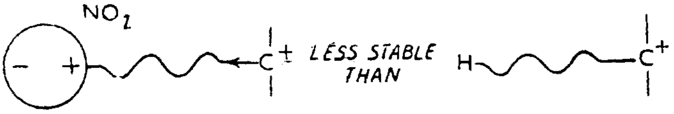
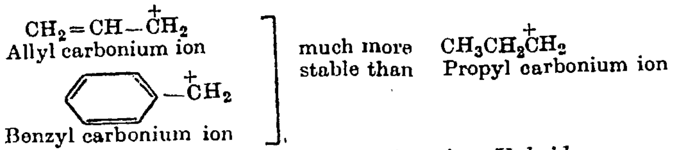


Fig. 8·2. The NO_2 group withdraws electrons through the connecting bond (shown wavy), thus enhancing the positive charge of the central carbon and reducing the stability of the carbonium ion.

The stability of carbonium ions could also be explained in terms of resonance. A particular carbonium ion may delocalise its positive charge through the analogous canonical structures in its hybrid. Thus the positive charge on the central carbon of the carbonium ion declines by distribution over other carbon atoms and this makes the ion stable. As a rule, the more canonical structures which may be written, the more stable the carbonium ion proves to be. Benzyl carbonium ion and allyl carbonium ion are considerably more stable than propyl carbonium ion because of the marked stabilisation of their resonance hybrids through the canonical structures shown below :



$CH_2=CH-\overset{+}{C}H_2$
Allyl carbonium ion

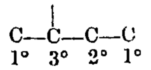
$-\overset{+}{C}H_2$
Benzyl carbonium ion

much more stable than $CH_3CH_2\overset{+}{C}H_2$
Propyl carbonium ion

Canonical structures of the Allyl carbonium ion Hybrid :

$$CH_2=CH-\overset{+}{C}H_2 \leftrightarrow \overset{+}{C}H_2-CH=CH_2$$

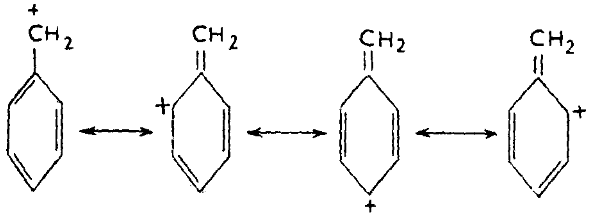
***Primary carbon atom** is that which is linked directly to one or two other carbon atoms ; **Secondary carbon** is linked to two and **tertiary carbon** to three other carbon atoms. These are designated 1°, 2° and 3° respectively.



$$\underset{1°}{C}-\underset{3°}{\overset{C}{\overset{|}{C}}}-\underset{2°}{C}-\underset{1°}{C}$$

The carbonium ions containing 1°, 2° and 3° carbon atoms are, therefore, called *primary, secondary* and *tertiary* carbonium ions respectively.

Canonical structures of the Benzyl carbonium ion Hybrid :



Since the carbon of the carbonium ion is an sp^2 hybrid, the ion is planar with a vacant p orbital prependicular to the plan of the three covalent bonds to carbon.

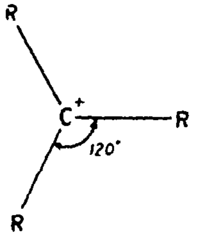
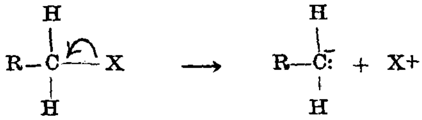


Fig. 8·3. The geometry of alkyl carbonium ion.

CARBANIONS

Let us revert for a while to the heterolytic fission of the bond C—X present in an organic molecule. If the carbon atom has greater electronegativity than the atom X, the former takes away the bonding electron pair and acquires a negative charge while a positive ion X+ is produced. Thus :



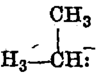
$$R-CH_2-X \longrightarrow R-\overset{-}{C}H_2{:} + X^+$$

Carbanion

An organic ion with a pair of available electrons and a negative charge on the central carbon atom is called a CARBANION (CARB, *from carbon*+ANION, *negative ion*).

Individual carbanions are named after the parent alkyl group and adding the word carbanion. Thus :

$CH_3—\overset{-}{C}H_2{:}$ Ethyl carbanion



$CH_3—\overset{-}{C}H{:}(CH_3)$ Isopropyl carbanion

Though carbanions are electron-rich fragments of heterolytic fission but they are very reactive intermediates. They are readily attacked by electron-poor reagents (electrophiles).

Ordinarily carbanions are unstable because of their negative charge. They are stabilised by the presence of an adjacent electron-attracting group as $-C{\equiv}N$ or $>C{=}O$.

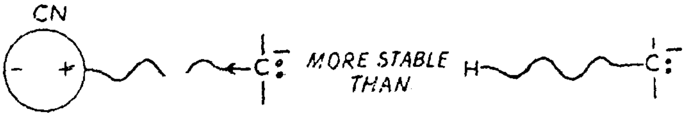


Fig. 8·4. The —C≡N group withdraws electrons through the connecting bond (shown wavy) and thus the negative charge on the carbon decreases while the carbanion becomes more stable.

On the other hand, the presence of an adjacent electron-releasing group such as alkyl group increases the negative charge on the central carbon atom and thus makes the carbanion less stable.

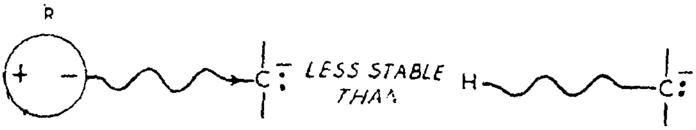
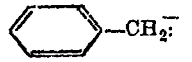


Fig. 8·5. The group R pumps electrons through the wavy bond to the central carbon atom thereby increasing its negative charge and rendering the carbanion less stable.

Carbanions can also be stabilised due to resonance when they have double bond or an aromatic ring adjacent to the charged carbon centre. Thus :

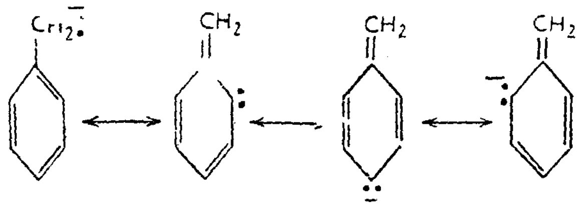


more stable than $CH_3—CH_2:^-$

Benzyl carbanion

Ethyl carbanion

The stabilisation by resonance is due to the delocalisation of the negative charge which is then distributed over other carbon atoms in the hybrid structure. The canonical forms of Benzylcarbanion in its resonance hybrid structure responsible for its stabilisation are :



ATTACKING REAGENTS AND THEIR ROLE

We have described before that an organic reaction proceeds by the attack of a reagent on substrate. Under the influence of the attacking reagent and suitable experimental conditions, the substrate molecule undergoes heterolysis to form reactive intermediates such as carbonium ions and carbanions. These then combine with the attacking reagent to give the final product. Therefore, to understand the reaction mechanisms it is imperative to know the nature of the various attacking reagents. They can be classified as :

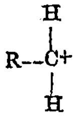
(*i*) *Electrophilic reagents* ;

and (*ii*) *Nucleophilic reagents.*

Electrophilic Reagents. As signified by the name electrophilic (*electro* = electron ; *philic* = loving), these reagents are often referred to as **electrophilic**. Their lust for electrons is accounted for by the fact that they are short of a pair of electrons than the stable number (duplet or octet)

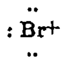
The electrophilic reagents are of two types :

(*a*) POSITIVE ELECTROPHILES (E^+) that are deficient in two electrons and carry a positive charge *e.g.*, Carbonium ions and Bromonium ions,



$R-\overset{H}{\underset{H}{C^+}}$

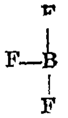
Carbonium ion
(C atom has 6 electrons
in the outer shell).



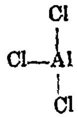
$:\overset{..}{\underset{..}{Br}}{}^+$

Bromonium ion
(has 6 electrons in the
outer shell).

(*b*) NEUTRAL ELECTROPHILES (E) such as boron trifluoride (BF_3) and aluminium chloride ($AlCl_3$) in which the central atom has six electrons but no charge



$F-\overset{F}{\underset{F}{B}}$

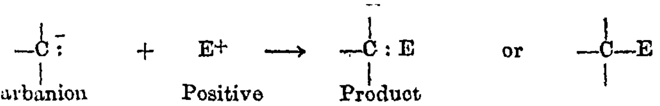


$Cl-\overset{Cl}{\underset{Cl}{Al}}$

(one covalent bond implies two electrons)

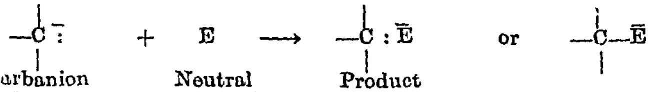
How electrophiles attack the substrate ?

Both types of electrophiles can attack the substrate ion or molecule which is electron-rich and can donate an electron-pair to the attacking reagent to form a new bond.



$$-\overset{|}{\underset{|}{C}}\,\overset{-}{:} \quad + \quad E^+ \longrightarrow -\overset{|}{\underset{|}{C}}:E \quad \text{or} \quad -\overset{|}{\underset{|}{C}}-E$$

Carbanion (substrate) | Positive electrophile | Product



$$-\overset{|}{\underset{|}{C}}\,\overset{-}{:} \quad + \quad E \longrightarrow -\overset{|}{\underset{|}{C}}:\bar{E} \quad \text{or} \quad -\overset{|}{\underset{|}{C}}-\bar{E}$$

Carbanion (substrate) | Neutral electrophile | Product

How positive electrophiles are produced ?

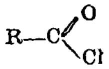
Positively charged electrophiles are produced as a result of heterolytic fission of neutral molecules. For example, bromonium ions are obtained by heterolysis of bromine molecule (Br—Br).

$$\underset{\text{Bromine molecule}}{:\ddot{\underset{..}{Br}}:\ddot{\underset{..}{Br}}:} \xrightarrow{\text{heterolysis}} \underset{\text{Bromide ion}}{:\ddot{\underset{..}{Br}}:^{-}} + \underset{\text{Bromonium ion}}{\ddot{\underset{..}{Br}}:}$$

So are produced carbonium ions by heterolytic fission of carbon bonds as described before.

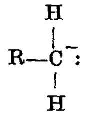
It may be noted that it is sometime difficult to distinguish between an attacking reagent and a substrate. Compounds such as acid chlorides (RCOCl) could be either reagent or substrate. Carbonium ions and carbanions both could play the role of a reagent as also of substrate.

TABLE : *Some Electrophiles*

POSITIVE (+)		NEUTRAL	
Hydrogen ion	H^+	Sulphur trioxide	SO_3
Hydroxonium ion	H_3O^+	Boron trifluoride	BF_3
Nitronium	NO_2^+	Aluminium trichloride	$AlCl_3$
Nitrosonium	NO^+	Ferric chloride	$FeCl_3$
Sulphonium	$SO_2^+.OH$	Acid chlorides	 $R-C\begin{smallmatrix}\nearrow O\\ \searrow Cl\end{smallmatrix}$
Bromonium	Br^+	Carbonyl group	$>C=O$
Diazonium ions	$C_6H_5N_2^+$		
Carbonium ion	$-\overset{\vert}{\underset{\vert}{C}}{}^{+}$		

Nucleophilic Reagents. As implied by the name nucleophilic (*nucleo*=nucleus ; *philic*=loving), these reagents are nucleus-loving and are often referred to as **nucleophiles**. Since the nucleus is electrically positive, the nucleophiles would be electrically negative or electron-rich substances. Thus there are two types of nucleophiles.

(*a*) NEGATIVE NUCLEOPHILES ($\bar{Nu}:$) which have an excess electron-pair and carry a negative charge *e.g.*, carbanions and chloride ion.



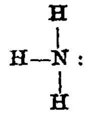
$$R-\overset{H}{\underset{H}{\overset{|}{\underset{|}{C}}}}{}^{-}:$$

Carbanion
(C atom has a spare pair of electrons and a negative charge)

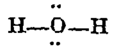
$$:\ddot{\underset{..}{Cl}}:^{-}$$

Chloride ion
(has available pairs of electrons and a negative charge)

(*b*) **Neutral Nucleophiles** (Nu:) such as ammonia and water whose molecules possess spare pairs of electrons but no charge.



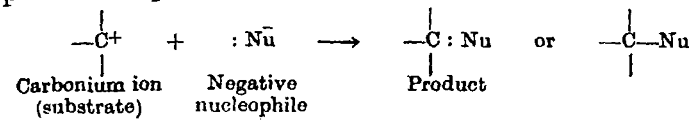
Ammonia

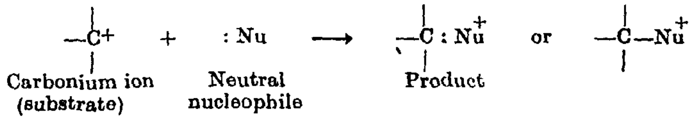


Water

How nucleophiles attack the substrate ?

Both charged and neutral nucleophiles have a spare pair of electrons. When they attack a substrate deficient in two electrons, the latter accepts the spare electron-pair from the reagent to establish a new bond. Let us illustrate the result of attack of both types of nucleophiles on the carbonium ion as the substrate.





It may be noted that with the charged nucleophile the product is neutral while with the neutral nucleophile the Nu part of the product develops a positive charge.

TABLE : *Some Nucleophiles*

Negative (−)		Neutral	
Hydroxyl ion	$-\overset{-}{\ddot{\underset{\cdot\cdot}{O}}}-H$	Ammonia	$\ddot{N}H_3$
Halide ion	$:\overset{-}{\underset{\cdot\cdot}{\ddot{X}}}:$ ($X=Cl, Br, I$)	Water	$H-\ddot{\underset{\cdot\cdot}{O}}-H$
Cyanide ion	$-C\equiv\overset{-}{N}:$	Alcohols	$R-\ddot{\underset{\cdot\cdot}{O}}-H$
Bisulphide ion	$-\overset{-}{\ddot{\underset{\cdot\cdot}{S}}}-H$	Other molecules containing linkages $>\ddot{O},\ >\ddot{S},\ \equiv\ddot{N}$	
Alkoxy ion	$R-\overset{-}{\ddot{\underset{\cdot\cdot}{O}}}:$		
Carbanion	$-\overset{|}{\underset{|}{C}}\overset{-}{:}$		

Electron Displacement Effects

We have seen that most of the attacking reagents bear either a positive or a negative charge. Naturally these could not attack the substrate successfully unless the latter somehow possessed oppositely charged centre in its molecule. In other words, the substrate molecule although as a whole electrically neutral, must develop polarity on some of its carbon atoms and substituents linked together. This is made possible by the displacement of the bonding electrons (partially or completely) resulting in the development of polarity in the molecule. Such changes or 'effects' involving the displacement of electrons in the substrate molecule are often referred to as ELECTRON DISPLACEMENT EFFECTS and are of great importance in understanding reaction mechanisms. Two such effects are :

(*a*) *Inductive effect* ;

and (*b*) *Electromeric effect*.

Inductive effect. When a carbon atom is joined to a hydrogen atom by a covalent (σ) bond (C—H) such as in alkanes, it is understood that the shared electron-pair is symmetrically placed between them. If instead of hydrogen atom, we have a substituent X having higher electronegativity or electron-attracting power than the C-atom, in the bond C—X, the shared electron-pair will be displaced away from the carbon atom and toward the more electronegative substituent X. On the other hand if a substituent Y having lower electronegativity is attached to it, the shared pair of the bond C—Y will be displaced toward the carbon atom and away from the electron releasing group Y. In other words the symmetry of the molecular orbital of C—X will be disturbed in favour of X, the more electronegative substituent while in case of C—Y the molecular orbital will be disturbed in favour of the carbon atom which is more electronegative.

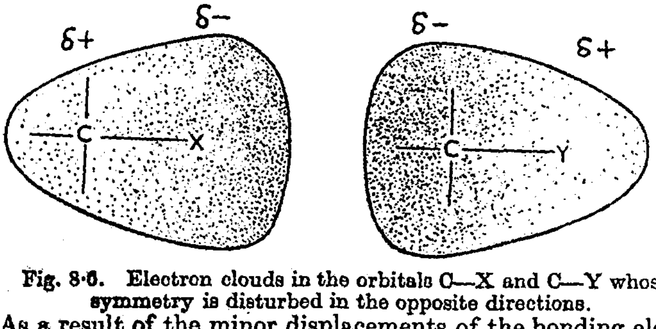


Fig. 8·6. Electron clouds in the orbitals C—X and C—Y whose symmetry is disturbed in the opposite directions.

As a result of the minor displacements of the bonding electron-pair, the joined atoms develop small fractional charges on them as illustrated below :

C :H or C——H (standard)
C :X or $\overset{\delta_+}{\text{C}}\text{——}\overset{\delta_-}{\text{X}}$ (—*I*)
C: Y or $\overset{\delta_-}{\text{C}}\text{——}\overset{\delta_+}{\text{Y}}$ (+*I*)

The polarisation thus induced in the substrate molecule is of a permanent nature.

The permanent effect whereby polarity is induced on the carbon atom and the substituent attached to it due to minor displacement of bonding electron-pair caused by their different electronegativities, is known as **Inductive effect** *or simply as* **I-effect.** When the substituent linked to carbon is electron-attracting (X), it develops a negative charge and it is said to exert a negative inductive effect or **−I effect.** If the substituent Y bonded to carbon atom is electron-releasing it acquires a positive charge and the inductive effect produced is called **+I effect.**

Writing structural formula of the polar molecules, the inductive effect is represented by an arrow-head in the middle of the covalent bond pointing in the direction of the electron displacement. Thus :

$$\underset{(-\text{I})}{\text{C}\rightarrow\text{X}} \qquad\qquad \underset{(+\text{I})}{\text{C}\leftarrow\text{Y}}$$

Now let us consider an organic molecule having a highly electron-attracting substituent X attached to the terminal carbon atom.

$$\overset{\gamma}{\text{C}}-\overset{\beta}{\text{C}}-\overset{\alpha}{\text{C}}-\text{X}$$

The substituent X pulls towards it the electron-pair between α-carbon and X. This produces a slight positive charge (δ_+) on the α-carbon. When a small positive charge is acquired by the α-carbon, it will tend to attract to itself the electron-pair linking it with β-carbon. This causes β-carbon also to acquire a fractional positive charge which, of course, would be smaller than of the α-carbon due to the decreasing influence of X. Similarly, the β-carbon influences the electron-pair bonding it with γ-carbon, but to a lesser degree and a still smaller positive charge is developed on the γ-carbon. Denoting the decreasing magnitude of positive charge on α, β and γ carbon atoms by δ_+, δ_{++} and $\delta\delta\delta_+$, the inductive effect relayed along the carbon chain may be represented as follows.

$$\overset{\delta\delta\delta_+}{\text{C}}\rightarrow\overset{\delta\delta_+}{\text{C}}\rightarrow\overset{\delta_+}{\text{C}}\rightarrow\overset{\delta_-}{\text{X}}$$

With an electron-pumping substituent Y, the inductive effect will be reversed and the situation would be

$$\overset{\delta\delta\delta_-}{\text{C}}\leftarrow\overset{\delta\delta_-}{\text{C}}\leftarrow\overset{\delta_-}{\text{C}}\leftarrow\overset{\delta_+}{\text{Y}}$$

Some common groups which can cause negative or positive I-effect are given below in order of their decreasing effect (*a*) *—I effect groups* (*electron-attracting*) :

$$NO_2 > F > COOH > Cl > Br > I > OH > C_6H_5$$

(*b*) *+I effect groups* (*electron-pumping*) :

$$\underset{\text{Tertiary butyl}}{(CH_3)_3C-} > \underset{\text{Isopropyl}}{(CH_3)_2CH-} > \underset{\text{Ethyl}}{CH_3CH_2-} > \underset{\text{Methyl}}{CH_3-}$$

In general the inductive effect of the alkyl groups is in the order 3°>2°>1° groups. In other words the electron-releasing power of a primary carbon (1°) is less than that of a secondary carbon (2°), while that of a tertiary carbon (3°) is the minimum. The inductive effect caused by the presence of an electron-attracting or electron-pumping substituents relayed along a chain falls rapidly as the distance from the functional group increases. Actually, it dies down completely after the third or fourth carbon atom of the chain.

Electromeric effect. This effect is very helpful in explaining polarisation produced in a substrate molecule containing multiple bonds. When a double or a triple bond is exposed to attack by an electrophilic reagent, a pair of bonding electrons is transferred completely from one atom to the other. The atom that takes charge of the electron-pair becomes negatively charged and the other positively charged. Thus, taking a very general case :

$$\overset{\curvearrowright}{A = B} \xrightarrow[\text{reagent}]{\text{Electrophilic}} \overset{+}{A}—\overset{-}{\ddot{B}}$$

This is a purely temporary effect and remains into play only in the presence of the electrophilic reagent. As soon as the attacking reagent is removed, the polarised molecule reverts to its original electronic state.

$$A = B \underset{\text{Reagent removed}}{\overset{\text{Reagent added}}{\rightleftharpoons}} \overset{+}{A}—\overset{-}{\ddot{B}}$$

The effect which causes a temporary polarisation in the substrate molecule at the seat of a multiple bond by shift of an electron-pair from one atom (*or part*) *to the other under the influence of an electrophilic reagent, is called* **Electromeric effect** (*electro* = electron ; *meros* = part).

The electromeric effect differs from the inductive effect in the following respects.

ELECTROMERIC EFFECT	INDUCTIVE EFFECT
1. Shown by substrate molecules containing double (C=C) or triple (C≡C) bonds.	1. Shown by molecules containing single bond.
2. Takes place when the molecule is exposed to an attack by electrophilic reagent.	2. Takes place under the influence of a substituent (electron-attracting or electron-pumping) linked to the terminal carbon atom.
3. Polarity caused by complete transfer of an electron-pair to one of the two atoms joined by multiple bond.	3. Polarity caused by the displacement of bonding electron-pair from one atom towards the other.
4. The charge acquired by the atom that gains the electron-pair is +1 while the other gets −1.	4. The charge developed by the carbon linked to the substituent is small fractional δ_+ or δ_- according as the substituent is electron attracting or electron-pumping.
5. Temporary effect ; disappears with the removal of the attacking reagent.	5. Permanent effect ; depending on the structure of the substrate molecule.

Let us discuss the example where an electrophile attacks a carbon-to-carbon double bond in the substrate molecule. According to modern concepts, a double bond is made of one σ bond (—) and one π bond (⌒). The electron cloud of the π bond is rather extensive and surrounds that of the σ bond in space. Under the influence of the electric field of an electrophile symmetry of the π electrons cloud is disturbed entirely in favour of one carbon atom as shown in the illustration given below :

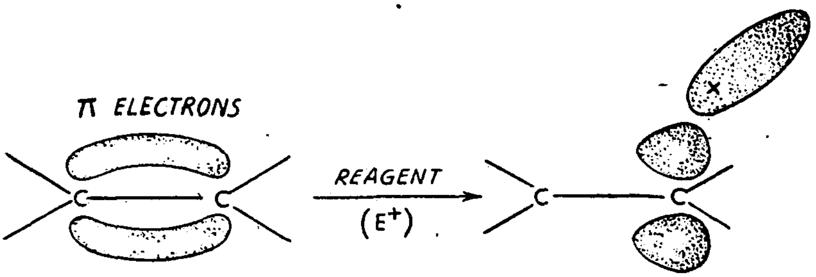
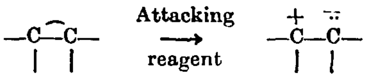


Fig. 8·7. The presence of an electrophile disturbs the symmetry of the π electrons cloud completely in favour of one of the doubly bonded carbon atoms.

This gives a negative charge to the carbon atom to which the π electron-pair shifts, while the other atom gets a positive charge. For the convenience of writing, the above change may be represented as



$$-\overset{|}{\underset{|}{C}}\overset{\frown}{-}\underset{|}{C}- \xrightarrow[\text{reagent}]{\text{Attacking}} -\overset{+}{\underset{|}{C}}-\overset{-}{\underset{|}{C}}-$$

The π bond is ruptured by the attack of the electrophile and one carbon to which the bonding electrons shift becomes negative while the other that loses its own shared electron gets a positive charge. Therefore, a more correct definition of the electromeric effect would be :

"A temporary effect which causes extreme (or whole unit) polarity on atoms joined by a multiple bond owing to a complete transfer of the π electron-pair to one or the other atom under the influence of an electrophile."

While writing reaction mechanism, electromeric effect or change is represented by a curved arrow pointing away from the centre of the π bond towards the carbon that gains the electron-pair. To be more correct π bond should be represented by (⌒) to distinguish it from σ bond (—). But for convenience, a π bond is also generally written as a straight line like the σ bond. Thus :

$$\mathrm{C} \overset{\curvearrowright}{=} \mathrm{C} \xrightarrow{\text{Electrophile}} \overset{+}{\mathrm{C}}\text{—}\ddot{\mathrm{C}}$$

Let us now consider the example of ethylene molecule. Here under the influence of an electrophile the direction of displacement of electron-pair can take place on to any of the two carbon atoms.

$$\mathrm{H_2C{=}CH_2} \xrightarrow[\text{Reagent}]{\text{Attacking}} \mathrm{H_2\overset{+}{C}\text{—}\ddot{C}H_2} \quad \text{or} \quad \mathrm{H_2\overset{-}{\ddot{C}}\text{—}\overset{+}{C}H_2}$$

However, if one of the doubly bonded carbon atoms is linked also to an electron-withdrawing or electron releasing group, the electromeric effect is regulated by the inductive influence of the attached group. For example, the electromeric effect in propylene molecule could operate in two ways :

$$(i) \quad \mathrm{CH_3\text{—}CH} \overset{\curvearrowright}{=} \mathrm{CH_2} \xrightarrow{(\mathrm{E}+)} \mathrm{CH_3\text{—}\overset{+}{C}H\text{—}\overset{-}{\ddot{C}}H_2}$$

$$(ii) \quad \mathrm{CH_3\text{—}\overset{\curvearrowleft}{C}H{=}CH_2} \xrightarrow{(\mathrm{E}+)} \mathrm{CH_3\text{—}\overset{-}{\ddot{C}}H\text{—}\overset{+}{C}H_2}$$

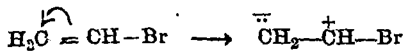
Since methyl group is electron-repelling, the electromeric effect at the double bond will take place as shown in (*i*) above. Here the inductive effect between the CH_3 group and the adjacent carbon dictates the direction of transfer of the electron-pair and the electromeric effect is depicted as follows :

$$\mathrm{CH_3{\rightarrowtail}CH} \overset{\curvearrowright}{=} \mathrm{CH_2} \longrightarrow \mathrm{CH_3{\rightarrowtail}\overset{+}{C}H\ \ddot{C}H_2}$$

Had there been an electron-attracting group in place of the methyl group, the situation would have been reversed. Halogen substituents, which have normally electron-attracting property, behave in an astonishing manner while directing the electromeric effect. For example, vinyl bromide could possibly undergo electromeric effect in two ways :

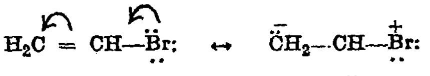
(i) 

$$H_2C = CH—Br \longrightarrow \overset{+}{C}H_2—\overset{-}{\ddot{C}}H—Br$$

(ii) 

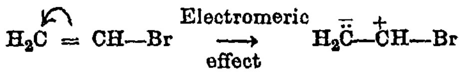
$$H_2C = CH—Br \longrightarrow \overset{-}{\ddot{C}}H_2—\overset{+}{C}H—Br$$

Ordinarily, Br atom being electron-attracting would have directed the electromeric effect as in (i). But vinyl bromide is also capable of existing as the resonance hybrid of the following structures.



$$H_2C = CH—\ddot{B}r: \leftrightarrow \overset{-}{C}H_2—CH—\overset{+}{B}r:$$

Here the Br atom displays electron-releasing effect (+*I* effect) due to the presence of an available lone pair to be donated to the adjacent carbon atom. *Such an electron movement from the octet of an atom to that of another atom without rupturing its bond,* is called **Conjugate effect**. In vinyl bromide the inductive and the conjugate effect of bromine atom operate simultaneously in opposite directions and the latter being stronger overweighs the inductive effect. Hence the electromeric change follows the course described in (ii) above *i.e.,*



$$H_2C = CH—Br \xrightarrow[\text{effect}]{\text{Electromeric}} H_2\overset{-}{\ddot{C}}—\overset{+}{C}H—Br$$

REACTION MECHANISMS – THEIR TYPES

From the mechanistic viewpoint described earlier in this chapter, organic reactions could be divided into two classes :

(i) *Homolytic reactions involving homolytic bond fission* ;

(ii) *Heterolytic reactions involving homolytic bond fission.*

The reaction mechanism in the two cases is of entirely different type.

Free-Radical mechanism. In homolytic reactions, the first step is the production of a free radical (R·) from a normal molecule by the application of energy (heat or light). The free radical then attacks the substrate to bring about homolytic fission.

$$R\cdot + \underset{\text{Substrate}}{X—Y} \longrightarrow R—X + \cdot Y$$

This type of reaction mechanism when the attacking species is a free radical, is called **free-radical mechanism.**

The free-radical mechanism may be illustrated by the chlorination of methane in sunlight. In the first step, illumination causes a molecule of chlorine to break homolytically into two chlorine atoms. These then attack a molecule of methane forming hydrogen chloride and methyl radical ($H_3C\cdot$). In turn, the methyl free-radical attacks a molecule of chlorine giving methyl chloride (CH_3Cl) and fresh chlorine atom.

$$\mathrm{Cl:Cl} \xrightarrow{light} 2\mathrm{Cl}\cdot$$

$$\left.\begin{array}{lll} \mathrm{Cl}\cdot + \mathrm{CH_4} & \longrightarrow & \mathrm{HCl} + \mathrm{H_3C}\cdot \\ \mathrm{H_3C}\cdot + \mathrm{Cl_2} & \longrightarrow & \mathrm{CH_3Cl} + \mathrm{Cl}\cdot \end{array}\right\}\text{ Chain reactio}$$

Once the free radical $H_3C\cdot$ is produced, the reaction proceeds by the last two steps in a sort of endless chain. Such a self-propagating reaction is often referred to as a **Chain reaction.**

Since the free radical carries no charge, it can attack any part of the substrate molecule regardless of the electronic distribution of the latter.

Polar or Ionic mechanism. This type of mechanism applies to organic reactions in which heterolytic fission takes place. Here the substrate molecule develops negative and positive charged centres, or partial ionic character, by the displacement of electrons due to inductive effect, electromeric effect etc. These negative and positive parts or poles of the molecule are so to say activated for attack by an electrophilic or nucleophilic reagent. The mechanism of reactions involving the attack of electrophilic or nucleophilic reagents on the polar or ionic molecules of the substrate is referred to as *Polar* or *Ionic mechanism.*

The cardinal principle of electrostatics that 'the unlike charges attract while like charges repel each other' forms the basis of polar or ionic mechanism. The negatively charged nucleophilic reagents are anionic in character and attack the substrate molecule at the positive centre causing a *nucleophilic reaction.* On the other hand, the positively charged electrophilic reagent would attack the molecule at the negative centre causing *electrophilic reaction.*

The Polar or Ionic mechanism may be beautifully illustrated as follows. The imaginary molecule AB of the substrate has a positive end A and a negative end B. This would be expected to be attacked by anionic nucleophilic reagent at A and cationic electrophilic reagent at B.

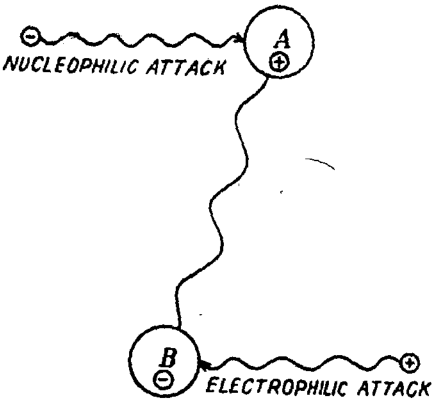
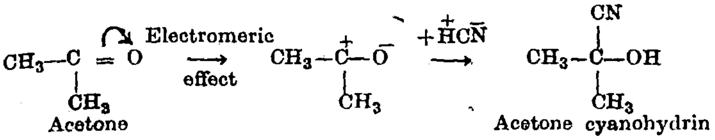


Fig. 8·8. How a nucleophilic and electrophilic reagent attacks the polar AB molecule.

An example of the above reaction mechanism is afforded by the addition of HCN $(H^+ + CN^-)$ to acetone.



$$\underset{\text{Acetone}}{CH_3-\underset{\underset{CH_3}{|}}{C}=O} \xrightarrow[\text{effect}]{\text{Electromeric}} CH_3-\underset{\underset{CH_3}{|}}{\overset{+}{C}}-\overset{-}{O} \xrightarrow{+\overset{+}{H}\overset{-}{CN}} \underset{\text{Acetone cyanohydrin}}{CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CN}{|}}{C}}-OH}$$

More examples of the ionic mechanism will be discussed in the subsequent treatment.

ENERGY REQUIREMENTS OF A REACTION

In an organic reaction, some bonds break while some new ones are formed. Energy is required for the breaking of bonds and also it is liberated in the formation of bonds. Let us consider, for example, the reaction between methane and chlorine to give chloromethane (CH_3Cl) and hydrogen chloride. Here one C—H bond and one C—Cl bond is broken, requiring a total energy of 157 kcal/mole. At the same time one C—Cl bond and H—Cl bond is formed, liberating total energy of 184 kcal/mole. The net result is that the reaction occurs with a liberation of energy equal to 27 kcal/mole and is, therefore, said to be **exothermic**. Thus :

$$\underset{99}{CH_3-H} + \underset{58}{Cl-Cl} \longrightarrow \underset{81}{CH_3-Cl} + \underset{103}{H-Cl}$$

Bond energy
Kcal/mole

Conversely, the reverse reaction would require the consumption of 27 Kcal/mole energy, and will be **endothermic**. Thus an exothermic reaction could be considered like a ball rolling down a hill side and would be expected to occur of its own accord. On the other hand an endothermic reaction which is like a ball rolling uphill, would not occur normally, unless heat is supplied to the system. The total 'chemical energy' stored in the molecules before and after the reaction could be described as the 'potential energy' of the system.

Activation Energy. We have discussed above that a reaction proceeds by breaking of bonds in the reacting molecules. Therefore, whether a reaction is exothermic or endothermic, to start with energy must come from some source to break the bonds.

We know from our knowledge of Physical Chemistry that molecules of the reactants are in a state of rapid motion and possess kinetic energy. The reaction occurs when the reacting molecules approach in proper alignment with respect to one another and collide. On such collisions, the kinetic energy possessed by the molecules is transformed into 'chemical energy' or 'potential energy of the system. Thus to start a reaction, the required energy is supplied by the collisions of the reacting molecules, whose rate could be enhanced if necessary, say by heating.

Not all collisions between the reacting molecules are fruitful. Rather, it is only the collisions of such molecules as possess a certain minimum energy which bring about the reaction, while others do not The molecules that come to possess higher potential energy through collisions are said to have been *'activated'* to enter into reaction.

The minimum amount of 'chemical' or 'potential' energy that must be provided by collisions of the reacting molecules for the reaction to occur is termed the **Activation energy.**

It is true that for an exothermic reaction, the collisions of the reactant molecules readily supply the required initial energy and the reaction takes place spontaneously. On the other hand, for an endothermic reaction the molecules need to be activated by supplying energy, say in the form of heat to make the reaction go.

For illustration, imagine some balls attempting to climb over a hill from one valley to another. Only those will cross over which possess a certain minimum of energy to reach the hilltop from where they would get over the barrier.

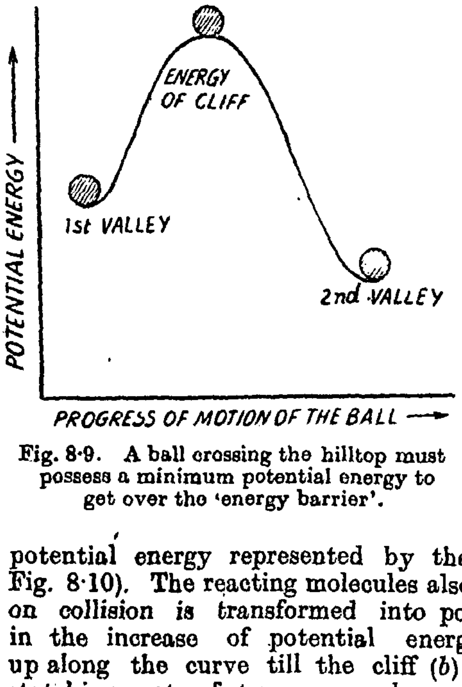


Fig. 8·9. A ball crossing the hilltop must possess a minimum potential energy to get over the 'energy barrier'.

From analogy, only such reacting molecules that possess a certain minimum energy could change into products but before doing so, these would have to cross over the 'activation energy barrier'.

Let us consider the energy changes during the course of the reaction.

$$X + Y{-}Z \longrightarrow X{-}Y + Z$$

In the beginning both X and Y—Z possess certain potential energy represented by the point *(a)* on the curve *(see* Fig. 8·10). The reacting molecules also possess kinetic energy which on collision is transformed into potential energy. This results in the increase of potential energy and the system moves up along the curve till the cliff *(b)* is reached. The 'energy cliff state' is a sort of temporary phase and leads to the products *(c)*, when the potential energy of the system is again changed into kinetic energy and then into heat or any other form of energy.

The following figure illustrates that for an exothermic reaction, the system originally possesses more potential energy than the products and the excess energy (ΔH) is liberated as heat. For an endothermic reaction, the system to start with has less potential energy than at the end ($-\Delta H$) and, therefore, it absorbs heat from the surroundings.

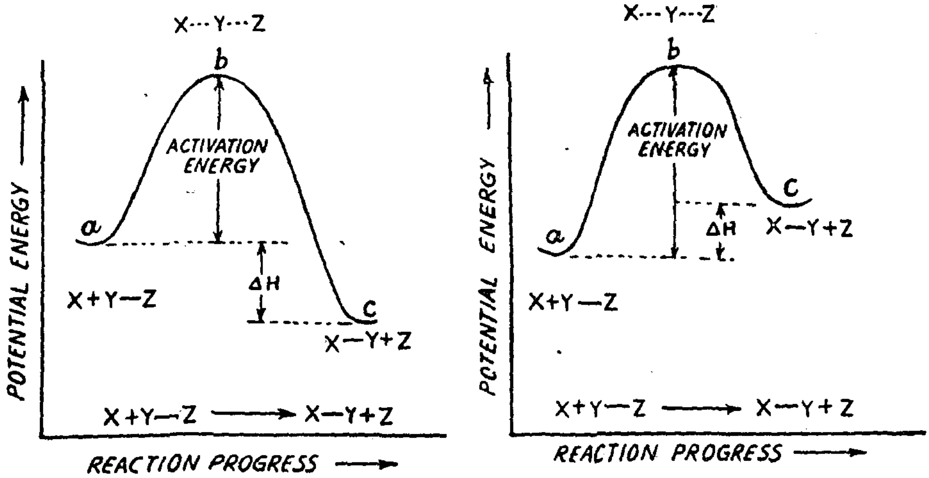


Fig. 8·10. Energy changes in exothermic and endothermic reactions.

The reaction $X + Y\text{—}Z \rightarrow X\text{—}Y + Z$ could be visualised to take place by the following steps. The molecule X approaches Y—Z from a direction remote from Z (proper alignment). While X draws nearer to Y, Z starts being repelled from Y until a stage is reached when X and Z are rather loosely attached to Y and are approximately equidistant from it. Thus an 'activated complex' $X\cdots Y\cdots Z$ is formed in which X to Y and Y to Z distances are slightly more than the normal bond length. This is the least stable arrangement and is called the **Transition state** or **Activated complex**. The sequence of events may be represented by the following equation.

$$\underset{\text{Reactants}}{X + Y\text{—}Z} \longrightarrow \underset{\substack{\text{Transition state}\\ \text{(activated complex)}}}{X\cdots Y\cdots Z} \longrightarrow \underset{\text{Products}}{X\text{—}Y + Z}$$

The activated complex is not a true molecule, the bonds being partial. In this state, the system possesses maximum energy and is most unstable. Hence the transition state of a system could be described as an extremely transitory specific arragement of atoms and groups through which a reaction system must pass on its way to the products. In other words, the activated complex has infinitesimally short life-time and at once decomposes to give the products.

APPLICATION OF GENERAL MECHANISTIC CONCEPTS

The concepts discussed above are successfully employed to interpret the course of the bulk of organic reactions known so far, as also to transgress the possibility of reaction between any two species. Almost all types of reactions mentioned earlier in this chapter can be explained in the light of the general mechanistic concepts.

Substitution Reactions

Reactions proceeding by the replacement or substitution of one or more atoms or groups of a compound by other atoms or groups are referred to as *substitution reactions.* They are known to proceed by a free radical or ionic mechanism.

Free radical substitution. These reactions are initiated by free radicals. The replacement of hydrogen atoms in alkane molecules is probably the best example of this type.

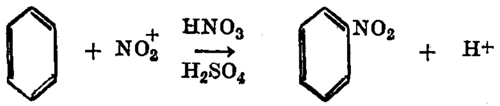
$$Cl_2 \xrightarrow{h\nu} \underset{\text{(free radicals)}}{2Cl\cdot}$$

$$\underset{\text{Methane}}{CH_4} + Cl\cdot \longrightarrow \underset{\text{Methyl chloride}}{CH_3Cl}$$

A detailed account of the conditions of the reaction and its mechanism will be dealt under alkanes.

Ionic substitution. Substitution reactions may be brought about by electrophiles or nucleophiles acting as attacking reagents. Most of such reactions are initiated by Nucleophiles, while substitution reactions involving electrophiles are very rare indeed.

(*i*) *Electrophilic substitution* (S_E). When a substitution reaction involves an attack by an electrophile, the reaction is referred to as S_E (here S stands for substitution and E for electrophile). The substitution reactions of benzene are the best examples of electrophilic substitution *e.g.*, the nitration of benzene is brought about with the help of nitronium ion NO_2^+ (an electrophile).



A detailed mechanism will be discussed in the chapter on Benzene.

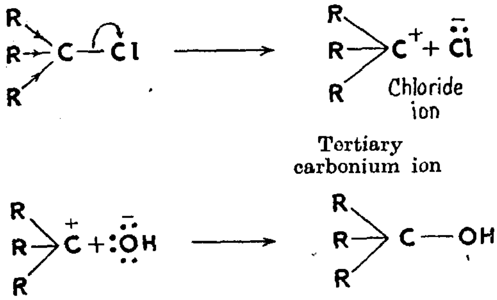
(*ii*) *Nucleophilic substitution* (S_N). If a substrate is attacked by a nucleophile in a substitution reaction, the reaction is represented as S_N (S for substitution and N for a nucleophile). A general nucleophilic substitution reaction may be represented as

$$\bar{N}: + R—X \longrightarrow N-R + \bar{X}:$$

where N is the attacking nucleophile, RX the substrate, NR the substitution product and X is the leaving group.

Such reactions may be classed into two further divisions *viz.*, $S_N{}^1$ and $S_N{}^2$ depending upon whether the reaction in question is a first order or second order one. Familiar examples of the two types are :

$S_N{}^1$ type. Conversion of a tertiary alkyl halide into a tertiary alcohol by substitution of -OH group by Cl atom.

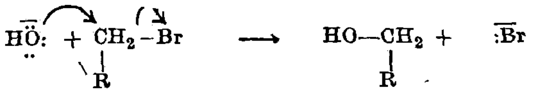


Tertiary carbonium ion

Nucleophile

Tertiary alcohol

S_N2 *type.* Conversion of primary alkyl halide into a primary alcohol.



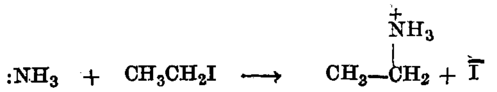
$$\bar{H\ddot{O}}: + \underset{R}{CH_2}-Br \longrightarrow HO-\underset{R}{CH_2} + :\bar{Br}$$

Alkyl bromide

Primary alcohol

Bromide ion

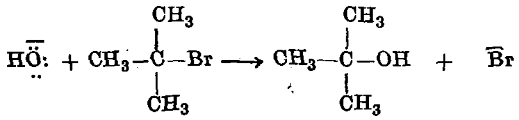
Some nucleophilic substitution reactions of primary importance are cited below :



$$:NH_3 + CH_3CH_2I \longrightarrow CH_3-\overset{\overset{+}{N}H_3}{C}H_2 + \bar{I}$$

$$R_2\ddot{S}: + R'I \longrightarrow [R_2SR'] + \bar{I}$$

$$\bar{H\ddot{O}} + R-Br \longrightarrow H-O-R + \bar{Br}$$

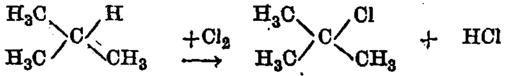


$$\bar{H\ddot{O}}: + CH_3-\overset{CH_3}{\underset{CH_3}{C}}-Br \longrightarrow CH_3-\overset{CH_3}{\underset{CH_3}{C}}-OH + \bar{Br}$$

It may be clearly understood that in an electrophilic substitution reaction an electron deficient species attacks the substrate and gets bonded to it through a pair of electrons furnished by the nucleophile ; at the same time a second electron deficient species is generated. A reference to such reactions will be made in the forthcoming chapter.

Notes on Substitution. (1) In some *compounds* substitution proceeds readily while in others with difficulty, depending upon the nature of the compound and experimental conditions.

(2) In hydrocarbons with a branched chain, the hydrogen atom attached to a tertiary *carbon atom is* substituted first, then the hydrogen atoms attached to a secondary carbon atom, and last of all those which are attached to a primary carbon atom. Thus in isobutane the tertiary H atom is replaced first and if chlorine is in excess, other hydrogens will be subsequently replaced.



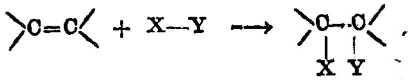
Isobutane

Isobutyl chloride

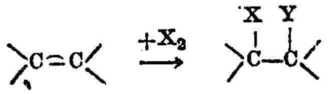
(3) In benzene hydrocarbons, the position occupied by the atom or group entering the benzene nucleus depends upon the nature of substituents already present in the nucleus.

Addition Reactions

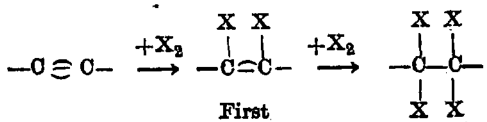
This type of reaction is characteristic of (*a*) alkenes, (*b*) alkynes, and (*c*) aromatic hydrocarbons. In fact, all organic compounds containing double or triple bonds display addition reactions. Thus :



We have already studied that a double bond is made of one σ bond and one π bond, while a triple bond consists of one σ bond and two π bonds. It requires less energy to break a π bond than the σ bond, since the *p* orbitals experience a sidewise overlap to a lesser extent and form a weak π bond, while a σ bond that is formed by a head-on overlap of orbitals which is quite significant lends strength to the bond. An ethylenic π bond is approximately 15 Kcal/mole weaker than a σ bond. Therefore, in addition reactions of a double linkage, which consists of one σ bond and one π bond, the weaker π bond breaks open leaving the stronger σ bond intact.



As already stated, a triple bond or acetylene linkage is made of one σ bond and two π bonds. Here the addition of a reagent will take place in two steps, when first one π bond will break open and then the second. The σ bond being the strongest remains intact in the final addition product.



The reagents which readily add to double or triple bonds are halogens, hydrogen, halogen acid, sulphuric acids, hypohalous acids, etc. The addition of hydrogen to unsaturated hydrocarbons is commonly referred to as **Hydrogenation.**

Electrophilic Addition Reactions. It has been observed that when an alkane is treated with bromine (or chlorine) dissolved in a solvent (ethanol, petrol), a rapid reaction takes place and the bromine solution is decolorised. Further, this reaction is seen to be catalysed by polar reagents, indicating a polar mechanism of the addition reaction. The polar reagent is believed to push the π electrons (forming the weaker bond) in one direction, thereby polarising the alkene molecule.

$$\overset{\curvearrowright}{CH_2 = CH_2} \xrightarrow[\text{effect [E+]}]{\text{Electromeric}} \overset{+}{C}H_3—\overset{-}{C}H_2$$

Likewise, the bromine molecule tends to get cleaved unsymmetrically, one of the atoms getting complete control of the shared pair of electrons constituting the covalent bond.

$$Br:Br \xrightarrow[\text{fission}]{\text{Heterolytic}} \overset{+}{Br} + \overset{-}{\ddot{B}r}$$

As the ethylene and bromine molecules approach each other, the bromine molecule enhances the electromeric effect in ethylene molecule whereas the latter helps the heterolytic fission of bromine molecule. However, the overall reaction is believed to be taking place in two steps.

In the first place, the electrophile (Br^+) attacks the polarised ethylene molecule and forms a carbonium ion.

$$CH_2{=}CH_2 + Br—Br \longrightarrow \overset{+}{C}H_2-CH_2Br + \overset{-}{\ddot{B}r}$$

This ion has a transitory existence and combines readily with bromide ion at the positively charged carbon atom.

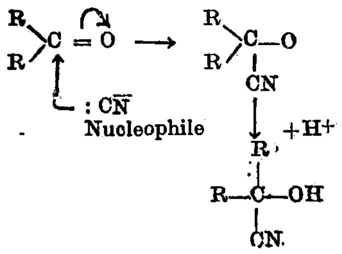
$$\overset{+}{C}H_2-CH_2Br + \overset{-}{\ddot{B}r} \longrightarrow Br—CH_2—CH_2-Br$$

Combining the above two equations,

$$\begin{aligned} CH_2 \overset{\curvearrowright}{=} CH_2 + Br \overset{\curvearrowright}{—} Br &\longrightarrow \overset{+}{C}H_2—CH_2Br + \overset{-}{\ddot{B}r} \\ &\longrightarrow Br—CH_2—CB_2—Br \end{aligned}$$

The mechanism of other electrophilic addition reactions will be dealt with in detail at appropriate places in the text of the book.

Nucleophilic Addition Reactions. These are started by nucleophilic attack in substrate molecule. The additions of HCN $NaHSO_3$ and NH_3 to aldehydes and ketones afford an excellent example of this type. Thus :



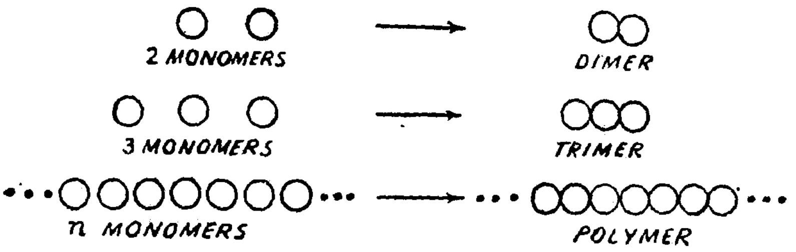
Polymerization

This is one of the most significant reactions of alkenes and conjugated dienes (containing alternate single and double bonds) and several other compounds containing multiple bonds. Under suitable conditions, two or more molecules of such compounds react together by combination to yield complex molecules.

The union of two or more molecules of a substance to form a large single molecule is called **Polymerization** *and the product thus obtained is called a* **Polymer.**

$$nX \xrightarrow{\text{Ploymerization}} X_n$$

The simple molecules are called **monomers**, and the products are named as **dimers**, **trimers** and **polymers** according as the number of molecules joining in the formation of the complex molecule is 2, 3, or, *n* (many). Thus :



Polymerization reactions are again of two types :

(*a*) *Addition Polymerization* ; and

(*b*) *Condensation Polymerisation.*

Addition polymerization involves the joining together of many simple molecules (monomers) to give a new compound (*addition polymer*) having the same empirical formula but higher molecular weight. For example, when ethylene is heated under pressure in the presence of oxygen, an open-chain alkane-like compound, having a very high molecular weight (20,000) is obtained.

$$\underset{\text{Ethylene}}{n\,CH_2{=}CH_2} \xrightarrow[\text{[O}_2\text{]}]{\text{200°C, 1000 Atmos.}} \underset{\text{Polyethylene}}{(-CH_2-CH_2-)_n}$$

Polyethylene, commonly called *'polythene'*, is a useful plastic material for the preparation of toys, flexible bottles and laboratory ware as also for packing films.

Polymerization reactions require the presence of an *'initiator'* —a foreign substance which simply starts the reaction and thus acts as a catalyst. Peroxides are very common initiators : these contain —O—O— group in the molecule. Peroxides are believed to furnish a free radical which adds to a molecule of alkene and then generates another free radical which in turn adds to still another molecule of ethylene giving a free radical, and so on. This 'chain reaction' set up results in the formation of complex polymers. Peroxide simply starts the chain reaction. Its oxygen supplies the free radical in the polymerization of ethylene as a result of the homolytic fission of its molecule.

(*i*)* $\text{Peroxide} \longrightarrow F\cdot$ (free radical)

(*ii*) $F\cdot + CH_2{=}CH_2 \longrightarrow FCH_2{-}\dot{C}H_2$

(*iii*) $FCH_2{-}\dot{C}H_2 + CH_2{=}CH_2 \longrightarrow FCH_2{-}CH_2{-}CH_2{-}\dot{C}H_2$; and so on

Polymerization of conjugated dienes is of special interest since the polymer obtained resembles natural rubber. Thus :

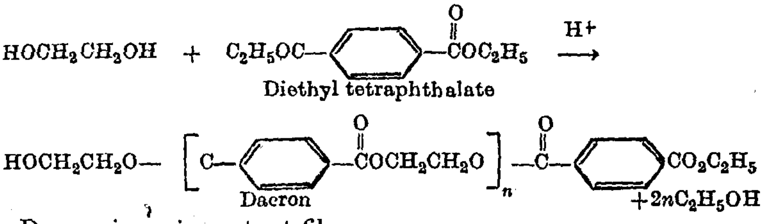
(*i*) $\text{Peroxide} \longrightarrow F\cdot$ (free radical)

(*ii*) $F\cdot + \underset{\text{1, 3-Butadiene}}{CH_2{=}CH{-}CH{=}CH_2} \longrightarrow FCH_2{-}CH{=}\dot{C}H{-}CH_2$

(*iii*) $FCH_2{-}CH{=}CH{-}\dot{C}H_2 + CH_2{=}CH{-}CH{=}CH_2$

$\longrightarrow FCH_2{-}CH{=}CH{-}CH_2{-}CH_2{-}CH{=}CH{-}\dot{C}H_2$; and so on.

In **Condensation Polymerization**, two or more simple molecules join together with the elimination of a simple molecule (*e.g.*, water, ammonia, hydrogen chloride) to form a new substance of high molecular weight. Thus the polyester of ethylene glycol and terephthalic acid is obtained by condensation-polymerization.



Dacron is an important fibre.

Note. Polymerisation generally (but not always) implies that the original simple substance should be recoverable from the complex compound. The splitting of such compounds to their originals is termed **Depolymerisation.**

Condensation

The term condensation is very loosely used in organic chemistry and it is difficult to give an exact definition of this type of reaction. It refers to all possible changes which result in the lengthening of the carbon chain and may be defined as follows :

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*F· should not be confused by the beginner as the fluorine atom ; it is simply a fragment of the peroxide molecule having an odd electron.

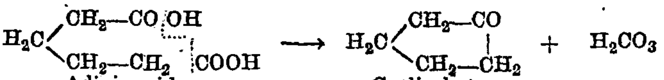
All reactions which proceed by a direct union between the carbon atoms of the same molecules or different molecules of the same or different substances, to form a new compound are termed **Condensation reactions** *and the products so obtained are termed* **Condensation products**. The condensation between molecules is very frequently attended by the elimination of H_2O, HCl, HBr, Br_2, etc. but that is not always necessary. The term condensation has also been extended to the union between carbon and nitrogen atoms. Some typical examples of condensation are given below :

(1) In the presence of sodium metal, two molecules of alkyl halides condense to form a longer molecule of a higher hydrocarbon.

$$CH_3CH_2Br + BrCH_2CH_3 + 2Na \longrightarrow CH_3CH_2CH_2H_3 + 2NaBr$$

Ethylene bromide (2 molecules) n-Butane

(2) Distillation of calcium salt of adipic acid (*Internal Condensation*).



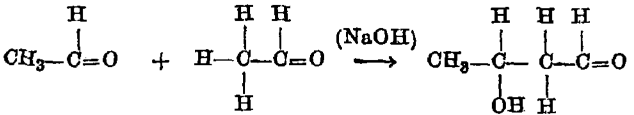
Adipic acid Cyclic ketone

(3) Condensation of aldehydes and ketones with hydroxylamine, NH_2OH.

$$CH_3CH{=}O + H_2NOH \longrightarrow CH_3CH{=}NOH + H_2O$$

Acetaldehyde Oxime

(4) **Aldol condensation.** In the presence of a dilute base (catalyst) two molecules of an aldehyde or a ketone may combine to form a β-hydroxy-aldehyde or a β-hydroxy-ketone. The reaction is termed 'aldol condensation' since originally it was applied to aldehydes and the product obtained was both an 'ald'- ehyde and an alcoh-'ol'.



$$CH_3-\overset{H}{C}{=}O + H-\overset{H}{\underset{H}{C}}-\overset{H}{C}{=}O \xrightarrow{(NaOH)} CH_3-\overset{H}{\underset{OH}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{C}{=}O$$

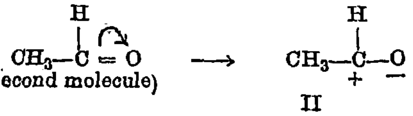
(Acetaldehyde-2 molecules)

Here, the α-carbon atom of one molecule of acetaldehyde becomes attached to the carbonyl group of other molecule.

The possible mechanism of aldol condensation involves the following steps :

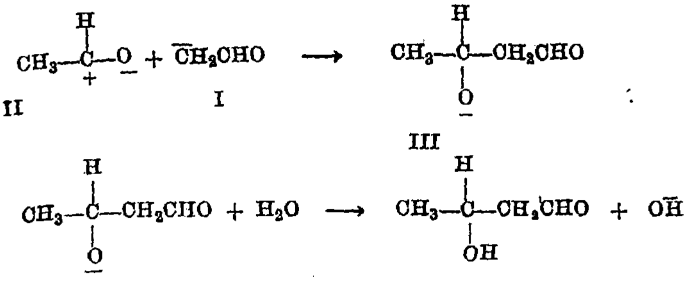
$$CH_3CHO + \overline{OH} \rightleftharpoons \overline{C}H_2.CHO + H_2O$$

(from base) I



$$CH_3-\overset{H}{C}{=}O \longrightarrow CH_3-\overset{H}{\underset{+}{C}}-\underset{-}{O}$$

(Second molecule) II

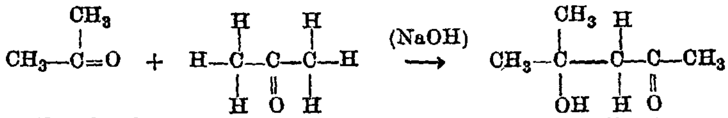


$$\underset{\text{II}}{CH_3-\underset{+}{\overset{H}{C}}-\underset{-}{O}} + \underset{\text{I}}{\bar{C}H_2CHO} \longrightarrow \underset{\text{III}}{CH_3-\underset{\underset{-}{O}}{\overset{H}{C}}-CH_2CHO}$$

$$CH_3-\underset{\underset{-}{O}}{\overset{H}{C}}-CH_2CHO + H_2O \longrightarrow CH_3-\underset{OH}{\overset{H}{C}}-CH_2CHO + \bar{O}H$$

The first step is the formation of a carbanion as a result of the removal of hydrogen ion by a hydroxyl ion of the base. In the second step the electromeric effect operates and creates a carbonium ion. The carbanion produced in step I attacks the carbonium ion and another nucleophile with negative charge on oxygen atom is generated. The third nucleophile then extracts hydrogen ion from water and OH⁻ ion is regenerated.

A similar mechanism explains the formation of β-hydroxydiacetone from two molecules of acetone in the presence of dilute sodium hydroxide solution, which as already stated, is also an example of aldol condensation.



$$CH_3-\overset{CH_3}{C}=O + H-\underset{H}{\overset{H}{C}}-\underset{\overset{\|}{O}}{C}-\underset{H}{\overset{H}{C}}-H \xrightarrow{(NaOH)} CH_3-\underset{OH}{\overset{CH_3}{C}}-\underset{H}{\overset{H}{C}}-\underset{\overset{\|}{O}}{C}-CH_3$$

(2 molecules of acetone) β-Hydroxydiacetone

Difference between Condensation and Polymerisation. It is true that polymerisation and condensation present many common examples, but **polymerisation is not necessarily condensation.** The points of difference between the two types of reactions are :

1. Condensation always proceeds by new union between carbon atoms while in polymerisation it is not necessary. For instance, in the polymerisation of aldehydes any change in structures only involves oxygen bonds.

2. Unlike polymerisation, condensation reactions are not reversible.

3. In polymerisation the reaction takes place between identical molecules but in condensation the reaction may take place even between different molecules.

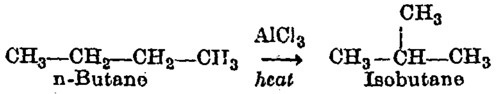
Intramolecular Change

We have already studied that molecules of organic compounds are built of carbon, hydrogen, and other atoms arranged in a characteristic way. Naturally a slight change effected in the molecular structure will lead to the formation of a new compound.

All such reactions which proceed by the internal re-arrangement of the molecule are designated **Intramolecular changes.** Such changes may be due to a spatial or structural re-arrangement in the molecule. The intramolecular change, since it results in the formation of an isomer of the original compound, is also referred to as an **Isomeric change.**

Some examples of intramolecular change are given below :

(1) Butane is converted to iso-butane when heated with aluminium chloride.



$$\underset{\text{n-Butane}}{CH_3{-}CH_2{-}CH_2{-}CH_3} \xrightarrow[\textit{heat}]{AlCl_3} \underset{\text{Isobutane}}{CH_3{-}\overset{\overset{\displaystyle CH_3}{|}}{C}H{-}CH_3}$$

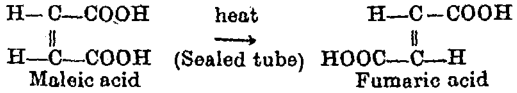
Such a reaction which refers to a change in the 'chain structure' of the molecule and results in a compound which is a 'chain isomer' of the original compound, is commonly termed **Isomerisation**. Butane is said to have isomerised to isobutane.

(2) n-Propyl bromide on heating becomes isopropyl bromide.

$$\underset{\text{n-Propyl bromide}}{CH_3.CH_2.CH_2.Br} \xrightarrow{\text{heat}} \underset{\text{Isopropyl bromide}}{CH_3.CHBr.CH_3}$$

It may be noted that in this case the isomeric change results in a position-isomer of the original substance.

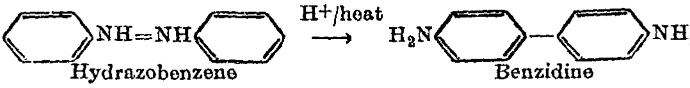
(3) Maleic acid when heated in a sealed tube is converted to fumaric acid.



$$\underset{\text{Maleic acid}}{\begin{matrix} H{-}C{-}COOH \\ \| \\ H{-}C{-}COOH \end{matrix}} \xrightarrow[\text{(Sealed tube)}]{\text{heat}} \underset{\text{Fumaric acid}}{\begin{matrix} H{-}C{-}COOH \\ \| \\ HOOC{-}C{-}H \end{matrix}}$$

This change presents a case when the product is a 'space isomer' of the original compound.

(4) Hydrazobenzene when treated with mineral acids, yields benzidine (*Benzidine change*),



In most cases, intra-molecular changes are goaded by the urge for a stable arrangement under the conditions of the experiment. Such changes differ from the tautomeric changes in that they are not reversible.

Reduction and Oxidation reactions

Reduction and oxidation reactions are very common in organic chemistry. They are shown especially by compounds containing double and triple bonds such as alcohols, aldehydes and ketones. The definition of reduction and oxidation as applied in organic chemistry is very simple.

A reaction which proceeds by the addition of hydrogen is termed **Reduction** *and the one that involves the addition of oxygen is called* **Oxidation**. The products formed in the two cases are referred to as **Reduction products** and **Oxidation products** respectively.

The result of reduction and oxidation depends upon the nature of the original compound and that of the reagent employed to effect the change. While reduction seldom causes a rupture of the carbon chain, oxidation does it very often.

Examples of Reduction. The hydrocarbons ethylene, acetylene and benzene when mixed with hydrogen and passed over finely divided nickel at an elevated temperature, add hydrogen yielding ethane, ethylene and hexahydrobenzene respectively.

$$CH_2{=}CH_2 + H_2 \xrightarrow{\text{Ni/heat}} \underset{\text{Ethane}}{CH_3{-}CH_3}$$

$$CH{\equiv}CH + H_2 \longrightarrow \underset{\text{Ethylene}}{CH_2{=}CH_2}$$

$$C_6H_6 + 3H_2 \longrightarrow \underset{\text{Hexahydrobenzene}}{C_6H_{12}}$$

The addition of hydrogen at the double or the triple bond is termed HYDROGENATION. The hydrogenation carried with finely divided nickel as a catalyst is often spoken of as **Sabatier and Senderens reaction.**

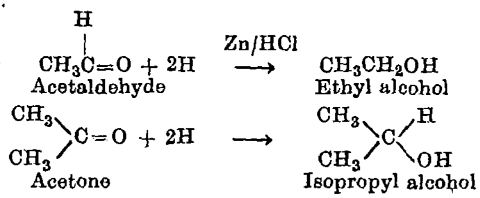
(2) Alcohols, aldehydes and ketones when reduced with hydrogen iodide and phosphorus at high temperature yield the corresponding hydrocarbons.

$$\underset{\text{Methyl alcohol}}{CH_3OH} + 2H \xrightarrow{HI/P} \underset{\text{Methane}}{CH_4} + H_2O$$

$$\underset{\text{Acetaldehyde}}{CH_3.CHO} + 4H \longrightarrow \underset{\text{Ethane}}{CH_3.CH_3} + H_2O$$

$$\underset{\text{Acetone}}{CH_3.CO.CH_3} + 4H \longrightarrow \underset{\text{Propane}}{CH_3.CH_2.CH_3} + H_2O$$

(3) Aldehydes and ketones on reduction with H_2 and nickel, or zinc and hydrochloric acid, yield alcohols.



$$\underset{\text{Acetaldehyde}}{CH_3\overset{H}{\overset{|}{C}}{=}O} + 2H \xrightarrow{Zn/HCl} \underset{\text{Ethyl alcohol}}{CH_3CH_2OH}$$

$$\underset{\text{Acetone}}{(CH_3)_2C{=}O} + 2H \longrightarrow \underset{\text{Isopropyl alcohol}}{(CH_3)_2C(H)OH}$$

(4) Nitrocompounds on reduction with tin and hydrochloric acid give primary amines.

$$\underset{\text{Nitroethane}}{C_2H_5NO_3} + 6H \xrightarrow{Sn/HCl} \underset{\text{Ethylamine}}{C_2H_5NH_2} + 2H_2O$$

Nitrobenzene yields a variety of reduction products, depending on the nature of the reducing agent.

Examples of Oxidation. (1) Unsaturated hydrocarbons oı oxidation under different conditions yield different products. Thi is illustrated by the following examples.

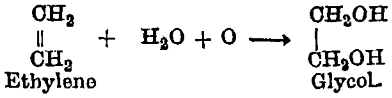
(*a*) With a strong oxidising agent like conc. HNO_3, ethylene i oxidised to carbon dioxide and water.

$$\underset{\text{Ethylene}}{C_2H_4} + 6O \longrightarrow 2CO_2 + 2H_2O$$

(*b*) Mild oxisiding agent such as $KMnO_4$, causes a splitting of the molecule at the double bond

$$\underset{\text{Butene}}{CH_3.CH_2.CH{=}CH_2} + 4O \longrightarrow \underset{\text{Propionic acid}}{CH_3.CH_2.COOH} + \underset{\text{Formic acid}}{HCOOH}$$

(*c*) Very mild oxidising agent like alkaline $KMnO_4$ yields a glycol.



$$\underset{\text{Ethylene}}{\begin{array}{c}CH_2\\ \| \\ CH_2\end{array}} + H_2O + O \longrightarrow \underset{\text{Glycol.}}{\begin{array}{c}CH_2OH\\ | \\ CH_2OH\end{array}}$$

(2) Alcohols and aldehydes when oxidised with a mixture of potassium dichromate and sulphuric acid, ultimately yield fatty acids. The nature of oxidation products largely depends upon whether the alcohol is primary, secondary or tertiary.

$$\underset{\text{Ethyl alcohol}}{CH_3CH_2OH} + [O] \longrightarrow \underset{\text{Acetaldehyde}}{CH_3CHO} + H_2O$$

$$CH_3CHO + [O] \longrightarrow \underset{\text{Acetic acid}}{CH_3COOH}$$

Common Reducing Agents. (1) *Molecular hydrogen* with finely divided nickel or platinum as catalyst at an elevated temperature.

(2) *Sodium amalgam*; $2Na+2H_2O=2NaOH+H_2$. It is better than sodium alone as the presence of mercury moderates the evolution of hydrogen and reduction proceeds smoothly.

(3) *Sodium and alcohol*; $Na+C_2H_5OH=C_2H_5ONa+H$.

(4) *Zinc (or Tin) and hydrochloric acid*; $Zn+2HCl=ZnCl_2+2H$.

(5) *Zinc and sodium hydroxide*; $Zn+2NaOH=Na_2ZnO_2+H_2$

(6) *Zinc and water*; $Zn+H_2O=ZnO+2H$.

(7) *Zinc Copper Couple.* It can be prepared by placing granulated zinc in copper sulphate solution when it is covered with copper. By an 'electrolytic reaction' it liberates hydrogen from water. Aluminium-mercury couple is also used in place of Zn-Cu couple.

(8) *Hydrogen iodide and Phosphorus (red).* It is a very effective reducing agent.

$$2HI \rightleftharpoons 2H+I_2$$

The iodine formed is at once taken up by phosphorus and transformed into hydrogen iodide in presence of water.

$$2P+3I_2 = 2PI_3$$

$$PI_3+3H_2O = H_3PO_3+3HI$$

Common Oxidising Agents. (1) *Oxygen gas* in the presence of Vanadium pentoxide (V_2O_5) as catalyst at high temperature.

(2) *Ozone*; $O_3=O_2+O$.

(3) *Aqueous and Alkaline Potassium permanganate*;

$$2KMnO_4+H_2O = 2KOH+2MnO_2+3O.$$

(4) *Acidified Potassium permanganate*;

$$2KMnO_4+3H_2SO_4 = K_2SO_4+2MnSO_4+3H_2O+5O.$$

(5) *Acidified Potassium dichromate* ;
$K_2Cr_2O_7+4H_2SO_2 = K_2SO_4+Cr_2(SO_4)_3+4H_2O+3O.$

(6) *Conc. Nitric acid* ; $2HNO_3 = H_2O+2NO_2+O.$

(7) *Potassium chlorate* ; $2KClO_3 = 2KCl+3O_2.$

Biochemical Reactions

There are a number of reactions which are apparently carried through the agency of living organisms. These reactions are generally referred to as the **Biochemical reactions.** It was originally believed that these reactions are purely, physiological in nature and depend upon the life-process of the organisms. This view has, however, been shown to be incorrect. Now it has been proved beyond doubt that all such reactions are brought about by the catalytic activity of '*highly complex organic compounds*' which are secreted by the living organisms and not by the life-force of the organisms. These 'complex nitrogenous compounds' which may rightly be called '*organic catalysts*' are termed *enzymes* (meaning yeast), since a number of them were originally found to be present in yeast. Some examples of *enzyme catalysis* are given below :

(1) The enzyme ZYMASE obtained from yeast can cause the decomposition of glucose to give ethyl alcohol and carbon dioxide.

$$\underset{\text{Glucose}}{C_6H_{12}O_6} \longrightarrow \underset{\text{Ethyl alcohol}}{2C_2H_5OH} + 2CO_2$$

(2) The enzyme INVERTASE converts cane sugar to glucose and fructose.

$$\underset{\text{Cane sugar}}{C_{12}H_{22}O_{11}} + H_2O \longrightarrow \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

(3) The enzyme DIASTASE converts starch to maltose.

$$\underset{\text{Starch}}{2(C_6H_{10}O_5)_n} + nH_2O \longrightarrow \underset{\text{Maltose}}{nC_{12}H_{22}O_{11}}$$

(4) The enzyme LIPASE causes the hydrolysis of esters of fatty acids.

$$\underset{\text{Ester}}{RCOOC_2H_5} + H_2O \longrightarrow \underset{\text{Acid}}{RCOOH} + \underset{\text{Alcohol}}{C_2H_5OH}$$

Notes on Enzyme Catalysis. (1) Like the inorganic catalysis, enzymes act as 'contact catalysts'.

(2) Enzymes are highly specific in action. In a number of cases certain enzymes will catalyse a specific reaction and none other.

(3) The speed of reaction catalysed by a certain enzyme is proportional to the amount of the enzyme present.

(4) In certain cases the accumulation of the products of the reaction slows down the enzymatic action.

(5) The activity of an enzyme is maximum at a certain temperature (*optimum temperature*), not very much above the room temperature.

(6) While enzymes are activated by the presence of certain other enzymes (*Co-enzymes*), they are poisoned by substances like H_2S, HCN, etc.

Meaning of the term Fermentation

Yeast is a single-celled living plant. It grows rapidly under suitable conditions. If we put some yeast in dilute solution of grape sugar, after some time the whole liquid begins to froth and offers a boiling appearance. On testing it is found that the sugar has been converted to alcohol and the 'boiling' is in fact due to the brisk evolution of carbon dioxide during the reaction.

$$\underset{\substack{\text{Glucose}\\ (\textit{Grape sugar})}}{C_6H_{12}O_6} \longrightarrow \underset{\text{Alcohol}}{2C_2H_5OH} + 2CO_2$$

This process of conversion of grape sugar into alcohol induced by yeast was known to the ancients who named it **Fermentation** (*Ferver*=to boil).

Pasteur studied very carefully the fermentation of sugar and established that the change did not take place unless some living organism was present in sugar solution. He thought that the change was brought about by the physiological action of yeast cells. Buchner, however, disproved this view. He showed that if yeast is killed by grinding with sand and then squeezed, the resulting extract is capable of changing sugar into alcohol. This extract is free from any living substance but, of course, contains some 'complex compound' that was originally present in the yeast cells. Thus, he proved beyond doubt that it was not the life-force of yeast but rather the catalytic activity of the 'complex compound' present in it which caused fermentation.

Later researches showed that the process of 'fermentation' is not restricted to the conversion of sugar to alcohol. A number of other reactions have been discovered which are likewise caused by yeast or 'complex compounds' derived from other sources. In its modern form *the term 'fermentation' covers all such reactions in which an organic substance is slowly decomposed in the presence of a 'complex organic compound'*. The complex compound that acts as a catalyst for reaction is often referred to as **ferment**. To distinguish it from other fermentation reactions, the conversion of sugar into alcohol has been termed **Alcoholic Fermentation**.

QUESTIONS

1. What are the major types of organic reactions ? Define each type and illustrate by one example.

2. Describe what you understand by : (*i*) Substitution reactions, (*ii*) Addition reactions, (*iii*) Elimination reactions, and (*iv*) Rearrangement reactions. Give one example of each.

3. What do you mean by the terms : (*a*) substrate, (*b*) attacking reagent, and (c) intermediates. Apply these terms to a substitution reaction.

4. Describe homolytic and heterolytic fission of covalent bonds. How do these lead to the formation of carbonium ions and carbanions ?

5. Classify the two types of attacking reagents giving at least four examples of each type. How do they react ?

6. Give an account of tne mode of formation of carbonium ions and carbanions. What determines their relative stabilities.

7. Explain inductive effect. Why does it die down as the length of the chain increases ? What is meant by $+I$ effect and $-I$ effect ?

8. "Unlike inductive effect, the electromeric effect is not a permanent polarisation effect." Elaborate the statement.

9. Define (*i*) Inductive, and (*ii*) Electromeric effects. Give examples to illustrate these.

10. What do you understand by mechanism of an organic reaction ? Describe the various types of reaction mechanisms.

11. Give a brief account of the free radical mechanism of substitution and polymerisation reactions.

12. Discuss Polar or Ionic mechanism and illustrate by taking one example of each type of reaction.

13. What do you mean by S_E and S_N ? What are the types of S_N reactions.

14. What do you understand by (*a*) energy of activation, and (*b*) transition state complex ? How are exothermic and endothermic reactions brought about ?

15. How does classical structural theory fail to explain a number of reactions ? What were its limitations and make out a few leading principles of modern theory of organic reactions ?

16. Give the simplified definitions of Reduction and Oxidation as applied in organic chemistry. Give examples of the two types of reactions and mention the common oxidising and reducing agents.

17. What are enzymes ? How do they differ from inorganic catalysts ? Give *five* examples of enzyme catalysis.

18. Write a short note on condensation. Give electronic mechanism of aldol condensation.

19. What are fermentation reactions ? Why are they called so ? Explain briefly Alcoholic Fermentation.

20. Write an essay on : "Nucleophilic substitution in Aliphatic compounds." (*Ceylon B.Sc., 1967*)

21. Write an essay on : "Oxidation reduction processes in organic chemistry. (*Ceylon B.Sc., 1968*)

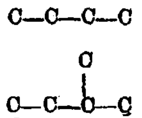
9

Classification and Systematic Nomenclature

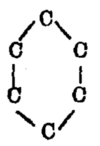
PRINCIPAL SERIES OF ORGANIC COMPOUNDS

Organic Chemistry is a vast subject. About two million organic compounds are now known. Their study would be well nigh impossible if they are not divided into 'groups' or 'series' on the basis of their properties and structure. The principal series which embrace the entire population of organic compounds so far known, have been described below :

Acyclic and cyclic series. By definition organic compounds contain one or more carbon atoms joined to each other by covalent bonds. The carbon atoms could be joined either in open chains or cyclic structures. Thus :



Open chains

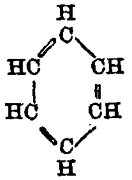


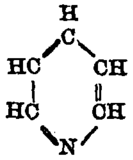
Cyclic or ring structure

The compounds whose molecules are open-chained or noncyclic, are known as **Open chain** or **Acyclic compounds**. All such compounds are said to constitute *Acyclic* or *Open-chain series*. For example, the hydrocarbons methane, ethane, propane, ethylene, acetylene, etc. having open-chains of carbon atoms in their molecules belong to this series.

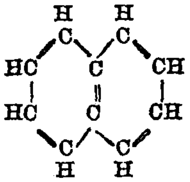
The organic compounds which contain one or more rings of atoms, are called **Cyclic** or **Ring compounds**. These form the *Cyclic series.*

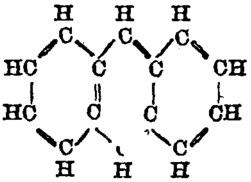
Carbocyclic and Heterocyclic series. The cyclic compounds which have rings made of only carbon atoms, are named as **Carbocyclic compounds**. The series of cyclic compounds which may also include one or more noncarbon (*hetero*, meaning different) atoms such as O, N, S are called **Heterocyclic compounds**. For example, benzene (C_6H_6)is carbocyclic while pyridine (C_5H_5N) is heterocyclic.


Benzene
(*Carbocyclic*)


Pyridine
(*Heterocyclic*)

The carbocyclic and heterocyclic compounds could be further classified as **monocyclic, bicyclic** and **tricyclic** according as they contain one, two or three rings in their molecules. Thus, while benzene and pyridine are monocyclic, naphthalene ($C_{10}H_8$) is bicyclic and anthracene ($C_{14}H_{10}$) is tricyclic.


Naphthalene
(*Bicyclic*)

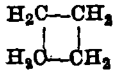

Anthracene
(*Tricyclic*)

Aliphatic and Aromatic Series. These are the most important series of organic compounds and embrace all types of compounds mentioned above.

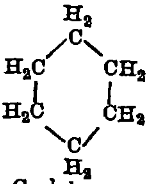
The aliphatic series includes all open-chain compounds, whether of straight or branched chains. These possess characteristic physical and chemical properties and are commonly known as **aliphatic compounds**. The term aliphatic is derived from the Greek word *aleipher* meaning fatty, since the earliest known compounds of this type were obtained from fats.

The carbocyclic compounds are again of two types : (1) *Alicyclic* ; and (2) *Aromatic.*

Such carbocyclic compounds in which the carbon atoms of the ring are joined by single covalent bonds and resemble with aliphatic compounds in properties, are called **Alicyclic compounds** For example,



Cyclobutane
(*alicyclic*)

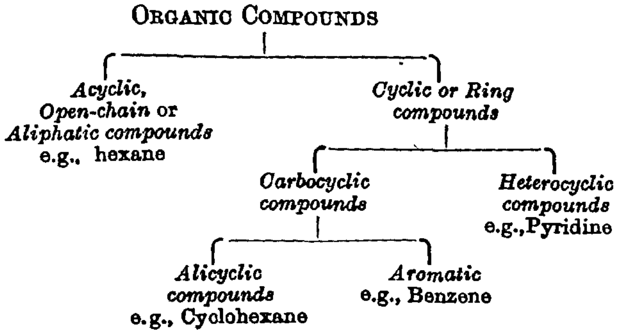


Cyclohexane
(*alicyclic*)

although having ring structure show aliphatic character. For that reason, the study of alicyclic compounds is included in the aliphatic section of the text.

The carbocyclic compounds which contain one or more benzenoid rings in their molecules possess distinctive properties from those of the aliphatic compounds. These are popularly known as **aromatic compounds** (Greek *aroma,* meaning fragrant smell) since many of these were found to have peculiar agreeable smell. Thus benzene, naphthalene, anthracene and their derivatives belong to the *Aromatic series.*

A complete genealogical table given below indicates the broad classification of organic compounds.



We will take up the study of organic compounds in two parts. First of all we will devote ourselves mainly to the discussion of aliphatic compounds. The aromatic compounds will form a subject for separate study at a later stage. We do not recommend the study of aliphatic and aromatic compounds simultaneously because this is likely to lead to overlapping of subject matter in the mind of the beginners.

DIVISION INTO CLASSES

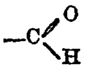
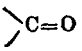
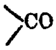
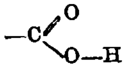
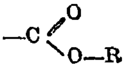
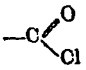
Hydrocarbons are regarded as the parent organic compounds. All other compounds are considered as derived from them by substituting one or more hydrogen atoms of hydrocarbons by more reactive atoms or groups (X).

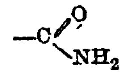
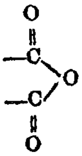
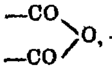
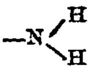
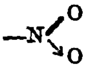
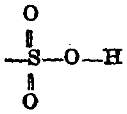
$$\underset{\text{Hydrocarbon}}{R{-}H} \xrightarrow[+X]{-H} \underset{\text{Organic compound}}{R{-}X}$$

In the molecule R—*X* which stands for any organic compound, R represents the carbon-hydrogen framework and *X* the functional group. In the aliphatic series R would be determined by the structure of the parent alkane, alkene or alkyne. In the aromatic compounds the framework of R would be based on the benzene ring.

The second part *X* of the organic compound is called the 'functional group'. A **functional group** *is an atom or a group of atoms defining the function or mode of activity of a given compound.* In other words, the functional group is that part of a compound which largely determines its properties. For example, an alcohol covers its alcoholic properties to the functional group -OH (hydroxy), an aldehyde to —CHO (formyl) and a carboxylic acid to -COOH (carboxy). The typical functional groups are shown in the following table.

Table : *Functional groups and their corresponding classes of compounds.*

STRUCTURE		NAME	CORRESPONDING CLASS
—X (—Cl, —Br, —I)		Halo	Halogen compounds
—O—H	—OH	Hydroxy	Alcohols
—O—R	—OR	Alkoxy	Ethers
	—CHO	Formyl	Aldehydes
	, —CO—	Carbonyl	Ketones
	—COOH, —CO_2H	Carboxyl	Carboxylic acids
	—COOR	Ester	Esters
	—COCl	Acid chloride	Acid chlorides

STRUCTURE		NAME	CORRESPONDING CLASS
	$—CONH_2$	Amide	Amides
	 $—CO.O.CO—$	Anhydride	Acid anhydrides
	$—NH_2$	Amino	Amines
	$—NH—$	Imino	Imines
$—C\equiv N$	$—CN$	Cyanide	Cyanides or Nitriles
	$—NO_2$	Nitro	Nitro compounds
$—N=O$	$—NO$	Nitroso	Nitroso compounds
	$—SO_2.OH$, $—SO_3H$	Sulphonic acid	Sulphonic acids

The properties of an organic compound depend on both the carbon-hydrogen framework and the functional group present. The compounds with the same functional group react in a similar manner if they have the same type of carbon-hydrogen framework. All such compounds possessing similar properties are said to form a **Class**. Thus the compounds CH_3OH, C_2H_5OH, C_4H_9OH etc. which contain the same functional group -OH and alkane carbon-hydrogen structure, constitute a class of compounds known as alcohols. It may, however, be noted that the reactivity of the functional group may be modified to some extent by the difference in the carbon-hydrogen structure.

Homologous Series. When the number of a class of compounds are arranged in order of increasing molecular weights, they form what we call a *Homologous Series.* Let us illustrate by taking the case of normal (straight-chain) alcohols which form the following homologous series.

FORMULA	NAME
CH_3OH	Methyl alcohol
CH_3CH_2OH	Ethyl alcohol
$CH_3CH_2CH_2OH$	Propyl alcohol
$CH_3CH_2CH_2CH_2OH$	Butyl alcohol, etc.

The characteristics of a homologous series are :

(1) Each member of the series differs in formula from the member above or below it by —CH_2— (methylene) group.

(2) The molecular weight of a compound in the series differs by 14 ($CH_2 = 12 + 2 \times 1 = 14$) from that of its neighbour.

(3) The series has a general formula *e.g.*, the above homologous series of alcohols can be represented by $C_nH_{2n+1}OH$ and the molecular formulas of the various members in order can be obtained by putting $n = 1, 2, 3, 4$ etc.

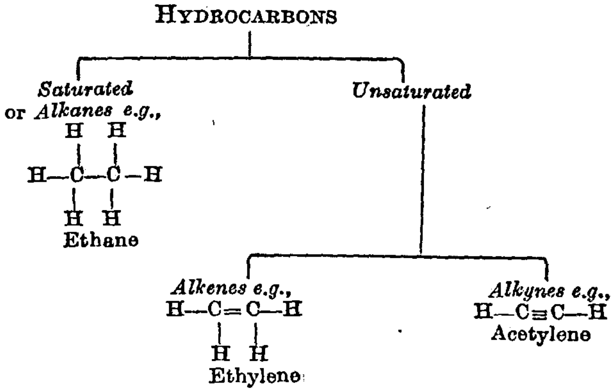
(4) The chemical properties of the members of the series are similar, though the first compound may vary considerably from others.

(5) The physical properties such as density, melting point, and boiling point of the members in a homologous series vary with increase of molecular weight by and large in a regular fashion.

The concept of functional groups and the homologous series, has led to the division of organic compounds into classes. These include hydrocarbons, halides, alcohols, ethers, aldehydes, ketones, carboxylic acids, amines, etc. This makes the study of the very large number of compounds easier as instead of the individual compounds we now study them in groups or classes.

The important classes of compounds of the aliphatic series are mentioned below :

Hydrocarbons. The compounds made of carbon and hydrogen only are called *Hydrocarbons.* These are of two types : *Saturated* and *Unsaturated.* Those hydrocarbons in which all the bonds of carbon atoms are fully utilised and thus cannot take up more hydrogen, are referred to as *Saturated hydrocarbons* or *Alkanes.* The second type of hydrocarbons are those in which all the bonds of carbon atoms are not fully satisfied and can, therefore, take up more hydrogen or other atoms. These have been called *Unsaturated hydrocarbons.* While the alkanes contain carbon atoms linked by single covalent bonds, the unsaturated hydrocarbons are characterised by the presence of double (=) and triple (≡) bonds. Those having a double bond are named as Alkenes and the ones having a triple bond Alkynes.



The type formulas of the hydrocarbons could be written as :

$RCH_2—CH_3$	Alkanes
$RCH = CH_2$	Alkenes
$RC \equiv CH$	Alkynes

The functional groups of alkenes and alkynes are $\rangle C{=}C\langle$ and $-C{\equiv}C-$ respectively.

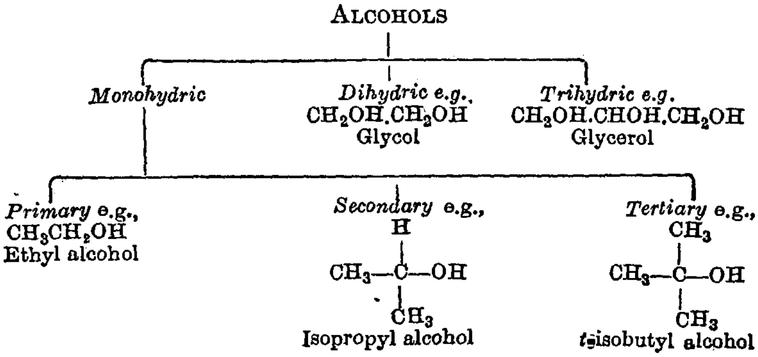
Halogen compounds. They contain the functional group X=Cl, Br, I. They are called *mono-*, *di-* or *trihalogen* compounds according to the number of halogen atoms present. For example,

CH_3Cl	CH_2Cl_2	$CHCl_3$	CCl_4
Chloromethane, Methyl chloride	Dichloromethane, Methylene chloride	Trichloromethane, Chloroform	Tetrachloromethane, Carbon tetrachloride

Methane forms similar bromo and iodo compounds.

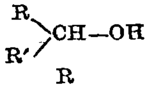
Mono-haloalkanes are called *Alkyl halides* and have the type formula *R—X* or *RX.*

Alcohols. The class of compounds containing the functional group —OH(hydroxy) are termed alcohols. They are classified as *mono-*, *di-* and *trihydric* alcohols according as they possess 1, 2 or 3 hydroxy groups. Monohydroxy alcohols are further designated as *primary*, *secondary* and *tertiary* when the —OH group is attached to a carbon atom which in turn is attached to one (or none), two or three carbon atoms respectively.



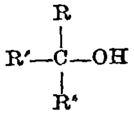
The type formulas of primary (1°), secondary (2°) and tertiary (3°) alcohols are :

$R—CH_2—OH$ Primary alcohol



$$\begin{matrix} R \\ R' \end{matrix} > CH—OH$$

Secondary alcohol



$$R'—\overset{\displaystyle R}{\underset{\displaystyle R''}{C}}—OH$$

Tertiary alcohol

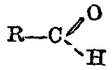
where R, R′ and R″ may be same or different.

Ethers. They have the functional group divalent oxygen atom —O— linked to two carbon atoms. The type formula of ethers is R—O—R′, where R and R′ are hydrocarbon radicals which may be same or different. Thus :

$CH_3—O—C_2H_5$ Ethyl methyl ether

$C_2H_5—O—C_2H_5$ Diethyl ether

Aldehydes. This class of compounds has the functional group —CHO which is named as *formyl* or *aldehyde group.* Aldehydes are represented by the type formula



$$R—C\begin{matrix} \nearrow O \\ \searrow H \end{matrix}$$

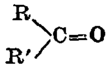
or RCHO

where R is the hydrocarbon radical. In the first member of the series we have H atom in place of R. Thus :

HCHO Formaldehyde

CH_3CHO Acetaldehyde

Ketones. They are characterised by the presence of the functional group $>$CO *i.e.*, a bivalent carbonyl group which is called a **ketonic group.** They have the type formula



$$\begin{matrix} R \\ R' \end{matrix} > C=O$$

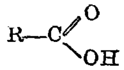
or R—CO—R′ or RCOR′

where R and R′ are hydrocarbon radicals which may be same or different. Thus :

CH_3COCH_3 Acetone

$CH_3COC_2H_5$ Ethyl methyl ketone

Carboxylic acids. They nave the functional group —COOH which is called *carboxy* or *carboxyl group.* Their type formula is represented as



$$R—C\begin{matrix} \nearrow O \\ \searrow OH \end{matrix}$$

or RCOOH or RCO_2H

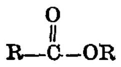
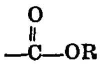
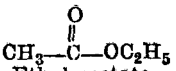
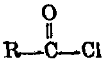
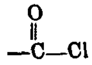
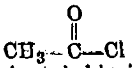
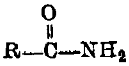
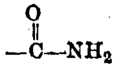
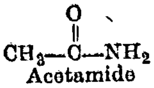
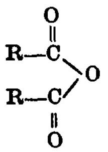
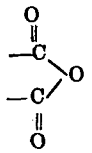
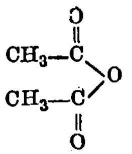
where R stands for a hydrocarbon radical. In the first member of this class R = H. Thus :

HCOOH Formic acid

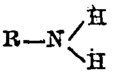
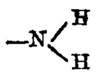
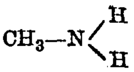
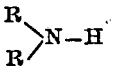
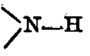
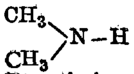
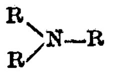
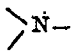
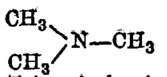
CH_3COOH Acetic acid

The compounds containing two or three —COOH groups are termed *di-* and *tri-*carboxylic acids.

Derivatives of Carboxylic acids. The more important derivatives of carboxylic acids are *esters, acyl hylides, amides* and *acid* *anhydrides.* Their type formulas, functional groups and examples are given in the table below:

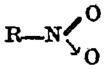
DERIVATIVE	TYPE FORMULA	FUNCTIONAL GROUP	EXAMPLE
Esters	 $R-\overset{O}{\overset{\|}{C}}-OR$	 $-\overset{O}{\overset{\|}{C}}-OR$	 $CH_3-\overset{O}{\overset{\|}{C}}-OC_2H_5$ Ethyl acetate
Acyl halides	 $R-\overset{O}{\overset{\|}{C}}-Cl$	 $-\overset{O}{\overset{\|}{C}}-Cl$	 $CH_3-\overset{O}{\overset{\|}{C}}-Cl$ Acetyl chloride
Amides	 $R-\overset{O}{\overset{\|}{C}}-NH_2$	 $-\overset{O}{\overset{\|}{C}}-NH_2$	 $CH_3-\overset{O}{\overset{\|}{C}}-NH_2$ Acetamide
Anhydrides	 $\begin{matrix} R-\overset{O}{\overset{\|}{C}} \\ R-\underset{O}{\underset{\|}{C}} \end{matrix}\rangle O$	 $\begin{matrix} -\overset{O}{\overset{\|}{C}} \\ -\underset{O}{\underset{\|}{C}} \end{matrix}\rangle O$	 $\begin{matrix} CH_3-\overset{O}{\overset{\|}{C}} \\ CH_3-\underset{O}{\underset{\|}{C}} \end{matrix}\rangle O$ Acetic anhyride

Amines. This class of compounds are structurally related to ammonia (NH_3), and are named as amines. In ammonia, the trivalent nitrogen atom is bonded to hydrogen atoms but in amines it may be bonded to one, two or three alkyl radicals, in place of H atoms. The amines are further classified into *primary*, *secondary* and *tertiary* amines according as 1, 2 or 3 alkyl groups are attached to the nitrogen atom. The type formulas, functional groups and examples of amines are listed below:

AMINE	TYPE FORMULA	FUNCTIONAL GROUP	EXAMPLE
Primary	 $R-N\langle\begin{smallmatrix} H \\ H \end{smallmatrix}$	 $-N\langle\begin{smallmatrix} H \\ H \end{smallmatrix}$ (amino)	 $CH_3-N\langle\begin{smallmatrix} H \\ H \end{smallmatrix}$ Methylamine
Secondary	 $\begin{smallmatrix} R \\ R \end{smallmatrix}\rangle N-H$	 $\rangle N-H$ (*Imino*)	 $\begin{smallmatrix} CH_3 \\ CH_3 \end{smallmatrix}\rangle N-H$ Dimethylamine
Tertiary	 $\begin{smallmatrix} R \\ R \end{smallmatrix}\rangle N-R$	 $\rangle N-$ (*Nitrile*)	 $\begin{smallmatrix} CH_3 \\ CH_3 \end{smallmatrix}\rangle N-CH_3$ Trimethylamine

The alkyl groups bonded to the nitrogen atom may be same or different.

Nitro-compounds. They contain the functional group $—NO_2$ which is called *Nitro group.* They have the type formula



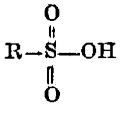
or RNO_2

where R stands for a hydrocarbon radial. For example, $C_2H_5NO_2$ is nitroethane.

Nitriles and Isonitriles. These classes are represented by the type formulas RCN and RNC respectively. The functional group —CN is called nitrile or cyanide, while the group —NC is called isonitrile or isocyanide. The compounds belonging to these classes are named as *Alkyl nitriles* (or *cyanides*) and *Alkyl isonitriles* (or *isocyanides*). Their type formulas, functional groups and examples are listed below :

CLASS NAME	TYPE FORMULA	FUNCTIONAL GROUP	EXAMPLE
Alkyl nitriles, Alkyl cyanides	$R—C\equiv N$	$—C\equiv N$	$CH_3—C\equiv N$ Methyl nitrile, Methyl cyanide
Alkyl isonitriles, Alkyl isocyanides	$R—N\underset{\rightarrow}{=}C$	$—N\underset{\rightarrow}{=}C$	$CH_3—N\underset{\rightarrow}{=}C$ Methyl isonitrile, Methyl isocyanide

Sulphonic acids. The functional group characterising this class of compounds is the *sulphonic acid group* which may be written as $—SO_2.OH$ or $—SO_3H$. The type formula for Alkane sulphonic acids is



$$R—\overset{\overset{\large O}{\|}}{\underset{\underset{\large O}{\|}}{S}}—OH \quad \text{or} \quad R—SO_2—OH \quad \text{or} \quad R—SO_3H$$

when R stands for alkyl radical. Ethanesulphonic acid $C_2H_5SO_3H$ is an example.

Thioalcohols and Thioethers. Thioalcohols and thioethers differ from alcohols and ethers in that they contain sulphur in place of oxygen. Thiols are also called *mercaptans* and thioethers or *organic sulphides.*

CLASS NAME	TYPE FORMULA	FUNCTIONAL GROUP	EXAMPLE
Thioalcohols, Mercaptans	R–S—H	—S—H	CH_3SH Methyl thioalcohol, Methyl mercaptan
Thioethers, Sulphides	R–S–R	—S—	CH_3SCH_3 Dimethyl thioether, Dimethyl sulphide

Organometallic compounds. Compounds containing one or more alkyl groups directly linked to metallic atom by covalent bonds are called *Organometallic compounds.* The best example is offered by *Alkylmagnesium halides* (Grignard reagents). Thus :

$$\underset{\text{Alkylmagnesium halide}}{R—Mg—X} \quad e.g., \quad \underset{\text{Methylmagnesium iodide}}{CH_3—Mg—I}$$

SYSTEMATIC NOMENCLATURE

In the early days of the development of Organic chemistry, any new compound that was discovered, was given a separate name. These names often depended on one or the other property or source of the substance. Thus CH_4 was named as *marsh gas* because it was produced in marshes and was also called *fire damp* since it formed explosive mixtures with air (German, *feur*=fire ; *damp*=vapour). Such names of organic compounds which remained in common use for a pretty long time, are called **Common names** or **Trivial names.** The common names were assigned at the whim of the discoverer and had no system. It was no wonder that the same substance was given different names in literature produced by different authors in different countries (CH_4=methane, fire damp, marsh gas) which naturally gave rise to confusion. To eliminate this confusion and to coordinate the knowledge of organic chemistry in all parts of the world, it became necessary to have a common system of naming organic compounds. Moreover, with the large number of organic compounds known with the passage of time (now about 2 million) it would be a mad man's job to even entertain the idea of assigning common names to each one of them. Thus chemists felt the need of evolving a comprehensive and systematic scheme of nomenclature having a structural bearing and which could cover the whole array of organic compounds known

The first rational system of naming organic compounds was given in 1892 by the International Chemical Congress at Geneva. The *Geneva Nomenclature* gave systematic names to various classes and framed set rules naming higher individual compounds. Although chemists made good headway at Geneva, the work was admittedly incomplete. This was revised and extended by the International Union of Chemistry (IUC) at Liege in 1930. The *IUC System* as it was called, was a great advance over the previous one but by no means complete and in places gave names that were ambiguous. The Union which later assumed the name International Union of Pure and Applied Chemistry (IUPAC) published its new report on organic nemenclature in 1957. This was followed by an improved version released in 1967.

The system of nomenclature accepted and used all over the world today is that approved by IUPAC which is commonly referred to as the **IUPAC System of Nomenclature.** The IUPAC rules are also under constant revision by actual usage in *Chemical Abstracts* and research papers.

In the following treatment of the IUPAC nomenclature, we will be frequently using the terms *Common Names* and *Systematic Names.*

The **Common Name** of a compound is *one which has a history behind and is accepted on account of its long usage.* Such names have no structural bearing and were assigned to compounds even before their structure was known.

The **Systematic Name** of a compound *is based on its structure.* Knowing systematic name of a given compound, you can at once write its structural formula.

According to IUPAC, *a systematic name is one which is wholly composed of coined or selected syllables.* An outline of IUPAC NOMENCLATURE for the various classes of organic compound is given below:

Alkanes. For the first four members the common names are retained. The remaining hydrocarbons of the series are named by putting a prefix indicating the number of carbon atoms, with the termination '*ane*'. Thus :

FORMULA	COMMON NAME	IUPAC NAME
CH_4	Methane	Methane
C_2H_6	Ethane	Ethane
C_3H_8	Propane	Propane
C_4H_{10}	Butane	Butane
C_5H_{12}	—	Pentane
C_6H_{14}	—	Hexane
$C_{10}H_{22}$	—	Decane

The monovalent radicals or groups formed by the loss of one hydrogen atoms from alkanes are called **Alky groups** or **Alkyl radicals**. Their IUPAC names are derived by replacing '*ane*' of the corresponding alkane by '*yl*'. Thus :

$$\textit{Alkane} - \textit{ane} + \textit{yl} \longrightarrow \textit{Alkyl}\ .$$

FORMULA	COMMON NAME	IUPAC NAME
$CH_3—$	Methyl	Methyl
$C_2H_5—$	Ethyl	Ethyl
$CH_3CH_2CH_2—$	n-Propyl	Propyl
$CH_3\overset{\vert}{C}HCH_3$	Isopropyl	Isopropyl, etc.

Alkenes. The name of a particular member of this class of hydrocarbons is obtained from the name of the corresponding alkene (containing same number of carbon atoms) by simply changing the terminal '*ane*' to '*ene*'. Thus :

Alkane -ane + ene → Alkene

FORMULA	COMMON NAME	IUPAC NAME
C_2H_4	Ethylene	Ethylene (Ethene)
C_3H_6	Propylene	Propene
C_4H_8	Butylene	Butene
C_5H_{10}	—	Pentene
C_6H_{12}	—	Hexene
C_8H_{16}	—	Octene, etc.

Alkynes. The name of an alkyne can be derived from the name of the corresponding alkane by changing the terminal '*ane*' to '*yne*'. Thus :

Alkane -ane + yne → Alkyne

FORMULA	COMMON NAME	IUPAC NAME
C_2H_2	Acetylene	Acetylene (Ethyne)
C_3H_4	—	Propyne
C_4H_6	—	Butyne
C_8H_{14}	—	Octyne

Alcohols. Alcohols have been given the class name ALKANOLS. The systematic name of an individual alcohol can be derived from the parent alkane by replacing '*e*' of the terminal '*ane*' by '*ol*'.

Alkane -e + ol → Alkanol

Thus we have,

FORMULA	COMMON NAME	IUPAC NAME
CH_3OH	Methyl alcohol	Methanol
C_2H_5OH	Ethyl alcohol	Ethanol
C_3H_7OH	Propyl alcohol	Propanol
$C_{10}H_{21}OH$	—	Decanol

The alcohols containing two -OH groups are named as '*diols* and those with three -OH groups '*triols*'

Ethers. This systematic name is ALKOXYALKANES. The name of an individual ether is derived by naming the Alkoxy group (RO) present in it and suffixing the name of the alkane containing the same number of carbon atoms as the larger radical. Thus :

FORMULA	COMMON NAME	IUPAC NAME
CH_3OCH_3	Dimethyl ether	Dimethyl ether, Methoxymethane
$CH_3OC_2H_5$	Ethyl methyl ether	Ethyl methyl ether, Methoxyethane
$C_2H_5OC_2H_5$	Diethyl ether	Diethyl ether, Ethoxyethane

Aldehydes. They have been given the class name ALKANALS. The systematic name of an individual aldehyde is obtained by replacing '*e*' of the corresponding alkane by '*al*'.

Alkane – *e* + *al* ⟶ *Alkanal*

FORMULA	COMMON NAME	IUPAC NAME
HCHO	Formaldehyde	Methanal
CH_3CHO	Acetaldehyde	Ethanal
C_2H_5CHO	Propionaldehyde	Propanal
$C_9H_{19}CHO$	–	Decanal

Ketones. The general name assigned to this class of compounds is ALKANONES. The systematic name of an individual ketone may be derived by substituting the suffix '*one*' for the final '*e*' in the name of the alkane.

Alkane – *e* + *one* ⟶ *Alkanone*

Thus we have :

FORMULA	COMMON NAME	IUPAC NAME
$CH_3.CO.CH_3$	Acetone	Propanone
$CH_3.CO.C_2H_5$	Ethyl methyl ketone	Butanone
$C_2H_5.CO.C_2H_5$	Diethyl ketone	Pentanone

Carboxylic acids. As a class carboxylic acids containing one carboxyl group have been assigned the systematic name ALKANOIC ACIDS. The name of a particular member is obtained by substituting terminal '*e*' from the name of the corresponding alkane by '*oic*' and adding the word acid at the end.

Alkane – *e* + *oic* + *acid* ⟶ *Alkanoic acid*

FORMULA	COMMON NAME	IUPAC NAME
HCOOH	Formic acid	Formic acid, Methanoic acid
CH_3COOH	Acetic acid	Acetic acid, Ethanoic acid
C_2H_5COOH	Propionic acid	Propanoic acid
C_3H_7COOH	Butyric acid	Butanoic acid
$C_9H_{19}COOH$		Decanoic acid

The dicarboxylic acids are called ALKANEDIOIC ACIDS

$HOOC.CH_2.CH_2.COOH$ Butanedioic acid

Derivatives of Carboxylic acids. The systematic name some important derivatives of acids are listed as follows.

FORMULA	COMMON NAME	IUPAC NAME
$CH_2COCC_2H_5$	Ethyl acetate	Ethyl acetate, Ethyl ethanoate
CH_3COCl	Acetyl chloride	Acetyl chloride, Ethanoyl chloride
CH_3CONH_2	Acetamide	Acetamide, Ethanamide
$\left.\begin{matrix}CH_3CO\\CH_3CO\end{matrix}\right>O$	Acetic anhydride	Acetic anhydride, Ethanoic anhydride

Amines. In the IUPAC system, primary amines are regarded as AMINOALKANES, Secondary amines as ALKYLAMINOALKANES, and tertiary amines as DIALKYLAMINOALKANES.

FORMULA	COMMON NAME	IUPAC NAME
CH_3NH_2	Methylamine	Methylamine, Aminomethane
$C_2H_5NH_2$	Ethylamine	Ethylamine, Aminoethane
$CH_3.NH.C_2H_5$	Ethylmethylamine	N-Methylethylamine, Methylaminoethane
$(CH_3)_2N.C_2H_5$	Ethyldimethylamine	N-Dimethylamino-ethane

Derivatives of Inorganic acids. Some important derivatives of inorganic acids are assigned systematic names as follows :

FORMULA	COMMON NAME	IUPAC NAME
CH_3Cl	Methyl chloride	Chloromethane
$C_2H_4Br_2$	Ethylene dibromide	Dibromoethane
$C_2H_5NO_2$	—	Nitromethane
$C_6H_{13}SO_3H$	—	Hexanesulphonic acid
C_2H_5CN	Ethyl nitrile	Ethanenitrile
C_2H_5SH	Ethyl mercaptan, Ethyl thioalcohol	Ethanethiol
$(C_2H_5)_2S$	Ethyl sulphide, Ethyl thioether	Ethylthioethane

IUPAC RULES FOR ASSIGNING NAMES TO COMPLEX MOLECULES

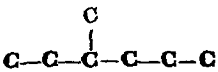
The International Union of Pure and Applied Chemistry has done a commendable job in framing set rules for assigning names to organic compounds having relatively complex structure. We will now describe how these rules can be applied for deriving systematic names for (*i*) branched-chain hydrocarbons ; and (*ii*) other classes of compounds. We will first consider the naming of hydrocarbons because the naming of the other classes of compounds is also dependent on a correct name being given to the carbon skeleton.

Naming of Branched-chain hydrocarbons. The higher branched-chain hydrocarbons are assigned systematic names according to the following procedure laid down by IUPAC.

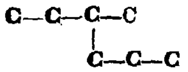
I. *Select the longest continuous carbon chain in the molecule which need not necessarily have to be horizontal (straight).* This is called the parent chain or 'main chain', while other chains attached to it are referred to as 'side-chains'.

The number of carbon atoms constituting the main chain determines the parent name of the hydrocarbon.

EXAMPLE.



(Longest chain horizontal)
I

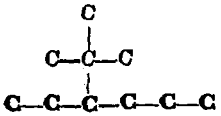


(Longest chain zig-zag)
II

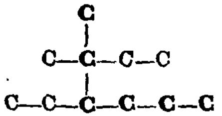
In the above carbon skeletons the longest chain is made of six carbon atoms which is horizontal in I and zig-zag in II. Therefore, the parent name of the hydrocarbon is hexane and the seventh carbon attached to it represents a substituent.

In case a molecule contains two carbon chains of the same length, the one that carries larger number of branches is designated as the parent chain.

EXAMPLE.



(one branch only)
I

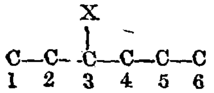


(three branches)
II

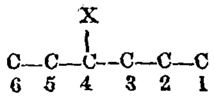
The above carbon skeleton has two chains, each made of six carbon atoms. One of these is shown in bold type in I and the other in II. The chain indicated in I has one branch only while that in II carries as many as three branches. Therefore, the chain shown in II is selected as the parent chain.

II. *Number the carbon atoms of the parent chain as 1, 2, 3, 4 etc. starting from the end that gives the smallest possible number to the carbons carrying the substituents or branches.*

EXAMPLE :



(Correct)

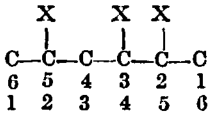


(Incorrect)

When the above carbon chain is numbered from left to right it puts the substituent on C3 (carbon No. 3) but if numbering is done from the other end the substituent is put at C4 which would, therefore, be incorrect.

The term LOCANT is now used to denote *the numeral that indicates the position of the substituent on the carbon chain.* Thus locant for X in the above structure is 3.

In case there are two or more substituents present on the parent chain, two sets of locants are obtained according as the numbering is done from the left or right. Thus for the following structure

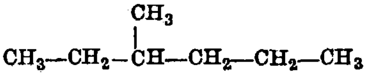


$$\begin{array}{cccccccccccc} & & \mathrm{X} & & & & \mathrm{X} & & \mathrm{X} & & \\ & & | & & & & | & & | & & \\ \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} \\ 6 & & 5 & & 4 & & 3 & & 2 & & 1 \\ 1 & & 2 & & 3 & & 4 & & 5 & & 6 \end{array}$$

I set of locants is = 2,3,5 and II set = 2,4,5. Since I set is lower, the correct numbering is from right to left.

III. *Prefix the name of the substituent to the name of the parent hydrocarbon and indicate its position on the main chain by writing before it the locant.* A hyphen (-) is inserted between the locant and the substituent name.

Thus in the following hydrocarbon,

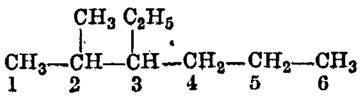


$$\begin{array}{c} \qquad\qquad\quad CH_3 \\ \qquad\qquad\quad | \\ CH_3-CH_2-CH-CH_2-CH_2-CH_3 \end{array}$$

the exact name of the substituent methyl group (CH_3-) is written as 3-methyl.

IV. *The complete name of the hydrocarbon is written as one word.* Hence the hydrocarbon mentioned in (3) above would be named as 3-methylhexane.

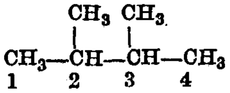
In case a number of substituents are present on the main chain, there names are prefixed to the name of the parent hydrocarbon in alphabetical order, inserting hyphen (-) in between the names of substituents. Thus the complete name of the hydrocarbon



$$\begin{array}{ccccccccccc} & & CH_3 & & C_2H_5 & & & & & & \\ & & | & & | & & & & & & \\ CH_3 & - & CH & - & CH & - & CH_2 & - & CH_2 & - & CH_3 \\ 1 & & 2 & & 3 & & 4 & & 5 & & 6 \end{array}$$

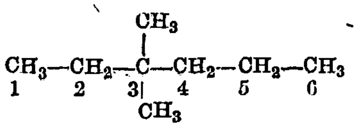
is 3-ethyl-2-methylhexane.

V. *If the same substituent is present two or more times, this is indicated by prefixing di-, tri-, tetra-, etc. to the substituent name.* The locants of individual substituents are set off from each other by commas and separated from the written name by a hyphen. Thus :



$$\underset{1}{CH_3}-\underset{2}{\overset{\overset{CH_3}{|}}{CH}}-\underset{3}{\overset{\overset{CH_3}{|}}{CH}}-\underset{4}{CH_3}$$

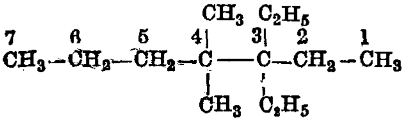
2, 3-dimethylbutane



$$\underset{1}{CH_3}-\underset{2}{CH_2}-\underset{\underset{CH_3}{3|}}{\overset{\overset{CH_3}{|}}{C}}-\underset{4}{CH_2}-\underset{5}{CH_2}-\underset{6}{CH_3}$$

3, 3-dimethylhexane

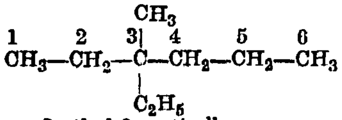
It may be noted that the names of the substituents are written in alphabetical order regardless of multiplying prefixes di-, tri-, etc. Thus ethyl comes before methyl in the name of the following compound the prefix *di* being neglected for the purpose.



$$\overset{7}{CH_3}-\overset{6}{CH_2}-\overset{5}{CH_2}-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{4|}}{C}}-\underset{\underset{C_2H_5}{|}}{\overset{\overset{C_2H_5}{3|}}{C}}-\overset{2}{CH_2}-\overset{1}{CH_3}$$

3, 3-diethyl-4, 4-dimethylheptane

If two different substituents are on the same carbon, the locant is repeated before the name of the second substituent. Thus :

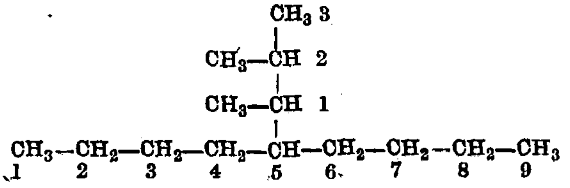


$$\overset{1}{CH_3}-\overset{2}{CH_2}-\underset{\underset{C_2H_5}{|}}{\overset{\overset{CH_3}{3|}}{C}}-\overset{4}{CH_2}-\overset{5}{CH_2}-\overset{6}{CH_3}$$

3-ethyl-3-methylhexane

VI. *In case the substituent on the parent chain is a complex one* (containing more than 4 carbon atoms) *it is named as a substituted alkyl group whose carbon chain is numbered from the carbon atom attached to the main chain.* The name of the complex substituent is given in brackets to avoid confusion with the numbers of the parent chain.

EXAMPLE.



$$\underset{1}{CH_3}-\underset{2}{CH_2}-\underset{3}{CH_2}-\underset{4}{CH_2}-\underset{5}{\overset{\overset{\overset{\overset{\overset{CH_3\ 3}{|}}{CH_3-CH\ 2}}{|}}{CH_3-CH\ 1}}{|}}{CH}}-\underset{6}{CH_2}-\underset{7}{CH_2}-\underset{8}{CH_2}-\underset{9}{CH_3}$$

The substituent at C5 is a substituted propyl group. The propyl chain is numbered 1, 2, 3 as indicated and the name of the substituent is written as 1, 2-dimethylpropyl. Hence the name of the hydrocarbon is

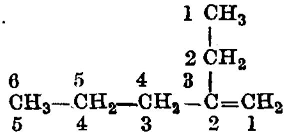
5-(1, 2-dimethylpropyl) nonane.

VII. *The position of a double (or triple) bond in alkenes (or alkynes) is indicated by prefixing the number of the carbon preceding such a bond, the carbon chain being numbered from the end which assigns lower positional number to the double (or triple) bond.* Thus :

$$\overset{1}{CH_3}-\overset{2}{CH}=\overset{3}{CH}-\overset{4}{CH_2}-\overset{5}{CH_3}$$ 2-pentene

In case the carbon chain has branches, we look for the longest carbon chain containing the double (or triple) bond and the hydrocarbon is named as a derivative of this alkene (or alkyne),

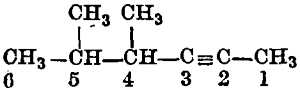
EXAMPLE 1.



$$\overset{6}{\underset{5}{CH_3}}-\overset{5}{\underset{4}{CH_2}}-\overset{4}{\underset{3}{CH_2}}-\underset{2}{\overset{\overset{\overset{1\,CH_3}{|}}{2\,CH_2}}{\overset{3}{\overset{|}{C}}}}=\underset{1}{CH_2}$$

In this structure the longest carbon-chain containing double bond has five carbon atoms and, therefore, the name of the hydrocarbon is 2-ethyl-1-pentene.

EXAMPLE 2.



$$\underset{6}{CH_3}-\underset{5}{\overset{\overset{CH_3}{|}}{CH}}-\underset{4}{\overset{\overset{CH_3}{|}}{CH}}-\underset{3}{C}\equiv\underset{2}{C}-\underset{1}{CH_3}$$

The structure has the largest chain containing triple bond made of six carbon atoms. Hence it is named as 4, 5-dimethyl-2-hexyne.

Naming of other classes of Compounds.

Having considered the IUPAC nomenclature of hydrocarbons, we proceed to the naming of other classes of compounds – alcohols, aldehydes, ketones, carboxylic acids etc. The compounds belonging to these classes are called **functional compounds** since they are characterised by the presence of one or more functional groups.

Monofunctional compounds. The compounds containing one functional group are referred to as *monofunctional.* These are named as derivatives of the parent hydrocarbons by the following rules :

I. *Select the longest carbon chain bearing the functional group. This is the parent chain and is numbered from the end that gives lower positional number to the functional group.*

II. *Write the name of the parent hydrocarbon and prefix the substituent names, if any, according to* IUPAC *rules described before regardless of the presence of the functional group.*

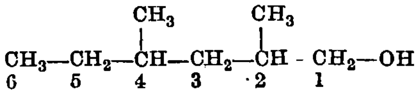
III. *Drop the terminal '-e' of the hydrocarbon name and add the suffix assigned to the functional group present. (See Table on page 197).*

IV. *Insert the positional number of the functional group (separated by hyphens on either side) before the name of the parent hydrocarbon if there is no ambiguity otherwise immediately before the functional syllable.*

V. *Halo and nitrocompounds are always named as substituted hydrocarbons.*

Let us now illustrate the above rules :

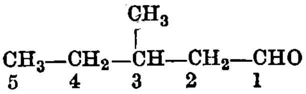
EXAMPLE 1.



$$\underset{6}{CH_3}-\underset{5}{CH_2}-\underset{4}{\overset{\overset{CH_3}{|}}{CH}}-\underset{3}{CH_2}-\underset{2}{\overset{\overset{CH_3}{|}}{CH}}-\underset{1}{CH_2}-OH$$

The longest carbon chain bearing the functional group -OH has six carbon atoms and its name will be based on the parent hydrocarbon hexane. Since it has two methyl groups on C2 and C4, the substituted parent hydrocarbon will be named as 2, 4-dimethylhexane. The compound is an alcohol and, therefore, the terminal '-*e*' is replaced by the syllable *ol*. This gives the name 2, 4-dimethylhexanol. Now insert the positional number '1' before the name of the parent hydrocarbon to get the IUPAC name of the compound 2, 4-dimethyl-1-hexanol.

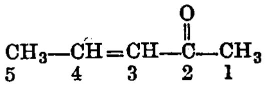
EXAMPLE 2.



$$\underset{5}{CH_3}-\underset{4}{CH_2}-\underset{3}{\overset{\overset{CH_3}{|}}{CH}}-\underset{2}{CH_2}-\underset{1}{CHO}$$

The longest carbon chain contains five carbon atoms and hence the parent hydrocarbon is pentane. The substituted hydrocarbon would be 3-methylpentane. The name of the aldehyde obtained by replacing -*e* of this hydrocarbon name by *al* (the syllable for the functional group aldehyde) is 3-methylpentanal. Therefore, putting the positional number '1' of aldehyde group before the parent hydrocarbon we have the IUPAC name of the compound 3-methyl-1-pentanal.

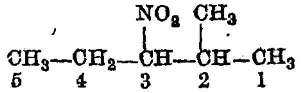
EXAMPLE 3.



$$\underset{5}{CH_3}-\underset{4}{CH}=\underset{3}{CH}-\underset{2}{\overset{\overset{O}{\|}}{C}}-\underset{1}{CH_3}$$

Here the carbon chain having the functional group >(C)=O has five carbon atoms and a double bond. Therefore, the name of the parent hydrocarbon is 3-pentene. The above compound is a ketone and hence the terminal -*e* of the hydrocarbon name is replaced by -*one*. This assigns to the compound the name 3-pentenone. In this case the positional number of the functional group cannot be placed before the parent hydrocarbon name and hence it is inserted before the functional syllable -*one*. Thus the IUPAC name of the compound is 3-penten-2-one.

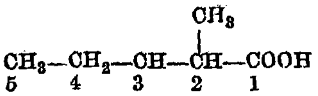
EXAMPLE 4.



$$\underset{5}{CH_3}-\underset{4}{CH_2}-\underset{3}{\overset{NO_2}{\overset{|}{C}}H}-\underset{2}{\overset{CH_3}{\overset{|}{C}}H}-\underset{1}{CH_3}$$

As already pointed out, nitro group is always to be treated as a substituent. The above compound will have the systematic name 2-methyl-3-nitropentane.

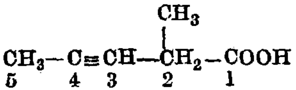
EXAMPLE 5.



$$\underset{5}{CH_3}-\underset{4}{CH_2}-\underset{3}{CH}-\underset{2}{\overset{CH_3}{\overset{|}{C}}H}-\underset{1}{COOH}$$

2-methyl-1-butanoic acid

EXAMPLE 6.



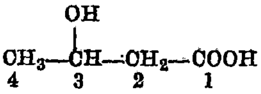
$$\underset{5}{CH_3}-\underset{4}{C}\equiv\underset{3}{CH}-\underset{2}{\overset{CH_3}{\overset{|}{C}}H_2}-\underset{1}{COOH}$$

2-methyl-3-hexyn-1-oic acid

Polyfunctional Compounds. The organic compounds which contain two or more different functional groups in the same molecule, are called *Polyfunctional compounds.* The 1965 IUPAC rules have introduced the concept of the 'Principal group' for assigning systematic names to such compounds.

When there are many functional groups present in a molecule, only one suffix can be used to form a systematic name. The group named as suffix is termed the **Principal group** (or class group) and is determined by its position in the 'seniority table' given on page 197. All other functional groups must be considered substituents. For example, if a compound contains both —COOH and —OH groups, the —COOH group ranks higher in the seniority table and is designated as the principal group while —OH group is to be regarded as a substituent.

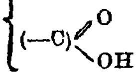
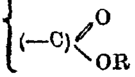
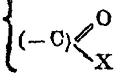
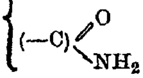
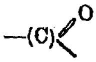
EXAMPLE 1.



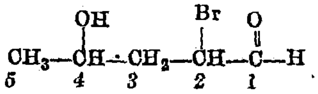
$$\underset{4}{CH_3}-\underset{3}{\overset{OH}{\overset{|}{C}}H}-\underset{2}{CH_2}-\underset{1}{COOH}$$

The longest carbon chain containing the principal group is the parent chain and is numbered so as to assign lowest position to this group. Here the principal function is —COOH and since the parent hydrocarbon would be butane, the above compound must be named 3-hydroxy-1-butanoic acid.

Seniority Table for Principal Groups

GROUP	SUFFIX NAME	PREFIX NAME
$-COOH$	carboxylic acid	carboxy
 $(-C){<}^{O}_{OH}$	oic acid	
$-COOR$	alkyl —carboxylate	alkoxycarbonyl
 $(-C){<}^{O}_{OR}$	alkyl —oate	
$-SO_3H$	sulphonic acid	sulpho
$-CO.X$	carbonyl halide	halocarbonyl
 $(-C){<}^{O}_{X}$	oyl halide	
$-CONH_2$	carboxamide	carbamoyl
 $(-C){<}^{O}_{NH_2}$	amide	
$-CHO$	aldehyde	formyl
 $-(C){<}^{O}$	al, one	oxo
$-CN$	carbonitrile	cyano
$-OH$	ol	hydroxy
$-SH$	thiol	mercapto
$-O-$	—	epoxy
$-NH_2$	amine	amino
$-X$ (halogen)	—	halo
$-NO_2$	—	nitro
$(C){=}(C)$	ene	
$(C){\equiv}(C)$	yne	

EXAMPLE 2.

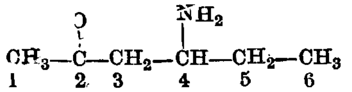


$$\overset{5}{CH_3}-\underset{4}{\overset{OH}{CH}}-\underset{3}{CH_2}-\underset{2}{\overset{Br}{CH}}-\underset{1}{\overset{O}{\overset{\|}{C}}}-H$$

In this structure —CHO, —OH and —Br are the functional groups present. Since —CHO group ranks highest in the seniority table, it is the principal group and the compound is named as aldehyde by using the suffix '*al*'. The other functions —OH and —Br are to be regarded as substituents. Therefore the IUPAC name of the above compound is

2-bromo-4-hydroxy-1-pentanal

EXAMPLE 3.

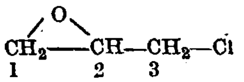


$$\underset{1}{CH_3}-\underset{2}{\overset{\overset{\textstyle O}{\|}}{C}}-\underset{3}{CH_2}-\underset{4}{\overset{\overset{\textstyle NH_2}{|}}{CH}}-\underset{5}{CH_2}-\underset{6}{CH_3}$$

Here the ketonic group $-(C)<^{O}$ is senior to amino group —NH_2. Therefore, the compound is to be named as a substituted ketone. The systematic name of the above structure is

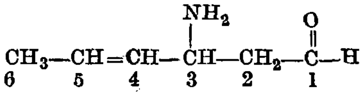
4-amino-2-hexanone

EXAMPLE 4.



Since the epoxy group (C)—O—(C) and chlorine both are always to be regarded as substituents, the above structure will be named as a substituted alkane. The epoxy group being senior, numbering of the carbon is done as indicated above and the systematic name assigned to the compound is 1, 2-epoxy-3-chloropropane.

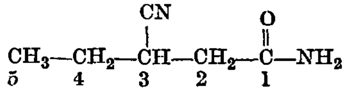
EXAMPLE 5.



$$\underset{6}{CH_3}-\underset{5}{CH}=\underset{4}{CH}-\underset{3}{\overset{\overset{\textstyle NH_2}{|}}{CH}}-\underset{2}{CH_2}-\underset{1}{\overset{\overset{\textstyle O}{\|}}{C}}-H$$

3-amino-4-penten-1-al

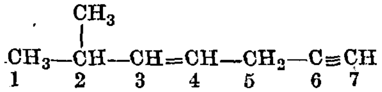
EXAMPLE 6.



$$\underset{5}{CH_3}-\underset{4}{CH_2}-\underset{3}{\overset{\overset{\textstyle CN}{|}}{CH}}-\underset{2}{CH_2}-\underset{1}{\overset{\overset{\textstyle O}{\|}}{C}}-NH_2$$

3-cyano-1-pentanoic amide

EXAMPLE 7.



$$\underset{1}{CH_3}-\underset{2}{\overset{\overset{\textstyle CH_3}{|}}{CH}}-\underset{3}{CH}=\underset{4}{CH}-\underset{5}{CH_2}-\underset{6}{C}\equiv\underset{7}{CH}$$

When a molecule contains both the functions — a double bond and triple bond, the numbering of the carbon chain is done so as to assign lower positional number to the double bond and the hydrocarbon is named as substituted alkene. Since the functions -ene (=) and -yne (≡) are always to be named as suffixes, the systematic name of the above structure is

2-methylheptene-6-yne

QUESTIONS

1. What are the principal series of organic compounds ? Give one example of each series.

2. Define the following terms : (*i*) Aliphatic compounds ; (*ii*) Aromatic compounds ; (*iii*) Carbocyclic compounds (*iv*) Heterocyclic compounds ; and (*v*) Alicyclic compounds.

3. Give a genealogical table listing the various broad classes of compounds giving an example in each case.

4. Give a concise definition of *functional group.* Write the structure and name of ten important functional groups.

5. Define a *'class'* with reference to organic compounds. Write the functional groups characterising the following classes of compounds : alcohols, aldehydes, ketones, ethers and carboxylic acids.

6. What do you understand by the term *homologous series* ? What are the main features of such a series ? Illustrate your answer by taking example of alkanes, alcohols or carboxylic acids.

7. Discuss the classification of aliphatic hydrocarbons into saturated and unsaturated hydrocarbons. Give the 'class name' and 'type formula' of each class.

8. List the various classes of organic compounds as also their functional groups. Name the first two members of each class.

9. Write a concise account of the *Systematic Nomenclature* of aliphatic organic compounds. In what respects a systematic name is superior to a common name.

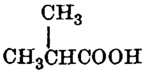
10. What do you understand by IUPAC System of Nomenclature ? Give the IUPAC names of the various classes of compounds.

11. Give the structure, and IUPAC name of the alkyl groups bearing the following common names :

$CH_3—$ $C_2H_5—$ $CH_3CH_2CH_2—$ $CH_3\overset{|}{C}HCH_3$

12. Give the common and IUPAC names of the following compounds :

$CH_3CH_2CH_2OH$



$CH_3\overset{\overset{CH_3}{|}}{C}HCOOH$

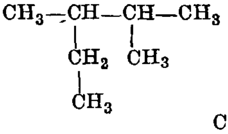
$C_2H_5CONH_2$

$C_2H_5OC_2H_5$ C_2H_5SH CH_3COCH_3

13. State the rules given by IUPAC to name complex hydrocarbons.

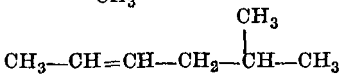
14. Assign names to the following structures :

(*i*)



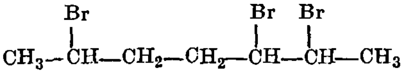
$CH_3-\underset{\underset{CH_3}{\underset{|}{CH_2}}}{\underset{|}{C}H}-\underset{\underset{CH_3}{|}}{C}H-CH_3$

(*ii*)



$CH_3—CH=CH—CH_2—\overset{\overset{CH_3}{|}}{C}H—CH_3$

(*iii*)



$CH_3-\overset{\overset{Br}{|}}{C}H—CH_2—CH_2—\overset{\overset{Br}{|}}{C}H—\overset{\overset{Br}{|}}{C}H—CH_3$

15. Give the graphic formulas for the isomers having the molecular formula $C_5H_{10}Br_2$.

16. What do you understand by the Principal group ? When the following functional groups are present in a molecule what will be its class name :

(i) $—OH, —COOH, —NO_2$;

(ii) $—Br, —CH_3, —CHO$;

(iii) $—NO_2, —NH_2, —CONH_2$.

17. Define the term 'locant' ? What are the locants of the following substituents :

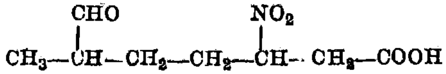
3-methyl, 4-amino 2, 3-dimethyl

18. Describe how the concept of Principal group introduced recently has been used to name complex polyfunctional compounds.

19. Write condensed line formulas of the following compounds :

(a) 2, 2, 3-trimethylhexane.
(b) 4-methyl-3-pentyne.
(c) 3-chloro-2-methylpropene.
(d) 1-bromo-3-pentanone.
(e) 3, 4-dimethylpentanal.

20. Name the following compounds :

(i) $(CH_3)_2CH—CH(C_2H_5)—CH_2—CH_2—CH_2—CH_3$
(ii) $CH_3\ CH_2—CH_2—CH(CH_2Cl)—CH_2—CHOH—CH_3$
(iii)


$$CH_3—\overset{\overset{\displaystyle CHO}{|}}{C}H—CH_2—CH_2—\overset{\overset{\displaystyle NO_2}{|}}{C}H—CH_2—COOH$$

(iv) $CH_3—CH_2—CH_2—O—CH_2—CH_3$.

21. Write names of the following structures :

(i) $CH_3CHICHNO_2CH_3$
(ii) $CH_3COCH_2CH_2CHO$
(iii) $CH_3CH=CHCOOCH_3$
(iv) $CH_3CHBr\ CH_2COCl$.

22. Give the graphic formulae of the compounds :

(a) Isopropyl alcohol ;
(b) 4-ethyl-6-methylhexane ;
(c) 2, 2, 4-trimethylpentane ;
(d) trimethylcarbinol ; and
(e) 3-ethyl-2, 2-dimethylheptane. (*Saugar B.Sc., 1965*)

23. Write down the structural formulae of the following compounds :

(a) 2-methylpentane ;
(b) tetramethylmethane ;
(c) 3, 5-dimethylhexan-2-ol ;
(d) pentane-2-one. (*Rangoon B.Sc., 1963*)

Aliphatic Compounds

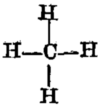
10

Alkanes

Friedrich Bergius
(1884— .)

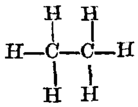
German Industrial Chemist. He is known for inventing the Bergius Process for synthetic petroleum. He has made sugar from wood. He won the Nobel Prize in 1931 for his contributions in high pressure synthesis.

Alkanes are the simplest organic compounds made of carbon and hydrogen only. The first member *methane* (CH_4) has the structural formula



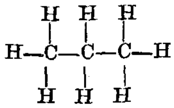
$$\begin{array}{c} H \\ | \\ H-C-H \\ | \\ H \end{array}$$

and its molecule is built of one carbon atom joined to four hydrogen atoms by covalent bonds. Other hydrocarbons of this series : ethane, propane, butane etc., contain two or more carbon atoms linked in chains by single covalent bonds, the rest of their valencies being satisfied by union with hydrogen atoms. Thus :



$$\begin{array}{ccccc} & H & & H & \\ & | & & | & \\ H- & C & - & C & -H \\ & | & & | & \\ & H & & H & \end{array}$$

Ethane



$$\begin{array}{ccccccc} & H & & H & & H & \\ & | & & | & & | & \\ H- & C & - & C & - & C & -H \\ & | & & | & & | & \\ & H & & H & & H & \end{array}$$

Propane

Since all the four valencies of the carbon atoms in these compounds are fully satisfied, they can take up no more hydrogen or any other atoms. Thus being 'fully saturated' in respect of chemical combination, these hydrocarbons are classed as **Saturated hydrocarbons**.

The saturated hydrocarbons are relatively stable to most chemical reagents. They react with nitric acid and sulphuric acid only under drastic conditions, while they are not attacked at all by oxidising agents such as potassium permanganate and chromic acid. On account of their feeble chemical activity they are also called **Paraffins** (Latin, *parum affinis*=little affinity).

The IUPAC name for the paraffin hydrocarbons is **Alkanes**.

The relative chemical inactivity of alkanes can be accounted for by the modern orbital theory of molecular structure. In the molecules of these hydrocarbons, all the carbon atoms are joined to four other atoms. According to Quantum mechanics when a carbon atom is linked to four other atoms, it is in sp^3 state of hybridisation with its bonding orbitals pointed towards the four corners of a regular tetrahedron. Each of these orbitals overlap the s orbital of hydrogen in methane forming the strongest σ bonds. In ethane and higher alkanes, the four hybridised orbitals of a carbon atom may overlap with the s orbital of hydrogen or sp^3 orbital of another carbon to form σ bonds. Since the σ bonds are remarkably strong, the alkanes are chemically inactive. The shapes of alkane molecules and their geometry will be discussed at appropriate places in the text.

NOMENCLATURE

Alkanes form a homologous series having the general formula C_nH_{2n+2} and their type formula is RH. The molecular formulae of the various members can be obtainod by putting $n = 1, 2, 3, 4,$ etc. in the general formula. There are three systems of naming these hydrocarbons.

(1) The COMMON SYSTEM. The first four members of the series are called by their trivial or common names : Methane, Ethane, Propane and Butane. From the fifth onwards, alkanes are named by prefixing the Greek numerals *pent* (5), *hex* (6), *hept* (7), *oct* (8) etc. indicating the number of carbon atoms in the molecule, to the terminal *-ane*. Thus the name of an individual alkane is a one-word name. The names of first twelve alkanes are given below.

CH_4	Methane	C_7H_{16}	Heptane
C_2H_6	Ethane	C_8H_{18}	Octane
C_3H_8	Propane	C_9H_{20}	Nonane
C_4H_{10}	Butane	$C_{10}H_{22}$	Decane
C_5H_{12}	Pentane	$C_{11}H_{24}$	Undecane
C_6H_{14}	Hexane	$C_{12}H_{25}$	Dodecane

There is one methane, one ethane and one propane known. Further alkanes containing four or more carbon atoms exist in two or more isomeric forms depending on the structure of the carbon skeleton. The alkanes having a straight or normal chain are called **normal** (or 'n-') **hydrocarbons**. This is indicated by prefixing n- to the name of the alkane. Thus :

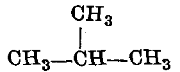
$CH_3CH_2CH_2CH_3$ — $C-C-C-C$

n-Butane — (Normal chain)

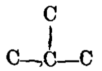
$CH_3CH_2CH_2CH_2CH_3$ — $C-C-C-C-C$

n-Pentane — *(Normal chain)*

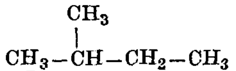
The alkanes in which the carbon chain has branches are called **branched chain hydrocarbons**. Such alkanes as possess a one-carbon branch on the second carbon of the normal or basic chain, are referred to as **Iso hydrocarbons** (Greek, *isos*=equal). Thus :


$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{C}H-CH_3$$

Isobutane


$$C-\overset{\overset{\displaystyle C}{|}}{C}-C$$

Isobutane skeleton

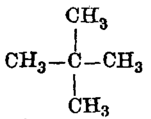

$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{C}H-CH_2-CH_3$$

Isopentane

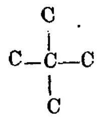

$$C-\overset{\overset{\displaystyle C}{|}}{C}-C-C$$

Isopentane skeleton

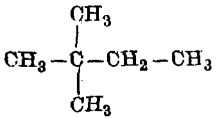
From pentane (C5) onwards, when the normal carbon chain present in the molecule has two one-carbon branches on the second carbon from the end, the alkane is referred to as **Neo hydrocarbon** (Greek, *neos*=new). Thus :


$$CH_3-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-CH_3$$

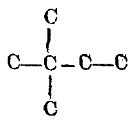
Neopentane


$$C-\underset{\underset{\displaystyle C}{|}}{\overset{\overset{\displaystyle C}{|}}{C}}-C$$

Neopentane skeleton

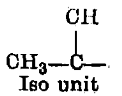

$$CH_3-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-CH_2-CH_3$$

Neohexane


$$C-\underset{\underset{\displaystyle C}{|}}{\overset{\overset{\displaystyle C}{|}}{C}}-C-C$$

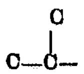
Neohexane skeleton

From an examination of the above structures you will note that branched chain alkanes in general are characterised by the following structural units.



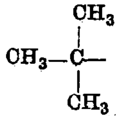
$CH_3-\overset{\displaystyle CH}{C}-$

Iso unit



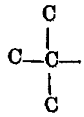
$C-\overset{\displaystyle C}{C}-$

Iso skeleton



$CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{C}}-$

Neo unit



$C-\underset{\displaystyle C}{\overset{\displaystyle C}{C}}-$

Neo skeleton

In modern practice, the symbols n-, iso- and neo- are not to be written in italics as was done earlier.

Types of Carbons atoms in Alkanes.

The structural formulas of alkanes and their derivatives contain four types of carbon atoms.

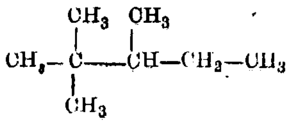
(1) **Primary (1°) carbon** atom which is bonded to one (or no other carbon atom.

(2) **Secondary (2°) carbon** atom which is bonded to two other carbon atoms.

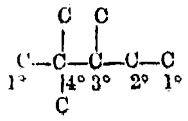
(3) **Tertiary (3°) carbon** atom which is bonded to three other carbon atoms.

(4) **Quaternary (4°) carbon** atom which is bonded to four carbon atoms.

Thus in the following structure beginning from the left, the first carbon is primary (1°), the second quaternary (4°), the third tertiary (3°), the fourth secondary (2°) and the fifth one again primary (1°).



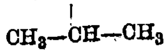
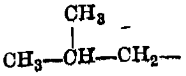
$CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{C}}-\overset{\displaystyle CH_3}{CH}-CH_2-CH_3$



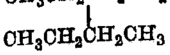
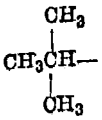
$\underset{1^\circ}{C}-\underset{\underset{\displaystyle C}{4^\circ}}{\overset{\displaystyle C}{C}}-\underset{3^\circ}{\overset{\displaystyle C}{C}}-\underset{2^\circ}{C}-\underset{1^\circ}{C}$

Naming of Alkyl radicals

A group of atoms that has an unused valency (represented by dash) is called a *radical*. The radicals derived from alkanes (R—H) by removal of one H atom are called **Alkyl radicals** (R –). The names of the alkyl radicals corresponding to normal and isoalkanes are obtained by simply changing the suffix *-ane* to *-yl*. In case of normal alkanes the hydrogen atom is removed from the end of the carbon chain while in isoalkanes it comes from the end opposite to the branched or 'iso' end. Thus :

STRUCTURE	NAME	ABBREVIATION
CH_3-	Methyl	Me
CH_3CH_2-	Ethyl	Et
$CH_3CH_2CH_2-$	n-Propyl	Pr^n
 $CH_3-\overset{\mid}{C}H-CH_3$	Isopropyl	Pr^i
$CH_3CH_2CH_2CH_2-$	n-Butyl	B^n
 $CH_3-\overset{\overset{CH_3}{\mid}}{C}H-CH_2-$	Isobutyl	B^i

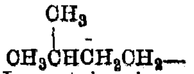
In more complex cases, the name of the alkyl radical depends on whether the hydrogen is removed from a primary, secondary or a tertiary carbon atom of the hydrocarbon structure. Thus :

$CH_3CH_2CH_2CH_2-$	n-Butyl	B^n
 $CH_3CH_2\overset{\mid}{C}H_2CH_3$	sec-Butyl, s-Butyl	B^s
 $CH_3\overset{\overset{CH_3}{\mid}}{\underset{\underset{CH_3}{\mid}}{C}}H-$	tert-Butyl t-Butyl	B^t

Proceeding similarly, pentane (C_5H_{12}) forms the following radicals.

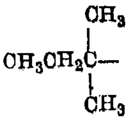
$CH_3CH_2CH_2CH_2CH_2-$

n-Pentyl or n-amyl



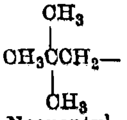
$CH_3\overset{\overset{CH_3}{\mid}}{C}HCH_2CH_2-$

Isopentyl or isoamyl



$CH_3CH_2\overset{\overset{CH_3}{\mid}}{\underset{\underset{CH_3}{\mid}}{C}}-$

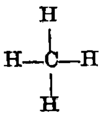
tert-Amyl or *t*-amyl



$CH_3\overset{\overset{CH_3}{\mid}}{\underset{\underset{CH_3}{\mid}}{C}}CH_2-$

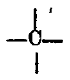
Neopentyl

(2) The SUBSTITUTED METHANE SYSTEM. This mode of naming complex branched chain alkanes is some time used when common names cannot be assigned conveniently This system names alkanes as if derived from methane (CH_4) by substitution of alkyl radicals for hydrogen atoms.



$$H-\overset{\overset{H}{\mid}}{\underset{\underset{H}{\mid}}{C}}-H$$

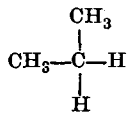
Methane



$$-\overset{\mid}{\underset{\mid}{C}}-$$

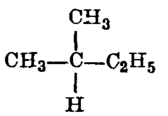
Methane carbon

To assign name to an individual alkane, the alkyl radicals are named in alphabetical order (ignoring prefixes di, tri etc.) and the word methane is added so as to get a continuous one-word name. For illustration,



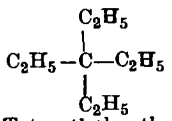
$CH_3-CH(CH_3)-H$

Dimethylmethane



$CH_3-CH(CH_3)-C_2H_5$

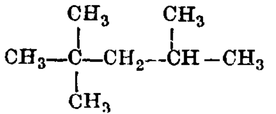
Ethyldimethylmethane



$C_2H_5-C(C_2H_5)_2-C_2H_5$

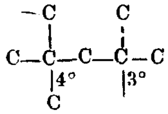
Tetraethylmethane

While naming complex alkanes the most highly branched carbon is designated as the methane carbon, the order of preference being 4°, 3°, 2°. Thus in the following structure the carbon atoms second and fourth from the left of the chain are 4° and 3° respectively. Therefore, the second carbon is regarded as the methane carbon.



$CH_3-C(CH_3)_2-CH_2-CH(CH_3)-CH_3$

Trimethylisobutylmethane



$C-C(C)(C)-C-C(C)-C$ (4°, 3°)

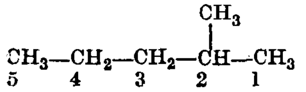
(3) The IUPAC SYSTEM retains the common names for the first ten (C_1 to C_{10}) alkanes as also for the simple alkyl radicals described earlier. This modern system of nomenclature is indispensable for naming branched chain alkanes. We have already discussed how a complex hydrocarbon can be assigned IUPAC name. The rules used for the purpose will be mentioned again by way of recapitulation.

(*i*) The longest carbon chain present in the molecule is selected and the complex hydrocarbon is regarded as alkyl derivative of the parent alkane containing this chain.

(*ii*) The positions of the substituents (alkyl radicals) attached to the parent chain are determined by numbering this chain from the end which puts them on carbons having the lowest numbers.

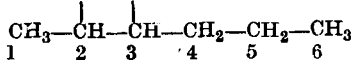
(*iii*) To write the IUPAC name of the complex hydrocarbon the names of the substituents with position numbers indicated in front of them and arranged in alphabetical order, are prefixed to the name of the parent alkane. The substituent names are hyphened on either side except the last one which is merged with the name of the alkane.

(*iv*) If the same substituent appears on the parent chain more than once, the positional numbers are set off by commas and the prefixes *di, tri, tetra* etc. are used to indicate the number of times it appears. Thus



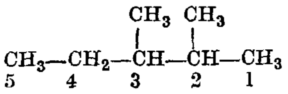
$\underset{5}{CH_3}-\underset{4}{CH_2}-\underset{3}{CH_2}-\underset{2}{CH}(CH_3)-\underset{1}{CH_3}$

2-Methylpentane



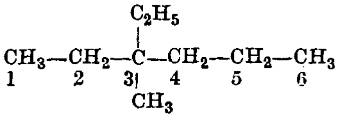
$\underset{1}{CH_3}-\underset{2}{CH}(CH_3)-\underset{3}{CH}(C_2H_5)-\underset{4}{CH_2}-\underset{5}{CH_2}-\underset{6}{CH_3}$

3-Ethyl-2-methylhexane



$$\underset{5}{CH_3}-\underset{4}{CH_2}-\underset{3}{\overset{\overset{CH_3}{|}}{CH}}-\underset{2}{\overset{\overset{CH_3}{|}}{CH}}-\underset{1}{CH_3}$$

2, 3-dimethylpentane



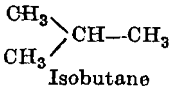
$$\underset{1}{CH_3}-\underset{2}{CH_2}-\underset{\underset{CH_3}{|}}{\overset{\overset{C_2H_5}{|}}{\underset{3}{C}}}-\underset{4}{CH_2}-\underset{5}{CH_2}-\underset{6}{CH_3}$$

3-Ethyl-3-methylhexane

ISOMERISM IN ALKANES

The alkanes offer for study an excellent example of *Chain Isomerism.* The first three hydrocarbons of the series *viz.*, methane, ethane and propane do not exhibit isomerism. The next hydrocarbon butane (C_4H_{10}) exists in two isomeric forms :

$CH_3—CH_2—CH_2—CH_3$ and
Butane



$$\begin{matrix} CH_3\diagdown \\ \quad CH—CH_3 \\ CH_3\diagup \end{matrix}$$

Isobutane

All higher hydrocarbons show chain isomerism and the number of isomers goes on increasing rapidly with the increase in the number of carbon atoms. Thus :

	C_4H_{10}	C_5H_{12}	C_6H_{14}	C_7H_{16}	C_8H_{18}
No. of Isomers	2	3	5	9	18

Prediction of Isomers according to theory. Since isomerism in hydrocarbons depends on the different structures of the carbon chains, the number of isomeric forms of a particular hydrocarbon can be worked out by building up the possible carbon chains of that hydrocarbon. Starting from the first hydrocarbon methane which contains only one carbon atom, the chain of ethane can be constructed in a simple way by adding to it another carbon atom.

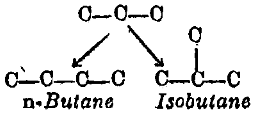
$$\underset{\textit{Methane}}{C} \longrightarrow \underset{\textit{Ethane}}{C—C}$$

Similarly, the carbon chain of propane can be obtained by adding a new carbon atom to the chain of ethane.

$$\underset{\textit{Ethane}}{C—C} \longrightarrow \underset{\textit{Propane}}{C—C—C}$$

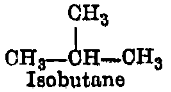
So far it is all simple, as the addition of the new carbon atom to the previous chain can be done only in one way and the resulting carbon chain has only one structure. Hence, methane, ethane, and propane are incapable of exhibiting isomerism. However, carbon chains of higher hydrocarbons built in this way can have two or more different structures and, therefore, show chain isomerism.

Isomeric Butanes, C_4H_{10}. The C-chain of butane can be obtained from that of propane by the addition of a new C-atom to it. Since the C-chain of propane contains two types of C-atoms (the middle C-atom being different from the side ones), this can be done in two ways :



Thus theory predicts the existence of two butanes. Their structural formulae can be written by applying the necessary hydrogen atoms to the C-atoms in the above chains.

$CH_3.CH_2.CH_2.CH_3$
n-Butane



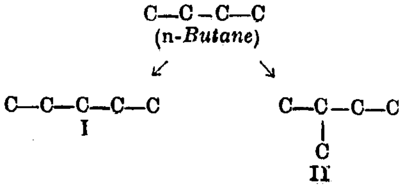
$CH_3—\overset{CH_3}{\overset{|}{C}}H—CH_3$

Isobutane

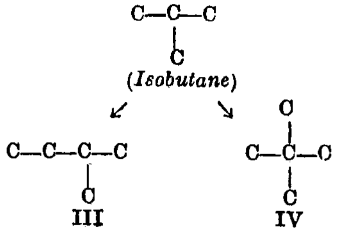
Both these hydrocarbons are actually known. Their boiling points are 1° and —10·2° respectively.

Isomeric Pentanes, C_5H_{12}. Carbon chains of pentanes can be built up from those of butanes by the addition of another C-atom.

The C-chain of n-butane has two types of C-atoms, those in the middle being different from those at the ends. Thus it will give rise to two chains of five carbon atoms.



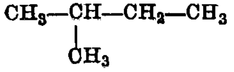
Isobutane has again two types of C-atoms, the central atom being different from the remaining three. Therefore, it can also give rise to two chains of five C-atoms.



Of the four possible chains derived for pentane, II and III are identical. Hence according to theory there should exist three isomeric pentanes. Supplying the necessary hydrogen atoms to C-chains I, II and IV, the full formulae of the three pentanes may be written. All these hydrocarbons are actually known. They are :

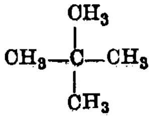
(*i*) $CH_3.CH_2.CH_2.CH_2.CH_3$ n-Pentane

(*ii*)



$CH_3—\underset{CH_3}{\underset{|}{C}}H—CH_2—CH_3$ Isopentane or 2-Methylbutane

(*iii*)



$CH_3—\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}—CH_3$ Neo-pentane or 2·Dimethylpropane

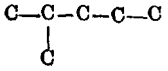
Isomeric Hexanes, C_6H_{14}. Carbon chains of hexanes can be obtained by adding a carbon atom to the chains of three pentanes.

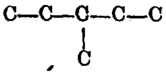
The C-chain of n-pentane has three types of C-atoms :

1 2 3 4 5
C—C—C—C—C
(n-*Pentane*)

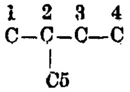
C-atom 1 is similar to 5, and 2 is similar to 4, while 3 is differently linked than all these. Thus, it can give rise to three chains of six carbon atoms :

C—C—C—C—C—C I

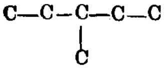

II

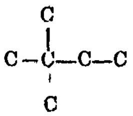

III

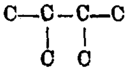
In the C-chain of isopentane only the C-atoms

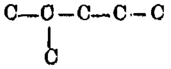


1 and 5 are similarly linked, hence there are only four ways of adding the next C-atom. Thus we have four possible chains of six C-atoms.

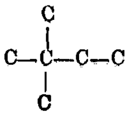

IV


V


VI

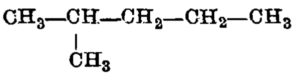

VII

In neo-pentane chain all the four available C-atoms are similarly linked and it can, therefore, give rise to only one chain of six C-atoms.

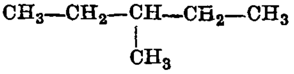

VIII

Now, of the eight chains of six carbon atoms II and VII, III and IV, V and VIII are identical. This reduces the number of possible C-chains of hexanes to only five. All the five hexanes predicted by theory are known. They are

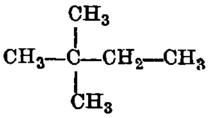
$CH_3-CH_2-CH_2-CH_2-CH_2-CH_3$ n-Hexane



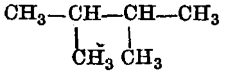
$CH_3-\underset{CH_3}{\underset{|}{CH}}-CH_2-CH_2-CH_3$ 2-Methylpentane



$CH_3-CH_2-\underset{CH_3}{\underset{|}{CH}}-CH_2-CH_3$ 3-Methylpentane



$CH_3-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-CH_2-CH_3$ 2,2-Dimethylbutane



$CH_3-\underset{CH_3}{\underset{|}{CH}}-\underset{CH_3}{\underset{|}{CH}}-CH_3$ 2,3-Dimethylbutane

Proceeding in a similar way the number of isomeric forms of any higher alkane can be theoretically predicted.

OCCURRENCE IN NATURE

The alkanes are distributed in nature in enormous quantities. *Natural gas* given off in petroleum regions is a mixture of chiefly methane and ethane. Lower alkanes are also produced on an industrial scale by the dry-distillation of fats and brown coal.

The liquid hydrocarbons are found in almost unlimited quantities in crude petroleum or mineral oil. Natural wax or *Ozokerite* found in large deposits in petroleum areas and elsewhere is a mixture of higher solid hydrocarbons.

METHODS OF FORMATION

Since the alkanes resemble each other very closely in their physical properties, they cannot be profitably separated from natural petroleum. Even repeated distillation or crystallisation of the oil does not yield pure hydrocarbons. Thus for the preparation of alkanes we have to depend entirely on the synthetic methods.

(1) **Direct synthesis from elements.** The lower hydrocarbons, methane and ethane are formed by passing the electric arc between carbon electrodes in an atmosphere of hydrogen. At the temperature of the arc (1200°) carbon and hydrogen combine together to form alkanes.

$$C + 2H_2 \longrightarrow \underset{\text{Methane}}{CH_4}$$

$$2C + 3H_2 \longrightarrow \underset{\text{Ethane}}{C_2H_6}$$

The hydrocarbons so obtained are mixed with ethane which is also produced in the process.

This method is of special theoretical interest as it forms the first step in the **Complete Synthesis** or **Total Synthesis** of any organic compound. By the term 'complete synthesis' we mean *the building up of a chemical compound starting from elements.*

(2) **Hydrogenation of unsaturated hydrocarbons.** Alkanes are formed by passing a mixture of an unsaturated hydrocarbon and hydrogen over finely divided nickel (or platinum) at 250° to 300°C. (*Sabatier and Senderens Reaction*).

(*i*)

$$\underset{\text{Alkene}}{C_nH_{2n}} + H_2 \longrightarrow \underset{\text{Alkane}}{C_nH_{2n+2}}$$

$$\underset{\text{Ethylene}}{CH_2{=}CH_2} + H_2 \longrightarrow \underset{\text{Ethane}}{CH_3.CH_3}$$

$$\underset{\text{1-Butene}}{CH_2 : CH.CH_2.CH_3} + H_2 \longrightarrow \underset{\text{n-Butane}}{CH_3.\,CH_2.CH_2.CH_3}$$

(*ii*)

$$\underset{\text{Alkyne}}{C_nH_{2n-2}} + 2H_2 \longrightarrow \underset{\text{Alkane}}{C_nH_{2n+2}}$$

$$\underset{\text{Acetylene}}{CH{\equiv}CH} + 2H_2 \longrightarrow \underset{\text{Ethane}}{CH_3.CH_3}$$

Since unsaturated hydrocarbons are obtained in large quantities by the cracking of petroleum, this method is now used for the technical preparation of alkanes.

(3) **Decarboxylation of a fatty acid.** When the sodium salt of a fatty acid RCOOH, is heated with soda lime (NaOH+CaO), a molecule of carbon dioxide is split off as carbonate and an alkane obtained.

$$\underset{\text{Sod. salt of acid}}{R\boxed{COONa + NaO}H} \longrightarrow \underset{\text{Alkane}}{RH} + Na_2CO_3$$

$$\underset{\text{Sod. acetate}}{CH_3COONa} + NaOH \longrightarrow \underset{\text{Methane}}{CH_4} + Na_2CO_3$$

Obviously, the hydrocarbon obtained by this method contains one carbon atom less than the acid from which it is prepared. However, it is a convenient method for the preparation of lower alkanes in the laboratory.

Writing this reaction in a simple way we have

$$R\boxed{COO}H \longrightarrow RH + CO_2$$

Since the carboxyl group in the original acid has been removed in the process, the action has been designated as DECARBOXYLATION.

(4) **Reduction of alkyl halides.** When reduced with nascent hydrogen, alkyl halides are converted to the corresponding alkanes.

$$\underset{\text{Alkyl halide}}{RXI + 2H} \longrightarrow \underset{\text{Alkane}}{RH} + \underset{\text{Halogen acid}}{HX}$$

e.g.,

$$\underset{\text{Methyl iodide}}{CH_3I} + 2H \longrightarrow \underset{\text{Methane}}{CH_4} + HI$$

The common reducing agents employed for the purpose are zinc and hydrochloric acid ; hot hydrogen iodide ; and zinc-copper couple and alcohol.

This method for the preparation of alkanes is used when pure hydrocarbons are needed.

(5) **Reduction of alcohols, ketones and fatty acids.** Alcohols, ketones and fatty acids when reduced with hot hydriodic acid and red phosphorus form alkanes.

Thus :

(*i*) $$\underset{\text{Alcohol}}{ROH} + 2HI \longrightarrow \underset{\text{Alkane}}{RH} + H_2O + I_2$$

$$\underset{\text{Methanol}}{CH_3OH} + 2HI \longrightarrow \underset{\text{Methane}}{CH_4} + H_2O + I_2$$

(*ii*) $$\underset{\text{Ketone}}{R.CO.R} + 4HI \longrightarrow \underset{\text{Alkane}}{R.CH_2.R} + H_2O + 2I_2$$

$$\underset{\text{Acetone}}{CH_3.CO.CH_3} + 4HI \longrightarrow \underset{\text{Propane}}{CH_3.CH_2.CH_3} + H_2O + 2I_2$$

(*iii*) $$\underset{\text{Fatty acid}}{R.COOH} + 6HI \longrightarrow \underset{\text{Alkane}}{R.CH_3} + 2H_2O + 3I_2$$

$$\underset{\text{Acetic acid}}{CH_3COOH} + 6HI \longrightarrow \underset{\text{Ethane}}{CH_3.CH_3} + 2H_2O + 3I_2$$

The red phosphorus reacts with iodine produced in the reaction to regenerate HI which is re-used.

This method is particularly important for the preparation of higher alkanes from fatty acids which are easily obtained by the hydrolysis of fats.

(6) **Action of sodium on alkyl halides** (*Wurtz Reaction*). Higher alkanes are produced by heating an alkyl halide with sodium metal in dry ether solution. Two molecules of the alkyl halide react with two atoms of sodium to give alkane with double the number of carbon atoms present in the former.

$$\underset{\text{Alkyl halide}}{R|X} + 2Na + X|R \longrightarrow \underset{\text{Alkane}}{R.R} + 2NaBr$$

$$\underset{\text{Methyl bromide}}{CH_3|Br} + 2Na + Br|CH_3 \longrightarrow \underset{\text{Ethane}}{CH_3.CH_3} + 2NaBr$$

It is now believed that the sodium metal first acts on the alkyl halide yielding alkyl free radicals which momentarily unite to form the higher alkane.

$$2CH_3Br + 2Na \longrightarrow 2CH_3\cdot + 2NaBr$$

$$\underset{\text{Methyl}}{2CH_3\cdot} \longrightarrow \underset{\text{Ethane}}{CH_3.CH_3}$$

Instead of a pure alkyl halide we can also take a mixture of two different alkyl halides. For example, methyl bromide and ethyl bromide when treated with sodium yield propane.

$$\underset{\substack{\text{Methyl}\\\text{bromide}}}{CH_3|Br} + 2Na + \underset{\substack{\text{Ethyl}\\\text{bromide}}}{Br|C_2H_5} \longrightarrow \underset{\text{Propane}}{CH_3.C_2H_5} + 2NaBr$$

Along with propane small amounts of ethane and butane are also obtained. This can be explained by the fact that besides the union of methyl radicals with ethyl radicals they also unite with themselves forming ethane and butane.

$$2CH_3\cdot \longrightarrow C_2H_6 \; ; \; 2C_2H_5\cdot \longrightarrow C_4H_{10}$$

As shown by the above examples *Wurtz reaction is a good method for building up higher alkanes from lower members.* The lower alkanes can be converted into the corresponding halide and treated with sodium. Thus methane can be converted into ethane as follows :

$$\underset{\text{Methane}}{CH_4} + Cl_2 \longrightarrow \underset{\text{Methyl chloride}}{CH_3Cl} + HCl$$

$$2CH_3Cl + 2Na \longrightarrow \underset{\text{Ethane}}{C_2H_6} + 2NaCl$$

Wurtz reaction proceeds easily with alkyl iodides and bromides. Instead of sodium, metallic zinc or finely divided silver can also be used.

(7) **From Grignard Reagents.** Alkylmagnesium halides (Grignard reagents) when decomposed with water yield pure alkanes.

$$\underset{\text{Grignard reagent}}{RMgI} + HOH \longrightarrow \underset{\text{Alkane}}{RH} + MgI(OH)$$

$$\underset{\substack{\text{Methylmagnesium}\\ \text{iodide}}}{CH_3MgI} + HOH \longrightarrow \underset{\text{Methane}}{CH_4} + MgI(OH)$$

(8) **Electrolysis of salts of fatty acids** (*Kolbe's Method*). When concentrated solution of sodium or potassium salt of a fatty acid is electrolysed, a higher alkane is obtained.

$$\underset{\substack{\text{Pot. Salt}\\ \text{of fatty acid}}}{2RCOOK} \longrightarrow 2RCOO^- + 2K^+$$

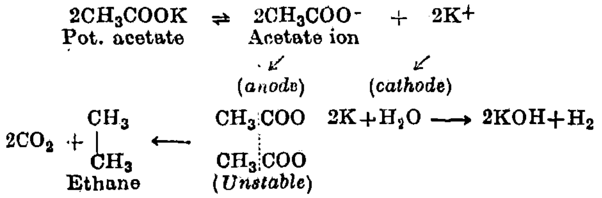
By electrolysis we get : (*i*) *At anode*—

$$2RCOO^- \xrightarrow{-2e} \underset{\textit{Unstable}}{2RCOO} \longrightarrow \underset{\text{Alkane}}{R.R} + 2CO_2$$

(*ii*) *At cathode*—

$$2K^+ \xrightarrow{+2e} 2K \;\; ; \;\; 2K + 2H_2O \longrightarrow 2KOH + H_2$$

Thus potassium acetate solution yields ethane upon electrolysis as follows :



$$\underset{\text{Pot. acetate}}{2CH_3COOK} \rightleftharpoons \underset{\text{Acetate ion}}{2CH_3COO^-} + 2K^+$$

$$(\textit{anode}) \qquad (\textit{cathode})$$

$$2CO_2 + \underset{\text{Ethane}}{\begin{matrix} CH_3 \\ | \\ CH_3 \end{matrix}} \longleftarrow \underset{(\textit{Unstable})}{\begin{matrix} CH_3{:}COO \\ \vdots \\ CH_3{:}COO \end{matrix}} \qquad 2K + H_2O \longrightarrow 2KOH + H_2$$

The acetate ions move to the anode and are discharged there. The resulting groups being unstable, two of them split out to give ethane and carbon dioxide.

The Kolbe's method stated above, in fact, involves the electrolytic decomposition of a fatty acid and may be represented in a simple way as

$$\underset{\text{Acid}}{\begin{matrix} R{:}COO\,H \\ \vdots \quad \vdots \\ R{:}COO{:}H \end{matrix}} \longrightarrow \underset{\text{Alkane}}{\begin{matrix} R \\ | \\ R \end{matrix}} + 2CO_2 + H_2$$

Wurtz used this method for the preparation of higher alkanes by taking a mixture of salts of two different fatty acids instead of one.

PHYSICAL CHARACTERISTICS

(1) The first four hydrocarbons methane, ethane, propane and butane are colourless, odourless gases. The next eleven members (C_5H_{12} to $C_{15}H_{32}$) are colourless liquids having "benzine" odour. The higher alkanes are solids with no colour or odour.

(2) Alkanes are the most volatile organic compounds, their *boiling points being the lowest when compared with those of any of* their derivatives.

(3) The liquid alkanes are lighter than water.

(4) They are almost insoluble in water but dissolve freely in organic solvents like ether acetone, and carbon tetrachloride.

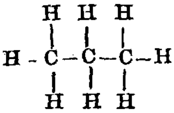
(5) Their boiling points and specific gravities increase with rise of molecular weight. Among the lower members, a difference of CH_2 corresponds to an increase of about 30° in the boiling point.

NAME	FORMULA	B. PT. °C	M. PT. °C	SP. GR.
Methane	CH_4	—164	—184	0·415 at —164°
Ethane	C_2H_6	— 93	—171·4	0·546 at --88°
Propane	C_3H_8	— 45	—190	0·585 at —44·5°
Butane	C_4H_{10}	+0·6	—135	0·601 at —0°
Pentane	C_5H_{12}	+36	—130·8	0·631 at 20°
Hexane	C_6H_{14}	*+69*	*—93·7*	*0·660 at 20°*
Heptane	C_7H_{16}	+98·3	—90	0·684 at 17°
Octane	C_8H_{18}	+125·8	—57	0·707 at 20°
Nonane	C_9H_{20}	+145·5	—51	0·718 at 20°
Decane	$C_{10}H_{22}$	+173	—32	0·747 at 20°

(6) As a rule the boiling points of the hydrocarbons having branched carbon-chains are lower than those of the isomeric normal hydrocarbons. The increased branching of the chain results in a consequent decrease of the boiling point.

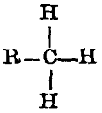
CHEMICAL CHARACTERISTICS

Excepting methane which contains only one carbon atom, the molecules of alkanes consist of two or more carbon atoms united to each other by single covalent bonds and their remaining valencies are fully satisfied by combination with hydrogen atoms. Thus :



$$\begin{array}{ccccccccc} & & H & & H & & H & & \\ & & | & & | & & | & & \\ H & - & C & - & C & - & C & - & H \\ & & | & & | & & | & & \\ & & H & & H & & H & & \end{array}$$

Propane



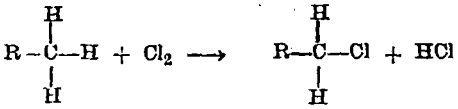
$$\begin{array}{ccccc} & & H & & \\ & & | & & \\ R & - & C & - & H \\ & & | & & \\ & & H & & \end{array}$$

Alkane ; R=alkyl group

The chemical behaviour of alkanes may, therefore, be *summarised* as follows :

(*i*) STABILITY. They are characterised by their stability to most chemical reagents. The four valencies of the carbon atoms being fully satisfied, there is no scope for further addition of hydrogen, halogens, etc. Moreover *a carbon-to-carbon linkage is unusually strong* and cannot be ruptured by even such reagents as potassium permanganate, chromic acid, etc.

(*ii*) SUBSTITUTION REACTIONS. The linkage between carbon and hydrogen is comparatively weak so that the hydrogen atoms can be replaced by other atoms or groups giving substitution products. Thus :

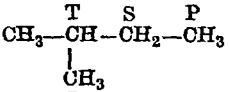


$$\begin{array}{ccccc} & & H & & \\ & & | & & \\ R & - & C & - & H \\ & & | & & \\ & & H & & \end{array} + Cl_2 \longrightarrow \begin{array}{ccccc} & & H & & \\ & & | & & \\ R & - & C & - & Cl \\ & & | & & \\ & & H & & \end{array} + HCl$$

Alkane Substitution product

(*iii*) OXIDATIOH REACTIONS. When burnt in air or oxygen, the alkanes are decomposed to form carbon dioxide and water. On slow combustion the products are found to contain aldehydes and fatty acids.

As a general rule reactivity of the alkanes increases as one proceeds from primary, through a secondary to a tertiary hydrogen atom*. Thus the H-atoms in isopentane will be attacked in the order T > S > P



$$\begin{array}{ccccccc} & & T & & S & & P \\ CH_3 & - & CH & - & CH_2 & - & CH_3 \\ & & | & & & & \\ & & CH_3 & & & & \end{array}$$

Isopentane

The general reactions of alkanes are described below :

(1) **Halogenation.** Chlorine and bromine can substitute the hydrogen atoms of alkanes with considerable ease,

$$\underset{\text{Alkane}}{RH} + X_2 \xrightarrow{\textit{Light}} \underset{\text{Alkyl halide}}{RX} + HX$$

chlorine being more reactive than bromine. Thus by the action of chlorine at ordinary temperature in diffused daylight all the four

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*A hydrogen atom linked to a primary carbon (attached to one more carbon only) is termed a primary H-atom ; one linked to a secondary carbon (attached to two more carbons) a secondary H-atom ; and the one linked to a tertiary carbon (attached to three more carbons) is termed a tertiary H-atom.

hydrogen atoms of methane can be successively replaced by chlorine atoms.

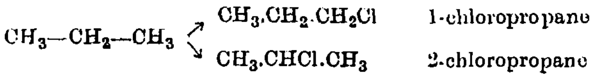
$$CH_4 + Cl_2 \longrightarrow \underset{\text{Methyl chloride}}{CH_3Cl} + HCl$$

$$CH_3Cl + Cl_2 \longrightarrow \underset{\text{Methylene chloride}}{CH_2Cl_2} + HCl$$

$$CH_2Cl_2 + Cl_2 \longrightarrow \underset{\text{Chloroform}}{CHCl_3} + HCl$$

$$CHCl_2 + Cl_2 \longrightarrow \underset{\text{Carbon tetrachloride}}{CCl_4} + HCl$$

Ethane and higher homologues react with chlorine in a similar way and all possible products are obtained. Thus, in the first instance the chlorination of propane yields both 1-chloro and 2-chloropropane.



$$CH_3-CH_2-CH_3 \begin{array}{l} \nearrow CH_3.CH_2.CH_2Cl \quad \text{1-chloropropane} \\ \searrow CH_3.CHCl.CH_3 \quad \text{2-chloropropane} \end{array}$$

Iodine does not substitute directly in alkanes as the hydriodic acid formed during iodination reduces the alkyl iodide back to the alkane, making the reaction reversible.

$$\underset{\text{Alkane}}{RH} + I_2 \rightleftharpoons \underset{\text{Alkyl iodide}}{RI} + HI$$

However, alkanes can be iodinated in the presence of an oxidising agent such as iodic acid (HIO_3) or nitric acid, which destroys the hydriodic acid (HI) as it is formed.

$$5HI + HIO_3 \longrightarrow 3I_2 + 3H_2O$$

A detailed study of the action of chlorine on methane reveals the following facts :

(*a*) Equimolecular mixture of methane and chlorine remains unchanged when kept at 20°C in the dark.

(*b*) A rapid reaction takes place—(*i*) in the dark at a temperature of 250°C ; or (*ii*) under the influence of ultraviolet or visible light radiations at room temperature.

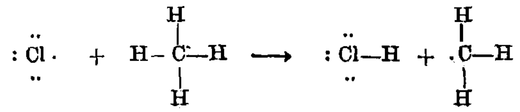
(*c*) Many molecules of halogenated alkane are produced by each photon ($h\nu$) or quantum of light absorbed by the system when the reaction is initiated by light.

(*d*) The presence of a small amount of oxygen slows down the reaction.

The **mechanism** which explains these facts most satisfactorily, involves the following steps :—

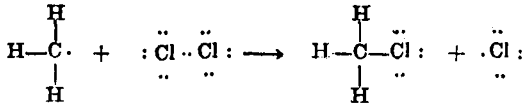
(*i*) $$;\overset{..}{\underset{..}{Cl}}..\overset{..}{\underset{..}{Cl}}: + \text{energy } (h\nu) \longrightarrow :\overset{..}{\underset{..}{Cl}}\cdot + \cdot\overset{..}{\underset{..}{Cl}}:$$

(*ii*)



$$:\overset{..}{\underset{..}{Cl}}\cdot + H-\overset{\displaystyle H}{\underset{\displaystyle H}{\overset{|}{\underset{|}{C}}}}-H \longrightarrow :\overset{..}{\underset{..}{Cl}}-H + \cdot\overset{\displaystyle H}{\underset{\displaystyle H}{\overset{|}{\underset{|}{C}}}}-H$$

(iii)



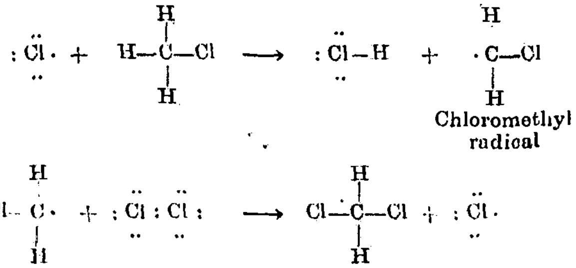
$$H_3C\cdot + :\ddot{Cl}:\ddot{Cl}: \longrightarrow H_3C{-}\ddot{Cl}: + \cdot\ddot{Cl}:$$

Then the steps (*ii*), (*iii*), (*ii*), (*iii*) are repeated over and over again.

Explanation.—The step (*i*) involves the homolytic fission of the chlorine molecule due to the action of heat or light, when each Cl atom retains one electron of the pair that constituted the covalent bond. The *odd electron* present on each Cl atom now lacks a partner of opposite spin and hence is very reactive. As defined in the foregoing chapter, such an atom or group of atoms having an unpaired or odd electron is called a **free radical.** The increased reactivity of such a free radical is attributed to its urge to acquire an additional electron for completing the octet. Since the formation of free radicals is attended by an absorption of energy (58 K. cal./mole in present case), it stands to reason that they are 'energy rich' particles ready to form new covalent bond by losing energy.

In step (*ii*), one of the free radicals generated as above, attacks a molecule of methane and gives a stable molecule of HCl together with another free radical-methyl radical. This radical has an odd electron on the carbon atom and is unstable, since the C atom has only seven electrons. It reacts with a molecule of chlorine in step (*iii*), and regenerates another chlorine free radical capable of reacting with methane as in step (*ii*), to form a methyl radical. The methyl radical so produced repeats the step (*iii*) to give yet another chlorine free radical. In this fashion the sequence of reactions (*ii*), (*iii*), (*ii*), (*iii*) is repeated over and over again. Such a mechanism which involves a cycle of steps each of which produces a free radical that conducts the following step, is termed as the **Free Radical mechanism** or **Chain mechanism.** The step (*i*) is the chain initiating step and requires the supply of sufficient energy for the homolytic fission of the bond between chlorine atoms.

When the concentration of methyl chloride as a result of the 'chain reaction' described above increases sufficiently, it combines with chlorine free radical to form chloromethyl radical. This radical then participates further in chain reaction to form dichloromethane.



$$:\ddot{Cl}\cdot + H_3C{-}Cl \longrightarrow :\ddot{Cl}{-}H + \cdot CH_2{-}Cl$$

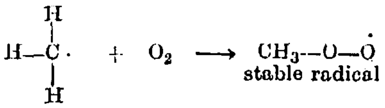
Chloromethyl radical

$$Cl{-}\dot{C}H_2 + :\ddot{Cl}:\ddot{Cl}: \longrightarrow Cl{-}CH_2{-}Cl + :\ddot{Cl}\cdot$$

Dichloromethane

Similarly trichloromethane and tetrachlormethane are formed by further chain reactions.

The inhibitory action of oxygen as envisaged in fact (*d*) above, is explained by saying that the methyl radical $CH_3\cdot$ reacts with an oxygen molecule to give a much less reactive free radical $CH_3O\dot{O}$. This contributes very little towards the propagation of the chain reaction and its lesser activity slows down the reaction considerably.



$$H_3C\cdot + O_2 \longrightarrow CH_3{-}O{-}\dot{O}$$

stable radical

(2) **Nitration.** Nitric acid has no action on lower alkanes but by its long, continued action on higher hydrocarbons one of their

hydrogen atoms may be replaced by a nitro-group, NO_2 (*Nitration*).

$$\underset{\text{Alkane}}{RH} + HONO_2 \longrightarrow \underset{\text{Nitroalkane}}{RNO_2} + H_2O$$

For example, when hexane is heated with fuming nitric acid for forty hours, about ten per cent of the hydrocarbon is converted to NITROHEXANE,

$$\underset{\text{Hexane}}{C_6H_{13}\boxed{H + HO}NO_2} \longrightarrow \underset{\text{Nitrohexane}}{C_6H_{13}NO_2} + H_2O$$

More recently, the *vapour-phase nitration processes* of the lower hydrocarbons have been developed with great success and it has been made possible to nitrate all alkanes except methane. For example, when ethane is mixed with vapours of nitric acid and heated to 400°C, they react to form nitroethane

$$\underset{\text{Ethane}}{C_2H_5}\boxed{H + HO}\underset{\text{Nitric acid}}{NO_2} \longrightarrow \underset{\text{Nitroethane}}{C_2H_5NO_2} + H_2O$$

Since the reaction is carried at high temperature, some of the carbon-to-carbon linkages are also attacked resulting in the formation of simpler nitro-compounds. Thus in the above case, some nitromethane is also produced along with nitroethane.

(3) **Sulphonation.** Alkanes react with fuming sulphuric acid at elevated temperatures to produce alkanesulphonic acids.

$$R\boxed{H + HO}\underset{(\textit{fuming})}{SO_3H} \xrightarrow{400^\circ} \underset{\text{Alkanesulphonic acid}}{RSO_3H} + H_2O$$

$$\underset{\text{Hexane}}{C_6H_{13}}\boxed{H + HO}SO_3H \longrightarrow \underset{\text{Hexane-sulphonic acid}}{C_6H_{13}.SO_3H} + H_2O$$

Lower hydrocarbons do not respond to the reaction.

The process involves the replacement of one H of the alkane by sulphonic acid group, SO_3H and is known as *Sulphonation.*

While tertiary alkanes undergo sulphonation readily, the secondary and tertiary ones may not sulphonate under equivalent conditions. Hence this reaction can be used to separate tertiary alkanes from the secondary and tertiary hydrocarbons by sulphonation and subsequent washing with water in which sulphonic acids are soluble.

(4) **Oxidation.** (*i*) Normal alkanes are not oxidised by potassium permanganate but the latter oxidises a tertiary hydrogen atom to a hydroxy group. Thus isobutane is oxidised to tertiary butanol.

$$\underset{\text{Isobutane}}{(CH_3)_3CH} + [O] \longrightarrow \underset{\textit{Ter.}\text{ butanol}}{(CH_3)_3C.OH}$$

(*ii*) Alkanes when burnt in air or oxygen are completely oxidised to carbon dioxide and water. Thus

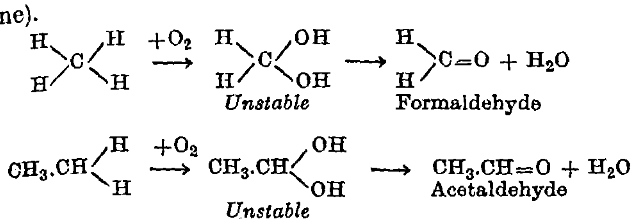
$$C_nH_{2n+2} + \left(\frac{3n+1}{2}\right)O_2 \longrightarrow nCO_2 + (n+1)H_2O + \textit{Heat}$$

$$\underset{\text{Methane}}{CH_4} + 2O_2 \longrightarrow CO_2 + 2H_2O + 210{\cdot}8 \text{ Cals.}$$

$$\underset{\text{Ethane}}{C_2H_6} + 7/2O_2 \longrightarrow 2CO_2 + 3H_2O + 368{\cdot}4 \text{ Cals.}$$

The reaction is highly exothermic and is widely applied where alkanes (natural gas, petrol, kerosene) are used as fuel. The heat of combustion of alkanes increases gradually as we go higher in the series.

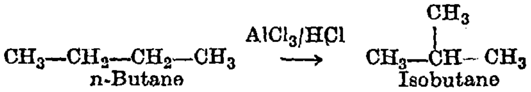
(*iii*) The lower alkanes when heated with a limited supply of air at 350–500°C, yield the corresponding aldehydes and ketones (Bone).



The aldehydes and ketones on further oxidation eventually may give fatty acids.

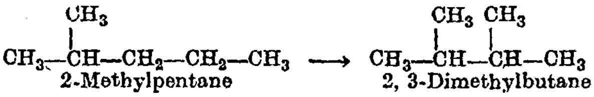
The controlled oxidation of alkanes is the modern source of large-scale production of a number of alcohols, aldehydes and acids. Since the higher alkanes from petroleum could be easily oxidised to the respective acids by treatment with air at moderately high temperatures, it has opened a way for the artificial preparation of fats and soaps.

(5) **Isomerisation.** n-Alkanes in the presence of aluminium chloride and hydrogen chloride or of aluminium bromide and hydrogen bromide are converted to their branched-chain isomers. Thus :



$$\underset{\text{n-Butane}}{CH_3{-}CH_2{-}CH_2{-}CH_3} \xrightarrow{AlCl_3/HCl} \underset{\text{Isobutane}}{CH_3{-}\overset{\overset{CH_3}{|}}{C}H{-}CH_3}$$

Similarly other less branched alkanes isomerise to more branched ones. Thus :



$$\underset{\text{2-Methylpentane}}{CH_3{-}\overset{\overset{CH_3}{|}}{C}H{-}CH_2{-}CH_2{-}CH_3} \longrightarrow \underset{\text{2, 3-Dimethylbutane}}{CH_3{-}\overset{\overset{CH_3}{|}}{C}H{-}\overset{\overset{CH_3}{|}}{C}H{-}CH_3}$$

Isomerisation of alkanes is of considerable importance in the petroleum industry.

(6) **Pyrolysis.** By the term pyrolysis (Gr., *pyr*=fire ; *lysis*= loosing) is meant the conversion of an organic substance to one or more new substances by the action of heat alone. When the vapours of a higher alkane are heated at elevated temperature (500° or more) in the absence of oxygen, chemical decomposition occurs in two ways : (*i*) by fission of C—H linkages to form an unsaturated hydrocarbon and hydrogen gas ; and (*ii*) by fission of C—C linkages t give simpler hydrocarbons — one alkane and one alkene. Thus propane when pyrolysed at about 600°, is decomposed as follows :

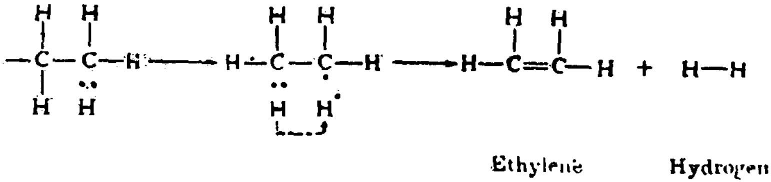
(*i*) $\underset{\text{Propane}}{CH_3{-}CH_2{-}CH_3} \longrightarrow \underset{\text{Propene}}{CH_3{-}CH{=}CH_2} + H_2$

(*ii*) $\underset{\text{Propane}}{CH_3{-}CH_2{-}CH_3} \longrightarrow \underset{\text{Ethylene}}{CH_2{=}CH_2} + \underset{\text{Methane}}{CH_4}$

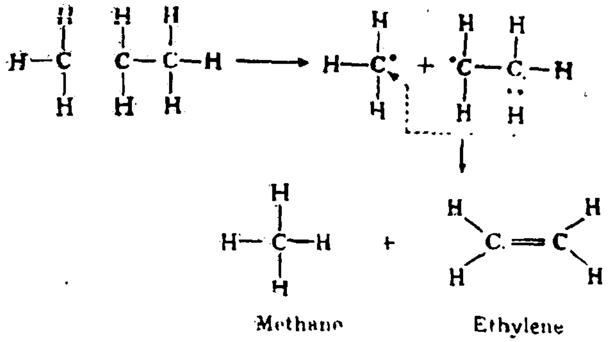
Mechanism

Cracking, which in a way is carbon-carbon bond cleavage, is believed to take place as a result of homolytic bond fissions. The carbon skeleton breaks into smaller units some of which should invariably be unsaturated. The homolytic fission of various bonds is shown below :

Cracking of Ethane :

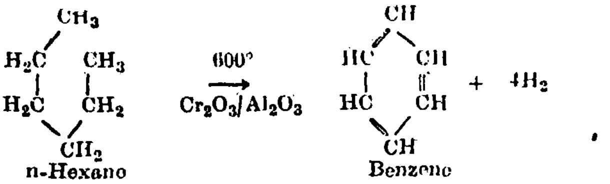


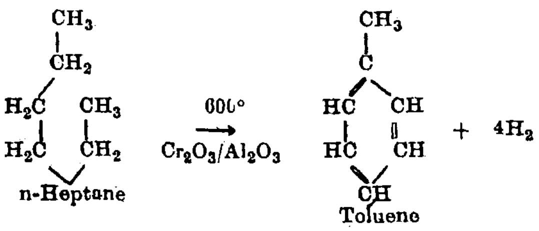
Cracking of Propane :



The catalytic thermal decomposition of alkanes is used technically for the production of the more reactive unsaturated hydrocarbons needed in the modern chemical organic industry.

(7) **Aromatisation.** One of the most striking developments of recent years is that the alkanes containing six or more carbon atoms are converted into aromatic hydrocarbons at high temperature in the presence of catalyst. Thus, n-hexane and n-heptane when passed over Cr_2O_3 supported on Al_2O_3 at 600°, yield benzene and toluene respectively.





This reaction known as *aromatisation*, proceeds by simultaneous cyclization and dehydrogenation of the aliphatic compounds. It provides an excellent method for passing from aliphatic to aromatic series.

INDIVIDUAL MEMBERS

METHANE, CH_4

It is the first member of the alkane series and is the only hydrocarbon which contains a single carbon atom in the molecule. Methane is found bubbling from marshy places where it is produced by the bacterial decomposition of dead vegetable matter and hence its name **marsh gas.** Also, it occurs in coal mines, pockets of the gas being opened up during the process of mining. Here it forms an explosive mixture with air and the miners call it *fire damp*, a name which probably originated from the German word *Feuer* (fire) and *Damp* (vapour). The natural gas issuing from the petroleum wells contains on average 85 per cent of methane and is the chief household fuel in U.S.A. It is present to the extent of 35 per cent in coal gas. Methane is also present in the intestinal gases. It is also found in the gases from cracked petroleum.

Preparation. Methane can be obtained by the general methods 1, 2, 3, 4, 5 and 7. It is prepared :

(1) By heating sodium acetate with soda-lime.

$$\underset{\text{Sod. acetate}}{CH_3COONa} + NaOH \longrightarrow \underset{\text{Methane}}{CH_4} + Na_2CO_3$$

(2) By reduction of methyl iodide with zinc-copper couple and methanol.

$$\underset{\text{Methyl iodide}}{CH_3I} + 2[H] \longrightarrow \underset{\text{Methane}}{CH_4} + HI$$

(3) By dropping water on aluminium carbide.

$$\underset{\text{Aluminium carbide}}{Al_4C_3} + 12H_2O \longrightarrow 4Al(OH)_3 + \underset{\text{Methane}}{3CH_4}$$

(4) By the fermentation of wet cellulose.

$$\underset{\text{Cellulose}}{(C_6H_{10}O_5)} + nH_2O \longrightarrow 3nCO_2 + \underset{\text{Methane}}{3nCH_4}$$

Thus if wet filter-paper pulp is mixed with horse dung and kept at 50° C, a mixture of methane and carbon dioxide is evolved. To recover methane, carbon dioxide may be removed by absorption in KOH solution.

In addition to the above, the following synthetic methods are available for the preparation of methane.

(5) By the direct combination of carbon and hydrogen in the electric arc (*Direct or Complete synthesis*).

$$C + 2H_2 \xrightarrow{1200°} \underset{\text{Methane}}{CH_4}$$

(6) By passing a mixture of carbon monoxide and hydrogen over nickel at 200—500°C.

$$CO + 3H_2 \longrightarrow CH_4 + H_2O$$

Laboratory Methods. (1) *From Sodium Acetate.* A mixture of fused sodium acetate and soda-lime is heated in a copper test-tube.

$$CH_3COONa + NaOH \longrightarrow CH_4 + Na_2CO_3$$

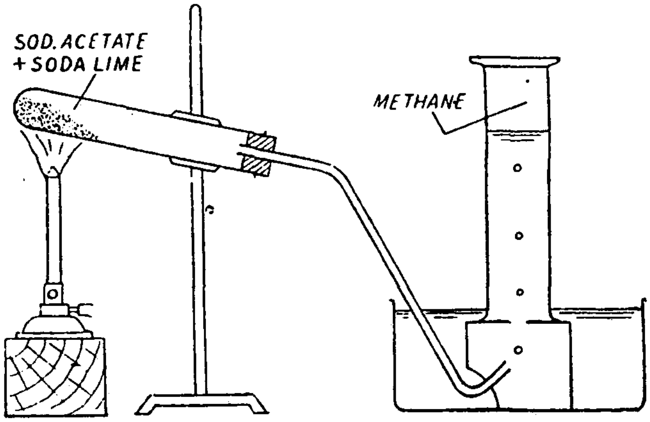


Fig. 10·1. Preparation of methane from sodium acetate.

Powdered sodium acetate (20 gms.) is mixed with thrice its weight of soda-lime. The mixture is placed in a copper test-tube fitted with a delivery tube and the apparatus is set up as shown in Fig. 10·1. The test-tube is now strongly heated. At first, some air is allowed to escape from the apparatus and then the gas is collected over water in a gas jar. Methane so prepared contains some ethylene and hydrogen as impurities. If desired, ethylene can be removed by bubbling the gas through concentrated sulphuric acid before collection.

(2) *From Methyl Iodide.* The method is employed when pure methane is needed. It consists in the reduction of methyl iodide with the help of zinc-copper couple and methanol.

$$CH_3I + [2H] \longrightarrow CH_4 + HI$$

ms of pure granulated zinc are immersed in dilute copper sulphate solution until it is coated with a film of copper. The zinc copper couple so obtained is washed several times with water and then with alcohol. It is placed in the flask and U-tube (see Fig. 10·2). A mixture of methyl iodide and 95 per cent ethanol (1 : 1) is added from the dropping funnel. Methane gas is evolved in cold and is collected by the downward displacement of water. The zinc-copper couple placed in the U-tube helps in removing any methyl iodide vapour that are mixed with methane.

Industrial Preparation. Large quantities of methane are available in U.S.A. as natural gas from petroleum wells. The methods used for the large scale preparation of methane are :

(1) By the catalytic reduction of water gas ($CO+H_2$).

(2) By passing carbon monoxide and steam over heated (250—270°) nickel carbonate.

$$4CO + 2H_2O \longrightarrow CH_4 + 3CO_2$$

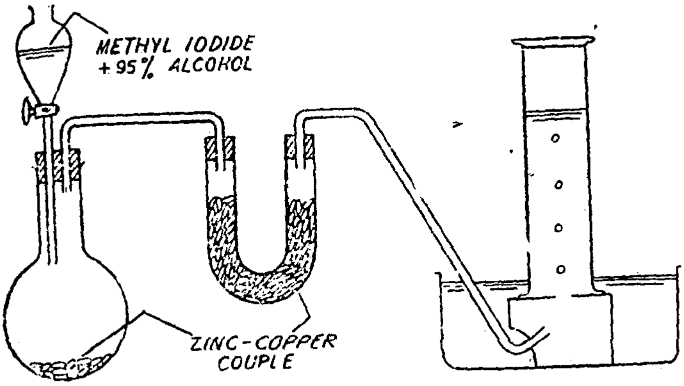


Fig. 10·2. Preparation of pure methane.

(3) By the bacterial decomposition of wet cellulosic material. This method has become particularly important in Great Britain where large volumes of gas are now obtained by the bacterial decomposition of sewage.

Properties (*Physical*). Methane is a colourless and odourless gas which liquefies at −161·4°C and soldifies at —184°C. Its molecular weight is less than that of any other compound and it is, therefore, the lightest compound gas known. Its specific gravity is 0·559 as compared with air. It is only slightly soluble in water but is much more soluble in organic solvents like acetone, ether and alcohol.

Chemical. (*i*) Chemically methane shows absolute inertness to reagents such as fuming sulphuric acid, nitric acid, alkalis, potassium permanganate, etc.

(*ii*) Methane behaves like a typical alkane responding to almost all the general reactions of the class.

(1) STABILITY. It shows remarkable stability and absolute inertness to most reagents. Sulphuric acid, nitric acid, alkalis and potassium permanganate have no action on methane.

(2) ACTION OF HALOGENS. Methane reacts with chlorine and bromine in diffused daylight, to form derivatives in which one, two, three or all the four X-atoms are replaced by chlorine atom.

CH_3Cl	CH_2Cl_2	$CHCl_3$	CCl_4
Methyl chloride	Methylene chloride	Chloroform	Carbon tetrachloride

In the presence of direct sunlight or on ignition, chlorine reacts with methane with explosive violence to form hydrogen chloride and free carbon.

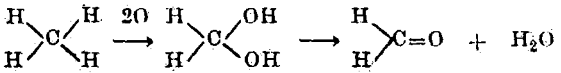
$$CH_4 + 2Cl_2 \longrightarrow C + 4HCl$$

(3) OXIDATION. Methane burns in air or oxygen with a pale-blue non-luminous flame to give carbon dioxide and water.

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O + \textit{heat}$$

Within certain limits of composition, methane forms explosive mixtures with air.

On incomplete combustion in air at 350—500°C or by oxidation with ozone, it is converted to formaldehyde.



Methane (unstable) Formaldehyde

Formaldehyde is at once detected by smell and hence this reaction (oxidation by ozone) is used as a test for the presence of methane.

(4) ACTION WITH STEAM. Methane reacts with steam in the presence of nickel catalyst yielding carbon monoxide.

$$CH_4 + H_2O \xrightarrow[\text{Cat.}]{1000^\circ} CO + 3H_2$$

This reaction is used for the large-scale production of hydrogen from natural gas.

(5) PYROLYSIS. When heated in the absence of oxygen, methane splits up to form carbon and hydrogen.

$$CH_4 \xrightarrow{1000^\circ} C + 2H_2$$

The free carbon thus produced (*carbon black*) is used for making paints, black printing ink, and in the production of rubber products (automobile tyres).

According to a most recent cracking process, methane (natural gas) is converted to acetylene by passing it through electric arc or by subjecting it to high temperature obtained by partial combustion.

$$\underset{\text{Methane}}{2CH_4} \longrightarrow \underset{\text{Acetylene}}{HC\equiv CH} + \text{Other products}$$

(6) CONVERSION TO HCN. Methane is converted to hydrogen cyanide by reaction with nitrogen or ammonia as follows (*Industrial*).

$$2CH_4 + N_2 \xrightarrow[\text{arc}]{\text{electric}} 2HCN + 3H_2$$

$$CH_4 + NH_3 \xrightarrow[Al_2O_3]{1000^\circ} HCN + 3H_2$$

Uses : Methane is used :

(1) as *illuminant* and *domestic fuel* in the form of natural gas ;

(2) for making 'carbon black' needed as a black pigment and for compounding rubber tyres ;

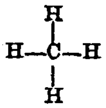
(3) as fuel for generating power for plants ;

(4) for the preparation of CH_3Cl, CH_2Cl_2, $CHCl_3$, and CCl_4 by regulated chlorination ; and

(5) for the technical production of methanol, formaldehyde, acetylene, hydrogen cyanide and hydrogen.

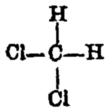
Structure. (1) The molecular formula of methane as shown by eudiometric analysis is CH_4.

(2) Since methane, forms only one mono-chloro derivative CH_3Cl, all the four hydrogen atoms in its molecule are similar. Keeping in view the tetra-covalency of carbon, the structural formula for methane could be written as

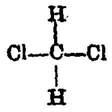


$$\mathrm{H{-}\overset{\displaystyle H}{\underset{\displaystyle H}{C}}{-}H}$$

(3) If the above planar formula is correct, methane should be able to form two dichloromethanes :



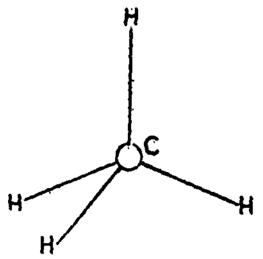
$$\mathrm{Cl{-}\overset{\displaystyle H}{\underset{\displaystyle Cl}{C}}{-}H}$$

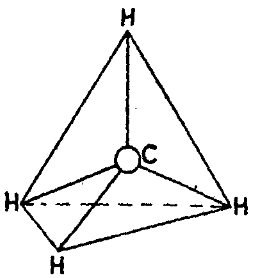


$$\mathrm{Cl{-}\overset{\displaystyle H}{\underset{\displaystyle H}{C}}{-}Cl}$$

Actually one dichloromethane is known to exist and hence the planar formula for methane is untenable.

(4) If, however, methane is assigned a tetrahedral structure, the four valencies of the carbon atom are distributed symmetrically in space and it can be represented as





In this formula all the H atoms are similarly placed in the molecule which justifies the existence of only one dichloromethane. The tetrahedral structure of methane is further supported by the phenomenon of optical isomerism.

(5) The modern orbital structure of methane (Page 73 ; Fig. 5·4) supports the tetrahedral model of its molecule. The carbon atom linked to the four hydrogen atoms is in sp^3 hybridisation state. The four equivalent hybrid orbitals are directed towards the four corners of regular tetrahedron. Each of these orbitals overlap with the spherical *s* orbital of hydrogen atom forming a strong σ bond. Thus in methane molecule there are four σ bonds of equal strength. The electron diffraction and spectroscopic data of methane points to the fact that in its molecule the bond angle H—C - H is 109°28′ and the bond length C – H is 1·09 Å. The geometry of methane molecule is given below :

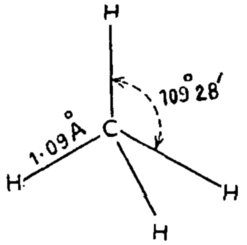


Fig. 10·3. The geometry of methane molecule.

ETHANE, C_2H_6

It is the second member of the homologous series of alkancs. It may be regarded as derived from methane by replacing one H atom by methyl group and may thus be named as *methylmethane*. Being made up of two methyl groups. CH_3CH_3, it may be called dimethyl.

It occurs dissolved in the natural mineral oil, and is evolved in the gaseous state when the oil comes to the surface. Natural gas contains small quantities (10—21%) of ethane along with methane. To a small extent it is also present in coal gas and in 'cracked petroleum'.

Preparation. Ethane can be prepared by the general methods described earlier.

(1) By heating a mixture of sodium propionate with soda-lime in a hard-glass test-tube.

$$\underset{\text{Sod. propionate}}{C_2H_5COONa} + NaOH \longrightarrow \underset{\text{Ethane}}{C_2H_6} + Na_2CO_3$$

(2) By the reduction of ethyl iodide with zinc-copper couple and ethanol.

$$\underset{\text{Ethyl iodide}}{C_2H_5I} + 2H \longrightarrow \underset{\text{Ethane}}{C_2H_6} + HI$$

(3) By the action of sodium on methyl iodide in dry ethereal solution (*Wurtz reaction*).

$$\underset{\text{Methyl iodide}}{CH_3I} + 2Na + ICH_3 \longrightarrow \underset{\text{Ethane}}{CH_3.CH_3} + 2NaI$$

Thin slices of sodium metal are suspended in dry ether contained in small flask fitted with a reflux condenser and a tap-funnel. Methyl iodide is slowly added from the tap funnel and the ethane evolved is collected over water.

(4) By passing a mixture of ethylene and hydrogen over heated nickel (*Sabatier and Senderens*).

$$\underset{\text{Ethylene}}{CH_2{=}CH_2} + H_2 \longrightarrow \underset{\text{Ethane}}{C_2H_6}$$

(5) By the electrolysis of an aqueous solution of sodium or potassium acetate (*Kolbe's method*). Acetate ions are discharged at the anode giving ethane and carbon dioxide.

$$\underset{\text{Pot. acetate}}{CH_3COOH} \longrightarrow \underset{\text{Acetate ion}}{CH_3COO^-} + K^+$$

$$2CH_3COO^- \xrightarrow{\text{discharged}} \underset{(\textit{Unstable})}{2CH_3COO} \longrightarrow \underset{\text{Ethane}}{CH_3CH_3} + 2CO_2$$

Carbon dioxide is removed by absorption in potassium hydroxide solution.

LABORATORY METHODS. (1) *From Ethyl iodide.* Pure ethane is obtained in the laboratory by the reduction of ethyl iodide with zinc-copper couple and ethanol mixed with about 5 per cent water.

$$C_2H_5I + 2[H] \longrightarrow C_2H_6 + HI$$

The experimental details of the procedure are the same as described under similar method for the preparation of methane.

(2) *From Potassium acetate.* Ethane can also be prepared conveniently by the electrolysis of a concentrated solution of potassium acetate.

$$2CH_3COOK \longrightarrow C_2H_6 + 2CO_2 + 2K$$

The apparatus used for the purpose is shown in Fig. 10·4. It consists of a porous pot fitted with a platinum anode and a delivery tube. The pot is placed

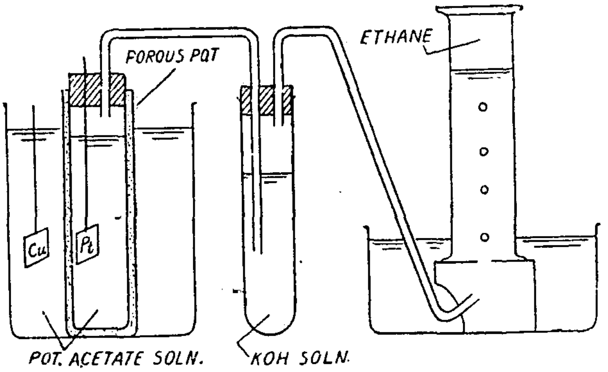


Fig. 10·4. Preparation of Ethane by electrolysis.

in an outer vessel in which is hung a copper cathode. Both the porous pot and the outer vessel are filled with potassium acetate solution. On passing the current hydrogen is evolved at the cathode, and ethane and carbon dioxide at the anode. The mixture of ethane and carbon dioxide coming from the porous pot is bubbled through potassium hydroxide solution contained in a test tube or a wash-bottle. This removes carbon dioxide and allows ethane gas to pass on. It is then collected over water.

COMMERCIAL METHODS. (1) Ethane is obtained in large amounts by cracking of petroleum during its distillation when it escapes in the uncondensed gases.

(2) It can also be prepared technically by the catalytic hydrogenation of ethylene which is formed in large quantities during the cracking of petroleum.

Properties (*Physical*). Ethane is a colourless and odourless gas at ordinary temperature. It can be more easily liquefied than methane: liquid ethane boils at −88·3°C and solidifies at −172°C. It is sparingly soluble in water but dissolves readily in ethanol.

(*Chemical*). In its chemical behaviour ethane closely resembles with methane.

(1) STABILITY. It is extremely stable to most reagents. Thus strong oxidising agents like potassium permanganate and chromic acid, alkalis, concentrated nitric and sulphuric acids have no action on ethane.

(2) HALOGENATION. Ethane reacts with chlorine in diffused daylight when all the 6 H-atoms are replaced in turn by chlorine atoms yielding a mixture of various chloro-derivatives.

(*i*) $$\underset{\text{Ethane}}{CH_3.CH_3} + Cl_2 \longrightarrow \underset{\text{Ethyl chloride}}{CH_3.CH_2.Cl}$$

(*ii*) $$CH_3.CH_2Cl + Cl_2 \longrightarrow \underset{\text{Ethylene chloride}}{CH_2Cl.CH_2Cl} + HCl$$

(also) $$\longrightarrow \underset{\text{Ethylidene chloride}}{CH_3CHCl_2} + HCl$$

The final product of chlorination is hexachloroethane, C_2Cl_6. Bromine reacts with ethane much less readily giving similarly bromo substitution products. It is difficult to replace more than two H-atoms from the molecule by bromine. Iodine does not react with ethane.

(3) NITRATION. Ethane reacts with nitric acid vapour at 400°C to form nitroethane.

$$\underset{\text{Ethane}}{C_2H_5}\boxed{H + HO}NO_2 \xrightarrow{400^\circ} \underset{\text{Nitroethane}}{C_2H_5NO_2} + H_2O$$

Some nitromethane is also produced by cleavage of the carbon bonds at elevated temperature.

(4) OXIDATION. Ethane burns in air or oxygen with a slightly luminous flame, yielding carbon dioxide and water.

$$\underset{\text{Ethane}}{2C_2H_6} + 7O_2 \longrightarrow 4CO_2 + 6H_2O + 736\cdot8 \text{ Cals.}$$

Thus like methane it forms expl
On incomplete combustion in air, ethane forms acetald
later decomposes by heat giving formaldehyde, carbon dioxide and water.

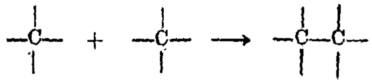
(5) THERMAL DECOMPOSITION. Ethane when heated in the absence of oxygen and in the presence of a catalyst at 450°C, dehydrogenates to produce ethylene.

$$\underset{\text{Ethane}}{CH_3.CH_3} \xrightarrow[\text{Cat.}]{450^\circ} \underset{\text{Ethylene}}{CH_2{=}CH_2} + H_2$$

Uses. Ethane does not find many uses in industry. It is, however, the more luminous constituent of natural gas and coal gas. Since it produces considerable heat on burning, ethane is also used for melting purposes.

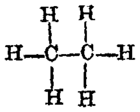
Structure. (1) From elementary analysis and the determination of its molecular weight by combustion methods, ethane has been shown to possess the molecular formula C_2H_6.

(2) Since ethane does not give addition and oxidation reactions characteristic of unsaturated hydrocarbons, it has no double or triple bond in the molecule. This suggests that the two carbon atoms in it are linked through a single valency bond as follows :



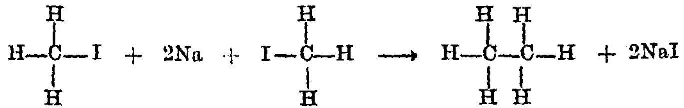
$$-\overset{|}{\underset{|}{C}}- + -\overset{|}{\underset{|}{C}}- \longrightarrow -\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-$$

(3) Now, there are six hydrogen atoms to be attached and there are also six free valencies in the above skeletal formula of ethane. Hence the only possible structure for ethane is



$$H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-H$$

(4) The structural formula of ethane has been confirmed by its synthesis from methyl iodide (*Wurtz Reaction*)



$$\underset{\text{Methyl iodide}}{H-\overset{H}{\underset{H}{C}}-I} + 2Na + I-\overset{H}{\underset{H}{C}}-H \longrightarrow \underset{\text{Ethane}}{H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-H} + 2NaI$$

(5) The orbital structure of ethane molecule has already been describ on page 73. Since each carbon atom is linked to four other atoms, it must l in sp^3 state of hybridisation with four bonding orbitals directed in spa towards the corners of a regular tetrahedron. One such orbital of each of t two carbon atoms is used in forming σ bond between them while the rest th orbitals overlap with *s* orbitals of hydrogen atoms to construct the eth molecule.

From electron diffraction and spectro scopic measurements it has revealed that in ethane molecule the bond angles H—C—H are equ

109° 28′; C—H length 1·10Å; C—C length 1·5Å. The geometry of the molecule is indicated by the following diagram.

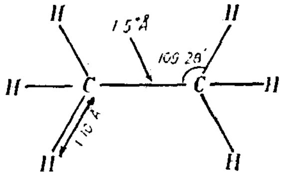


Fig. 10·5. The geometry of Ethane molecule.

PROPANE, C_3H_8

It occurs dissolved in petroleum in small amounts and is, therefore, obtained in the gaseous fractions during petroleum distillation. It can be prepared by the action of metallic sodium upon a mixture of methyl iodide and ethyl iodide.

$$CH_3I + 2Na + IC_2H_5 \longrightarrow \underset{\text{Propane}}{CH_3.C_2H_5} + 2NaI$$

This synthesis of propane also proves its constitution. Propane prepared in this way contains ethane and butane as impurities. Pure propane may be obtained by the action of zinc-copper couple on propyl iodide.

$$\underset{\text{n-Propyl iodide}}{CH_3CH_2CH_2I} + 2H \longrightarrow \underset{\text{Propane}}{CH_3CH_2CH_3} + HI$$

Properties. It is a colourless and odourless gas which can be condensed to liquid at —44·5°C. It is insoluble in water. It exhibits the same inertness in chemical reagents as is shown by other alkanes. On chlorination it yields two isomeric monohalogen derivatives.

$$\underset{\text{n-Propyl chloride}}{CH_3CH_2CH_2Cl} \qquad \underset{\text{Isopropyl chloride}}{CH_3.CHCl.CH_3}$$

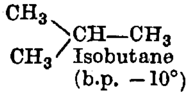
according as chlorine is attached to the end carbon atom or to the middle one.

Uses. It is used as a fuel and as a refrigerant in the petroleum industry.

BUTANES, C_4H_{10}

There are two isomeric hydrocarbons known which have the molecular formula C_4H_{10}.

$$\underset{\text{(b.p. +1°)}}{\underset{\text{n-Butane}}{CH_3.CH_2.CH_2.CH_3}}$$



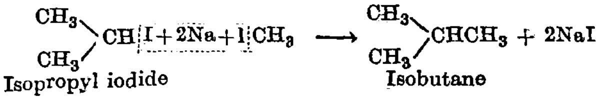
$$\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!CH—CH_3$$

Isobutane
(b.p. −10°)

Both these hydrocarbons are present dissolved in natural petroleum and are obtained along with methane, ethane and propane, during its distillation. They can be prepared by the action of sodium on appropriate alkyl halides (*Wurtz reaction*).

$$CH_3CH_2CH_2\boxed{I+2Na+I}CH_3 \longrightarrow CH_3CH_2CH_2CH_3 + 2NaI$$

n-Propyl iodide n-Butane



$$(CH_3)_2CH\boxed{I+2Na+I}CH_3 \longrightarrow (CH_3)_2CHCH_3 + 2NaI$$

Isopropyl iodide Isobutane

In their chemical behaviour they resemble other alkanes.

Both the hydrocarbons are gases which can readily be converted into liquid form. The liquefied hydrocarbons are stored in cylinders and used as gaseous fuel.

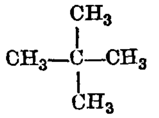
PENTANES, C_5H_{12}

There are three isomeric pentanes known :

$CH_3.CH_2.CH_2.CH_2.CH_3$ n-Pentane (b.p. 30°)

$$(CH_3)_2CH.CH_2.CH_3$$

Isopentane (b.p. 28°)



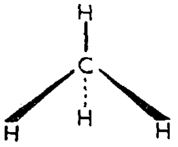
$$CH_3-C(CH_3)_2-CH_3$$

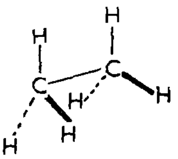
Neopentane (b.p. 9°)

Normal and isopentanes occur in petroleum. Their chemical behaviour is marked by the usual inertness. They are stable to acids, alkalis or oxidising agents. They react with chlorine and bromine forming substitution products.

CONFORMATIONS

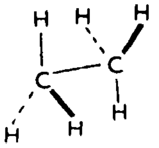
Using the tetrahedral arrangement of the carbon bonds, proposed by Le Bel and van't Hoff and established by the orbital theory, the stereochemistry of organic molecules presents certain interesting aspects of their structures. We have seen that the valency bonds about a saturated carbon atom are all at an angle 109° 28′ to each other. The sigma bond joining the two carbon atoms is cylindrically symmetrical about the nuclear axis (a line joining the two carbon nuclei). The symmetry of the bond permits free rotation about the bond axis without rupture. The three dimensional models of methane and ethane could be represented as follows :





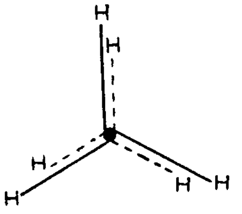
(a) Eclipsed form

The methane molecule can have only one shape as shown above, but in ethane molecule, the atoms can be arranged in different ways without breaking any bond and keeping the valency angles unchanged. These different molecular arrangements are made possible only due to free rotation of the molecule about the single bond (σ) joining the two carbon atoms. Thus another possible form of ethane molecule is as follows :

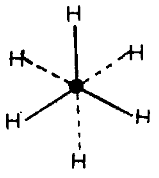


(b) Staggered form

The two formulae for ethane as viewed along the carbon-carbon bond axis, would appear as :



(a) Eclipsed form



(b) Staggered form

These two represenations are called **Newman projections** where the thick black dot represents the two carbons (the front carbon eclipsing the second carbon lying exactly behind it) ; the full lines – the C—H bonds of front carbon, and the dotted lines... the bonds between hind carbon and its hydrogen atoms. In (b) the hydrogen atoms of the nearer methyl group are seen exactly between those of farther away methyl group. With hydrogen atoms lying completely staggered, this form is often called **Staggered form**. In (a) the hydrogen atoms of one carbon lie exactly opposite to the hydrogen atoms of the other, eclipsed in a way. This arrangement is often referred to as **Eclipsed form**. These two forms have maximum diversity in regard to the position of hydrogen atoms of the two carbon atoms. As free rotation about the single bond is allowed, it will be observed for ethane, that an infinite number of different arrangements are possible depending upon the angular relationship between the hydrogens on each carbon. *All such spatial arrangements of the atoms of a given molecular structure that are obtained merely by rotation about a σ bond in the molecule are called* **Conformations** *of the molecule.*

The conformations of a compound possess identical physical character but differ in their energy content. If we consider the conformations of ethane molecule, it will be observed that in the eclipsed form the H-atoms on the two carbons are closer together than in any other possible conformation. The H-atoms on the two carbons though not linked directly, exert repulsive forces on one another. The closer the H-atoms, the greater will be the repulsion. It is, therefore, evident that a greater repulsive force operates in the eclipsed form than in the staggered one. As a result *the staggered conformations will be more stable energetically than the eclipsed conformation.* It is illustrated by the following graph depicting the energy of the molecule against the degree of rotation about the C—C bond.

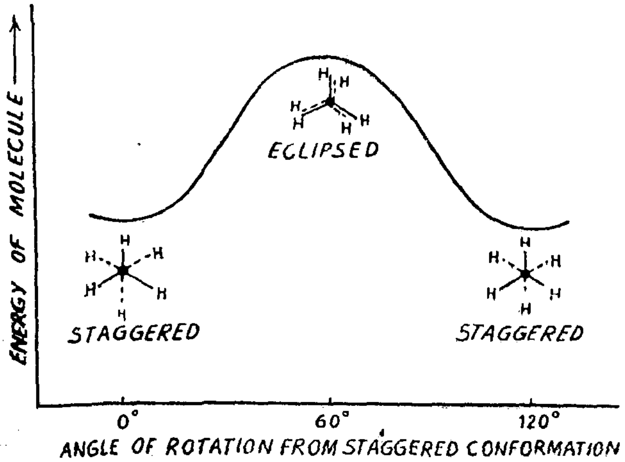
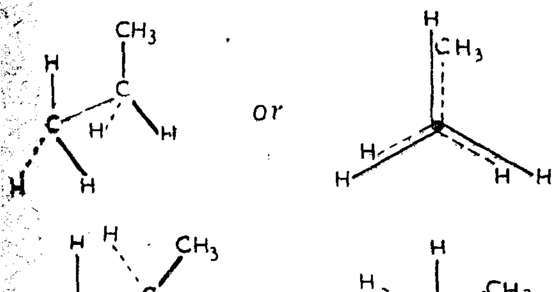


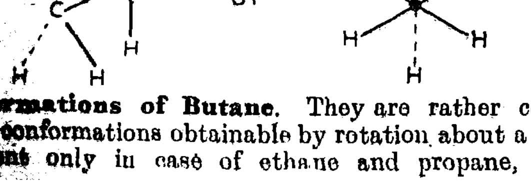
Fig. 10·6. Degree of Rotation from the staggered form and energy of the molecule of ethane.

It is thus clear that of all the conformations of ethane molecule, the staggered one possesses the least energy, maximum stability and thus is the most favoured conformation. The energy difference between the eclipsed and the staggered conformation is nearly equal to 3Kcal./mole. In an attempt to pass the staggered conformation into the eclipsed one, the energy cliff of 3 Kcal./mole has got to be reached which is, therefore, regarded as the potential energy barrier to exercise free rotation in the molecule.

Conformations of Propane In conformations of propane molecule, a situation identical with ethane molecule obtains except that one of the H-atoms is replaced by a methyl group. The two extreme conformations —the eclipsed and the staggered conformations are shown by the formulae (*a*) and (*b*) respectively.

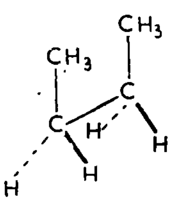


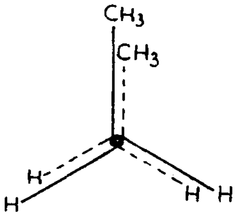
...(*a*)



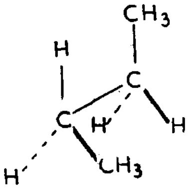
...(*b*)

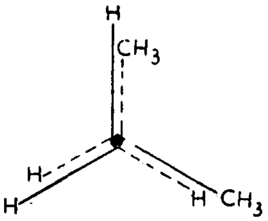
Conformations of Butane. They are rather complicated. All eclipsed conformations obtainable by rotation about a C—C bond are equivalent only in case of ethane and propane, whereas in butane molecule there are two distinct eclipsed conformations ; one in which two methyl groups are eclipsed by methyl groups and the other in which the methyl groups are eclipsed by hydrogen atoms.





...(a)

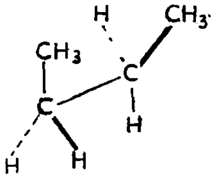




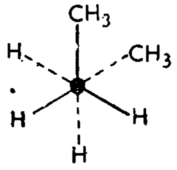
...(b)

Of these two eclipsed conformations, the one having larger methyl groups eclipsing (*a*), will naturally experience more repulsive forces than the one where a methyl group is faced with a H-atom (smaller than methyl group). Thus (*a*) conformation is naturally more favoured form from stability standpoint.

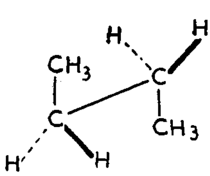
In likewise fashion, it will be observed that the two different staggered conformations are possible. In (*a*) the methyl groups are at an angle of 60° to each other and is called **skew** or **gauche conformation.**



or



...(a)



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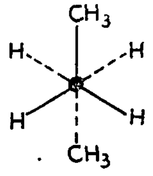
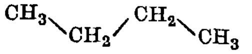


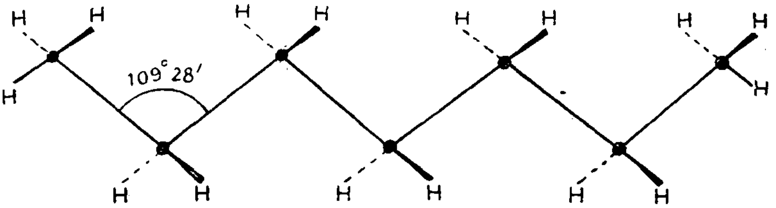
...(b)

The second staggered conformation (*b*), having an angle 180° between the methyl groups is called **transoid** or **anti conformation**. The repulsive forces will be greater in the conformation (*a*) than in conformation (*b*) due to the proximity of the methyl groups in the former. Consequently the conformation (*b*) is associated with the least energy and maximum stability. Hence most of the molecules of butane will take up the staggered conformation (*b*). In fact this molecule presents a zig-zag form as most of the saturated aliphatic molecules are known to possess.



$$\mathrm{CH_3\diagdown CH_2\diagup CH_2\diagdown CH_3}$$

Thus for reasons of stability as described above the long chain aliphatic molecules assume a similar zig-zag shape.



n-Heptane molecule.

Infrared Spectra of Alkanes. The alkanes show characteristic infrared spectra which are helpful in determining their structure. For example, the infrared spectrum of normal hexane indicates that there is maximum absorption (or minimum transmittance) at the wave number 2882—2940 and 1370—1452 which correspond to the presence of —C—H and C—C bonds.

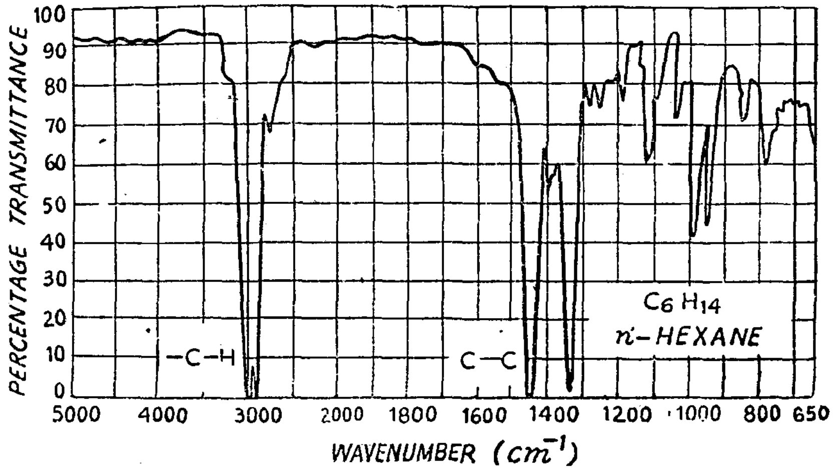


Fig. 10·7. Infrared spectrum of n-Hexane.

PETROLEUM OR MINERAL OIL

Huge deposits of liquid alkanes are found under the earth's crust in certain parts of the world. When freshly obtained from this source, the oily liquid is called Petroleum (*petra*=rock+*oleum*= oil) or **Crude oil.** The United States of America is the biggest oil producing country and has for many years produced about two-third of the world's output. Other great producers of crude oil are Venezuela, Russia, Indonesia, Mexico, etc. but the greatest reserves are found in the Arab countries of the Middle East.

Table—*Production of Crude Petroleum (1966)*

COUNTRY	'000 TONS	COUNTRY	'000 TONS
United States	403,702	Iraq	66,680
U.S.S.R.	263,570	Canada	42,856
Venezuela	173,172	Indonesia	23,150
Saudi Arabia	117,569	Mexico	17,700
Kwait	112,500	China	8,500
Iran	98,820	India	4,647
Libya	71,100	Pakistan	500

Nature has not been favourable to India in the distribution of oil and our resources so far discovered are inadequate indeed. The search of new oil fields is vigorously going on in India and the Oil Gas Commission set up by the Union Government has achieved some fruitful results. The yield of crude oil from oil fields in Assam has been stepped up and oil has been struck at Cambay (Bombay) and Ankleshwar (Gujarat). There are signs of the occurrence of petroleum in Kangra Valley but drilling at Jwalamukhi has proved futile. The oil fields at Cambay and Ankleshwar have started yielding handsome quantities of crude oil.

The Standard Vacuum Co of America, the Burma Shell of the U.K. and Caltex of America have set up refineries for the imported crude oil (largely from Middle East). Indian Oil Corporation also has recently started the marketing of Indian oil on a big scale.

On the whole, since 1963 the Petroleum Industry in India has grown considerably as shown by the figures in the following table. The total crude oil refined in 1967 was 14,430,000 tons which nearly meets the consumption of the country.

Table—*Growth of Petroleum Industry in India*

YEAR	PRODUCTION OF CRUDE OIL '000 TONS	REFINERIES CRUDE CHARGE '000 TONS	CONSUMPTION '000 TONS
1963	1,652	8,138	10.347
1964	2,212	8,932	11,361
1965	3,022	9,754	12,279
1966	4,647	12,030	12,968
1967	5,667	14,430	14,084

However, with the growing automobile industry, the aeroplanes, the tanks and the tractors, the demand of India for petroleum will be ever on the increase. In the interest of our national development, we must strive to achieve petroleum self-sufficiency by stepping up crude oil production from our own sources.

COMPOSITION OF PETROLEUM

Petroleum is essentially a mixture of the alkane hydrocarbons which are present in it right from methane up to the higher members containing as many as thirty-five carbon atoms. It also contains varying amounts of aromatic hydrocarbons and cycloalkanes. The actual composition of the oil, however, varies with the place of origin. Besides the various types of hydrocarbons there are present in petroleum organic compounds containing nitrogen and sulphur. Most of the natural oils are found to be optically active.

Since petroleum has entirely different composition from that of the vegetable and animal oils, to differentiate it from them it is commonly called *mineral oil*. This name points to its origin in mines.

At some places in America, the crude oil is accompanied by large volumes of a gas commonly known as **Natural gas**. This gas consists chiefly of methane, ethane and propane, along with small amounts of other hydrocarbons.

ORIGIN OF PETROLEUM IN NATURE

Many theories have been put forward to explain the formation of petroleum in nature. Of these, the more important are :

(1) **Carbide Theory.** This theory was originally suggested by Mendeleeff and supported by Moissan, Sabatier and Senderens. It regards petroleum as of inorganic origin being formed by the action of steam or water on metallic carbides in the inner portion of earth's crust. The Carbide theory describes the formation of petroleum by the following steps.

(*i*) *Formation of Carbides.* The molten metals in the hot interior of the earth came in contact with coal and carbides were formed. Thus :

$$4Al + 3C \longrightarrow \underset{\text{Aluminium carbide}}{Al_4C_3}$$

$$Ca + 2C \longrightarrow \underset{\text{Calcium carbide}}{CaC_2}$$

(*ii*) *Action of Steam with Carbides.* Carbides reacted with steam under high pressure and at high temperature forming hydrocarbons.

$$Al_4C_3 + 12H_2O \longrightarrow 4Al(OH)_3 + \underset{\text{Methane}}{3CH_4}$$

$$CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + \underset{\text{Acetylene}}{C_2H_2}$$

(*iii*) *Reduction of Unsaturated Hydrocarbons.* The unsaturated hydrocarbons formed by step (*ii*) are reduced with hydrogen in the presence of metallic catalyst at high temperature.

$$C_2H_2 + H_2 \longrightarrow \underset{\text{Ethylene}}{C_2H_4}$$

$$\underset{}{C_2H_4} + H_2 \longrightarrow \underset{\text{Ethane}}{C_2H_6}$$

The hydrogen needed for reduction is obtained by the action of hot metals with steam.

(*iv*) *Polymerisation.* Unsaturated hydrocarbons polymerised in the presence of hot metals forming aromatic hydrocarbons, cycloalkanes, and higher open-chain hydrocarbons.

$$\underset{\text{Acetylene}}{3CH : CH} \longrightarrow \underset{\text{Benzene}}{C_6H_6}$$

$$\underset{\text{Ethene}}{2CH_2 : CH_2} \longrightarrow \underset{\text{2-Butene}}{CH_3CH : CHCH_3}$$

$$\underset{\text{Ethene}}{3CH_2 : CH_2} \longrightarrow \underset{\text{Cyclohexane}}{(CH_2)_6}$$

2-Butene will again be hydrogenated forming butane.

There is no doubt that the Carbide theory explains the formation of petroleum in a rational way but there are serious objections against it and at present this theory commands little consideration. The two main facts which go against it are :

(*a*) *Natural petroleum contains sulphur and nitrogen compounds, chlorophyll, haemin, etc* The Carbide theory fails to explain their presence in petroleum as they are all essentially of organic origin.

(*b*) *Petroleum contains optically active compounds.* According to the Carbide theory, the natural mode of formation of petroleum is a strict laboratory one and we know that we cannot get optically active substances by ordinary synthetic methods in the laboratory.

(2) **Engler's Theory.** Engler (1900) discovered that by the destructive distillation of fish-blubber, a product exactly similar to natural petroleum could be obtained. It contained sulphur and nitrogen compounds commonly found in petroleum, and was also optically active. This affords a direct experimental evidence of the production of petroleum from sea animals by some natural process akin to destructive distillation. This can happen if, say, there is a volcano by the sea-side. The volcanic gases contain sulphur dioxide which dissolves in sea-water. Thus fish and other sea animals coming towards this region would die there of suffocation. In due course of time a huge accumulation of dead animals formed in this

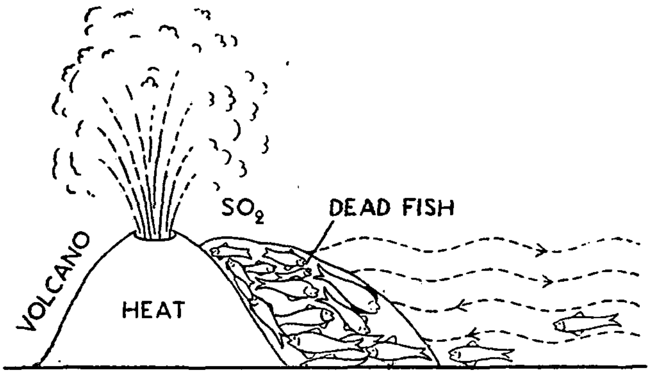


Fig. 10·8. Formation of petroleum from sea animals.

way would be covered by earth's crust. Under the influence of heat from the volcano, decomposition sets in, which ultimately results in a petroleum deposit.

Another fact that lends weight to Engler's theory is that mineral oil is always found in company with salt and brine which must have been obtained from sea-water.

(3) **Modern Views.** It has been described above that petroleum is very probably of animal origin. The presence of compounds which are derived from haemin, the pigment of the red blood corpuscles, and the discovery of fossils in petroleum areas are enough proof to support this theory.

Many oils contain compounds derived from chlorophyll, the green of the plants, thus pointing to the vegetable origin of petroleum. May be that some upheaval brought a forest well under the earth's crust whereby the action of heat and water, the plants were converted to petroleum. This view is supported by the fact that coal is found in the neighbourhood of oil deposits. The high resin content of Burma oil is also accounted for by the vegetable origin of the oil.

In face of the above evidence, it appears very likely that while some oils are of animal origin, there are others of vegetable origin.

Astronomers have recently established that the atmosphere of the large planets Jupiter and Saturn consists chiefly of methane. This has led to the idea that at one time our earth's crust also contained huge quantities of methane. Since methane is converted to higher hydrocarbons by the action of ultra-violet rays and radio-active rays, it has been conjectured that radio-active substances in the earth's crust may have transformed methane into petroleum. The fact that helium, which is a disintegration product of radio elements, is often present in natural gas issuing in petroleum areas lends support to this view.

PETROLEUM MINING

Petroleum usually occurs at moderate depths sometimes 5,000 feet or more deep. The oil is found in porous strata beneath the impervious rock (Fig. 10·9). It is often associated with *natural gas* which exerts pressure on the oil surface and drives it out with great velocity through natural openings.

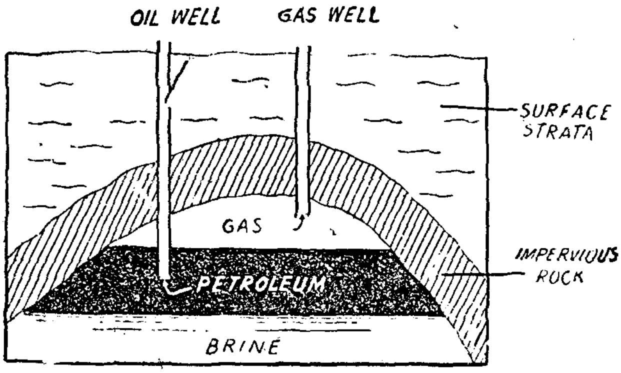


Fig. 10·9. Occurrence and mining of petroleum.

In case of artificial mining, mines are bored in the upper crust. When the oil pocket is pierced, the gas pressure forces the oil out. As the gas pressure subsides or when there is no gas, air pressure is applied to raise the oil from the well.

The oil obtained from the mine is conveyed by a system of pipe-lines to a distant place and distilled. The distillation is not carried out on the spot so that the inflammable *natural gas* or other dissolved gases may not catch fire and thus damage whole mine.

PETROLEUM REFINING

Petroleum as it comes from the ground is a rather viscous and highly coloured liquid. It often possesses unpleasant odour which is largely due to the presence of sulphur compounds in it. Technically, it is called **Crude Oil**.

Crude oil consists chiefly of mixtures of alkanes boiling between a wide range, say 0° and 400°, and as such it is unsuitable for most technical purposes. If, however, the oil is subjected to fractional distillation, it can be separated into a number of fractions each of which has a technical name and finds use in industry. The process of dividing petroleum into fractions with different boiling ranges and free from undesirable impurities, is termed **Refining**.

The distillation of petroleum is carried in a tubular furnace with a tall steel fractionating column (bulb). The crude oil is pumped continuously through heated pipes and flashed into the fractionating column. The vapours of the oil as they rise up the fractionating column become cooler and condense at the shelves at various heights. The highest boiling fraction condenses, at the bottom and the lowest boiling fraction at the top. The uncondensed gases escape along with the gasoline vapours at the head of the column. Outlets are provided in the side of the column at suitable heights to withdraw a number of fractions, the actual number of fractions and their boiling point ranges depending on the source of the petroleum and the trade demand. In the following table are used the details of the fractions commonly separated in modern practice. The main fractions are written in bold type and the 'sub-fractions' obtained from them by refractionation are given in small type. According to the most recent processes, the lubricating oil is now obtained from the residual oil by vacuum distillation.

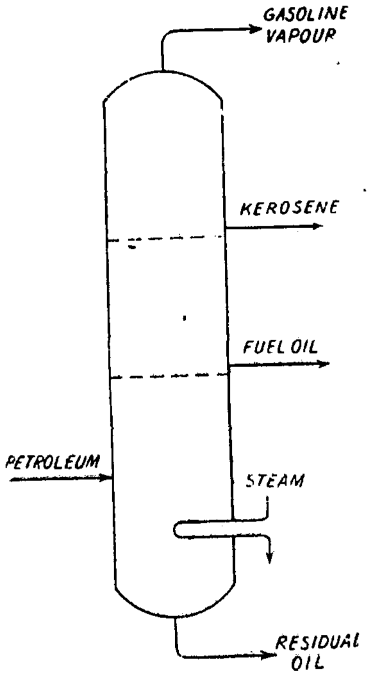


Fig. 10·10. Flowsheet of petroleum refining.

Name	Boiling Range°C	Composition	Uses
1. Gases	Upto room temperature	C_4—C_5	Fuel gas,
2. Gasoline—Refractionated to yield :	40—200	C_5-C_{11}	
(*i*) Petroleum ether	40—80	...	Solvent
(*ii*) Gasoline or Petrol	80—200	...	Motor fuel ; solvent ; dry-cleaning
3. Kerosene	200—300	$C_{11}-C_{16}$	Illuminant ; fuel for stoves ; for making oil gas
4. Gas oil or Fuel oil	Above 300	$C_{16}-C_{18}$	Fuel for diesel engines ; for conversion to gasoline by cracking.
5. Residual oil Refractionated under vacuum to give :	Above 400	...	
(*i*) Lubricating oil	...	$C_{17}-C_{20}$	Lubrication.
(*ii*) Paraffin Wax	...	$C_{20}-C_{30}$	Ointments ; candles ; toilets ; vaseline ; wax paper
(*iii*) Residue : (Asphalt and pitch)	...	...	Paints ; road surfacing.

The above method of refining of petroleum is called the *Straight run process* and the various fractions thus obtained are termed '*Straight run oils*'.

In order to secure a higher yield of petrol or gasoline, the higher boiling straight run " '*Gas oil*' or '*Residual oil*' are cracked and simultaneously fractionally distilled. The catalytic cracking is more modern and efficient. The process is used in preference to the simple *Thermal Cracking*. The stock is charged into the '*Reactor*' containing the catalyst at elevated temperature. The vapours of the cracked stock then pass to the fractionating unit and the products are : (*i*) cracked gasoline and ; (*ii*) cracked fuel oil.

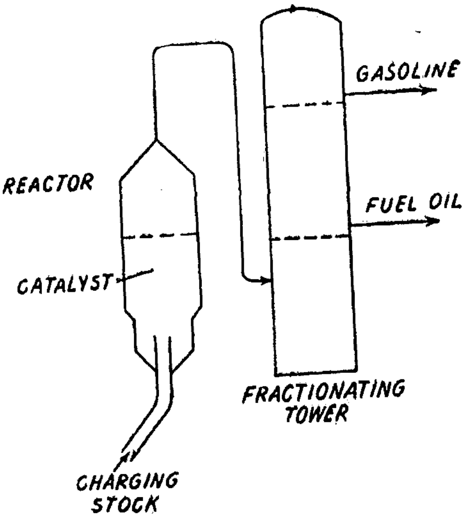


Fig. 10·11. Catalytic cracking process.

WHAT IS CRACKING ?

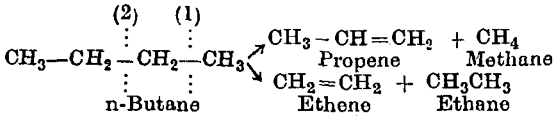
When liquid alkanes are heated under pressure, they are decomposed to give hydrocarbons of lower molecular weights which are more volatile. The products contain both alkanes and alkenes.

Thus :

$$\underset{\text{b.p. }216^\circ}{C_{12}H_{26}} \xrightarrow{700^\circ} \underset{\text{b.p. }98^\circ}{C_7H_{16}} + \underset{\text{b.p. }36^\circ}{C_5H_{10}}$$

This process of getting lower boiling hydrocarbons from higher boiling hydrocarbons by the application of heat is called **Cracking**.

The term cracking (*crack*= to break) is very descriptive of what happens when the molecules of hydrocarbons are heated to a high temperature. The kinetic energy of molecules increases and as a result they move faster, strike harder and are subject to more intense internal vibrations. These results of increased kinetic energy overcome some of the chemical bonds holding the atoms together, and the molecule may literally be said to have 'cracked' into simpler parts. This rupture of the molecule is accompanied by a redistribution of valencies and readjustment of some of the hydrogen atoms, resulting in the formation of lower hydrocarbons. The mechanism of the process of cracking may be illustrated by the decomposition of n-butane at 600°



$$\underset{\text{n-Butane}}{CH_3{-}CH_2\overset{(2)}{\vdots}CH_2\overset{(1)}{\vdots}CH_3} \begin{array}{l} \nearrow \underset{\text{Propene}}{CH_3-CH{=}CH_2} + \underset{\text{Methane}}{CH_4} \quad \ldots(1) \\ \searrow \underset{\text{Ethene}}{CH_2{=}CH_2} + \underset{\text{Ethane}}{CH_3CH_3} \quad \ldots(2) \end{array}$$

It is obvious that the carbon chain 'cracks' at positions (1) and (2), and the redistribution of valencies and hydrogen atoms in each case produces one alkane and one akene.

Actually the 'cracking reactions' are never clear-cut and the splitting of the molecules may take place at many points, yielding a number of small fragments, including alkanes, hydrogen and the carbon.

Applications of Cracking. The process of cracking has become very important on account of its useful applications.

(1) PREPARATION OF OIL GAS. Kerosene oil is cracked by pouring dropwise into a red-hot *iron retort*. It is thus converted into gaseous hydrocarbons (methane, ethane, ethene, hydrogen, etc.), which are mixed with a large amount of volatile, tarry matter. The cracked products are bubbled through water in the *hydraulic syphon* where the tar vapours are condensed and removed. The gas thus obtained, commonly named as **Oil Gas**, is then stored in an iron *gas holder* over water and conveyed to the laboratory through a pipe line. The burning oil gas is a very convenient and suitable agency of heating in the laboratory.

(2) PREPARATION OF PETROL GAS. *Petrol* can be converted into permanent gaseous hydrocarbons by cracking. This is done by passsng the petrol vapour through electrically heated coils or by heating it in a closed retort. The preparation of petrol gas is con-

venient as compared to that of oil gas, and the initial cost of the plant is low.

(3) 'Cracked Gasoline' from 'Residual oil' or 'Gas oil'. As mentioned earlier, the less useful fractions of petroleum, *viz.*, the

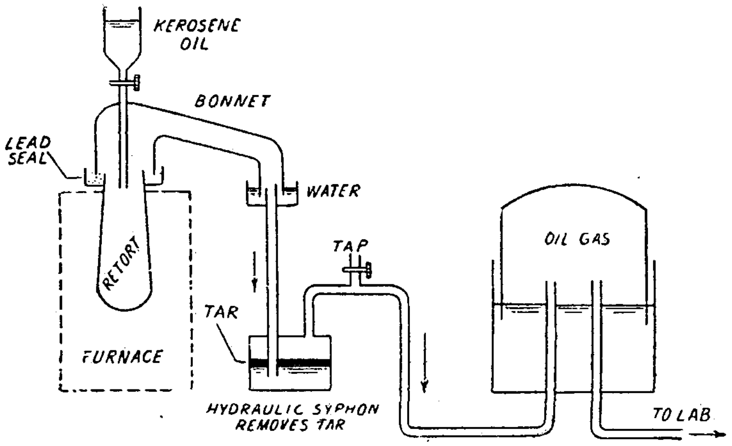


Fig. 10·12. Manufacture of oil gas for laboratory use.

Residual oil (Heavy oil) or the Gas oil are cracked with or without a catalyst at elevated temperature. The higher boiling hydrocarbons are thus split out into lower ones which constitute 'cracked gasoline.' The increased demand of motor fuel has been greatly met by this method.

SYNTHETIC PETROL

.With the extraordinary development of the automobile and *aeroplane* industry the world's demand for petrol has increased enormously. In spite of the great number of oil-fields which have been discovered, our supply of petrol is inadequate. The increasing demand for petrol has been largely shouldered by the introduction of cracking methods and actually more petrol is now obtained by cracking than in the original petroleum distillation process. But that is no satisfaction as the world's oil supply cannot last indefinitely.

In a country like India with practically no oil fields so far, we are immediately confronted with the problem of 'synthetic petrol'. To recoup from the aftermath of past slavery and then to rise again to occupy a respectable position in the comity of nations India must have enough of the motor fuel. Petrol has soon got to be produced somehow and it is left to the chemist to accomplish the task. The situation, however, is not so pessimistic as it seems to be. We can certainly count on our vast coal fields for a supply of the synthetic product. Already, the work on production of the fuel oil from this source has progressed enough in countries like U.K. and Germany. The chief methods of preparing 'Synthetic Petrol' are given below :

(1) **Bergius Process.** In this method, finely powdered coal

and a suitable catalyst is made into a paste with *Heavy oil* produced in the process. The coal paste is then preheated and pumped to the *converter*. Here the paste is heated to 450° and hydrogen bubbled through it at 250 atmos. pressure. The coal, which is really a mixture of high molecular complex organic compounds deficient in hydrogen, and elementary carbon, combines with hydrogen to form higher saturated compounds. These as a result of cracking and simultaneous hydrogenation yield mixtures of alkanes. Thus the vapours leaving the *converter* upon condensation yield 'Synthetic Petroleum' or *Crude oil*. This crude oil upon fractional distillation produces :

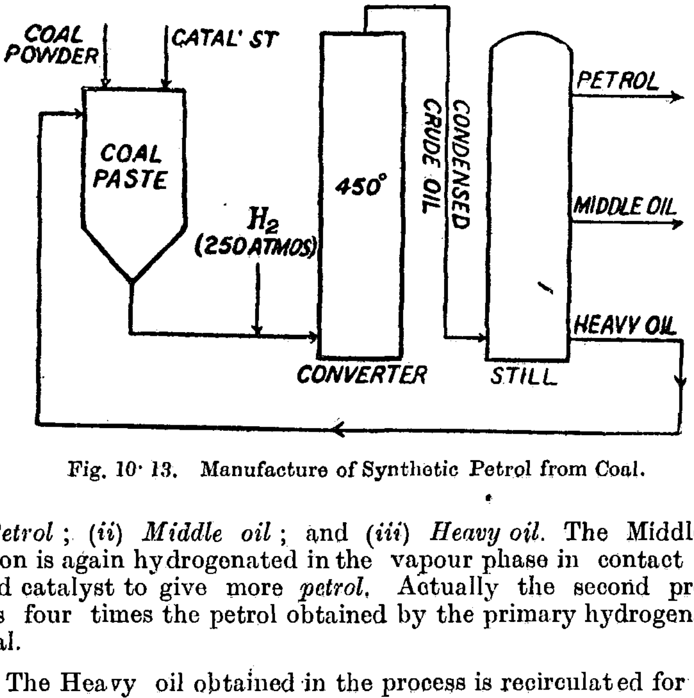


Fig. 10· 13. Manufacture of Synthetic Petrol from Coal.

(*i*) *Petrol* ; (*ii*) *Middle oil* ; and (*iii*) *Heavy oil*. The Middle oil fraction is again hydrogenated in the vapour phase in contact with a solid catalyst to give more *petrol*. Actually the second process yields four times the petrol obtained by the primary hydrogenation of coal.

The Heavy oil obtained in the process is recirculated for making fresh coal paste. One ton of soft coal treated as above yields 140 gallons of petrol. The Bergius process is at present the most promising of all methods so far invented for the production of synthetic motor fuel.

(2) **Fischer-Tropsch Process** (*Reduction of Carbon monoxide*). This method was given in 1923 by two German chemists, Franz Fischer and Hans Tropsch. Carbon monoxide needed in this process is made by passing steam over red-hot 'coke'. The water gas thus obtained is mixed with hydrogen and passed at a pressure of 5-10 atmospheres into a chamber containing a 'cobalt catalyst' at 200°C. The product is a mixture consisting mainly of liquid hydrocarbons.

$$n\text{CO} + (2n+1)\text{H}_2 \longrightarrow \underset{\text{Alkane}}{\text{C}_n\text{H}_{n+2}} + n\text{H}_2\text{O}$$

The 'artificial petroleum' so obtained is separated by fractional distillation as described under the Bergius Process. The various fractions separated are petrol, kerosene oil, lubricating oil, diesel oil and paraffin wax. Germany employed this method for producing 'artificial petroleum'; the annual output exceeding 1,000,000 tons. The Fischer-Tropsch Process has also a bright future in India.

The Fischer-Tropsch Process is now also worked in the United States. Here, the carbon monoxide-hydrogen mixture is obtained by the oxidation of natural gas by oxygen.

$$\underset{\text{Methane}}{2CH_4} + 3O_2 \longrightarrow 2CO + 4H_2O$$

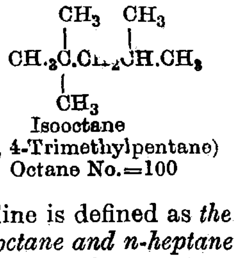
WHAT IS MEANT BY OCTANE NUMBER ?

The structure of a hydrocarbon determines its efficiency in an automobile engine. The straight chain alkanes are very poor fuels and cause the engine to 'knock', while the use of branched-chain hydrocarbons and alkanes eliminates the knocking considerably.

The knocking quality of an automobile fuel is measured in term of the so-called *'Octane Number'*. The hydrocarbon *'isooctane'* (2, 2, 4-trimethylpentane), which was found to be free from knocks in highest compression motors was arbitrarily given an 'octane number' of 100, whereas n-heptane, which knocked badly, was rated at 0.

$CH_3.CH_2.CH_2.CH_2.CH_2.CH_2.CH_3$

n-Heptane
Octane No.=0



$$CH_3.\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}.CH_2.\overset{\overset{CH_3}{|}}{C}H.CH_3$$

Isooctane
(2, 2, 4-Trimethylpentane)
Octane No.=100

The **Octane Number** of a gasoline is defined as *the percentage of isooctane present in a mixture of isooctane and n-heptane, when the mixture has the same knocking performance in the experimental engine as the gasoline under examination.*

Thus a motor fuel is said to have an octane number of 80 when it is as good as a mixture of 20 per cent n-heptane and 80 per cent isooctane. The higher the octane-number, the better the gasoline. Commercial gasolines have octane numbers 81, 74, and 65 for the *premium*, *regular*, and *third grade* gasolines.

The modern cracking methods of producing gasoline not only increase its yield but also give better quality of fuel having higher octane number. This is so because during cracking of petroleum, alkanes are formed which also undergo isomerization, polymerisation, etc. to give branched-chain hydrocarbons. Other methods of raising the octane number of a poor fuel are *'alkylation'*, *'reforming'*, *'hydroforming'* etc., the discussion of which is beyond the scope of this book. The addition of tetraethyl lead also improves the anti-knocking character of gasoline.

FLASH POINT

Kerosene oil is used in lamps for illuminating purposes. The burning oil should not be sufficiently volatile at ordinary temperatures, otherwise its vapours would form explosive mixtures with air and thus making its use in lamps a source of danger. Just a lighted match-stick or a smouldering cigarette-end if thrown into the oil godown might put the whole stock on fire. To ensure safety, the government of every country requires that only those oils should be used which do not give enough vapours at a certain minimum temperature. This temperature which is commonly known as the **Flash Point** or the **Ignition temperature** may be defined as :

The minimum temperature at which an oil gives off enough vapours to form a momentary flash of light when a naked flame is brought near its surface.

The ignition temperature of an oil depends on the proportion of volatile hydrocarbons present in it. An oil used in cold climates must necessarily be 'low boiling' and the one used in tropical climates must be 'high boiling'. Thus the flash point fixed in cold countries is low, while in hot countries it is high.

Determination of Flash point. The flash point of an oil is usually determined by means of ABEL'S APPARATUS a modified form of which is shown in Fig. 10·13. A beaker is fitted with a cork having a big hole in its centre. A thermometer and two platinum electrodes are fitted through the cork so that their tips are about 5—10 mm. apart just above the oil. The bulb of the thermometer should be kept dipped in the oil. The beaker containing the whole arrangement is then fixed in a water-bath as shown in the diagram. The central cork is covered with a watch-glass or a thin glass-plate. The temperature of the bath is now gradually raised and sparks are sent across the electrodes by connecting them with an induction coil and accumulator. Just when the temperature of the oil reaches the flash point, the watch glass or the plate is lifted by an explosion. The temperature shown by the inner thermometer at this point is recorded.

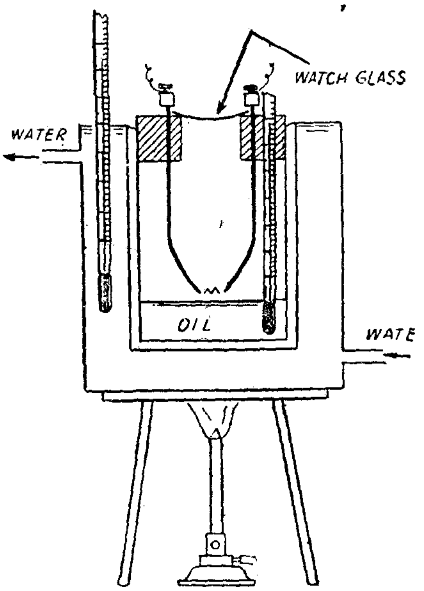


Fig. 10·13. Abel's apparatus.

PETROCHEMICAL INDUSTRY

A recent development of the petroleum industry is the manufacture of a large number of chemicals. In fact, petroleum is today the biggest and the cheapest source of organic compounds.

In the last decade or so, variety of useful organic compounds have been prepared from alkanes and alkenes obtained from natural gas and petroleum. These are known as **Petrochemicals** and include halogen and nitro-compounds, alcohols, aldehydes, ketones acids and their derivatives. The alkenes produced in enormous volumes by cracking of petroleum, in particular, form excellent raw materials for numerous compounds.

Alkanes and alkenes upon reaction with halogens give numerous halogen derivatives both by substitution and addition reactions. Vapour-phase nitration of alkanes yields nitroalkanes. Controlled oxidation of alkanes gives alcohols, aldehydes and acids. The oxidation of paraffin wax gives higher acids which are further used for the manufacture of soaps and artificial fats. Very recently it has been possible to convert n-hexane and n-heptane to benzene and toluene respectively by aromatisation. Thus petroleum is beginning also to compete with coal-tar as a source of aromatic hydrocarbons.

Table—*Compounds obtained from Hydrocarbons of Petroleum*

HYDROCARBONS	COMPOUNDS OBTAINED
1. Methane	Methyl chloride, Methylene chloride, Chloroform, Methanol, Farmaldehyde, Acetylene
2. Ethane	Ethyl chloride, Acetic acid, Nitroethane, Ethane.
3. Ethylene	Ethanol, Ethylene oxide, Ethylene glycol, Ethylene chlorohydrin. Ethylene chloride, Vinyl chloride, Butadiene.
4. Propane	Nitromethane, Nitroethane, Nitropropane, Propene, Propanol, Propionic acid.
5. Propene	Allyl chloride, Allyl alcohol, Glycerol.
6. Butene	Butyl alcohol, Butadiene.
7. n-Hexane	Benzene, Gammexane ($C_6H_6Cl_6$), D.D.T.,
8. n-Heptane	Toluene.

The compounds listed above in turn serve as raw material for many more derivatives. At present about 200 aliphatic and aromatic compounds are prepared from petroleum and the petrochemical industry is developing rapidly in America.

QUESTIONS

I. ALKANES

1. What are saturated hydrocarbons ? Why are they so called ? What reactions are typical of this series of hydrocarbons.

2. Describe the important methods of preparing methane. Give an account of its properties showing clearly thereby why it is called a 'saturated hydrocarbon.'

3. What is chain isomerism ? How many isomeric pentanes are possible ? Give their names and structural formulas.

4. Give the general methods of formation of alkanes.

5. How is it that while chlorination and bromination in alkanes proceeds fairly readily, their direct iodination is not possible ? Describe conditions under which the iodo derivatives of alkanes can be obtained.

6. Describe the laboratory preparation and properties of ethane. How has its structure been arrived at ?

7. Give three general methods for the preparation of the hydrocarbon of the general formula C_nH_{2n+2}. Give the structural formulae of the two isomeric butanes. What reactions would you expect to result from gently heating paraffin wax with bromine ?

8. Outline the methods available for the preparation of saturated aliphatic hydrocarbons and review their chemical properties. *(Mysore B.Sc., 1968)*

II. PETROLEUM

9. Describe the occurrence, composition and probable origin of natural petroleum. Give an outline in brief, of the method of treatment of the crude product and indicate the main applications of the derived materials.

10. What are the main products of distillation of crude petroleum ? How are they obtained ? State their uses. What do you understand by the cracking of petroleum ?

11. Give an account of the modern petroleum industry. How are the different products obtained from petroleum utilised in art and industries ?

12. Write an essay on petroleum and the various products obtained from it. What theories have been advanced to account for the occurrence of petroleum ?

13. Mention briefly some of the methods of obtaining synthetic petroleum.

14. Name some important substances obtainable today from natural petroleum. From what other sources, and how is petroleum obtainable ?

15. What are the uses of petrol ? Describe the different methods of producing it on a commercial scale.

16. Define *Flash Point*. How can it be determined ?

17. Give a short description of petroleum industry also mentioning briefly some important methods for obtaining synthetic petroleum.

18. Describe briefly 'Petroleum refining'. Explain the basis of the statement by a distinguished statesman that "Who has oil has empire".

19. Write a note on the use of petroleum for the manufacture of chemicals.

20. What are the theories put forward to explain the formation of petroleum in nature ? Write a note on cracking and on flash point.
(Banaras B.Sc. I, 1963)

21. Write a short note on petroleum industry with special reference to the methods of obtaining petrol. Explain the terms :

(1) Cracking, (2) Octane value, (3) Reforming. *(Vikram B.Sc., 1963)*

22. Petrol obtained from 'Petroleum' is insufficient to meet the world's requirements of today. What chemical methods are employed now-a-days to produce petrol artificially to meet the growing demands of the present age? How is the anti-knocking property of a fuel improved? (*Allahabad B.Sc., 1967*)

23. Write a short note on Synthetic Petrol.
(*J. & K., Udaipur. Gorakhpur, B.Sc., 1967*)

24. Write an essay on: "The industrial importance of a Petroleum Refinery" (*Ceylon B.Sc., 1961*)

25. Name the fractions obtained by the fractional distillation of crude petroleum with the percentage yield of each product. Give the boiling range of each fraction and mention its uses. (*Panjab B.Sc., 1968*)

26. Write an essay on Petroleum industry. (*Udaipur B.Sc., 1969*)

27. (*a*) Describe the different theories that have been put forward on the origin of petroleum.

(*b*) Give an account of the methods employed for the production of synthetic petrol. (*Kurukshetra B.Sc., 1969*)

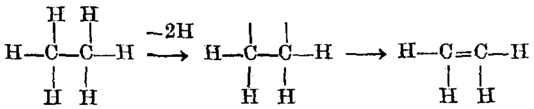
11

Alkenes

Paul Sabatier
(1854—1941)

French Chemist. He won the Nobel Prize in 1912 for his work in catalytic hydrogenation of hydrocarbons and other organic compounds.

The members of this class of hydrocarbons contain two hydrogen atoms less than the corresponding alkanes. The two valency bonds left free on the adjacent carbon atoms unite to form a second union between them, establishing a double bond in the molecule.



$$H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-H \xrightarrow{-2H} H-\underset{H}{\overset{|}{C}}-\underset{H}{\overset{|}{C}}-H \longrightarrow H-\underset{H}{C}=\underset{H}{C}-H$$

Ethane Ethylene

Since all the valencies of the carbon atoms in alkenes are not fully satisfied, they can take up more H-atoms and are called **Unsaturated hydrocarbons**.

The hydrocarbons of this class are frequently called **Olefines** (*Olefiant*=oil forming) as the first member of the class, ethylene reacted with chlorine to form an oily product.

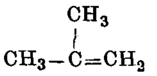
They are also called **Ethylenic hydrocarbons** after the first hydrocarbon of the class, ethylene. The modern IUPAC class name **Alkenes** *is now used in preference.*

Alkenes being much more reactive than alkanes, seldom occur free in nature. They are, however, produced in large amounts during the cracking of petroleum and the decomposition of almost all organic substances. The cracking of cotton seed oil gives as much as 30 per cent yield of ethylene. The lower alkenes occur to a minor extent in coal gas.

NOMENCLATURE

There are three ways of naming alkenes :

(1) The COMMON NAMES of the first four members (C_2 to C_5) are derived from those of the corresponding alkanes (having same No. of carbons) by changing the ending *-ane* to *-ylene*. Thus :

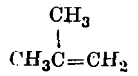
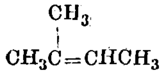
$CH_2{=}CH_2$	Ethylene (Ethane — ane + ylene)
$CH_2{=}CHCH_3$	Propylene
 $CH_3-\overset{\overset{CH_3}{\vert}}{C}{=}CH_2$	Isobutylene
$CH_2{=}CHCH_2CH_3$	α-Butylene
$CH_3CH{=}CHCH_3$	β-Butylene
$CH_2{=}CHCH_2CH_2CH_3$	Pentylene or Amylene

Greek letters are used to distinguish isomers having double bond at the first (α) or the second (β) carbon of the chain as illustrated above for butylenes.

The common names of certain radicals derived from these hydrocarbons are listed below :

$CH_2{=}CH$:	Vinyl
$CH_2{-}CHCH_2$—	Allyl
$CH_3CH{=}CH$—	Propenyl
$-CH_2$—	Methylene
$CH_2\ CH_2$--	Ethylene

(2) The ETHYLENE-SUBSTITUTED SYSTEM. According to this system which is no longer in common use, alkenes can be named as derivatives of ethylene ($CH_2{=}CH_2$) in which two or more hydrogen atoms have been substituted by alkyl groups. Thus :

$CH_3CH{=}CHCH_3$	sym-Dimethylethylene
 $CH_3\overset{\overset{CH_3}{\vert}}{C}{=}CH_2$	unsym-Dimethylethylene
 $CH_3\overset{\overset{CH_3}{\vert}}{C}{=}CHCH_3$	Trimethylethylene

The prefix sym- and unsym- in the above names are abbreviations of symmetrical and unsymmetrical.

(3) The IUPAC NAMES of alkenes are derived from those of the corresponding alkanes by changing the terminal *-ane* to *-ene*. Thus to get the name of an individual member, first name the alkane with the same number of carbon atoms and then replacing the ending -ane by-ene. Thus :

$CH_2{=}CH_2$	Ethene (Ethane – ane + ene)
$CH_3CH{=}CH_2$	Propene

For the first member the common name ethylene is also its IUPAC name while all other alkenes are assigned systematic names. The IUPAC names of higher alkenes are obtained as follows :

(1) The name of the hydrocarbon is based on the parent alkene having the longest carbon chain of which double bond is a part.

(2) This chain is numbered from the end near the double bond (=) and its position is indicated by the number of the carbon at which the double bond originates.

(3) The name of the parent alkene with the position number of the double bond is written first and then the names of the other substituents are prefixed to it.

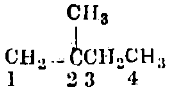
For illustration :

$\overset{4}{C}H_3\overset{3}{C}H_2\overset{2}{C}H{=}\overset{1}{C}H_2$

1-Butene

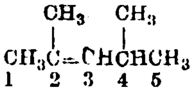
$\overset{1}{C}H_3\overset{2}{C}H{=}\overset{3}{C}H\overset{4}{C}H_3$

2-Butene



$\underset{1}{C}H_2{=}\underset{2}{C}(CH_3)\underset{3}{C}H_2\underset{4}{C}H_3$

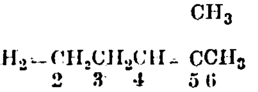
2-Methyl-1-Butene



$\underset{1}{C}H_3\underset{2}{C}(CH_3){=}\underset{3}{C}H\underset{4}{C}H(CH_3)\underset{5}{C}H_3$

2, 4-Dimethylpentene

When there are two or three double bonds in a molecule, the ending *-ane* of the respective alkane is replaced by *-adiene* or *-atriene* to get the name of the hydrocarbon. Thus



$\underset{1}{C}H_2{=}\underset{2}{C}H_2\underset{3}{C}H_2\underset{4}{C}H{=}\underset{5}{C}(CH_3)\underset{6}{C}H_3$

5-methyl-1, 4-hexadiene

Alkenyl radicals. The monovalent radicals obtained from alkenes are called alkenyl radicals. The common names vinyl radical and allyl radical are also the IUPAC names. All other alkenyl radicals are named by replacing the '*e*' of the parent alkene by '*-yl*.' The carbon atoms constituting the radical are numbered so that the carbon with free valency is always number 1. The IUPAC names of some alkenyl radicals are given below :

$CH_2{=}CH—$	Vinyl
$CH_2{=}CH—CH_2—$	Allyl (2-Propenyl)
$\overset{4}{C}H_3{=}\overset{3}{C}H\overset{2}{C}H_2\overset{1}{C}H_2—$	3-Butenyl
$CH_3CH{=}CHCH_2—$	2-Butenyl

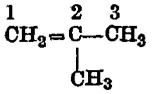
ISOMERISM

The presence of the double bond in alkenes increases the opportunity of isomerism. In addition to *chain isomerism*, they offer *position isomerism* due to the different positions of the double bond on the carbon chain.

The first two alkenes can have but one structural formula. The third member butene, however, can have three possible structural formulas.

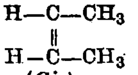
(1) $\overset{1}{CH_2}=\overset{2}{CH}-\overset{3}{CH_2}-\overset{4}{CH_3}$ 1-Butene

(2) $\overset{1}{CH_3}-\overset{2}{CH}=\overset{3}{CH}-\overset{4}{CH_2}$ 2-Butene

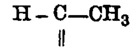
(3) 
$\overset{1}{CH_2}=\overset{2}{C}(CH_3)-\overset{3}{CH_3}$ 2-Methylpropene

All the three butenes are actually known. The compounds (1) and (2) present a case of *position isomerism* as they differ only in the location of the double bond. The compounds (2) and (3) illustrate both *position and chain isomerism*.

Besides the structural isomerism, certain alkenes also show *cis-trans isomerism*. Thus 2-Butene is known to exist in two forms.


$H-C-CH_3 \; \| \; H-C-CH_3$

(*Cis*)

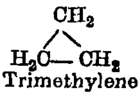

$H-C-CH_3 \; \| \; CH_3-C-H$

(*Trans*)

Alkene hydrocarbons are also isomeric with the corresponding members of another class of cyclic compounds, the *Polymethylenes*. Thus propene is isomeric with trimethylene.

$CH_3-CH=CH_2$

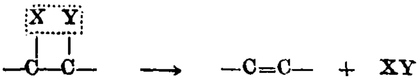
Propene


H_2C-CH_2 (bridged by CH_2)

Trimethylene

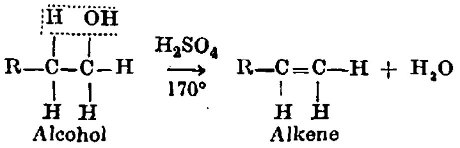
METHODS OF FORMATION

Most of the methods of preparation of alkenes depend upon the principle that the *removal of atoms or groups from adjacent carbon atoms of a chain results in the creation of a double bond.* For illustration,

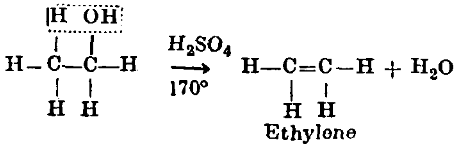

$-\overset{X}{C}-\overset{Y}{C}- \longrightarrow -C=C- + XY$

where X and Y may be same or different The general methods of formation of alkenes are :

(1) **By dehydration of alcohols.** When heated with a dehydrating agent like concentrated sulphuric acid or phosphoric acid, alcohols lose a molecule of water forming alkenes.



$$\mathrm{R{-}\overset{H}{\underset{H}{C}}{-}\overset{OH}{\underset{H}{C}}{-}H} \xrightarrow[170^\circ]{H_2SO_4} \mathrm{R{-}\underset{H}{C}{=}\underset{H}{C}{-}H} + H_2O$$



$$\mathrm{H{-}\overset{H}{\underset{H}{C}}{-}\overset{OH}{\underset{H}{C}}{-}H} \xrightarrow[170^\circ]{H_2SO_4} \mathrm{H{-}\underset{H}{C}{=}\underset{H}{C}{-}H} + H_2O$$

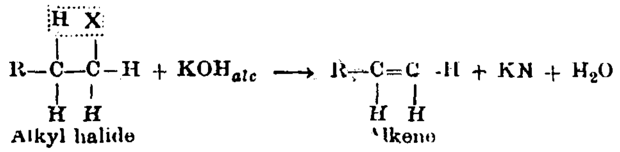
The alcohol first reacts with sulphuric acid to form the alkyl hydrogen sulphate which upon heating splits out a molecule of sulphuric acid to form alkene. Thus :

$$\underset{\text{Ethanol}}{C_2H_5OH} + \underset{\text{Sulphuric acid}}{H\,O.SO_3H} \longrightarrow \underset{\text{Ethyl hydrogen sulphate}}{C_2H_5O{\cdot}SO_3H} + H_2O$$

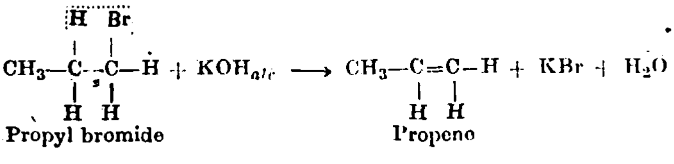
$$C_2H_5O.SO_3H \xrightarrow{170^\circ} \underset{\text{Ethylene}}{C_2H_4} + H_2SO_4$$

Alkenes can also be prepared by passing the vapour of alcohol over alumina (Al_2O_3) at 300°. Tertiary alcohols are dehydrated with greatest ease, and primary with greatest difficulty.

(2) **By dehydrohalogenation of alkyl halides.** When heated with alcoholic solution of potassium hydroxide (*alcoholic potash*), alkyl halides eliminate a hydrogen and halogen atom from adjacent carbon atoms to form alkenes.*



$$\mathrm{R{-}\overset{H}{\underset{H}{C}}{-}\overset{X}{\underset{H}{C}}{-}H} + KOH_{alc} \longrightarrow \mathrm{R{-}\underset{H}{C}{=}\underset{H}{C}{-}H} + KX + H_2O$$



$$\mathrm{CH_3{-}\overset{H}{\underset{H}{C}}{-}\overset{Br}{\underset{H}{C}}{-}H} + KOH_{alc} \longrightarrow \mathrm{CH_3{-}\underset{H}{C}{=}\underset{H}{C}{-}H} + KBr + H_2O$$

This is probably the most important method for preparing alkenes in the laboratory. In the preparation of alkenes from alkyl halides, as a rule, iodides are most reactive and chlorides least so.

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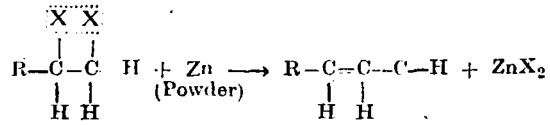
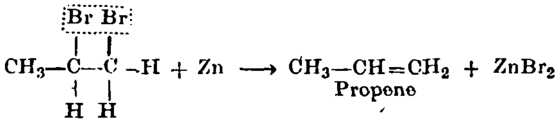
* A rule of thumb, *Saytzeff's Rule*, states that in the dehydration of alcohols or the dehydrohalogenation of alkyl halides, hydrogen atom is preferentially eliminated from the carbon atom with fewer number of hydrogen atoms.

(3) **By dehalogenation of dihaloalkanes with zinc.** When dihalogen derivatives of alkenes having the two halogen atoms on adjacent carbons are heated with an active metal like zinc, the latter removes the halogen atoms to form alkenes.

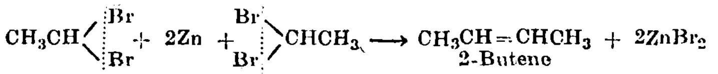


$$\underset{\text{Dihaloalkane}}{R-\overset{X}{\underset{H}{C}}-\overset{X}{\underset{H}{C}}-H} + \underset{\text{(Powder)}}{Zn} \longrightarrow \underset{\text{(Alkene)}}{R-\underset{H}{C}=\underset{H}{C}-H} + ZnX_2$$



$$\underset{\text{1, 2-dibromopropane}}{CH_3-\overset{Br}{\underset{H}{C}}-\overset{Br}{\underset{H}{C}}-H} + Zn \longrightarrow \underset{\text{Propene}}{CH_3-CH=CH_2} + ZnBr_2$$

When the two halogen atoms are attached to the same carbon, zinc eliminates four halogen atoms from two molecules of the dihaloalkene. Thus :



$$\underset{\text{Ethylidene bromide}}{CH_3CH\begin{smallmatrix}Br\\Br\end{smallmatrix}} + 2Zn + \begin{smallmatrix}Br\\Br\end{smallmatrix}CHCH_3 \longrightarrow \underset{\text{2-Butene}}{CH_3CH=CHCH_3} + 2ZnBr_2$$

(4) **By partial hydrogenation of alkynes.** The alkyne mixed with hydrogen gas is passed over finely divided platinum or palladium, or heated nickel, when it adds only two H-atoms to give alkene.

$$\underset{\text{Alkyne}}{RC\equiv CH} + H_2 \xrightarrow[\textit{heat}]{Ni} \underset{\text{Alkene}}{RCH=CH_2}$$

$$\underset{\substack{\text{1-Butyne}\\ \text{(Ethylacetylene)}}}{CH_3.CH_2C\equiv CH} + H_2 \xrightarrow[\textit{heat}]{Ni} \underset{\text{1-Butene}}{CH_3.CH_2.CH=CH_2}$$

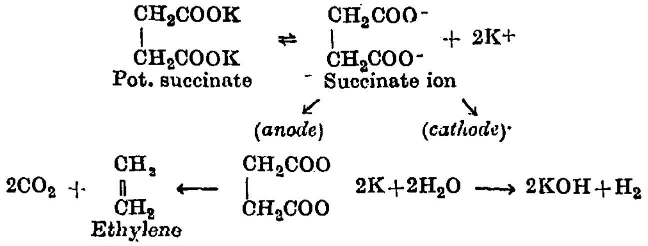
(5) **By Cracking.** The higher alkanes when heated to a high temperature decompose to give a lower alkene along with a lower alkane.

$$\underset{\text{Higher alkane}}{R'.CH_2.CH_2.R} \xrightarrow{\textit{Cracking}} \underset{\text{Alkene}}{R'HC=CH_2} + \underset{\text{Alkane}}{RH}$$

$$\underset{\text{n-Butane}}{CH_3.CH_2.CH_2.CH_3} \xrightarrow{\textit{Cracking}} \underset{\text{Propene}}{H_3C.CH=CH_2} + CH_4$$

The first three alkenes are thus obtained by the cracking of the petroleum hydrocarbons.

(6) **By Electrolysis of salts of dicarboxylic acids.** Alkenes are formed by the electrolysis of aqueous solutions of potassium salts of dibasic acids of the succinic acid series. Thus :



$$\begin{array}{c} CH_2COOK \\ | \\ CH_2COOK \end{array} \rightleftharpoons \begin{array}{c} CH_2COO^- \\ | \\ CH_2COO^- \end{array} + 2K^+$$

Pot. succinate   Succinate ion

(*anode*)   (*cathode*)

$$2CO_2 + \begin{array}{c} CH_2 \\ \| \\ CH_2 \end{array} \longleftarrow \begin{array}{c} CH_2COO \\ | \\ CH_2COO \end{array} \qquad 2K + 2H_2O \longrightarrow 2KOH + H_2$$

Ethylene

This reaction is, in fact, an extension of Kolbe's method for the preparation of alkanes and is seldom used in actual practice as the product obtained is not pure.

PHYSICAL CHARACTERISTICS

In general, alkenes resemble alkanes in their physical properties.

(1) The first three alkenes — ethene, propene, and butenes— are gases at ordinary temperature ; the next fourteen members are liquids ; and the hydrocarbons with more than 18 carbon atoms in the molecule are solids. They are all colourless and odourless except ethene which has a rather pleasant odour.

(2) They are a little less volatile than the corresponding alkanes. Their boiling and melting points are slightly higher than those of alkanes containing the same number of carbon atoms.

(3) They are only slightly soluble in water but dissolve freely in organic solvents.

(4) The lower alkenes are powerful general anaesthetics.

(5) Their boiling points, melting points, and specific gravities, in general, rise with increase of molecular weight in the homologous series. The physical constants of the first few straight-chain hydrocarbons are given in the table below :

NAME	FORMULA	M.P. °C	B.P. °C	SP. GR. 20°/4
Ethene	$CH_2=CH_2$	—169	—104	0·570
Propene	$CH_2=CH.CH_3$	—185	—98	0·610
1-Butene	$CH_2=CH.CH_2.CH_3$	—139	—5	0·625
1-Pentene	$CH_2=CH.(CH_2)_2CH_3$	—138	40	0·641
1-Hexene	$CH_2=CH.(CH_2)_3CH_3$	—98	64	0·673
1-Heptene	$CH_2=CH.(CH_2)_4CH_3$	—120	95	0·697
1-Octene	$CH_2=CH.(CH_2)_5CH_3$	—102	122	0·715
1-Nonene	$CH_2=CH.(CH_2)_6CH_3$	...	150	0·732
1-Decene	$CH_2=CH.(CH_2)_7CH_3$	—87	172	0·742

CHEMICAL CHARACTERISTICS

The molecule of an alkene (other than ethylene) consists of two parts :

(*a*) *an alkyl group*, R ; and

(*b*) the *alkene part* or group containing the doubly bonded carbon atoms.

$R— \vdots CH=CH_2$
Alkyl group ⋮ Alkene part

While the alkyl group is marked by the usual stability of alkanes and can give substitution reactions with difficulty, the alkene part is unusually reactive on account of the presence of the double bond in it. According to the classical Baeyer's Strain theory, the molecule at the double bond is under strain as the two valency bonds of each of the two carbon atoms are displaced from their normal directions.

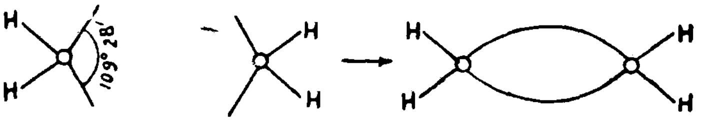
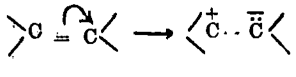


Fig. 11·1. In ethylene the normal bond angle of 109°28′ is reduced to 0° after the formation of double bond and this displacement of bond direction causes strain.

The alkene molecule at the double bond being under strain tends to shake off this strain and hence exhibits unusual chemical reactivity.

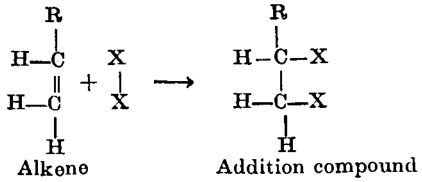
The greater reactivity of alkenes than alkanes can also be explained with the help of the modern orbital concept of bonding. On account of the presence of a weaker π bond in their molecules as against stronger σ bonds in alkanes, the former are unusually reactive. The electrons of the π bond are not held so firmly between the two C-atoms as the electrons of the σ bond. The π electrons are quite mobile and this lends the double bond a property of polarisability. In presence of the attacking reagent, the alkene molecule undergoes electromeric effect whereby a pair of electrons (π electrons) get transferred to one of the two C-atoms. Thus a negative charge is produced on one carbon and a positive charge on the other.



The molecule thus develops charged centres by virtue of which it is readily attacked by various reagents.

In general, alkenes give the following types of reactions.

(*i*) ADDITION REACTIONS. In these reactions, the reagent adds along the double bond which is then converted to a single bond



(*ii*) Oxidation Reactions. The double bond being a weak spot in the molecule is readily attacked by strong oxidising agents. The molecule of an alkene is, therefore, oxidised at this point, giving two simple oxidation products which may be aldehydes, ketones or fatty acids.

(*iii*) Substitution Reactions. The alkyl group is capable of undergoing substitution reactions and one or more hydrogen atoms in it may be replaced by monovalent atoms or groups. For example, it can be chlorinated easily. The alkene part of the molecule does not give substitution reactions.

(*iv*) Polymerisation. The valency bonds constituting the double bond are not in a stable condition. They become all the more labile at high temperature. Thus many molecules of an alkene may join together to form compounds of higher molecular weights.

The general reactions of alkenes are given below.

(1) **Addition of Hydrogen.** When the vapours of an alkene mixed with hydrogen are passed over finely divided nickel at high temperature, it adds a molecule of hydrogen at the double bond giving alkane. Thus :

$$\underset{\text{Alkene}}{RCH{=}CH_2} + H_2 \xrightarrow[\textit{heat}]{\text{Ni}} \underset{\text{Alkane}}{RCH_2.CH_3}$$

$$\underset{\text{Ethylene}}{CH_2{=}CH_2} + H_2 \xrightarrow[\textit{heat}]{\text{Ni}} \underset{\text{Ethane}}{CH_3.CH_3}$$

$$\underset{\text{Propene}}{CH_3CH{=}CH_2} + H_2 \xrightarrow[\textit{heat}]{\text{Ni}} \underset{\text{Propane}}{CH_3CH_2CH_3}$$

This reaction known as *hydrogenation* is characteristic of all organic compounds containing double bonds. It can also be carried by passing hydrogen through the alcoholic solution of an alkene containing suspended platinum or palladium as catalyst at ordinary temperature.

(2) **Addition of Halogens.** Alkenes react readily with halogens by addition, forming dihalogen derivatives.

$$RCH{=}CH_2 + X_2 \longrightarrow \underset{\text{1, 2-Dihaloalkane}}{RCHX.CH_2X}$$

$$\underset{\text{Ethylene}}{CH_2{=}CH_2} + Cl_2 \longrightarrow \underset{\text{Ethylene chloride}}{CH_2Cl.CH_2Cl}$$

$$\underset{\substack{\text{Propene}\\ \text{(Propylene)}}}{CH_3.CH{=}CH_2} + Cl_2 \longrightarrow \underset{\substack{\text{1, 2-dichloropropane}\\ \text{(Propylene chloride)}}}{CH_3.CHCl.CH_2Cl}$$

In these reactions, chlorine is the most reactive and iodine least so.

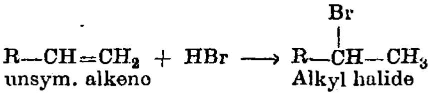
The mechanism of addition of halogens has already been discussed in Chapter 8.

(3) **Addition of Halogen acids.** Addition of halogen acids to alkenes gives alkyl halides.

$$\underset{\text{Alkene}}{R.CH{=}CH.R} + HBr \longrightarrow \underset{\text{Ethyl bromide}}{R.CH_2.CHBr.R}$$

$$\underset{\text{Ethylene}}{CH_2{=}CH_2} + HBr \longrightarrow \underset{\text{Ethyl bromide}}{CH_3CH_2Br}$$

The addition of halogen acids to unsymmetrical alkenes is governed by Markownikoff's Rule.



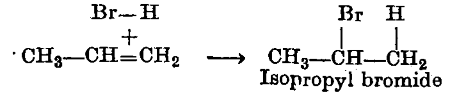
$$\underset{\text{unsym. alkene}}{R{-}CH{=}CH_2} + HBr \longrightarrow \underset{\text{Alkyl halide}}{R{-}\overset{\overset{\displaystyle Br}{|}}{C}H{-}CH_3}$$

$$\underset{\text{Propene}}{CH_3{-}CH{=}CH_2} + HBr \longrightarrow \underset{\text{Isopropyl bromide}}{CH_3{-}CHBr{-}CH_3}$$

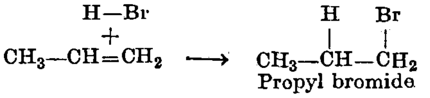
The order of reactivity of halogen acids is $HI > HBr > HCl$.

Markownikoff's Rule. The addition of halogen acids to an unsymmetrical alkene is governed by an empirical rule proposed by Markownikoff in 1870. In fact, it is a general rule and explains admirably the course of addition of any unsymmetrical reagent (HCl, HBr, HI, H_2SO_4, $HOCl$ etc.) to a double bond of an unsymmetrical alkene.

When HBr is added to a propene molecule, the reaction can take place in two ways.



$$CH_3{-}\overset{\overset{Br-H}{+}}{CH{=}CH_2} \longrightarrow \underset{\text{Isopropyl bromide}}{CH_3{-}\overset{\overset{\displaystyle Br}{|}}{C}H{-}\overset{\overset{\displaystyle H}{|}}{C}H_2} \qquad (A)$$



$$CH_3{-}\overset{\overset{H-Br}{+}}{CH{=}CH_2} \longrightarrow \underset{\text{Propyl bromide}}{CH_3{-}\overset{\overset{\displaystyle H}{|}}{C}H{-}\overset{\overset{\displaystyle Br}{|}}{C}H_2} \qquad (B)$$

On analysis, it is found that the reaction (A) dominates and very small quantity of propyl bromide is formed.

Markownikoff studied several such addition reactions and ultimately succeeded in framing a general rule to predict the direction of addition of halogen halides and such other reagents to unsymmetrical alkenes. This rule which bears his name will be stated as :

"The negative part of the molecule adding to the double bond goes to that carbon atom which is linked to the least number of hydrogen atoms."

The Markownikoff's rule has proved very useful to foretell the products of addition reactions when both the joining molecules happen to be unsymmetrical in nature. It is amazing that an empirical rule as this has stood gallantly the onslaughts of the modern theories and stands as firm today as a century back.

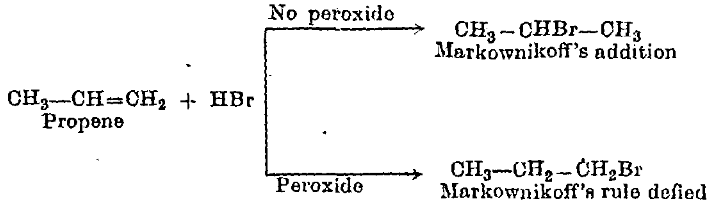
Let us examine the mechanism of the addition of HBr to $R-CH=CH_2$. In presence of the attacking polar reagent (HBr), the double bond in the alkene molecule experiences an electromeric effect. The alkyl radical being electron-releasing in nature regulates the direction of electron displacement as shown below :

$$R \rightarrow CH = CH_2 \xrightarrow[\text{effect}]{\text{Electromeric}} R-\overset{+}{C}H-\overset{-}{C}H_2$$

$$R-\overset{+}{C}H-\overset{-}{C}H_2 \xrightarrow{\overset{+}{H}-\overset{-}{Br}} R-\overset{+}{C}H-CH_2 + \overset{-}{Br}$$
$$\longrightarrow R-CHBr-CH_3$$

Markownikoff's rule is indeed quite general but certainly not universal. It must be clearly understood that in higher alkenes both the modes of addition (A and B) are simultaneously taking place. Under ordinary conditions, the first reaction (A) predominates but it is possible that under a different set of conditions the other reaction (B) may gain prominence.

Krash has actually shown that in the presence of oxygen or peroxides as catalysts, the addition of HBr to propene takes a course opposite to that predicted by Markownikoff's rule. This effect caused by the presence of peroxide is called *"peroxide effect"*. Thus :



No peroxide $\rightarrow$ $CH_3-CHBr-CH_3$ Markownikoff's addition

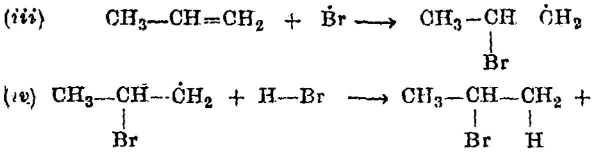
$CH_3-CH=CH_2 + HBr$ Propene

Peroxide $\rightarrow$ $CH_3-CH_2-CH_2Br$ Markownikoff's rule defied

Also, when the reactants are exposed to ultraviolet light, the addition defies the Markownikoff's rule. This suggests a 'free radical mechanism' of peroxide-initiated addition of HBr. The various steps are :

(*i*) Peroxide $\longrightarrow$ F· (free radical)

(*ii*) $F\cdot + H-Br \longrightarrow F:H + \dot{B}r$



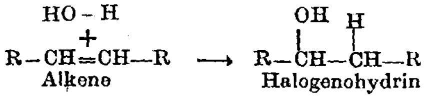
(*iii*) $CH_3-CH=CH_2 + \dot{B}r \longrightarrow CH_3-\underset{\displaystyle Br}{\underset{|}{C}H}\ \dot{C}H_2$

(*iv*) $CH_3-\underset{\displaystyle Br}{\underset{|}{C}H}-\dot{C}H_2 + H-Br \longrightarrow CH_3-\underset{\displaystyle Br}{\underset{|}{C}H}-\underset{\displaystyle H}{\underset{|}{C}H_2} + \dot{B}r$

This is a chain reaction involving the repetition of steps (*iii*) and (*iv*). This differs from the chain reaction of halogenation of alkanes in that it involves 'addition' rather than 'substitution' The fact that a very small quantity of peroxide changes the orientation of addition is amply borne out by the above 'chain mechanism'.

Strangely enough, the additions of HCl, HI, HF are not affected by the presence of peroxides. This anomaly is explained by the difficulty to generate $\dot{F}$ and $\dot{Cl}$ free radicals from their hydrides by step (*i*). Although $\dot{I}$ is readily obtained, it is by no way sufficiently reactive (probably due to a bigger size) to initiate a chain reaction.

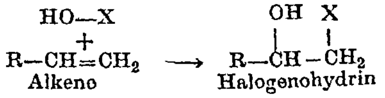
(4) **Addition of Hypohalous acids**. Hypochlorous acid, and to a less extent hypobromous acid, reacts with alkenes to form halogenohydrins.



$$\underset{\text{Alkene}}{R-CH=CH-R} + HO-H \longrightarrow \underset{\text{Halogenohydrin}}{R-\overset{OH}{\overset{|}{C}}H-\overset{H}{\overset{|}{C}}H-R}$$

$$\underset{\text{Ethylene}}{CH_2=CH_2} + HOCl \longrightarrow \underset{\text{Ethylene chlorohydrin}}{CH_2OH.CH_2Cl}$$

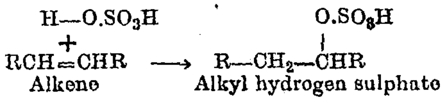
In hypohalous acids, the halogen is positive relative to (OH) group and thus the addition to unsymmetrical alkene would take place as



$$\underset{\text{Alkene}}{R-CH=CH_2} + HO-X \longrightarrow \underset{\text{Halogenohydrin}}{R-\overset{OH}{\overset{|}{C}}H-\overset{X}{\overset{|}{C}}H_2}$$

$$\underset{\text{Propylene}}{CH_3-CH=CH_2} + HOCl \longrightarrow \underset{\text{Propylene chlorohydrin}}{CH_3-CH(\quad -CH_2Cl}$$

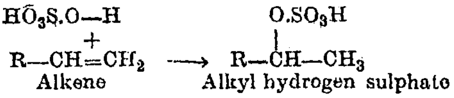
(5) **Addition of Sulphuric Acid**. Alkenes react with concentrated sulphuric acid to form alkyl hydrogen sulphates.



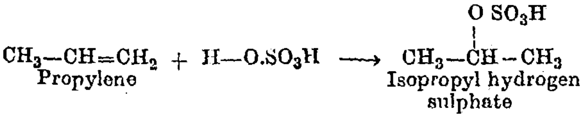
$$\underset{\text{Alkene}}{RCH=CHR} + H-O.SO_3H \longrightarrow \underset{\text{Alkyl hydrogen sulphate}}{R-CH_2-\overset{O.SO_3H}{\overset{|}{C}}HR}$$

$$\underset{\text{Ethylene}}{CH_2=CH_2} + \underset{\text{Sulphuric acid}}{H-O.SO_3H} \longrightarrow \underset{\text{Ethyl hydrogen sulphate}}{CH_3-CH_2.O.SO_3H}$$

Addition of sulphuric acid to unsymmetrical alkenes takes place according to Markownikoff's Rule.

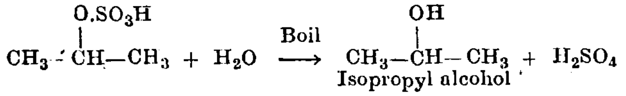


$$\underset{\text{Alkene}}{R-CH=CH_2} + HO_3S.O-H \longrightarrow \underset{\text{Alkyl hydrogen sulphate}}{R-\overset{O.SO_3H}{\overset{|}{C}}H-CH_3}$$



$$\underset{\text{Propylene}}{CH_3-CH=CH_2} + H-O.SO_3H \longrightarrow \underset{\text{Isopropyl hydrogen sulphate}}{CH_3-\overset{O\,SO_3H}{\overset{|}{C}}H-CH_3}$$

The alkyl hydrogen sulphate on boiling with water decompose to form an alcohol and sulphuric acid.



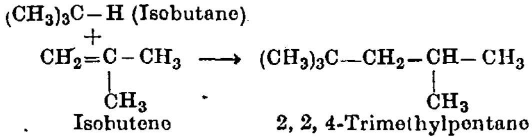
$$CH_3-\underset{}{\overset{O.SO_3H}{\overset{|}{C}H}}-CH_3 + H_2O \xrightarrow{\text{Boil}} CH_3-\overset{OH}{\overset{|}{C}H}-CH_3 + H_2SO_4$$

Isopropyl alcohol

Thus alkenes can be easily converted to alcohols by teatment with sulphuric acid and subsequent hydrolysis. Large quantities of alcohols are now produced from alkenes obtained from cracked petroleum.

(6) **Alkylation**. The addition of alkanes to alkenes is carried in the presence of an acid catalyst (HF, $AlCl_3$,H_2SO_4, etc.)

Thus :



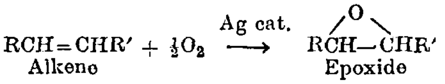
$$(CH_3)_3C-H \text{ (Isobutane)} + CH_2=\underset{CH_3}{\underset{|}{C}}-CH_3 \longrightarrow (CH_3)_3C-CH_2-\underset{CH_3}{\underset{|}{C}H}-CH_3$$

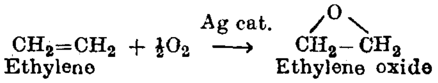
Isobutene 2, 2, 4-Trimethylpentane

The above reaction termed "Alkylation" of alkenes, has proved of great value in the manufacture of superior 'gasoline'.

(7) **Addition of Oxygen**. Lower alkenes react with oxygen by addition in the presence of a special catalyst to form **epoxides**.

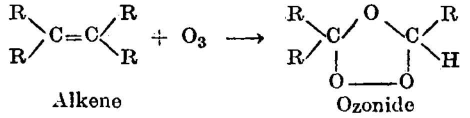
Thus :



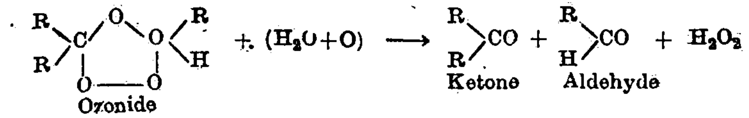


The direct oxidation of alkenes is of great industrial importance as the epoxides are the starting substances for many other organic compounds. On a smaller scale, the epoxides are obtained from alkenes by use of perbenzoic acid which is itself reduced to benzoic acid.

(3) **Addition of Ozone**. When ozone is passed through an alkene dissolved in an inert solvent, it adds across the double bond to form an **Ozonide**.



The ozonide on warming with water splits at the site of the double bond giving a mixture of ketones, aldehydes or of both, depending on the nature of the alkene.

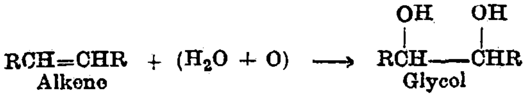


The hydrogen peroxide formed in the reaction is removed by the addition of zinc powder ($Zn + H_2O_2 = ZnO + H_2O$) as otherwise it would oxidise any aldehydes to acids.

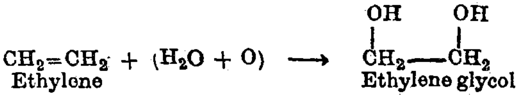
The addition of ozone and subsequent hydrolysis of an alkene as shown above, is termed **Ozonolysis.** It offers a valuable method of locating a double bond in long organic molecules.

(9) **Oxidation Reactions.** Alkenes are more readily oxidised than the alkanes, the site of attack being the double bond. The nature of the oxidation products obtained in a particular case depends upon the strength of the oxidising agent employed.

(*i*) WITH MILD OXIDISING AGENT. When treated with 1 per cent potassium permanganate solution, an alkene adds two (OH) groups at the double bond and thus forms a GLYCOL.



$$\underset{\text{Alkene}}{RCH{=}CHR} + (H_2O + O) \longrightarrow \underset{\text{Glycol}}{R\overset{OH}{\overset{|}{C}}H{-}\overset{OH}{\overset{|}{C}}HR}$$



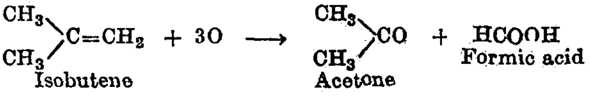
$$\underset{\text{Ethylene}}{CH_2{=}CH_2} + (H_2O + O) \longrightarrow \underset{\text{Ethylene glycol}}{\overset{OH}{\overset{|}{C}}H_2{-}\overset{OH}{\overset{|}{C}}H_2}$$

Since the pink colour of the permanganate ions is discharged during the reaction, it is used as a test for the presence of a double bond.

(*ii*) WITH MODERATE OXIDISING AGENT. When oxidised with a warm concentrated alkaline solution of potassium permanganate, the molecule is ruptured at the double bond yielding aldehydes, ketones or acids.

Thus :

$$\underset{\text{Propene}}{CH_3{-}CH{=}CH_2} + 4O \longrightarrow \underset{\text{Acetic acid}}{CH_3COOH} + \underset{\text{Formic acid}}{HCOOH}$$



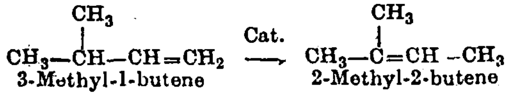
$$\underset{\text{Isobutene}}{(CH_3)_2C{=}CH_2} + 3O \longrightarrow \underset{\text{Acetone}}{(CH_3)_2CO} + \underset{\text{Formic acid}}{HCOOH}$$

The identification of the products of oxidation indicates the position of the double bond in the original molecule.

(*iii*) WITH STRONG OXIDISING AGENT. When burnt in air or treated with concentrated nitric acid, alkenes are oxidised to carbon dioxide and water.

(10) **Isomerisation.** The alkenes on heating or in the presence of a catalyst, undergo isomerisation when the double bond shifts to a carbon atom with greater branching or one centrally located in the molecule.

Thus :



$$\underset{\text{3-Methyl-1-butene}}{CH_3-\overset{CH_3}{\overset{|}{C}}H-CH=CH_2} \xrightarrow{\text{Cat.}} \underset{\text{2-Methyl-2-butene}}{CH_3-\overset{CH_3}{\overset{|}{C}}=CH-CH_3}$$

$$\underset{\text{1-Butene}}{CH_3-CH_2-CH=CH_2} \xrightarrow{\text{Cat.}} \underset{\text{2-Butene}}{CH_3-CH=CH-CH_3}$$

(11) **Substitution Reactions.** When alkenes are chlorinated at high temperature, it results in a product formed by substitution in the alkyl group.

Thus :

$$\underset{\text{Propene}}{CH_2=CH-CH_3} + Cl_2 \xrightarrow{400^\circ} \underset{\text{Allyl chloride}}{CH_2=CH-CH_2Cl} + HCl$$

(12) **Polymerisation.** At high temperature and in the presence of acid catalyst, alkene molecules add to one another to form *polymers.*

Thus :

$$\begin{array}{c} CH_2=CH-H \\ + \\ CH_2=CH_2 \\ \text{Ethylene} \\ \text{(2 molecules)} \end{array} \longrightarrow \underset{\text{1-Butene}}{CH_2=CH-CH_2-CH_3}$$

This process of addition of molecules may continue till hundreds of molecules have united to yield a complex product.

How to test the Presence of a Double Bond. Whether a given organic substance contains a double bond or not, can readily be detected by the following tests. Since a triple bond is in reality a fusion of two double bonds, these tests will also be given by acetylenic compounds. In fact, these could well be called as the **tests of unsaturation.**

(1) *Baeyer's Permanganate Test.* To the aqueous solution of the substance is added 1 per cent solution of potassium permanganate made alkaline with a little sodium carbonate. If on shaking, the pink colour of permanganate disappears rapidly and a brown precipitate of hydrated manganese dioxide appears, the given substance contains double bond. The test is untenable in the case of compounds which already contain a group with reducing properties.

(2) *Addition of Bromine.* A 5 per cent solution of bromine in carbon tetrachloride is added to the solution of the substance in carbon tetrachloride. If the brown colour of bromine is discharged at once, the given compound has a double bond in its molecule.

Both the above tests are not given by alkanes in which the doubly bound carbon atoms have no hydrogen atoms attached to them.

How to locate a Double Bond. There are two methods commonly used for locating the position of a double bond in organic molecules.

(1) *Ozonolysis.* This method consists in forming the ozonide of the given compound and then decomposing it by warming with water. The aldehydes or ketones so obtained are isolated and identified. Since by ozonolysis the molecule is split at the seat of the double bond, the carbon skeleton of the original compound can be constructed by uniting the oxidised carbon atoms of

the two products by a double bond. Thus a long alkene compound which upon ozonolysis yields two aldehydes containing $(n+1)$ and $(m+1)$ carbon atoms, can be written as

$$C_nH_{2n+1}CH{=}CHC_mH_{2m+1}$$

(2) *Oxidative Disruption.* In this method, the given compound is warmed with concentrated alkaline solution of potassium permanganate. The disruption of the carbon chain takes place at the seat of the double bond giving acids or ketones. The products obtained are identified. Obviously the double bond must have been present between the oxidised carbon atoms of the two compounds formed by oxidation. For example, in an alkene which upon oxidation gives one molecule of propionic acid and one molecule of acetic acid, the position of the double bond will be as follows :

$$CH_3CH\overset{\vdots}{\underset{\vdots}{=}}CHCH_2CH_3 + 4O \longrightarrow \underset{\text{Acetic acid}}{CH_3COOH} + \underset{\text{Propionic acid}}{CH_3CH_2COOH}$$

INDIVIDUAL MEMBERS

All attempts to prepare *Methylene*, CH_2, have invariably yielded ethylene. This is due to the fact that the methylene radical, $CH_2{=}$, (as it would be more appropriate to name this hydrocarbon) cannot exist in the free state. As soon as it is formed, two radicals combine to form ethylene.

ETHYLENE, ETHENE, C_2H_4

Since methylene does not exist in stable form, ethylene is virtually the first member of the series of alkenes. It is present in *natural gas* sometimes to the extent of 20 per cent. It is produced in large amounts by the cracking of the high-boiling fractions of petroleum. It occurs to the extent of 5 per cent in *coal gas* and the luminosity of the coal gas flame is largely due to the presence of ethylene. In small amounts ethylene is found to be present in *wood gas* and the products of destructive distillation of several organic substances.

Preparation. Ethylene can be obtained by any of the general methods described before.

(1) By heating ethyl alcohol with excess of concentrated sulphuric acid to 170°. The dehydration of alcohol giving ethylene takes place in two steps.

$$\underset{\text{Ethyl alcohol}}{C_2H_5OH} + H_2SO_4 \xrightarrow{100^\circ} \underset{\substack{\text{Ethyl hydrogen}\\ \text{sulphate}}}{C_2H_5HSO_4} + H_2O$$

Ethyl hydrogen sulphate first formed decomposes to form ethylene and regenerating sulphuric acid.

$$C_2H_5HSO_4 \xrightarrow{170^\circ} \underset{\text{Ethylene}}{C_2H_4} + H_2SO_4$$

The yield of ethylene is low due to charring which can be avoided by taking phosphoric acid in place of sulphuric acid.

(2) By passing ethyl alcohol vapour over alumina heated to 300°

$$\underset{\text{Ethyl alcohol}}{C_2H_5OH} \xrightarrow[Al_2O_3]{300^\circ} \underset{\text{Ethylene}}{C_2H_4} + H_2O$$

(3) By heating ethyl iodide with alcoholic potash solution.

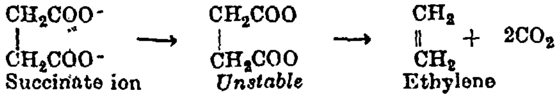
$$\underset{\text{Ethyl iodide}}{C_2H_5I} + KOH_{alc} \longrightarrow \underset{\text{Ethylene}}{C_2H_4} + H_2O + KI$$

This is a good laboratory method for preparing pure ethylene.

(4) By heating an alcoholic solution of ethylene bromide with granulated zinc, when pure ethylene is obtained.

$$\underset{\text{Ethylene bromide}}{CH_2Br.CH_2Br} + Zn \longrightarrow \underset{\text{Ethylene}}{CH_2{=}CH_2} + ZnBr_2$$

(5) By electrolysis of potassium succinate solution. The succinate ions are discharged at the anode where they decompose to form ethylene and carbon dioxide.



$$\underset{\text{Succinate ion}}{\begin{array}{l}CH_2COO^-\\ |\\ CH_2COO^-\end{array}} \longrightarrow \underset{\textit{Unstable}}{\begin{array}{l}CH_2COO\\ |\\ CH_2COO\end{array}} \longrightarrow \underset{\text{Ethylene}}{\begin{array}{l}CH_2\\ \|\\ CH_2\end{array}} + 2CO_2$$

The gases are passed through potassium hydroxide solution to remove carbon dioxide before collection.

(6) By thermal decomposition of alkanes. Thus propane decomposes at red heat to give ethylene.

$$\underset{\text{Propane}}{CH_3CH_2CH_3} \longrightarrow CH_4 + \underset{\text{Ethylene}}{CH_2{=}CH_2}$$

Laboratory Preparation. Ethylene is conveniently prepared in the laboratory from ethyl alcohol by heating it to 170° with

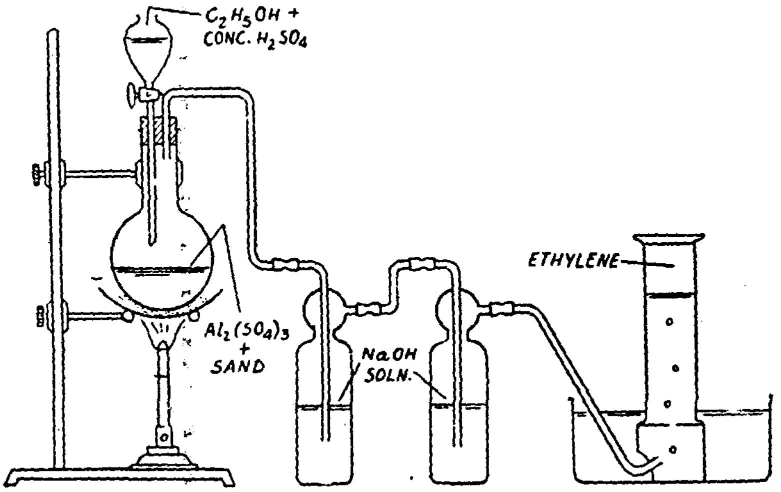


Fig. 11·2. Preparation of Ethylene from alcohol and sulphuric acid.

excess of concentrated sulphuric acid, preferably in the presence of anhydrous aluminium sulphate which lowers the working temperature to 140°

The apparatus used for the preparation is shown in *Fig.* 10·9. A litre flask is fitted with a tap-funnel, a thermometer and two wash-bottles in series. Both wash-bottles contain a strong solution of sodium hydroxide. The second wash-bottle is connected to an arrangement for the collection of the gas by the downward displacement of water.

A mixture of ethanol (50 mls.) and concentrated sulphuric acid (100 mls.) together with 8 grams of anhydrous aluminium sulphate and about 60 grams of sand is placed in the round-bottomed flask fitted as shown in the diagram above. The flask is then heated on a sand-bath till a steady stream of gas is evolved. As the gas bubbles through the caustic soda solution the latter absorbs carbon dioxide and sulphur dioxide. The pure ethylene gas goes to pneumatic trough. A little of the gas is allowed to escape uncollected. When a test-tube full of gas burns quietly, proceed to collect the gas in jars. If the supply of the gas becomes slow, a further amount of the mixture of alcohol and sulphuric acid in the ratio of 1 : 1 is added from the tap-funnel.

INDUSTRIAL PREPARATION

(1) Ethylene is now produced on a large scale by cracking the *natural gas* and high-boiling fractions of petroleum.

(2) By passing ethanol vapour through tubes containing alumina (Al_2O_3) at 300°.

(3) *By the partial reduction of acetylene.* At places where acetylene is produced commercially from calcium carbide, it is used for the manufacture of ethylene. A mixture of acetylene and hydrogen is passed over finely divided palladium or iron at 200°.

$$\underset{\text{Acetylene}}{CH \equiv CH} + H_2 \xrightarrow[\text{Pd}]{200°} \underset{\text{Ethylene}}{CH_2 = CH_2}$$

Properties. (*Physical*). Ethylene is a colourless gas with a rather sweet odour. Liquid ethylene boils under atmospheric pressure at −150° and the solid hydrocarbon melts at −169°. It is slightly soluble in water but dissolves more readily in organic solvents such as alcohol and ether. When inhaled, ethylene produces general anaesthesia.

(*Chemical*). Unlike ethane, ethylene is a very reactive hydrocarbon. All its important reactions are due to the presence of the double bond. The types of reactions shown by ethylene are : (*i*) Addition reactions, (*ii*) Oxidation reactions, and (*iii*) Polymerisation.

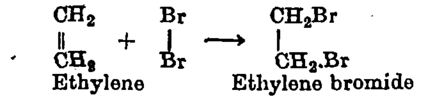
ADDITION REACTIONS

(1) *Addition of Hydrogen.* In the presence of finely divided nickel at 200—300°, ethylene takes up a molecule of hydrogen forming ethane.

$$\underset{\text{Ethylene}}{CH_2 = CH_2} + H_2 \longrightarrow \underset{\text{Ethane}}{CH_3.CH_3}$$

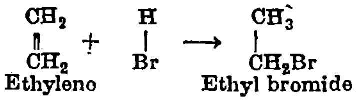
(2) *Addition of Halogens.* With halogens, in liquid phase or in solution, ethylene forms the dihalogen derivatives. Chlorine is

most easily added and iodine is very slightly reactive, bromine taking an intermediate position.



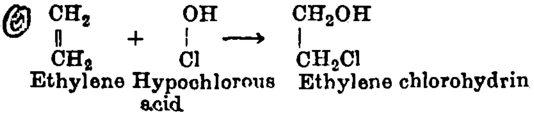
$$\underset{\text{Ethylene}}{\begin{array}{c}CH_2\\ \|\\ CH_2\end{array}} + \begin{array}{c}Br\\ |\\ Br\end{array} \longrightarrow \underset{\text{Ethylene bromide}}{\begin{array}{c}CH_2Br\\ |\\ CH_2.Br\end{array}}$$

(3) *Addition of Halogen acids.* Ethylene reacts with halogen acids HCl, HBr, and HI forming ethyl halides. The order of reactivity is HI>HBr>HCl.



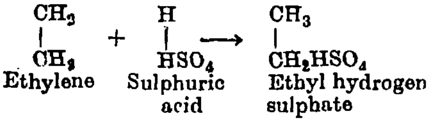
$$\underset{\text{Ethylene}}{\begin{array}{c}CH_2\\ \|\\ CH_2\end{array}} + \begin{array}{c}H\\ |\\ Br\end{array} \longrightarrow \underset{\text{Ethyl bromide}}{\begin{array}{c}CH_3\\ |\\ CH_2Br\end{array}}$$

(4) *Addition of Hypochlorous acid.* Ethylene reacts with aqueous solution of hypochlorous acid to form ethylene chlorohydrin.



$$\underset{\text{Ethylene}}{\begin{array}{c}CH_2\\ \|\\ CH_2\end{array}} + \underset{\text{Hypochlorous acid}}{\begin{array}{c}OH\\ |\\ Cl\end{array}} \longrightarrow \underset{\text{Ethylene chlorohydrin}}{\begin{array}{c}CH_2OH\\ |\\ CH_2Cl\end{array}}$$

(5) *Addition of Sulphuric acid.* Ethylene is readily absorbed by concentrated sulphuric acid to form ethyl hydrogen sulphate.



$$\underset{\text{Ethylene}}{\begin{array}{c}CH_2\\ |\\ CH_2\end{array}} + \underset{\text{Sulphuric acid}}{\begin{array}{c}H\\ |\\ HSO_4\end{array}} \longrightarrow \underset{\text{Ethyl hydrogen sulphate}}{\begin{array}{c}CH_3\\ |\\ CH_2HSO_4\end{array}}$$

Ethyl hydrogen sulphate upon heating regenerates ethylene and on boiling with water it yields ethanol.

$$\underset{\text{Ethyl hydrogen sulphate}}{C_2H_5HSO_4} \xrightarrow{\text{heat}} \underset{\text{Ethylene}}{C_2H_4} + H_2SO_4$$

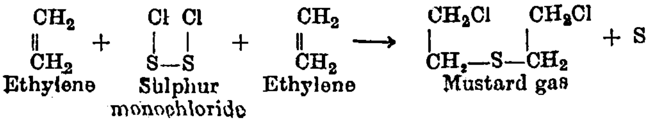
$$C_2H_5\boxed{HSO_4 + H}\underset{\text{Water}}{OH} \longrightarrow \underset{\text{Ethanol}}{C_2H_5OH} + H_2SO_4$$

Mixtures of ethylene and alkanes may be readily separated by treating with sulphuric acid ; ethylene is dissolved in sulphuric acid while alkanes do not. The ethyl hydrogen sulphate is heated to give back ethylene.

Another use of this reaction is the production of ethanol from ethylene obtained by cracking petroleum.

$$C_2H_4 \xrightarrow{+H_2SO_4} C_2H_5HSO_4 \xrightarrow{+H_2O} C_2H_5OH + H_2SO_4$$

(6) *Addition of Sulphur chloride.* Sulphur monochloride, S_2Cl_2 reacts with ethylene to give *mustard gas.*



$$\underset{\text{Ethylene}}{\begin{array}{c}CH_2\\ \|\\ CH_2\end{array}} + \underset{\text{Sulphur monochloride}}{\begin{array}{c}Cl\ \ Cl\\ |\ \ \ |\\ S-S\end{array}} + \underset{\text{Ethylene}}{\begin{array}{c}CH_2\\ \|\\ CH_2\end{array}} \longrightarrow \underset{\text{Mustard gas}}{\begin{array}{ccc}CH_2Cl & & CH_2Cl\\ | & & |\\ CH_2 & -S- & CH_2\end{array}} + S$$

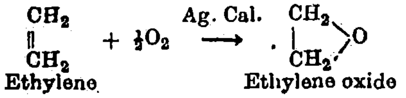
Mustard gas was used as a poison gas in the Gr 1914.

OXIDATION REACTIONS

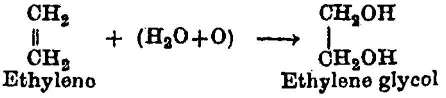
(7) *With Oxygen.* (*i*) Ethylene burns in air or ox luminous flame to produce carbon dioxide and water ; also it forms explosive mixtures with air or oxygen.

$$\underset{\text{Ethylene}}{C_2H_4} + 3O_2 \longrightarrow 2CO_2 + 2H_2O$$

(*ii*) Ethylene reacts with oxygen in the presence of a specia silver catalyst to form ethylene oxide.

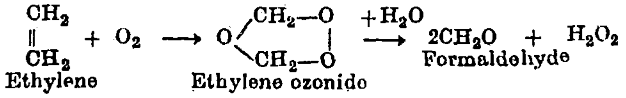


(8) *With Alkaline Potassium permanganate.* When treated with a cold dilute alkaline solution, ethylene yields ethylene glycol. Permanganate supplies an oxygen atom which with a water molecule gives two OH groups, and the latter add to the double bond.



$$\underset{\text{Ethylene}}{\begin{matrix}CH_2\\ \|\\ CH_2\end{matrix}} + (H_2O+O) \longrightarrow \underset{\text{Ethylene glycol}}{\begin{matrix}CH_2OH\\ |\\ CH_2OH\end{matrix}}$$

(9) *With Ozone.* When ozone is passed through ethylene solution dissolved in an inert solvent, ethylene reacts rapidly by addition forming ethylene *ozonide* which upon decomposition with water yields formaldehyde.



POLYMERISATION

(10) *Formation of Polyethylene.* When liquid ethylene is heated to 400° under high pressure, a large number of molecules unite end-to-end to form long chains. Thus ethylene is said to have undergone *addition polymerisation* and the product is known as **polyethylene** or **polythene**.

$$\underset{(n\text{ being }600\text{ to }1000)}{nCH_2{=}CH_2} \xrightarrow[\text{Cat}]{400°,\text{ h. pressure}} (-CH_2-CH_2-)_n$$

The product is a translucent solid (m.p. 110° to 137°). It is a tough plastic material, poor conductor of electricity and stable to most chemical reagents. Therefore, it is widely used for wire-making insulations, toys, packaging, pipes, squeeze bottles, laboratory containers and wearing apparel.

It is gratifying that a plant for the manufacture of high density polyethylene, which is the largest in Asia has gone into production in March 1968 in India (Thana). It utilises ethylene obtained by cracking of Naphtha and the product '*Hostalene*' is a superior quality plastic material. The hostalene pipes, buckets, baskets, bunch boxes, mugs, lamp shades, combs etc., in delightful colours are now available in the domestic market.

Uses. Ethylene is used : (1) for producing 'oxy-ethylene' flame for cutting and welding of metals :

(2) for 'ripening' of green fruits artificially by exposing them to the gaseous hydrocarbon ;

(3) as a general anaesthetic ;

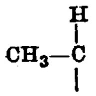
(4) for making a poison gas 'Mustard gas' ;

(5) as a starting material for ethylene glycol (*antifreeze*) ; ethylene dichloride (*solvent*) ; ethylene oxide (*fumigant*) ; ethanol. diethyl ether, etc. ; and

(6) for the manufacture of plastics for making bags, aprons, table-cloth, cables, etc.

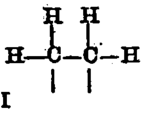
Structure of Ethylene. (1) The molecular formula of ethylene as determined by the gas combustion method is C_2H_4.

(2) The two carbon atoms in ethylene must be directly linked together. Keeping in view the tetravalency of carbon, the following three structural formulae are possible for this hydrocarbon :



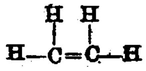
$CH_3-\overset{H}{\overset{|}{\underset{|}{C}}}$

I



$H-\overset{H}{\overset{|}{\underset{|}{C}}}-\overset{H}{\overset{|}{\underset{|}{C}}}-H$

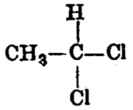
II



$H-\overset{H}{\overset{|}{C}}=\overset{H}{\overset{|}{C}}-H$

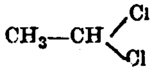
III

(3) Ethylene reacts with chlorine forming ethylene dichloride, $C_2H_4Cl_2$, which has a boiling point of 8·37°. If formula I for the hydrocarbon is correct, the dichloride would be presented as :



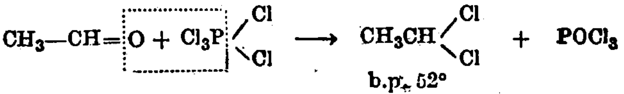
$CH_3-\overset{H}{\overset{|}{\underset{\underset{Cl}{|}}{C}}}-Cl$

or



$CH_3-CH\begin{matrix}\diagup Cl\\ \diagdown Cl\end{matrix}$

But a compound having this structure, as prepared by the action of PCl_5 on acetaldehyde,

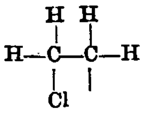


$$CH_3-CH=\boxed{O+Cl_3P}\begin{matrix}\diagup Cl\\ \diagdown Cl\end{matrix} \longrightarrow CH_3CH\begin{matrix}\diagup Cl\\ \diagdown Cl\end{matrix} + POCl_3$$

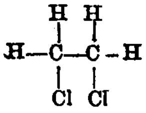
b.p. 52°
(Ethylidene dichloride)

is different from the dichloride actually formed from ethylene. Hence, the formula I for ethylene is untenable. This limits our choice to formulae II and III only.

(4) If ethylene contains free valencies as indicated in formula II, it should be able to form ethylene monochloride as well as the dichloride.

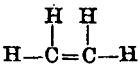


$H-\overset{H}{\overset{|}{\underset{\underset{Cl}{|}}{C}}}-\overset{H}{\overset{|}{\underset{|}{C}}}-H$



$H-\overset{H}{\overset{|}{\underset{\underset{Cl}{|}}{C}}}-\overset{H}{\overset{|}{\underset{\underset{Cl}{|}}{C}}}-H$

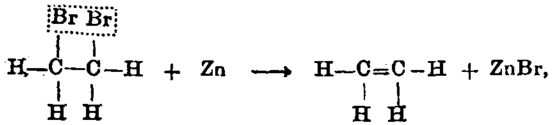
Actually no such compound as C_2H_4Cl is known as the addition of chlorine to ethylene invariably yields $C_2H_4Cl_2$. This rejects the formula II and supports the formula III.



$$H-\overset{H}{C}=\overset{H}{C}-H$$

in which the two carbon valencies are joined to each other to form a double bond.

(5) This structure of ethylene is further supported by its synthesis from ethylene dibromide and zinc.



$$H-\underset{H}{\overset{Br}{C}}-\underset{H}{\overset{Br}{C}}-H + Zn \longrightarrow H-\underset{H}{C}=\underset{H}{C}-H + ZnBr_2$$

Ethylene dibromide Ethylene

(6) According to the tetrahedral structure of the carbon atom, ethylene may be represented by the space model.

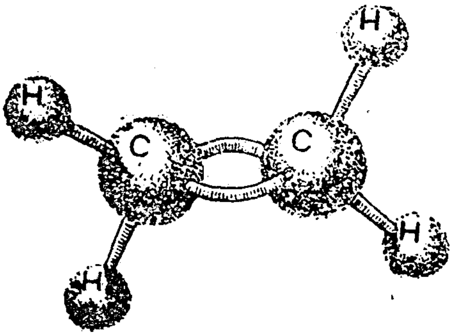


Fig. 11·3.

(7) The orbital structure of ethylene molecule has already been discussed. As ethylene molecule is known to be planer, its carbon atoms are in sp^2 hybridisation state. Each carbon has three sp^2 hybrid orbitals in one plane and another pure p orbital perendicular to this plane. One sp^2 orbital of each of the two carbon atoms is used in forming σ bond between them while the remaining two overlap with s orbitals of hydrogen atoms to form two σ bonds each. Their pure p orbitals overlap in the side-wise manner giving a π bond.

In all there are five σ and one π bond in ethylene molecule. From electron diffraction and spectroscopic measurements it has been revealed that in ethylene molecule the H—C—C and H—C—H angles are 121·6° and 117·5° respectively while C—C and C—H lengths are 1·34 Å and 1·10 Å.

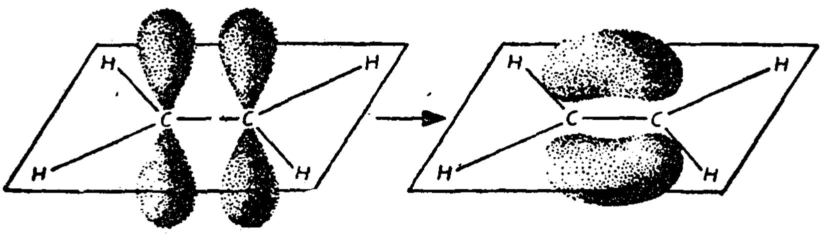


Fig. 11·4. Overlap of p orbitals to form π bond in ethylene.

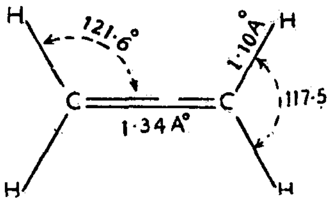
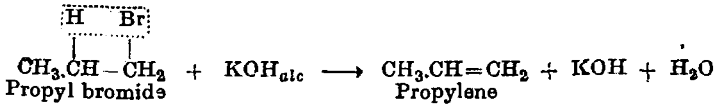


Fig. 11·5. Geometry of Ethylene molecule.

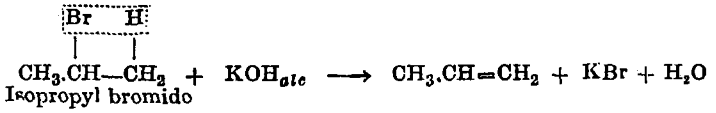
PROPYLENE, PROPENE, C_3H_6

It is a by-product of cracking of propane to ethylene, and is formed in large amounts during the cracking of petroleum.

Perparation. All the general methods for preparing alkenes are available for propylene. It may be prepared by boiling propyl bromide or isopropyl bromide with alcoholic potash.



$$\underset{\text{Propyl bromide}}{CH_3.\overset{\overset{H}{|}}{C}H-\overset{\overset{Br}{|}}{C}H_2} + KOH_{alc} \longrightarrow \underset{\text{Propylene}}{CH_3.CH{=}CH_2} + KOH + H_2O$$



$$\underset{\text{Isopropyl bromide}}{CH_3.\overset{\overset{Br}{|}}{C}H-\overset{\overset{H}{|}}{C}H_2} + KOH_{alc} \longrightarrow CH_3.CH{=}CH_2 + KBr + H_2O$$

Properties. It is a colourless gas. Liquid hydrocarbon boils at −48°.

The reactions of propylene are much the same as those of ethylene, However, owing to the fact that its molecule is not symmetrical and contains a methyl group, propylene differs from ethylene in certain respects.

(1) In addition the normal addition products, it forms substitution derivatives with halogens.

(2) It is absorbed by concentrated sulphuric acid forming propylene hydrogen sulphate which reacts with water to give isopropyl alcohol.

(3) It reacts with oxygen at 500° to form a variety of products which include butenes, pentenes, hexenes, methanal, ethanal and oxides of carbon.

Uses. Propylene prepared from petroleum by cracking is used for the commercial preparation of isopropyl alcohol, acetone and allyl chloride.

Infrared spectra of alkenes. Alkenes which are characterised by the presence of a double bond show absorption peaks in

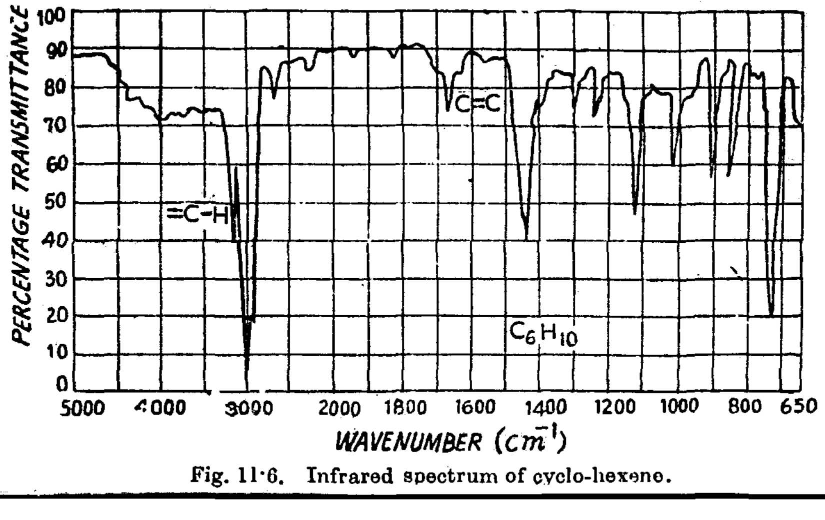
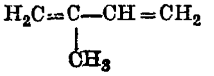


Fig. 11·6. Infrared spectrum of cyclo-hexene.

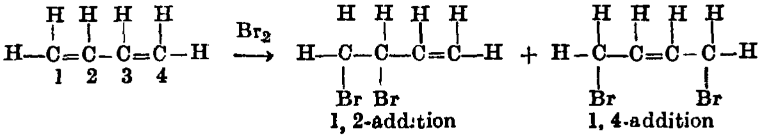
the regions between 1620—1680 cm^{-1}. There are also several regions of absorption due to $=C-H$ bonds. The infrared spectrum of cyclo-hexene is given below :

ALKADIENES OR DIOLEFINES

Olefines having two double bonds in their molecule are called *Diolefines.* Their IUPAC name is *Alkadienes.* It is derived from the name for the corresponding alkane by substituting the terminal *'diene'* for *'ne'*. Some of the important alkadienes are :

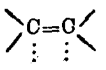
$CH_2=C=CH_2$	Propadiene or Allene
$CH_2=CH—CH=CH_2$	1, 3-Butadiene or Divinyl
 $H_2C=C(CH_3)—CH=CH_2$	2-Methyl-1, 3-butadiene or Isoprene

Alkadienes can be prepared by methods similar to those employed for alkenes. They give the usual reactions of a hydrocarbon containing two double bonds. However, in presence of alternate double and single bonds (**Conjugate System**), they give abnormal addition reactions. Thus, when a molecule of bromine is added to a molecule of 1, 3-butadiene, $\overset{1}{CH_2} : \overset{2}{CH} . \overset{3}{CH} : \overset{4}{CH_2}$, two dibromo-derivatives are obtained, the 'expected' 3, 4-dibromobut-1-ene (**1,2-addition**) and the 'unexpected' 1, 4 dibromobut-2-ene (**1,4-addition**).



Quite often 1, 4-addition product is the major product along with a reasonable amount of 1, 2-addition product depending upon the nature of the solvent and temperature of the reaction. In order to explain the abnormal addition reactions in dienes, Thiele proposed his **Theory of Partial Valency**. The theory makes the following assumptions :

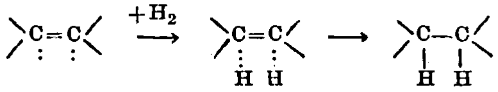
(1) *The valencies of the carbon atoms containing a double bond are not fully saturated and there is always a certain residual or* "PARTIAL VALENCY" *left on each carbon atom.* Thus a double bond be represented as



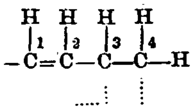
where the dotted lines indicate the partial valencies.

(2) *The addition of new atoms or groups along a double bond takes place through these partial valencies.* They first catch the partial valency and then take up the full valency with the

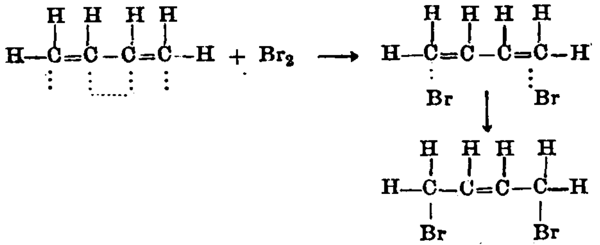
simultaneous disappearance of the double bond. The addition of hydrogen to a double bond can be represented as follows :



(3) *In a conjugated system of double bonds, the partial valencies at the carbon atoms 1 and 4 are free, while the partial valencies at the carbon atoms 2 and 3 are naturally satisfied.* Thus 1, 3-Butadiene can be written as

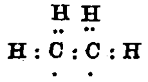


It is clear that according to Thiele's theory the addition can take place in positions 1 and 4 only as in 2 and 3 positions there are no free partial valencies available through which addition could take place. Thus :



1, 4-addition product

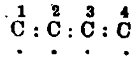
Electronic Interpretation of Thiele's theory. The application of the electronic concept has provided a sound basis for Thiele's theory. Ethylene molecule can be written as



$$\mathrm{H:\overset{\overset{H}{\cdot\cdot}}{\underset{\cdot}{C}}:\overset{\overset{H}{\cdot\cdot}}{\underset{\cdot}{C}}:H}$$

The odd electrons shown with the two carbon atoms tend to pair for greater stability but due to the 'distance factor' the pairing is incomplete. These electrons which are more or less available for chemical union, explain the existence of partial valencies at the doubly bonded carbon atoms.

In a molecule with conjugated double bonds which may be written (neglecting the hydrogen atoms) as



$$\mathrm{\overset{1}{\underset{\cdot}{C}}:\overset{2}{\underset{\cdot}{C}}:\overset{3}{\underset{\cdot}{C}}:\overset{4}{\underset{\cdot}{C}}}$$

the odd electrons in positions 2 and 3 being near can pair while those in positions 1 and 4 are left free. Since the free electrons lead to partial valencies, it stands to reason that in a conjugated system addition should take place in positions 1 and 4 only.

Thiele's theory explains 1, 4-addition reactions admirably but it does not account for the 1, 2-addition reactions.

Modern mechanism of addition to Conjugated Systems. The mechanism of additions to conjugated systems is now based on modern concepts. In 1, 4-addition, the centres of unsaturation function as one unit and the electromeric effect operates as :

$$H_2C{=}CH{-}CH = \overset{\overset{+}{Br}-\overset{-}{Br}}{CH_2} \longrightarrow H_2C{=}CH{-}\overset{+}{C}H{-}CH_2Br + \overset{-}{Br}$$

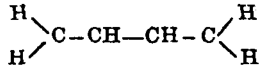
(carbonium ion)

The intermediate carbonium ion is capable of resonance :

$$H_2C{=}CH{-}\overset{+}{C}H{-}CH_2Br_2 \longleftrightarrow H_2\overset{+}{C}{-}CH{=}CH{-}CH_2Br$$

Hence the negative bromide ion (Br^-) can add at either positive carbon atom, forming 1, 2- and 1, 4-addition products.

Stability of Conjugated Systems. As clear from above, alkadienes having a system of two double bonds —C=C—C=C— are relatively inert, while they could be twice as reactive as alkenes. Let us apply the orbital concept to the simplest diene, butadiene. Each of the four carbons in its molecule have three sp^2 hybrid orbitals lying in one plane as in ethylene, and one pure *p* orbital disposed in a direction perpendicular to the plane. The three sp^2 orbitals on each carbon form three σ bonds — either two between a carbon and hydrogen atoms and one with the adjoining carbon, or two with adjoining carbon atoms and one with hydrogen atom, as shown below.



This leaves behind on each carbon one pure or free *p* orbital (See Fig. 11-7).

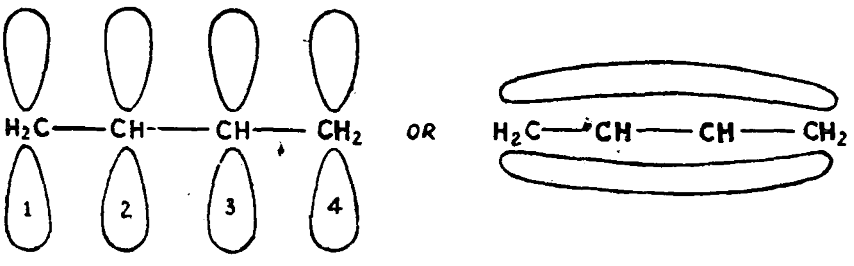


Fig. 11-7 Schematic representation of π electron cloud in Butadiene.

The *p* orbital on carbon (2) can overlap (side-wise) that on carbon (1) as much as it can overlap that on carbon (3). In this situation, all the four *p* orbitals may be visualised to form a Molecular orbital embracing all the four carbon atoms as shown in the diagram above. The four electrons, one each in a *p* orbital, are thus rendered polycentric and get 'delocalised'. In delocalised bond orbitals, the electrons attain a greater freedom of movement, thereby lowering the total energy of the system. Probably this accounts for the relative stability of a butadiene molecule

The most important of the alkadienes is **Isoprene**. It is formed by the destructive distillation of Indian rubber which has also been made from this hydrocarbon. Recently it has been found possible to prepare *Synthetic rubber* from butadiene even more easily than from isoprene. Butadiene obtained by high temperature cracking of petroleum or ethyl alcohol, is polymerised in the presence of metallic sodium, when a product resembling natural rubber is obtained.

QUESTIONS

1. What is meant by the term unsaturated compounds ? Give a few examples of such substances, showing how their reactions differ from those of saturated compounds.

2. Discuss the various methods available for the preparation of ethylene compounds.

3. Discuss the properties of unsaturated compounds. Give a method for preparing ethylene and name five of its characteristic reactions.

4. Discuss isomerism in olefines. Explain why a higher olefine can exist in more isomeric forms than the corresponding paraffin.

5. Comment on the statement. "While paraffins react by substitution, olefines react by addition".

6. You are given an unknown long chain compound. How will you test whether it contains a double bond or not ? Supposing it has one, then how will you ascertain its location on the carbon chain ?

7. How would you prepare ethylene in the laboratory ? How does it react with (*a*) bromine water (*b*) conc. sulphuric acid, (*c*) hydrogen chloride, and (*d*) acidified potassium permanganate ?

8. Show how the structural formula of ethylene has been arrived at. Prove clearly the existence of a double bond in its molecule.

9. *What are diolefines ? Write the structural formulae of the two* butadienes and point out differences in their behaviour. How is synthetic rubber prepared from 1, 3-butadiene ?

10. What is meant by 1, 4-addition ? Give Thiele's explanation as also the modern mechanism of addition to a conjugated system.

11. Write notes on :—
   (*a*) Unsaturation ·
   (*b*) Ozonolysis ;
   (*c*) Markownikoff's Rule. (*Vikram B.Sc. II, 1966*)

12. Which alkene of each pair would you expect to be more reactive towards the addition of H_2SO_4.
   (*a*) Ethylene or Propylene.
   (*b*) Ethylene or Vinyl bromide
   (*c*) Propylene or 2-butene.
   (*d*) 2-butene or isobutylene.
   (*e*) Vinyl chloride or 1, 2-dichloroethylene.
   (*f*) 1-Pentene or 2-methyl-1-butene.
   (*g*) Ethylene or $CH_2{=}CH.COOH$.
   (*h*) Propylene or 3, 3, 3-trifluoropropene (*Panjabi B.Sc. II. 1967*)

large quantities in the gases obtained by the cracking of petroleum. They are also produced by heating coal and several other organic substances.

NOMENCLATURE

The general formula for the series of alkynes is C_nH_{2n-2} They are characterised by the presence of a C-to-C triple bond (≡). There are three ways of naming this class of hydrocarbons.

(1) The COMMON NAMES for the simple members are :

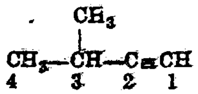
$CH\equiv CH$	Acetylene
$CH_3C\equiv CH$	Allylene
$CH_3C\equiv CCH_3$	Crotonylene

Except 'Acetylene' these names are now obsolete.

(2) The DERIVED NAMES. Here the higher alkynes are regarded as alkyl derivatives of acetylene, CH≡CH. Thus :

$H_3CC\equiv CH$	$CH_3C\equiv CCH_3$	 $C_2H_5C\equiv C\overset{CH_3}{\overset{\vert}{C}}HCH_3$
Methylacetylene	Dimethylacetylene	Ethylisopropylacetylene

(3) The IUPAC SYSTEM has adopted the name acetylene for the first member C_2H_2. The rest of the alkynes are named by dropping the ending *-ane* of the parent alkane and adding the suffix *-yne*. If necessary the carbon chain including the triple bond is numbered from the end nearest this bond. The position of the triple bond is indicated by prefixing the number of the carbon preceding it to the name of the alkyne. Thus :

FORMULA	IUPAC NAME
$CH\equiv CH$	Acetylene (Ethyne)
$CH_3C\equiv CH$	Propyne
1 2 3 4 $CH_3C\equiv CCH_3$	2-Butyne
4 3 2 1 $CH_3CH_2C\equiv CH$	1-Butyne
 $\underset{4}{CH_3}-\underset{3}{\overset{CH_3}{\overset{\vert}{C}H}}-\underset{2}{C}\equiv\underset{1}{CH}$	3-Methyl-1-butyne

ALKYNYL RADICALS. The monovalent radicals derived from the alkynes are named by deleting the final '*e*' of the parent hydrocarbon and adding the suffix *-yl*. Thus:

$HC\equiv C-$	Ethynyl (Ethyne —e + yl)
$H_3CC\equiv C-$	Propynyl

ISOMERISM

The presence of the triple bond provides the same opportunities of structural isomerism in alkynes as are offered by alkenes. Due to the linear nature of the alkyne molecule (Fig. 12·1) hydrocarbons of this class are incapable of showing geometrical isomerism.

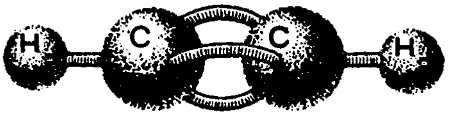


Fig. 12·1. Model of acetylene molecule.

Alkynes are also isomeric with the corresponding alkadienes.

$CH_3{-}C{\equiv}CH$ Propyne $CH_2{=}C{=}CH_2$ Propadiene, *Allene*

METHODS OF FORMATION

The methods of formation of alkynes are essentially of two types :

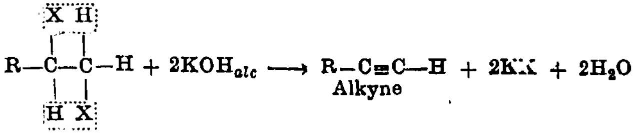
(*i*) Those in which a triple bond is created in a more saturated molecule by the elimination of sufficient atoms from adjacent carbon atoms.

(*ii*) Those in which a compound already containing a triple bond is taken as the starting material from which is built the length of the carbon chain.

Methods (1) and (2) given below are of the first type, while methods (3) and (4) belong to the second type.

(1) **Dehydrohalogenation of dihaloalkanes**. Dihalogen substituted alkanes with alcoholic potash eliminate two atoms of hydrogen and two atoms of halogen from the adjacent carbon atoms resulting in the formation of alkynes.

(*i*) *When the halogen atoms are on different carbons* :



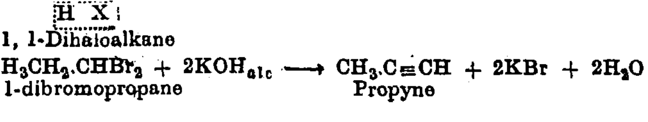
$$R{-}\overset{\overset{X}{|}}{\underset{\underset{H}{|}}{C}}{-}\overset{\overset{H}{|}}{\underset{\underset{X}{|}}{C}}{-}H + 2KOH_{alc} \longrightarrow \underset{\text{Alkyne}}{R{-}C{\equiv}C{-}H} + 2KX + 2H_2O$$

1, 2-dihaloalkane

$$\underset{\text{1, 2-dibromopropane}}{CH_3.CHBr.CH_2Br} + 2KOH_{alc} \longrightarrow \underset{\text{Propyne}}{CH_3.C{\equiv}CH} + 2KBr + 2H_2O$$

This gives a method for converting an alkene to alkyne.

(*ii*) *When the halogen atoms are on the same carbon* :



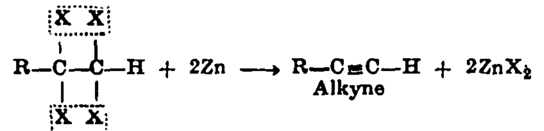
$$R{-}\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}{-}\overset{\overset{X}{|}}{\underset{\underset{X}{|}}{C}}{-}H + 2KOH_{alc} \longrightarrow \underset{\text{Alkyne}}{R{-}C{\equiv}C{-}H} + 2KX + 2H_2O$$

1, 1-Dihaloalkane

$$\underset{\text{1, 1-dibromopropane}}{CH_3CH_2.CHBr_2} + 2KOH_{alc} \longrightarrow \underset{\text{Propyne}}{CH_3.C{\equiv}CH} + 2KBr + 2H_2O$$

Since 1,1-dihaloalkanes can be obtained by the action of phosphorus pentachloride on aldehydes and ketones, the above method may be used for preparing alkynes from aldehydes.

(2) **Dehalogenation of Tetra-haloalkanes.** The halogen derivatives in which halogen atoms are linked to the adjacent carbon atoms, when treated with zinc yield alkynes.



$$\underset{X\ \ X}{\overset{X\ \ X}{R-C-C-H}} + 2Zn \longrightarrow \underset{\text{Alkyne}}{R-C\equiv C-H} + 2ZnX_2$$

1, 1, 2, 2-tetrahaloalkane

$$\underset{\text{1, 1, 2, 2-tetraiodobutane}}{CH_3.CH_2.CI_2.CHI_2} + 2Zn \longrightarrow \underset{\text{1-Butyne}}{CH_3CH_2C\equiv CH} + 2ZnI_2$$

(3) **Action of Water on Alkynides.** When treated with water or dilute acids, alkynides are hydrolysed to form alkynes.

$$\underset{\text{Alkynide}}{R.C\equiv C.M} + HOH \longrightarrow \underset{\text{Alkyne}}{R.C\equiv CH} + MOH$$

$$\underset{\text{Sod. methylacetylide}}{CH_3.C\equiv C.Na} + HOH \longrightarrow \underset{\text{Propyne}}{CH_3.C\equiv CH} + NaOH$$

$$\underset{\text{Silver acetylide}}{AgC\equiv CAg} + 2HOH \longrightarrow \underset{\text{Acetylene}}{HC\equiv CH} + 2AgOH$$

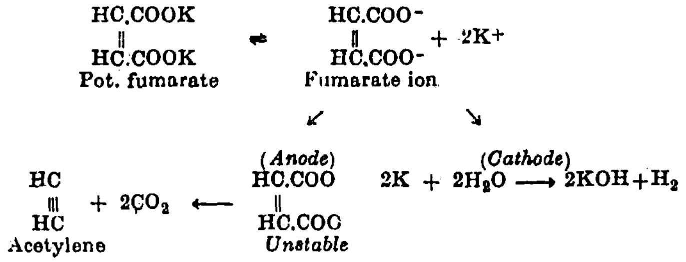
(4) **Action of Alkyl halides on alkynides of lower alkynes.**

$$\underset{\text{Alkynide}}{R.C\equiv C\boxed{M+X}R} \longrightarrow \underset{\text{Alkyne}}{R.C\equiv C.R} + MX$$

$$\underset{\text{Sod. methylacetylene}}{CH_3.C\equiv C\boxed{Na + I}CH_3} \longrightarrow \underset{\text{2-Butyne, Dimethylacetylene}}{CH_3.C\equiv C.CH_3} + NaI$$

The method is helpful only for the introduction of methyl groups as the action of higher alkyl halides gives different products.

(5) **Electrolysis of salts of unsaturated dicarboxylic acids.** Potassium salts of the acids of the fumaric acid series on electrolysis form alkynes.



PHYSICAL CHARACTERISTICS

Physical properties of alkynes are similar to those of alkenes.

(1) The first three members are gases, next eight are liquids,

and the higher alkynes are solids. They are all colourless and odourless except acetylene which has a characteristic garlic odour.

(2) For the corresponding members, alkynes are less volatile than alkanes as well as alkenes, the order of the boiling points being

alkynes > alkanes > alkenes.

(3) They are very slightly soluble in water but dissolve readily in organic solvents such as alcohol, benzene and acetone.

NAME	FORMULA	M.P. °C	B.P. °C
Acetylene, ethyne	$CH\equiv CH$	—82	—84
Propyne	$CH_3C\equiv CH$	—105	—27
1-Butyne	$C_3H_5C\equiv CH$	—130	18
Pentyne	$C_3H_7C\equiv CH$	—95	48
1-Hexyne	$C_4H_9C\equiv CH$	—150	75

(4) *The lowest members when inhaled produce* **general anaesthesia.**

(5) Their boiling points, melting points, and specific gravities show a regular increase with rising molecular weights. The physical constants of a few straight-chain hydrocarbons are given in the table above for illustration.

CHEMICAL CHARACTERISTICS

The chemical behaviour of alkynes *is very much similar to* **that of alkenes.** The molecule of typical alkyne is made of three distinct parts :

$$R-C\equiv C-H$$

(*i*) *the Alkyl group R* :

(*ii*) *the trebly bound pair of carbons* ; *and*

(*iii*) *the hydrogen atom.*

The alkyl groups attached to the trebly bound carbons are unusually inert. The triple bond being a fusion of two double bonds entails heavy strain which causes instability in the molecule. Thus like the alkenes, alkynes give addition reactions in duplicate adding two molecules of the reagent instead of one.

Alkynes also give oxidation, polymerisation and isomerisation reactions at the triple bond. The lonely H-atom linked to the trebly bound carbon is very reactive. Thus alkynes like hydrocyanic acid ($H.C\equiv N$) are acidic in character and form metallic derivatives.

The general reactions of alkynes are given below :

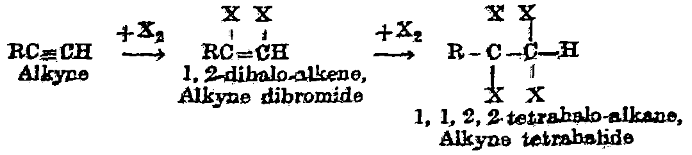
(2) **Addition of Hydrogen.** In the presence of a suitable catalyst alkynes add two molecules of hydrogen first forming the corresponding alkenes and finally the alkanes. Thus :

$$\underset{\text{Alkyne}}{RC\equiv CH} \xrightarrow[\text{Ni}]{+H_2} \underset{\text{Alkene}}{RCH=CH_2} \xrightarrow[\text{Ni}]{+H_2} \underset{\text{Alkane}}{RCH_2-CH_3}$$

$$\underset{\text{Propyne}}{CH_3C\equiv CH} \xrightarrow[\text{Ni}]{+H_2} \underset{\text{Propene}}{CH_3CH=CH_2} \xrightarrow[\text{Ni}]{+H_2} \underset{\text{Propane}}{CH_3CH_2CH_3}$$

While colloidal platinum catalyses the addition of halogen at room temperature, nickel does it at high temperature.

(2) **Addition of Halogens.** Halogens add to alkenes in two steps first forming a *dihalo-alkene* and then a *tetrahalo-alkane*.



$$\underset{\text{Alkyne}}{RC\equiv CH} \xrightarrow{+X_2} \underset{\substack{\text{1, 2-dihalo-alkene,}\\ \text{Alkyne dibromide}}}{R\overset{X}{C}=\overset{X}{C}H} \xrightarrow{+X_2} \underset{\substack{\text{1, 1, 2, 2-tetrahalo-alkane,}\\ \text{Alkyne tetrahalide}}}{R-\underset{X}{\overset{X}{C}}-\underset{X}{\overset{X}{C}}-H}$$

$$\underset{\text{Propyne}}{CH_3C\equiv CH} \xrightarrow{+Br_2} \underset{\substack{\text{1, 2-dibromopropene,}\\ \text{Propyne dibromide}}}{CH_3CBr=CHBr} \xrightarrow{+Br_2} \underset{\substack{\text{1,1,2,2-tetrabromopropane,}\\ \text{Propyne tetrabromide}}}{CH_3CBr_2.CHBr_2}$$

(3) **Addition of Halogen acids.** Halogen acids also add to alkynes in two stages. After one molecule of the acid has been added to a symmetrical alkyne the product is an unsymmetrical derivative of alkene so that the addition of a second molecule of the acid takes place in accordance with *Markownikoff's rule.* Thus both the halogens become united to the same carbon atom.

$$\underset{\text{Alkyne}}{RC\equiv CR} \xrightarrow{+HX} \underset{\text{1-haloalkene}}{RCH=CRX} \xrightarrow{+HX} \underset{\substack{\text{1, 1-dihaloalkane,}\\ \text{Alkylidene halide}}}{RCH_2-CRX_2}$$

$$\underset{\text{Acetylene}}{HC\equiv CH} \xrightarrow{+HBr} \underset{\text{Bromoethene}}{H_2C=CHBr} \xrightarrow{+HBr} \underset{\substack{\text{1, 1-dibromoethane,}\\ \text{Ethylidene bromide}}}{CH_3-CHBr_2}$$

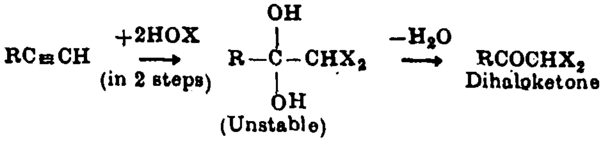
The addition of halogen acid to unsymmetrical alkynes follows Markownikoff's rule in the first as well as the second step and again both the halogens go to the same carbon.

$$\underset{\text{Alkyne}}{RC\equiv CH} \xrightarrow{+HX} RCX=CH_2 \xrightarrow{+HX} RCX_2-CH_3$$

$$\underset{\text{Propyne}}{CH_3C\equiv CH} \xrightarrow{+HBr} \underset{\text{2-Bromopropene}}{CH_3CBr=CH_2} \xrightarrow{+HBr} \underset{\substack{\text{2, 2-Dibromopropane,}\\ \text{Propylidene bromide}}}{CH_3CBr_2CH_3}$$

(4) **Addition of Hypohalous acid.** The addition of two molecules of hypochlorous acid to alkynes takes place in two steps.

Thus :



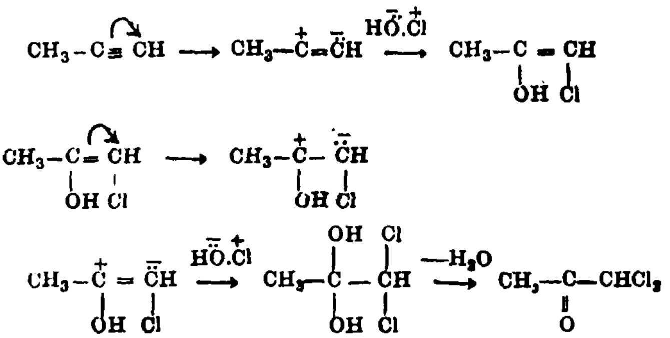
$$RC\equiv CH \xrightarrow[\text{(in 2 steps)}]{+2HOX} \underset{\text{(Unstable)}}{R-\underset{OH}{\overset{OH}{C}}-CHX_2} \xrightarrow{-H_2O} \underset{\text{Dihaloketone}}{RCOCHX_2}$$

$$\underset{\text{Propyne}}{CH_3C\equiv CH} \xrightarrow{+2HOCl} \underset{\text{(Unstable)}}{CH_3C(OH)_2-CHCl_2} \xrightarrow{-H_2O} \underset{\text{1, 1-dichloroacetone}}{CH_3COCHCl_2}$$

However, acetylene would react with hypochlorous acid to form dichloroacetaldehyde.

Hypobromous acid reacts similarly.

Mechanism. Hypochlorous acid is believed to ionise partially as indicated $\overset{+}{Cl}-\overset{-}{OH}$, the chlorine atom being less electronegative than O atom. Thus the mechanism of the reaction may be explained as shown below :

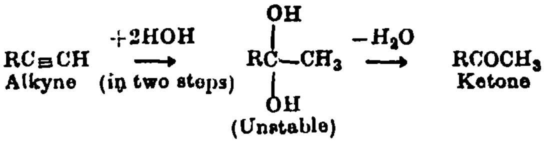


$$CH_3-C\equiv CH \longrightarrow CH_3-\overset{+}{C}=\overset{-}{C}H \xrightarrow{H\overset{-}{O}.\overset{+}{Cl}} CH_3-\underset{OH}{C}=\underset{Cl}{CH}$$

$$CH_3-\underset{OH}{C}=\underset{Cl}{CH} \longrightarrow CH_3-\underset{OH}{\overset{+}{C}}-\underset{Cl}{\overset{-}{C}H}$$

$$CH_3-\underset{OH}{\overset{+}{C}}=\underset{Cl}{\overset{-}{C}H} \xrightarrow{H\overset{-}{O}.\overset{+}{Cl}} CH_3-\underset{OH}{\overset{OH}{C}}-\underset{Cl}{\overset{Cl}{C}H} \xrightarrow{-H_2O} CH_3-\underset{\underset{O}{\|}}{C}-CHCl_2$$

(5) **Addition of Water.** Under the catalytic influence of mercury salts, alkynes combine with water to form an aldehyde or a ketone. Thus :

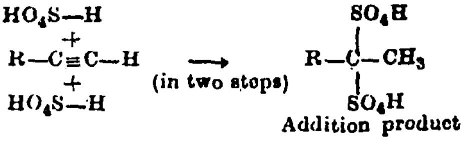


$$\underset{\text{Alkyne}}{RC\equiv CH} \xrightarrow[\text{(in two steps)}]{+2HOH} \underset{\text{(Unstable)}}{R\underset{OH}{\overset{OH}{C}}-CH_3} \xrightarrow{-H_2O} \underset{\text{Ketone}}{RCOCH_3}$$

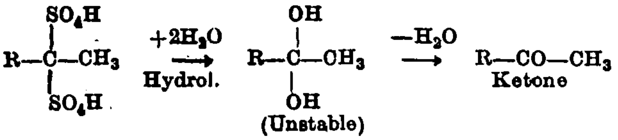
$$\underset{\text{Propyne}}{CH_3C\equiv CH} \xrightarrow{+2HOH} CH_3C(OH)_2CH_3 \xrightarrow{-H_2O} \underset{\text{Acetone}}{CH_3COCH_3}$$

Acetylene under the same conditions yields acetaldehyde.

The above change can also be brought about by absorption of the hydrocarbon in concentrated sulphuric acid and subsequent dilution and distillation of the product.

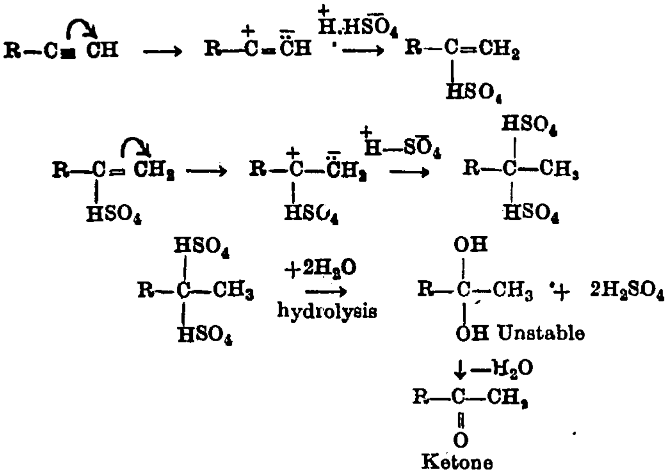


$$\begin{matrix} HO_4S-H \\ + \\ R-C\equiv C-H \\ + \\ HO_4S-H \end{matrix} \xrightarrow[\text{(in two steps)}]{} \underset{\text{Addition product}}{R-\underset{SO_4H}{\overset{SO_4H}{C}}-CH_3}$$



$$R{-}\overset{SO_4H}{\underset{SO_4H}{C}}{-}CH_3 \xrightarrow[\text{Hydrol.}]{+2H_2O} \underset{\text{(Unstable)}}{R{-}\overset{OH}{\underset{OH}{C}}{-}CH_3} \xrightarrow{-H_2O} \underset{\text{Ketone}}{R{-}CO{-}CH_3}$$

According to the modern electronic mechanism of hydration in presence of sulphuric acid, the addition of H_2SO_4 ($H^+{-}HSO_4^-$) takes place in two steps to yield the product $R{-}C(HSO_4)_2{-}CH_3$ which on subsequent hydrolysis gives $R{-}C(OH)_2{-}CH_3$. Since there are two $-OH$ groups on a carbon atom, it loses a water molecule to form a ketone $R{-}CO{-}CH_3$.



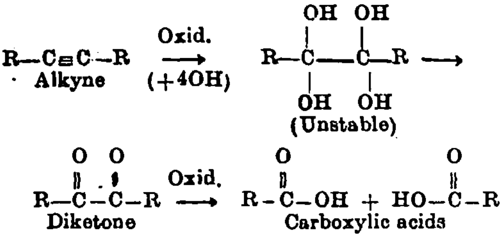
$$R{-}C\equiv CH \longrightarrow R{-}\overset{+}{C}{=}\overset{-}{\ddot{C}}H \xrightarrow{\overset{+}{H}.\overset{-}{HSO_4}} R{-}\underset{HSO_4}{C}{=}CH_2$$

$$R{-}\underset{HSO_4}{C}{=}CH_2 \longrightarrow R{-}\underset{HSO_4}{\overset{+}{C}}{-}\overset{-}{\ddot{C}}H_2 \xrightarrow{\overset{+}{H}{-}\overset{-}{SO_4}} R{-}\overset{HSO_4}{\underset{HSO_4}{C}}{-}CH_3$$

$$R{-}\overset{HSO_4}{\underset{HSO_4}{C}}{-}CH_3 \xrightarrow[\text{hydrolysis}]{+2H_2O} R{-}\overset{OH}{\underset{OH}{C}}{-}CH_3 + 2H_2SO_4 \quad \text{Unstable}$$

$$\xrightarrow{-H_2O} \underset{\text{Ketone}}{R{-}\underset{\underset{O}{\|}}{C}{-}CH_3}$$

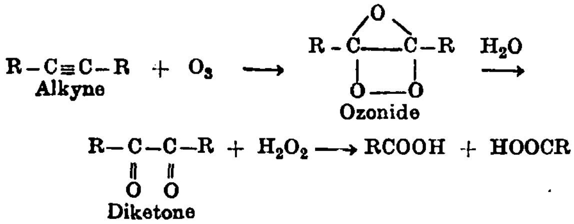
(6) **Oxidation.** Alkynes upon oxidation with strong alkaline potassium permanganate yield lower carboxylic acids.



$$\underset{\text{Alkyne}}{R{-}C\equiv C{-}R} \xrightarrow[(+4OH)]{\text{Oxid.}} \underset{\text{(Unstable)}}{R{-}\overset{OH}{\underset{OH}{C}}{-}\overset{OH}{\underset{OH}{C}}{-}R} \longrightarrow$$

$$\underset{\text{Diketone}}{R{-}\overset{O}{\overset{\|}{C}}{-}\overset{O}{\overset{\|}{C}}{-}R} \xrightarrow{\text{Oxid.}} \underset{\text{Carboxylic acids}}{R{-}\overset{O}{\overset{\|}{C}}{-}OH + HO{-}\overset{O}{\overset{\|}{C}}{-}R}$$

(7) **Ozonide formation.** Alkynes react with ozone to form ozonides that are decomposed by water to form diketones which are then oxidised to acids by the H_2O_2 produced in the reaction.

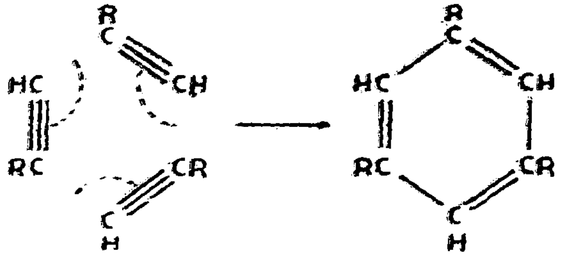


$$\underset{\text{Alkyne}}{R{-}C\equiv C{-}R} + O_3 \longrightarrow \underset{\text{Ozonide}}{\text{(ozonide ring: } R{-}C(O)C{-}R \text{ with } O{-}O)} \xrightarrow{H_2O}$$

$$\underset{\text{Diketone}}{R{-}\underset{\underset{O}{\|}}{C}{-}\underset{\underset{O}{\|}}{C}{-}R} + H_2O_2 \longrightarrow RCOOH + HOOCR$$

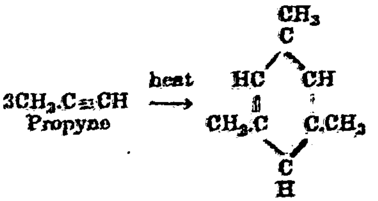
The identification of the acids produced enables the position of the triple bond in the chain to be determined.

(8) **Polymerisation.** Alkynes which passed through a red-hot quartz or iron tube polymerize to give benzene hydrocarbons.



Alkyne Sym-trialkylbenzene

Thus :



Sym-trimethyl benzene, Mesitylene

Acetylene upon passing through a red-hot tube gives benzene.

This reaction provides a method for passing from aliphatic to aromatic compounds.

(9) **Isomerisation.** In presence of traces of sodium amide, 2-alkynes *isomerise to* 1-alkynes. If the 1-alkyne is heated with alcoholic potash, isomerisation takes place in the reverse direction.

$$\underset{\text{2-alkyne}}{R-C\equiv C-CH_3} \underset{KOH_{alc}}{\overset{NaNH_2}{\rightleftharpoons}} \underset{\text{1-alkyne}}{R-CH_2-C\equiv C-H}$$

Thus :

$$\underset{\text{2-butyne}}{CH_3-C\equiv C-CH_3} \underset{KOH_{alc}}{\overset{NaNH_2}{\rightleftharpoons}} \underset{\text{1-butyne}}{CH_3-CH_2-C\equiv C-H}$$

This reaction also provides a method for passing from aliphatic to aromatic compounds.

(10) **Formation of Metal alkynides.** Alkynes differ from the alkenes in that they are acid in character and the H-atoms linked to the acetylenic carbon can be replaced by metals to form derivatives known as **alkynides.**

(*i*) COPPER AND SILVER ALKYNIDES. These can be prepared by merely mixing ammoniacal solutions of the salts and 1-alkynes.

$$\underset{\text{1-Alkyne}}{RC\equiv CH} + Ag(NH_3)_2^+ \longrightarrow \underset{\text{White ppt.}}{RC\equiv CAg} + NH_4^+ + NH_3$$

$$RC\equiv CH + Cu(NH_3)_2^+ \longrightarrow \underset{\text{Red ppt.}}{RC\equiv CCu} + NH_4^+ + NH_3$$

Acetylene having two replaceable H-atoms gives dimetal salts $Ag.C\equiv C.Ag$ and $Cu.C\equiv C.Cu$.

The copper and silver alkynides are covalent compounds, insoluble and unaffected by water. These are fairly stable while wet; but these are highly explosive when dry. These are decomposed by acids to give back the alkyne.

$$\underset{\text{Silver alkynide}}{R-C\equiv C-Ag} + HCl \longrightarrow \underset{\text{Alkyne}}{R-C\equiv C-H} + AgCl$$

Hence the formation of silver and copper alkynides may be used for the separation of alkynes from the gaseous mixtures.

(ii) Sodium Alkynides. These are best prepared by reaction of 1-alkynes with sodium amide in liquid ammonia.

$$\underset{\text{1-Alkyne}}{R-C\equiv C-H} + NaNH_2 \longrightarrow \underset{\text{Sod. alkynides}}{R-C\equiv \overset{-}{C}\overset{+}{Na}} + NH_3$$

They can also be prepared by passing the vapour of the alkyne over molten sodium.

$$R-C\equiv C-H + Na \xrightarrow{\text{heat}} R-C\equiv \overset{-}{C}\overset{+}{Na} + \tfrac{1}{2}H_2$$

Acetylene is capable of yielding mono- and di-sodium salts: C_2HNa, C_2Na_2.

The sodium alkynides hydrolyse readily when in contact with water to liberate the hydrocarbon.

$$\underset{\text{Sod. alkynide}}{R-C\equiv CNa} + HOH \longrightarrow \underset{\text{Alkyne}}{R-C\equiv C-H} + NaOH$$

Recently, these derivatives have become important as by the action of alkyl halides upon them, they yield higher homologues of the original hydrocarbons.

Individual Members

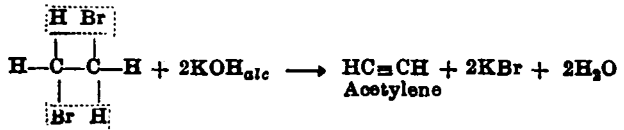
ACETYLENE, ETHYNE, C_2H_2

Edmund Davy (1836) discovered acetylene when he happened to pour water on crude calcium carbide. It is the first stable member of the alkyne series. It is produced by the cracking of alkanes present in natural gas and petroleum. Traces of acetylene are present in gases resulting from the incomplete combustion of coal gas and of oil gas during the striking back of Bunsen burner.

Acetylene is now becoming important as a key chemical for synthesising a large number of compounds, and for making synthetic rubber.

Preparation. Acetylene may be obtained by the following methods :

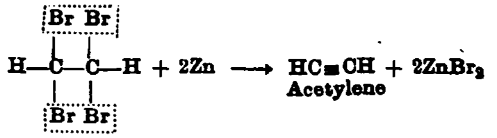
(1) By the action of alcoholic potash on ethylene bromide.



$$\mathrm{H-\overset{H}{\underset{Br}{C}}-\overset{Br}{\underset{H}{C}}-H + 2KOH_{alc} \longrightarrow \underset{Acetylene}{HC\equiv CH} + 2KBr + 2H_2O}$$

Ethylene bromide

(2) By heating 1, 1, 2, 2-tetrabromoethane with metallic zinc.



$$\mathrm{H-\overset{Br}{\underset{Br}{C}}-\overset{Br}{\underset{Br}{C}}-H + 2Zn \longrightarrow \underset{Acetylene}{HC\equiv CH} + 2ZnBr_2}$$

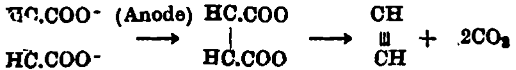
1, 1, 2, 2-Tetrabromoethane

(3) By heating iodoform with silver powder.

$CH\equiv I_3 + 6Ag + I_3\equiv CH \longrightarrow CH\equiv CH + 6AgI$.

Iodoform Acetylene

(4) By the electrolysis of aqueous solutions of potassium salts of maleic or fumaric acid (*Kolbe's Method*). Thus :



$$\begin{array}{l}\mathrm{HC.COO^-}\\ \mathrm{HC.COO^-}\end{array} \xrightarrow{\text{(Anode)}} \begin{array}{l}\mathrm{HC.COO}\\ \ \ |\\ \mathrm{HC.COO}\end{array} \longrightarrow \begin{array}{c}\mathrm{CH}\\ |||\\ \mathrm{CH}\end{array} + 2CO_2$$

Maleate ion (*Unstable*)

(5) By striking an electric arc between carbon electrodes in an atmosphere of hydrogen (*Berthelot's Synthesis*).

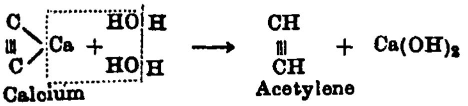
$2C + H_2 \longrightarrow C_2H_2$

Acetylene

The gas thus produced contains some methane and ethylene as impurities which are formed at the same time.

This method provides a basis for the total synthesis of compounds which can be formed from acetylene.

(6) By the action of water on calcium carbide.



$$\begin{array}{c}\mathrm{C}\\ |||\\ \mathrm{C}\end{array}\!\!>\mathrm{Ca} + \begin{array}{l}\mathrm{HO|H}\\ \mathrm{HO|H}\end{array} \longrightarrow \begin{array}{c}\mathrm{CH}\\ |||\\ \mathrm{CH}\end{array} + Ca(OH)_2$$

Calcium carbide Acetylene

LABORATORY PREPARATION

Acetylene is conveniently prepared in the laboratory by dropping water on calcium carbide and collecting the gas over water.

$CaC_2 + 2H_2O \longrightarrow C_2H_2 + Ca(OH)_2$

Cal. carbide Acetylene

A suitable apparatus for the preparation of acetylene is shown in Fig. 12·2. A layer of small lumps of calcium carbide is placed in the Buchner flask. It is then fitted with a dropping funnel using a rubber stopper. Some water is put in the dropping funnel and allowed to fall on calcium carbide, a drop at a time. The first gas coming from the generator is mixed with air and should be rejected. When a test portion of the gas collected in a test-tube burns quietly, the gas is collected in jars. *There should be no flame in the vicinity of the generator as acetylene forms explosive mixtures with air.*

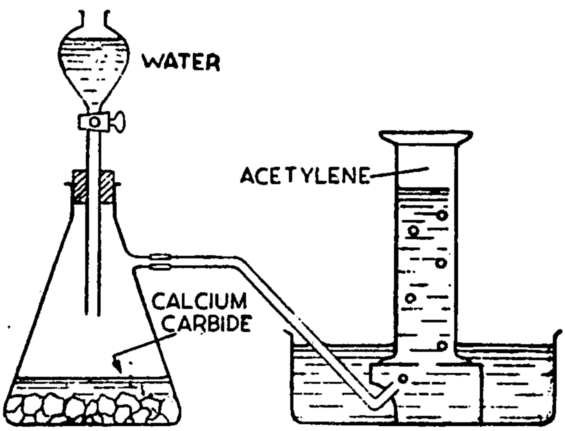


Fig. 12·2. Preparation of Acetylene from Calcium carbide.

MANUFACTURE

(1) *From Calcium carbide.* Acetylene is prepared on a large scale by the action of water on calcium carbide obtained by fusion of coke with quicklime in an electric furnace.

$$\underset{\text{Quicklime}}{CaO} + 3C \longrightarrow \underset{\text{Cal. carbide}}{CaC_2} + CO$$

$$CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + \underset{\text{Acetylene}}{C_2H_2}$$

With the development of hydroelectric projects, this method will become a potential source of acetylene in India.

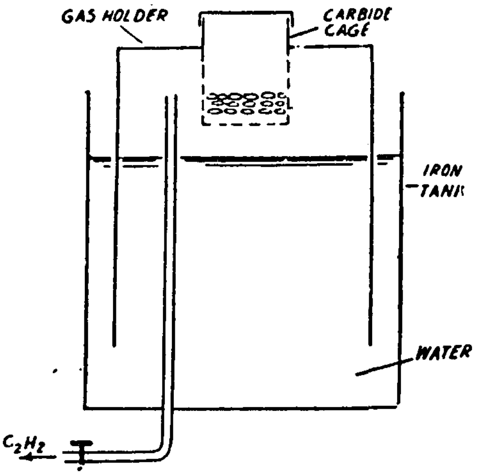


Fig. 12·3. Automatic plant for Acetylene.

(2) *From Natural Gas.* Methane obtained from natural gas is cracked at the temperature of electric arc to give acetylene.

$$2CH_4 \xrightarrow{1200^\circ} CH\equiv CH + 3H_2$$

Properties. *Physical.* Acetylene is a colourless gas with ethereal odour when pure. As prepared from calcium carbide it has a characteristic garlic odour owing to the presence of traces of phosphine and hydrogen sulphide gas. It can be liquefied at 1°C under a pressure of 48 atmospheres. Liquid acetylene boils at —82°C. It is very slightly soluble in water, somewhat more so in alcohol and very soluble in acetone. Thus, when needed for industrial purpose, acetylene is transported dissolved in acetone under high pressure as ordinary liquid acetylene explodes violently by shock or heat. Acetylene is somewhat poisonous and produces general anaesthesia when inhaled.

Chemical. The strain in acetylene molecule is more pronounced than in ethylene since it is here due to the distortion of three valency bonds instead of two in case of ethylene. A triple bond being equivalent to two double bonds, acetylene gives all the addition reactions of ethylene twice over, as also the oxidation and polymerisation reactions. However, it differs from ethylene as it forms metallic derivatives while ethylene does not.

(1) Addition of Hydrogen. (*i*) In the presence of finely divided nickel a 140°C, acetylene combines with hydrogen to form ethylene and then ethane.

$$\underset{\text{Acetylene}}{CH\equiv CH} \xrightarrow{+H_2} \underset{\text{Ethylene}}{CH_2=CH_2} \xrightarrow{+H_2} \underset{\text{Ethane}}{CH_3-CH_3}$$

If finely divided palladium or iron is used as a catalyst, it is possible to stop the addition of hydrogen at the first step when the product obtained would be ethylene.

(2) Addition of Halogens. (*i*) Acetylene adds on gaseous chlorine or bromine in the dark forming the respective di- and tetrahalogen derivatives.

$$\underset{\text{Acetylene}}{CH\equiv CH} \xrightarrow[\text{(dark)}]{+Cl_2} \underset{\substack{\text{1, 2-dichloroethylene,}\\ \text{Acetylene dichloride}}}{CHCl=CHCl} \xrightarrow{+Cl_2} \underset{\substack{\text{1, 1, 2, 2-tetra-}\\ \text{chloroethane,}\\ \text{Acetylene tetrachloride}}}{CHCl_2-CHCl_2}$$

It reacts explosively with chlorine gas in daylight, bursting into flame.

$$C_2H_2 + Cl_2 \longrightarrow 2C + 2HCl$$

(*ii*) Acetylene reacts with bromine water to form the dibromide and discharging the brown colour.

$$CH\equiv CH + \underset{(\textit{Aqueous})}{Br} \longrightarrow \underset{\substack{\text{1, 2-dibromoethene,}\\ \text{Acetylene dibromide}}}{CHBr=CHBr}$$

(*iii*) Acetylene adds on iodine with difficulty, yielding the diiodide in alcoholic solution only.

$$\underset{(alcoholic)}{C_2H_2 + I_2} \longrightarrow \underset{\text{Acetylene diiodide}}{C_2H_2I_2}$$

(3) ADDITION OF HALOGEN ACIDS. Acetylene adds on one or two molecules of halogen acids.

Thus :

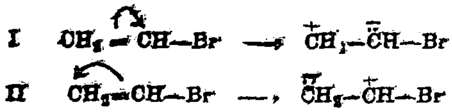
$$\underset{\text{Acetylene}}{CH{\equiv}CH} \xrightarrow{+HBr} \underset{\substack{\text{1-bromoethene,}\\ \text{Vinyl chloride}}}{CH_2{=}CHBr} \xrightarrow{+HBr} \underset{\substack{\text{1, 1-dibromoethane,}\\ \text{Ethylidene chloride}}}{CH_3{-}CHBr_2}$$

The addition of second molecule of hydrogen bromide at the double bond takes place according to Markownikoff's rule.

Mechanism

$$CH{\equiv}CH \xrightarrow[\text{effect}]{\text{Electromeric}} H\overset{+}{C}{=}\overset{-}{\ddot{C}}H \xrightarrow{\overset{+}{H}{-}\overset{-}{Br}} \underset{\text{Vinyl bromide}}{CH_2{=}CHBr}$$

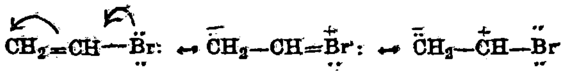
Vinyl bromide may undergo further electromeric effect in two ways.



$$\text{I} \quad CH_2{=}CH{-}Br \longrightarrow \overset{+}{C}H_2{-}\overset{-}{\ddot{C}}H{-}Br$$

$$\text{II} \quad CH_2{=}CH{-}Br \longrightarrow \overset{-}{\ddot{C}}H_2{-}\overset{+}{C}H{-}Br$$

Since Br is more electronegative than carbon, it would cause the electron drift towards itself thus favouring change I. Vinyl bromide is also capable of existing as resonance hybrid of the structures—



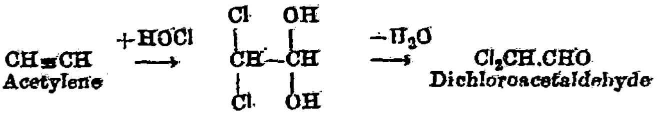
$$CH_2{=}CH{-}\ddot{Br}: \longleftrightarrow \overset{-}{\ddot{C}}H_2{-}CH{=}\overset{+}{Br}: \longleftrightarrow \overset{-}{\ddot{C}}H_2{-}\overset{+}{C}H{-}\ddot{Br}$$

Here we find the tendency is to push electrons in the opposite direction, to that in change I. Resonance effect is decidedly stronger than the electromeric effect, hence the displacement of electrons takes place as in change II, and the addition would be in accordance with Markownikoff's rule.

$$\overset{-}{\ddot{C}}H_2{-}\overset{+}{C}H{-}\ddot{Br}: \xrightarrow{\overset{+}{H}{-}\overset{-}{Br}} CH_3{-}CHBr_2$$

(4) ADDITION OF HYPOHALOUS ACIDS. Acetylene adds two molecules of hypochlorous acid and hypobromous acid to yield dihaloacetaldehyde.

Thus :



$$\underset{\text{Acetylene}}{CH{\equiv}CH} \xrightarrow{+HOCl} \underset{(Unstable)}{\begin{array}{cc} Cl & OH \\ | & | \\ CH{-} & CH \\ | & | \\ Cl & OH \end{array}} \xrightarrow{-H_2O} \underset{\text{Dichloroacetaldehyde}}{Cl_2CH.CHO}$$

(5) ADDITION OF SULPHURIC ACID. Acetylene reacts with concentrated sulphuric acid in two steps to form ethylidene sulphate.

$$\underset{\text{Acetylene}}{CH{\equiv}CH} \xrightarrow{+\overset{+}{H}\overset{-}{SO_4}H} \underset{\text{Intermediate}}{CH_2{=}CH(SO_4H)} \xrightarrow{+\overset{+}{H}\overset{-}{SO_4}H} \underset{\text{Ethylidene sulphate}}{CH_3{-}CH(SO_4H)_2}$$

Since the ethylidene sulphate upon hydrolysis yields acetaldehyde, the reaction is used for the industrial production of the latter.

$$CH_3CH(SO_4H)_2 + 2HOH \longrightarrow \underset{(\textit{Unstable})}{CH_3CH(OH)_2} + 2H_2SO_4$$

$$CH_3CH(OH)_2 \longrightarrow CH_3CHO + H_2O$$

(6) Addition of Water. Acetylene adds a molecule of water when passed through dilue sulphuric acid in the presence of mercuric sulphate at 60° to give acetaldehyde directly.

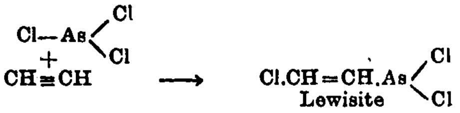
$$\begin{array}{c} H{-}OH \\ + \\ HC{\equiv}CH \end{array} \xrightarrow[80^\circ]{(H_2SO_4/HgSO_4)} \underset{\substack{\text{Vinyl alcohol} \\ (\textit{Unstable})}}{CH_2{=}CH{-}OH} \longrightarrow \underset{\text{Acetaldehyde}}{CH_3CHO}$$

The vinyl alcohol first produced is unstable and at once changes to the stable isomer, acetaldehyde.

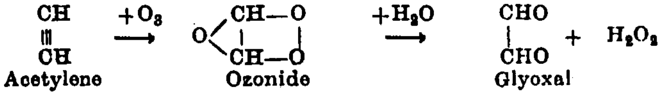
(7) Addition of HCN. It adds a molecule of hydrogen cyanide to form vinyl nitrile which is widely used in the manufacture of synthetic rubber and plastics.

$$CH{\equiv}CH + HCN \longrightarrow \underset{\text{Vinyl nitrile}}{CH_2{=}CH{-}CN}$$

(8) Addition of Arsenic trichloride. Acetylene adds to a molecule of arsenic trichloride to form β-chlorovinyl dichloroarsine which was used as poison gas **Lewisite** in the World War II.



(9) Oxidation. (*i*) Acetylene adds on a molecule of ozone across the triple bond to form an ozonide which on boiling with water yields glyoxal.



(*ii*) When passed through a solution of chromic acid, acetylene is oxidised to acetic acid. With dilute alkaline potassium permanganate, it is oxidised to oxalic acid.

$$\underset{\text{Acetylene}}{CH{\equiv}CH} + H_2O + O \longrightarrow \underset{\text{Acetic acid}}{CH_3COOH}$$

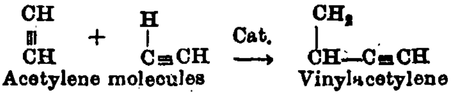
$$\underset{\text{Acetylene}}{\begin{array}{c} CH \\ ||| \\ CH \end{array}} + 4O \longrightarrow \underset{\text{Oxalic acid}}{\begin{array}{c} COOH \\ | \\ COOH \end{array}}$$

(*iii*) When mixed with oxygen and ignited, acetylene burns explosively undergoing oxidation to carbon dioxide and water.

$$2C_2H_2 + 5O_2 \longrightarrow 4CO_2 + 3H_2O + 620\ \text{Cal.}$$

However, when pure acetylene is burnt at a jet, it produces a strongly luminous flame owing to the presence of incandescent carbon particles. When fed into an acetylene flame, it insures complete combustion and a non-luminous flame (3000°) is obtained which is used for cutting and welding metals.

(10) **POLYMERISATION.** (*i*) When acetylene is passed into solution of cuprous chloride and ammonium chloride in hydrochloric acid, it adds to itself to form vinylacetylene, which is used for the preparation of synthetic rubber.



$$\underset{\text{Acetylene molecules}}{\begin{matrix}CH\\ \| \\ CH\end{matrix} + \begin{matrix}H\\ | \\ C\equiv CH\end{matrix}} \xrightarrow{\text{Cat.}} \underset{\text{Vinylacetylene}}{\begin{matrix}CH_2\\ | \\ CH-C\equiv CH\end{matrix}}$$

(*ii*) When passed through a red-hot tube (400°), three molecules of acetylene join together to form benzene.

$$3C_2H_2 \longrightarrow \underset{\text{Benzene}}{C_6H_6}$$

(11) **FORMATION OF ACETYLIDES.** (*i*) Copper and silver acetylides are formed as insoluble precipitates by passing acetylene through ammoniacal solutions of copper sulphate and silver nitrate repectively.

$$C_2H_2 + 2Cu(NH_3)_2^+ \longrightarrow \underset{\substack{\text{Copper acetylide}\\ (\textit{red})}}{C_2Cu_2} + 2NH_4^+ + 2NH_3$$

$$C_2H_2 + 2Ag(NH_3)_2^+ \longrightarrow \underset{\substack{\text{Silver acetylide}\\ (\textit{white})}}{C_2Ag_2} + 2NH_4^+ + 2NH_3$$

This serves as a delicate test for acetylene. Since acetylides are decomposed by acids to regenerate acetylene, the above reaction is used in gas analysis for the separation of this hydrocarbon from other gaseous hydrocarbons.

(*ii*) Acetylene reacts with sodium amide in liquid ammonia to form sodium acetylides.

$$C_2H_2 + NaNH_2 \longrightarrow \underset{\text{Sod. acetylide}}{C_2HNa} + NH_3$$

$$C_2H_2 + 2NaNH_2 \longrightarrow \underset{\text{Disod. acetylide}}{C_2Na_2} + 2NH_3$$

These can also be obtained by passing acetylene over fused sodium metal.

(12) **VINYLATION.** Walter Reppe in 1940 showed that alcohols and acids could be added to a molecule of acetylene at a temperature 120–180°C and 1–15 atm. pressure in presence of basic catalysts,

the products being vinyl ether and vinyl ester respectively. This process whereby an H atom is replaced by a vinyl group, is termed **Vinylation**.

$$CH\equiv CH + ROH \xrightarrow[\substack{120\text{-}180^\circ C \\ 1\text{-}15\ atm.}]{basic\ cat.} \underset{\text{Vinyl ether}}{R-O\ CH=CH_2}$$

$$CH\equiv CH + RCOOH \xrightarrow[\substack{120\text{-}180^\circ C. \\ 1\text{-}15\ atm.}]{basic\ cat.} \underset{\text{Vinyl ester}}{CH_2=CH-OOCR}$$

Vinyl ethers and vinyl esters may be polymerised to yield polyvinyl ethers and esters, the products of great commercial importance.

Uses. Acetylene is used : (1) For illumination in cycle lamps, hawker's lamps, buoys and in light houses, when it is obtained by dropping water on calcium carbide.

(2) For producing oxy-acetylene flame (2800°) for the welding and cutting of iron and steel.

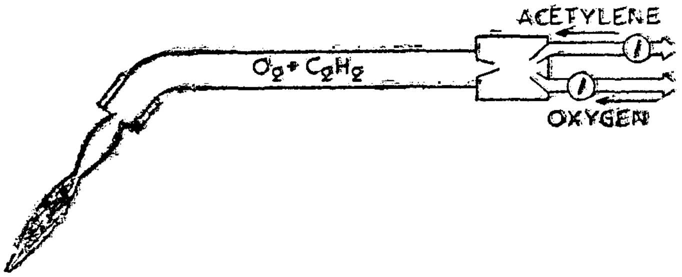


Fig. 124. Oxy-acetylene Torch.

(3) For the artificial ripening of fruits and vegetables.

(4) For the manufacture of hydrogen and *lamp black* by burning it in a limited supply of air.

(5) For the manufacture of a number of organic compounds such as acetaldehyde, acetic acid, ethanol ; as also for acetylene dichloride and acetylene tetrachloride both of which are excellent solvents.

(6) As a starting material for the preparation of plastics, synthetic rubbers and synthetic fibre *orlon*.

Tests. (1) Acetylene burns with a smoky luminous flame.

(2) It discharges the yellow colour of bromine water and pink colour of dilute alkaline permanganate solution.

(3) With ammoniacal solution of cuprous chloride, it gives a red precipitate of copper acetylide.

(4) With ammoniacal silver nitrate solution, it forms a white precipitate of silver acetylide.

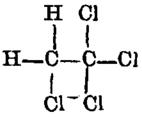
Structure. (1) The molecular formula of acetylene as determined by gas analysis is C_2H_2.

(2) Keeping in view the tetra-covalency of carbon, acetylene can have two possible structural formulae.

$$\overset{\overset{H}{|}}{H-C}=\overset{|}{C}- \qquad H-C\equiv C-H$$

I II

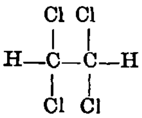
(3) Formula I is discarded as (*i*) it postulates the presence of free valencies which is an uncommon thing in organic chemistry; (*ii*) on addition of four chlorine atoms, it would give



$$H-\underset{\underset{Cl}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{Cl}{|}}{\overset{\overset{Cl}{|}}{C}}-Cl$$

1, 2, 2, 2-Tetrachloroethane

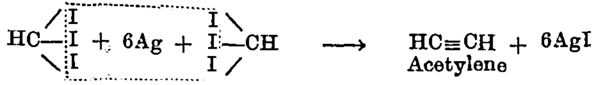
whereas actually we get



$$H-\underset{\underset{Cl}{|}}{\overset{\overset{Cl}{|}}{C}}-\underset{\underset{Cl}{|}}{\overset{\overset{Cl}{|}}{C}}-H$$

1, 1, 2, 2-Tetrachloroethane

(4) Formula II for acetylene is further supported by the synthesis from iodoform by heating it with silver powder.



$$HC\!\begin{smallmatrix}/I\\-I\\\backslash I\end{smallmatrix} + 6Ag + \begin{smallmatrix}I\backslash\\I-\\I/\end{smallmatrix}\!CH \longrightarrow \underset{\text{Acetylene}}{HC\equiv CH} + 6AgI$$

(5) The orbital structure of acetylene has already been discussed. Since acetylene molecule is known to be linear, the carbon atoms in it are in *sp* hybridisation state. Each of the two carbons possesses two *sp* hybrid orbitals and two pure *p* orbitals. The two carbons get bonded to each other by σ bond resulting from overlap of one *sp* orbital on them. Their second *sp* orbitals are utilized in forming σ bonds with *s* orbital of hydrogen atoms. The remaining two *p* orbitals on carbons overlap sidewise to give two π bonds. Thus there are in all three σ bonds and two π bonds. Geometry of the molecule as revealed by the diffraction experiments tells C—C length 1·20 Å, C—H length 1·06 Å and H—C—H angle equal to 180°.

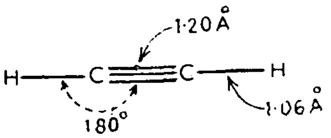
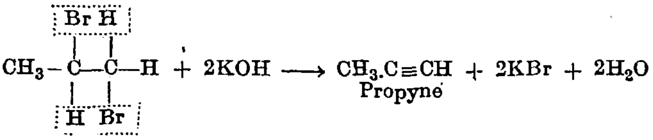


Fig. 12·5. Geometry of Acetylene molecule.

PROPYNE, ALLYLENE, C_3H_4

Preparation. (1) It can be prepared by heating propylene bromide with alcoholic potash.



$$CH_3-\underset{\underset{H}{|}}{\overset{\overset{Br}{|}}{C}}-\underset{\underset{Br}{|}}{\overset{\overset{H}{|}}{C}}-H + 2KOH \longrightarrow \underset{\text{Propyne}}{CH_3.C\equiv CH} + 2KBr + 2H_2O$$

(2) It can also be obtained by the action of methyl iodide on sodio acetylide.

$$HC{\equiv}CNa + CH_3I \longrightarrow CH{\equiv}C.CH_3 + NaI$$

Properties. Propyne is a colourless and odourless gas. The liquid hydrocarbon boils at —27°C.

It gives all the reactions typical of alkynes.

DIACETYLENES

The hydrocarbons containing two triple bonds are named as *Diacetylenes.* The two important members of this class are :

Formula	*Name*
$HC{\equiv}C{-}C{\equiv}CH$	Diacetylene
$CH{\equiv}C.CH_2.CH_2.C{\equiv}CH$	Dipropargyl

Dipropargyl is of special interest as it has the same molecular formula as that of benzene. However unlike benzene it readily forms addition products with halogens and is oxidised with potassium permanganate

QUESTIONS

1. What are alkynes ? How do they differ from alkanes and alkenes in respect of the structural formula ?

2. What types of isomerism are encountered in an alkyne hydrocarbons ? Why do they not show Geometrical Isomerism ?

3. Describe in detail the methods of producing triple bond in organic compounds. How will you synthesise propyne from elements ?

4. Describe the preparation of acetylene. How may acetylene be converted into (*a*) ethane, (*b*) acetaldehyde, (*c*) ethylidene bromide, (*d*) benzene, (*e*) acetone ?

5. How would you prepare acetylene ? State its properties and uses.

6. Justify the statement that acetylene will form the basic substance of the organic chemical industry of the future.

7. Elucidate the synthetic importance of acetylene.
(*Panjab B.Sc. II, 1964*)

8. Describe the preparation and properties of acetylene and indicate industrial applications of the substance as an intermediate product.
(*Calcutta B.Sc., 1964*)

9. Give the preparation and uses of acetylene. What is unsaturation ?
(*Dibrugarh B.Sc., 1967*)

10. Illustrate and describe briefly the geometrical and electronic structure of acetylene. Give three industrially important reactions of acetylene.
(*Panjab B.Sc. II, 1967*)

11. What are alkynes ? How are they distinguished from alkenes ?
(*Panjab B.Sc. II, 1968*)

12. How is acetylene prepared in the laboratory ? How can the following substances be prepared from acetylene (*a*) Ethyl alcohol and (*b*) Acetone ?

Discuss the synthetic and industrial uses of acetylene. How would you distinguish between a saturated hydrocarbon and an unsaturated hydrocarbon ? (*Viswa Bharati B.Sc., 1969*)

13. Give the general methods of preparing alkynes. What is the action of the following on acetylene :

(*i*) Ammoniacal cuprous chloride.

(*ii*) Ozone.

(*iii*) Sodium and liquid ammonia.

(*iv*) Sulphuric acid in the presence of mercuric sulphate.

(*Bombay B.Sc.*, *1969*)

14. How is acetylene prepared in the laboratory ? Give the reaction of acetylene with—

(*i*) Dilute sulphuric acid in the presence of mercurous sulphate.

(*ii*) Ammoniacal cuprous chloride.

(*iii*) HBr.

Give the names of commercial important compounds which are obtained from acetylene. (*Jammu & Kashmir B.Sc.*, *1969*)

13

Halogen Derivatives

CHARLES A. WURTZ
(1817–1884)
He worked with halogen compounds (Wurtz reaction), aliphatic amines, glycols, lactic acid. He synthesised alcohols by reduction of aldehydes and ethylene oxide.

GENERAL

We have seen that alkanes react with halogens forming products containing halogen atoms. *This class of compounds which are obtained by the replacement of one or more hydrogen atoms in hydrocarbons by a corresponding number of halogen atoms* are called **Halogen derivatives**. They are further termed **mono-**, **di-**, **tri-** and **tetrahalogen derivatives** according to the number of the halogen atoms present in the molecule. For instance, methane (CH_4) forms four chloro-derivatives :

CH_3Cl	Methyl chloride, Monochloromethane
CH_2Cl_2	Methylene chloride, Dichloromethane
$CHCl_3$	Chloroform, Trichloromethane
CCl_4	Carbon tetrachloride, Tetrachloromethane

The halogen derivatives of hydrocarbons are never found in nature and yet they are among the most useful of the aliphatic compounds. They are frequently used for introducing the hydrocarbon radicals in other molecules and form the basis for the synthesis of innumerable types of organic compounds. Besides, they are much used in medicine and some of them are excellent solvents.

Non-ionised Character. Halogen derivatives could well be compared with metallic halides.

C_2H_5I	$C_2H_4Br_2$	$CHCl_3$
Ethyl iodide	Ethylene bromide	Chloroform
NaI	$CaBr_2$	$AlCl_3$
Sodium iodide	Calcium bromide	Aluminium chloride

The similarity between them is, however, superficial. While inorganic halides are ionised, halogen derivatives are non-ionised in character. Thus, if we add a solution of silver nitrate to sodium iodide, at once a precipitate of silver iodide is formed, while the addition of the same reagent to ethyl iodide produces no precipitate at all.

MONOHALOGEN DERIVATIVES

As referred to above, monohalogen compounds may be regarded as derivatives of hydrocarbons in which one halogen atom has been substituted by a halogen atom.

$$C_nH_{2n+2} \xrightarrow[+X]{-H} C_nH_{2n+1}X$$

where X=Cl, Br, or I. They may thus be named as **monohaloalkanes**. Since their molecules are essentially built of an alkyl radical linked to a halogen atom, they are conveniently called **alkyl halides** and their type formula is written as RX.

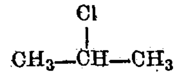
Alkyl halides may also be looked upon as derivatives of hydrogen halides HX, in which the hydrogen has been replaced by an alkyl radical. Thus they are **the esters of halogen hydracids.**

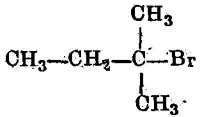
NOMENCLATURE

More simple alkyl halides are called by the common names while the higher complex members are named by the IUPAC system.

(1) The COMMON NAMES. These compounds are named as alkyl derivatives of hydrogen halides : HF hydrogen fluoride, HCl *hydrogen chloride, HBr hydrogen bromide, and HI hydrogen iodide.* Thus the common names of alkyl halides (RX) are two word names—the name of the alkyl group followed by the separate word fluoride, chloride, bromide or iodide as the the case may be. Branched chain alkyl halides may be distinguished as primary, secondary (sec-), or tertiary (tert-) where necessary.

CH_3I
Methyl iodide

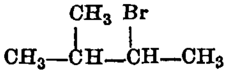

$$CH_3-\underset{}{\overset{Cl}{\overset{|}{C}}}H-CH_3$$
Isopropyl chloride


$$CH_3-CH_2-\underset{CH_3}{\overset{CH_3}{C}}-Br$$
tert-amyl bromide

(2) According to the IUPAC SYSTEM alkyl halides are named as monohalogen substituted alkanes. Thus their systematic name is

a one word name obtained by prefixing fluoro, chloro, bromo or iodo directly to the name of the parent hydrocarbon. In complex derivatives, the numeral indicating the position of the halogen atom is prefixed by the conventions of the IUPAC System.

C_2H_5Cl Chloroethane $CH_3CH_2CH_2I$ 1-iodopropane



$CH_3-\overset{CH_3}{\overset{|}{C}}H-\overset{Br}{\overset{|}{C}}H-CH_3$

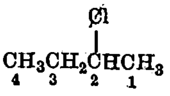
3-bromo-2-methylbutane

ISOMERISM

Alkyl halides show chain isomerism and position isomerism which is due to the different positions of the halogen atoms on the carbon chain. Thus butane can give rise to as many as four isomeric monohalogen derivatives.

(*i*) $\underset{4}{CH_3}\underset{3}{CH_2}\underset{2}{CH_2}\underset{1}{CH_2}Cl$ Primary butyl chloride or 1-chlorobutane

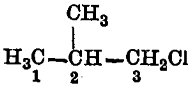
(*ii*)



$\underset{4}{CH_3}\underset{3}{CH_2}\underset{2}{\overset{Cl}{\overset{|}{C}}}H\underset{1}{CH_3}$

Secondary butyl chloride or 2-chlorobutane

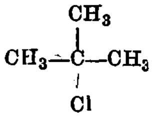
(*iii*)



$\underset{1}{H_3C}-\underset{2}{\overset{CH_3}{\overset{|}{C}}H}-\underset{3}{CH_2Cl}$

Primary isobutyl chloride or 2-methyl-3-chloropropane

(*iv*)



$CH_3-\underset{Cl}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CH_3$

Tertiary isobutyl chloride or 2-methyl-2-chloropropane

While compounds (*i*) and (*ii*) illustrate position isomerism, compounds (*i*) and (*iii*) present a case of chain isomerism.

METHODS OF FORMATION

Alkyl halides can be synthesised from three sources :

(*i*) FROM ALKANES : by direct halogenation.

(*ii*) FROM ALKENES : by addition with halogen acids.

(*iii*) FROM ALCOHOLS : by double decomposition with (*a*) halogen acids, (*b*) thionyl chloride, and (*c*) phosphorus halides.

(1) **Direct halogenation of alkanes.** Chlorine and bromine react directly with alkanes to form, in the first instance, an alkyl halide.

$$\underset{\text{Methane}}{CH_4} + Cl_2 \longrightarrow \underset{\text{Methyl chloride}}{CH_3Cl} + HCl$$

The reaction is facilitated by the action of heat, light and a catalyst. Bromine does not react so readily as chlorine while iodine does not react at all.

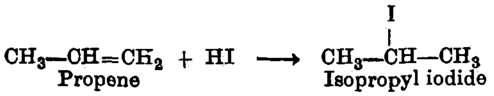
This method has only limited application. It does not give pure compounds because halogen derivatives containing two or more halogen atoms are formed along with the alkyl halides.

However, commercially the method is important because here cheapness and purity is the governing factor. Lower alkynes are available in large amounts from natural gas and can be converted to cheap halogenated products.

(2) **Addition of hydrogen halides to alkenes.** Alkyl halides can also be prepared by the addition of a hydrogen halide to an alkene.

$$\underset{\text{Ethylene}}{C_2H_4} + HI \longrightarrow \underset{\text{Ethyl iodide}}{C_2H_5I}$$

Addition of halogen acids to higher alkenes follows Markownikoff's rule, yielding secondary or tertiary alkyl halides depending upon the structure of the hydrocarbon. Thus :



$$\underset{\text{Propene}}{CH_3{-}CH{=}CH_2} + HI \longrightarrow \underset{\text{Isopropyl iodide}}{CH_3{-}\overset{\overset{\displaystyle I}{|}}{C}H{-}CH_3}$$

This method is well suited for the industrial preparation of alkyl halides as the lower alkenes are obtained in large quantities by cracking of petroleum products.

(3) **Action of thionyl chloride on alcohols.** Alkyl halides are conveniently prepared by the action of halogen acids on the corresponding alcohols.

$$\underset{\text{Ethyl alcohol}}{C_2H_5\boxed{OH + H}Cl} \overset{ZnCl_2}{\rightleftharpoons} \underset{\text{Ethyl chloride}}{C_2H_5Cl} + H_2O$$

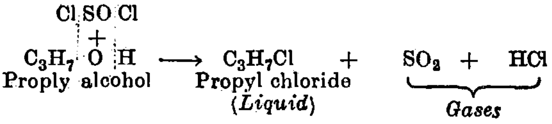
The reaction is reversible and can be made to go to completion by the use of a water-removing substance (*Law of Mass Action*). Anhydrous zinc chloride is generally used for the purpose.

Alkyl halides can also be obtained by passing a mixture of vapours of alcohol and hydrogen halide over a heated dehydration catalyst.

$$\underset{\text{Ethyl alcohol}}{C_2H_5OH} + HCl \xrightarrow[Al_2O_3]{350°} \underset{\text{Ethyl chloride}}{C_2H_5Cl} + H_2O$$

This is an excellent method for the preparation of alkyl halides in the laboratory and on a commercial scale.

(4) **Action of thionyl chloride on alcohols.** Alcohols react readily with thionyl chloride, $SOCl_2$, forming alkyl halides.



$$\underset{\text{Proply alcohol}}{C_3H_7\,\overset{\overset{\displaystyle Cl\,SO\,Cl}{+}}{O\,H}} \longrightarrow \underset{\substack{\text{Propyl chloride}\\ (\textit{Liquid})}}{C_3H_7Cl} + \underbrace{SO_2 + HCl}_{\textit{Gases}}$$

The gaseous by-products escape leaving behind the alkyl halide in the pure state.

(5) **Action of phosphcrus halides on alcohols** Alkyl halides can easily be prepared from alcohols by the action of phosphorus halides.

$$\underset{\text{Methyl alcohol}}{CH_3OH} + PCl_5 \longrightarrow \underset{\text{Methyl chloride}}{CH_3Cl} + POCl_3 + HCl$$

$$3CH_3OH + PI_3 \longrightarrow \underset{\text{Methyl iodide}}{3CH_3I} + H_3PO_3$$

In the preparation of iodo and bromo derivatives it is not necessary to use the phosphrous halides as such, but rather it is conveniently replaced by an appropriate mixture of red phosphorus and iodine or bromine.

This method is particularly suitable for the preparation of the lower bromides and iodides in the laboratory.

PHYSICAL CHARACTERISTICS

(1) The lower members are either colourless gases or volatile liquids with a sweetish ethereal odour. The higher members are odourless solids. Alkyl iodides become brown on standing due to the separation of iodine by decomposition.

(2) Their boiling points are of the same order as those of the alkanes and they are in general lower than those of the corresponding alcohols.

(3) Alkyl halides are only slightly soluble in water but dissolve readily in organic solvents.

(4) The boiling points of alkyl halides go on rising and the specific gravities go on falling with the increase of molecular weight. For the three types of alkyl halides, the boiling point and specific gravities are in the order : iodide > bromide > chloride. Boiling points of some lower member are given below for illustration.

ALKYL RADICAL	CHLORIDE	BROMIDES	IODIDE
Methyl	—22·7°	4·5°	45°
Ethyl	12·5°	38·4°	72·8°
n-Propyl	46·5°	71°	102·5°

(5) They burn easily producing a green edged flame.

CHEMICAL CHARACTERISTICS

Alkyl halides have an alkyl radical in union with a halogen atom. Thus the reactions given by these compounds will be due to

(*i*) *the hydrocarbon part* ;
and (*ii*) *the halogen atom.*

The hydrocarbon part shows its usual inertness toward most reagents and like alkanes undergoes halogenation yielding polyhalogen derivatives. The halogen atom of the alkyl halides is very reactive and can easily be replaced by many atoms or groups. This makes them valuable starting materials for preparing a variety of organic compounds.

In substitution reactions of alkyl halides the halogen atom of the latter is replaced by the nucleophilic reagent (Nu:) as indicated below :

$$\bar{Nu} \longrightarrow R\overset{\curvearrowright}{=}X \longrightarrow Nu{-}R + \bar{X}:$$

The covalent linkage between R and X is broken in the presence of the nucleophilic reagent while the lone pair of the nucleophile is donated to the carbonium ion. At the same time another nucleophile ($\bar{X}$:) is generated. This mechanism is illustrated by the examples given below.

The synthetic reactions of alkyl halides are :

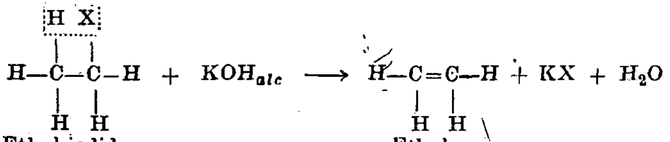
(1) On reduction with zinc and hydrochloric acid, alkyl halides form **alkanes.**

$$\underset{\text{Ethyl iodide}}{C_2H_5I} + 2H \longrightarrow \underset{\text{Ethane}}{C_2H_6} + HI$$

(2) On treatment with SODIUM OR ZINC POWDER two molecules of the alkyl halide are joined to form **higher alkanes.** (*Wurtz Reaction*).

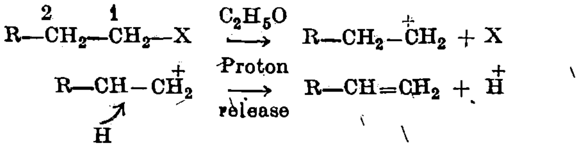
$$\underset{\text{Ethyl iodide}}{C_2H_5\boxed{I + 2Na + I}C_2H_5} \longrightarrow \underset{\text{Butane}}{C_2H_5.C_2H_5} + 2NaI$$

(3) When heated with ALCOHOLIC POTASH, they give **alkenes.**



$$\underset{\text{Ethyl iodide}}{H-\overset{\boxed{H\quad X}}{\underset{H}{C}-\underset{H}{C}}-H} + KOH_{alc} \longrightarrow \underset{\text{Ethylene}}{H-\underset{H}{C}=\underset{H}{C}-H} + KX + H_2O$$

Since alcohol (solvent) is a polar substance and is present in solution as ethoxide ions ($C_2H_5\bar{O}$), it causes the ionisation of alkyl halide. The second carbon atom of the halide then loses a proton which combines with the halide ions produced in the first step.



$$R-\overset{2}{C}H_2-\overset{1}{C}H_2-X \xrightarrow{C_2H_5O} R-CH_2-\overset{+}{C}H_2 + X$$

$$R-\underset{\underset{H}{\nearrow}}{CH}-\overset{+}{C}H_2 \xrightarrow[\text{release}]{\text{Proton}} R-CH=CH_2 + \overset{+}{H}$$

Potassium hydroxide serves to remove the hydrohalogen (HX) molecule as soon as it is formed.

(4) They react with SODIO-ACETYLIDES to form **higher alkynes.**

$$\underset{\text{Sodio-acetylide}}{HC\equiv C\boxed{Na + I}CH_3} \longrightarrow \underset{\text{Propyne}}{CH\equiv C.CH_3} + NaI$$

(5) With AQUEOUS POTASH or moist silver oxide (AgOH), they are hydrolysed to the corresponding **alcohols.**

$$C_2H_5\boxed{I + K}OH_{aq} \longrightarrow \underset{\text{Ethyl alcohol}}{C_2H_5OH} + KI$$

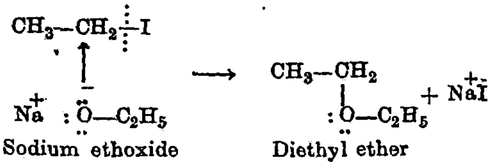
$$C_2H_5I + AgOH \longrightarrow C_2H_5OH + AgI$$

(6) They react with ALKOXIDES or dry silver oxide forming **ethers.**

$$\underset{\text{Sod. ethoxide}}{C_2H_5ONa} + IC_2H_5 \longrightarrow \underset{\text{Diethyl ether}}{C_2H_5OC_2H_5} + NaI$$

$$2C_2H_5I + Ag_2O \longrightarrow (C_2H_5)_2O + 2AgI$$

Mechanism. Sodium ethoxide furnishes nucleophilic anion as $C_2H_5-\overset{-}{\ddot{O}}:$ which reacts in the same manner as the hydroxide ion does.



(7) With ALCOHOLIC AMMONIA, alkyl halides form **amines** and the quaternary salts.

$$C_2H_5I + HNH_2 \longrightarrow \underset{\text{Ethylamine}}{C_2H_5NH_2} + HI$$

$$C_2H_5I + C_2H_5NH_2 \longrightarrow \underset{\text{Diethylamine}}{(C_2H_5)_2NH} + HI$$

$$C_2H_5I + (C_2H_5)_2NH \longrightarrow \underset{\text{Triethylamine}}{(C_2H_5)_3N} + HI$$

$$(C_2H_5)_3N + C_2H_5I \longrightarrow \underset{\text{Tetraethylammonium iodide}}{(C_2H_5)_4N.I}$$

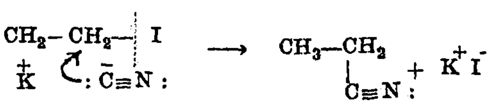
(8) With alcoholic POTASSIUM CYANIDE an alkyl halide gives the corresponding **nitrile** which upon hydrolysis with mineral acids forms **carboxylic acid.**

$$C_2H_5I + KCN \longrightarrow \underset{\text{Ethyl nitrile}}{C_2H_5CN} + KI$$

$$C_2H_5CN + 2H_2O \longrightarrow \underset{\text{Propionic acid}}{C_2H_5COOH} + NH_3$$

This reaction is helpful in building the length of a carbon chain.

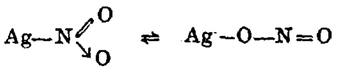
Mechanism. In this reaction, the cyanide ion acts as a carbon nucleophile.



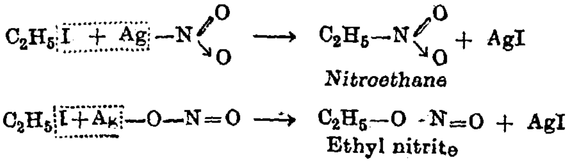
(9) They react with SILVER SALTS OF ACIDS forming **esters.**

$$\underset{\text{Silver acetate}}{CH_3COOAg} + IC_2H_5 \longrightarrow \underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + AgI$$

(10) When distilled with SILVER NITRATE, they yield **nitroalkanes and nitrites.** Like nitrous acid, silver nitrite exists in two forms.



Alkyl halides react with both these forms giving a mixture of alkyl nitrite and aliphatic nitro compound.



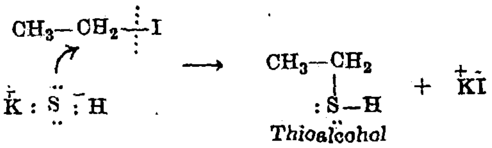
(11) WITH POTASSIUM HYDROSULPHIDE and POTASSIUM SULPHIDE they form **thioalcohols** and **thioethers** respectively.

$$C_2H_5I + KSH \longrightarrow \underset{\text{Thioalcohol}}{C_2H_5SH} + KI$$

$$2C_2H_5I + K_2S \longrightarrow \underset{\text{Thioether}}{(C_2H_5)_2S} + 2KI$$

Mechanism

KSH forms $H\overset{..}{\underset{..}{S}}:$ anions, the sulphur atom being quite analogous to oxygen — an element in the same group. The reaction between an alkyl halide and metal sulphides therefore leads to the replacement of halogen by the thiol group (SH) according to the mechanism :



Thioether formation follows the same mechanism.

(12) By the action of HALOGENS, they undergo further substitution yielding **Polyhalo-alkanes.**

$$\underset{\text{Chloroethane}}{C_2H_5Cl} \xrightarrow{Cl_2} \underset{\text{Dichloroethane}}{C_2H_4Cl_2} \xrightarrow{Cl_2} \underset{\text{Trichloroethane}}{C_2H_3Cl_3}$$

(13) In ether solution they react with ZINC and MAGNESIUM producing **Alkylzincs and Grignard Reagents** respectively.

$$C_2H_5I + Mg \longrightarrow \underset{\text{Ethylmagnesium iodide}}{C_2H_5MgI}$$

These metallic derivatives occupy a prominent position in organic synthesis.

INDIVIDUAL MEMBERS

METHYL CHLORIDE, CHLOROMETHANE, CH_3Cl

Preparation. (1) It is prepared commercially by the direct chlorination of methane.

$$CH_4 + Cl_2 \longrightarrow CH_3Cl + HCl$$

The mixture of methane and chlorine is passed through hot tubes containing antimony chloride catalyst maintained at 265° and at a pressure of 50—60 mm. The reaction being reversible excess of methane used ensures profitable yield.

(2) It is also obtained on a large scale by heating a mixture of methyl alcohol and hydrochloric acid gas, preferably in the presence of anhydrous zinc chloride.

$$CH_3OH + HCl \longrightarrow CH_3Cl + H_2O$$

(3) It can also be formed by heating trimethylamine with hydrochloric acid at 360°.

$$\underset{\text{Trimethylamine}}{(CH_3)_3N} + 4HCl \longrightarrow 3CH_3Cl + NH_4Cl$$

Properties and Uses. It is a colourless and sweet-smelling gas at ordinary temperature. Liquid methyl chloride boils at —23°C.

It is used (*i*) as a refrigerant, (*ii*) as a local anaesthetic, (*iii*) as a solvent for extraction of perfumes, and (*iv*) as a methylating agent.

METHYL IODIDE, IODOMETHANE, CH_3I

It is prepared by reacting together methyl alcohol, iodine and red phosphorus.

$$3CH_3OH + P + 3I \longrightarrow 3CH_3I + H_3PO_3$$

Properties and Uses. It is a pleasant smelling liquid, b.p. 45°C, sp. gr. 2·27. When freshly prepared, it is colourless but becomes brown on standing. This is due to its decomposition to form iodine. Methyl iodide being a liquid is convenient to handle and is often used as a methylating agent.

Laboratory Preparation. Fit up the apparatus as shown in Fig. 13·1. Place 5 grams of red phosphorus in a 250 ml. conical flask. Weigh 50 grams of iodine and 25 grams of methyl alcohol. Drop about 5 grams of iodine in the flask and then add a little alcohol through the condenser. Shake the flask under water. In the same way add the remaining iodine and alcohol. Allow the mixture to stand over-night to complete the reaction. Then distil the liquid using a water-bath to heat the flask and surrounding the receiver with ice-water.

METHYL BROMIDE, BROMOMETHANE, CH_3Br

It is prepared commercially by passing vapours of methyl alcohol and hydrogen bromide over a catalyst consisting of active carbon and orthophosphoric acid at high temperature.

$$CH_3OH + HBr \xrightarrow[(C+H_3PO_4)]{\text{heat}} CH_3Br + H_2O$$

Methyl bromide is a gas at ordinary temperature and pressure, B. pt. 75° ; sp. gr. 1·732. It is a potent fumigant, its toxicity to germs being equal to that of hydrogen cyanide. It can also be used as a fire extinguisher and as a refrigerant.

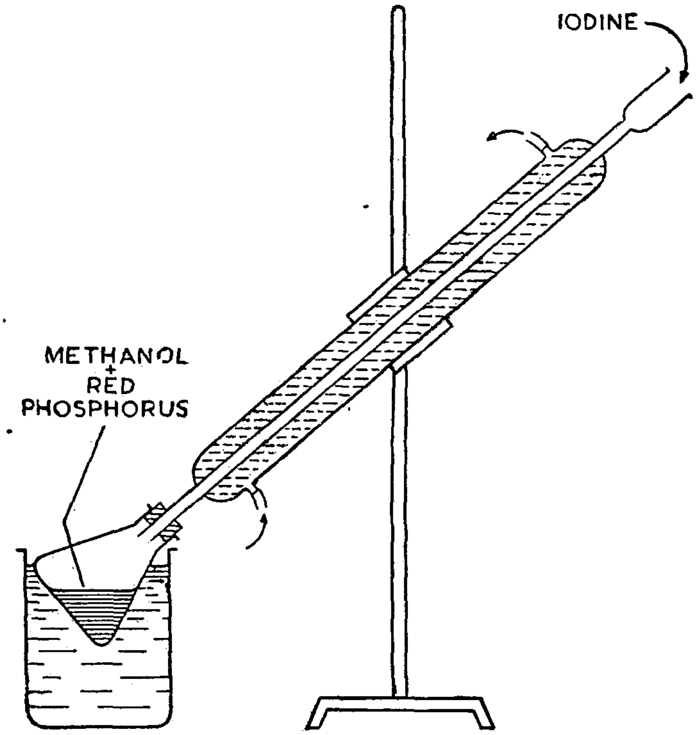


Fig. 13·1. Preparation of Methyl iodide.

ETHYL CHLORIDE, CHLOROETHANE, C_2H_5Cl

Preparation. It can be prepared by any of the general methods. The best yield is obtained when it is prepared by passing dry HCl gas into alcohol in the presence of zinc chloride.

$$C_2H_5OH + HCl \longrightarrow C_2H_5Cl + H_2O$$

It is prepared in large quantities by the addition of hydrogen chloride to ethylene in the presence of a suitable catalyst.

$$C_2H_4 + HCl \xrightarrow[ZnCl_2]{100-250°} C_2H_5Cl$$

Properties and Uses. It is a pleasant smelling gas under ordinary conditions. Liquid ethyl chloride boils at 12·2°C and has specific gravity 0·921 at 0°C.

It is used (*i*) as a refrigerant and local anaesthetic, (*ii*) in the preparation of ethyl cellulose and tetraethyl lead, and (*iii*) for the introduction of ethyl radical in organic molecules (*Ethylating agent*).

ETHYL BROMIDE, BROMOETHANE, C_2H_5Br

It is prepared technically by passing ethylene and hydrogen bromide vapour through a suspension of aluminium bromide in ethyl bromide maintained at low temperature.

$$\underset{\text{Ethylene}}{C_2H_4} + HBr \xrightarrow[\text{AlBr}_3]{\text{Low temp.}} C_2H_5Br$$

In the laboratory, ethyl bromide is prepared by the action of hydrogen bromide on ethyl alcohol.

Laboratory Preparation. Set up a one-litre round-bottomed flask on a wire-gauze placed on a ring stand. Fit the flask with a delivery-tube and connect it to a water-condenser as for distillation. Attach a bent adapter at the lower end of the condenser. Insert the end of the adapter in a 200 ml. conical flask. Put ice-cold water into it so that the end of the adapter is sealed. The receiving flask itself should be placed in a beaker containing ice-water.

Mix 60 gms. of ethyl alcohol and 50 gms. of water in the one-litre flask. Add to it 200 gms. of conc. H_2SO_4 by shaking and cooling. Continue shaking and cooling and add 100 gms. of potassium bromide which has been previously powdered. Attach the flask to the condenser and distil as rapidly as possible. The heating must be carefully regulated to avoid excessive frothing. Distil until no more oily drops of ethyl bromide fall into the receiver. Separate ethyl bromide from water with the help of a separating funnel. Wash the ethyl bromide with ice-water and separate as before. Now transfer the liquid to a dry conical flask containing some anhydrous calcium chloride and leave it overnight. Distil off pure ethyl bromide the next day.

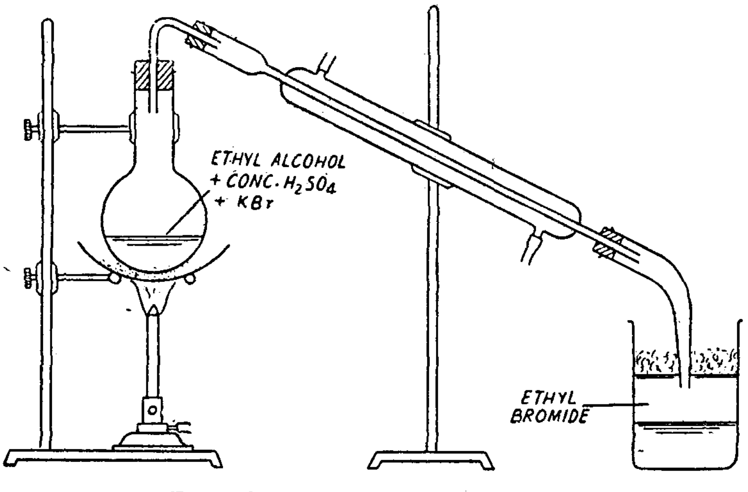
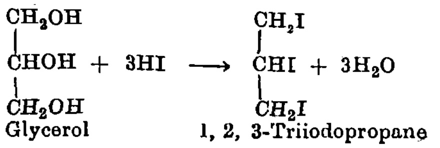


Fig. 13·2. Preparation of Ethyl bromide.

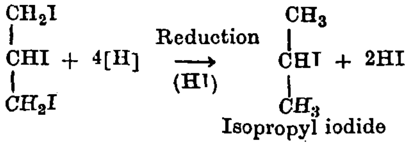
Properties and Uses. It is a colourless liquid having a pleasant smell. It boils at 31·4°C. It gives all the usual reactions of an alkyl halide and is used as an ethylating agent.

ISOPROPYL IODIDE, $CH_3.CHI.CH_3$

It is commonly prepared from glycerol by the action of hydrogen iodide, or phosphorus and iodine.



$$\begin{array}{l}CH_2OH\\ |\\ CHOH\\ |\\ CH_2OH\\ \text{Glycerol}\end{array} + 3HI \longrightarrow \begin{array}{l}CH_2I\\ |\\ CHI\\ |\\ CH_2I\\ \text{1, 2, 3-Triiodopropane}\end{array} + 3H_2O$$



$$\begin{array}{l}CH_2I\\ |\\ CHI\\ |\\ CH_2I\end{array} + 4[H] \xrightarrow[(HI)]{\text{Reduction}} \begin{array}{l}CH_3\\ |\\ CHI\\ |\\ CH_3\\ \text{Isopropyl iodide}\end{array} + 2HI$$

When pure, isopropyl iodide is a colourless liquid boiling at 89·5°C. It is heavier than water, its specific gravity being 1·703. It is used for the introduction of isopropyl radical in organic molecules.

DIHALOGEN DERIVATIVES

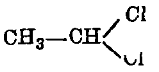
Dihalogen derivatives are compounds obtained by replacing two hydrogen atoms in a hydrocarbon by halogen atoms. Thus methane forms

CH_2Cl_2	CH_2Br_2	CH_2I_2
Methylene chloride	Methylene bromide	Methylene iodide

In higher members, two halogens may be linked to the same or different carbon atoms. Thus ethane gives two isomeric dihalides.

$Cl—CH_2—CH_2—Cl$

Ethylene chloride



$$CH_3—CH\begin{array}{l}\diagup Cl\\ \diagdown Cl\end{array}$$

Ethylidene chloride

METHODS OF FORMATION

The dihalogen derivatives of alkanes can be obtained by the following general methods :—

(1) *By further halogenation of monohalogen derivatives and reduction of tri- and tetrahalogen derivatives.*

$$CH_3Cl + Cl_2 \longrightarrow \underset{\text{Methylene chloride}}{CH_2Cl_2} + HCl$$

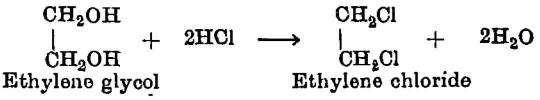
$$\underset{\text{Chloroform}}{CHCl_3} + 2H \longrightarrow CH_2Cl_2 + HCl$$

(2) *By the addition of halogens to alkenes and of halogen acids to alkynes.*

$$\underset{\text{Ethylene}}{CH_2{=}CH_2} + Cl_2 \longrightarrow \underset{\text{Ethylene chloride}}{CH_2Cl.CH_2Cl}$$

$$\underset{\text{Acetylene}}{CH{\equiv}CH} \xrightarrow{+HCl} \underset{\text{Vinyl chloride}}{CH_2{=}CHCl} \xrightarrow{+HCl} \underset{\text{Ethylidene chloride}}{CH_3CHCl_2}$$

(3) *By the action of halogen acids on glycols.*



$$\begin{array}{l}CH_2OH\\ |\\ CH_2OH\\ \text{Ethylene glycol}\end{array} + 2HCl \longrightarrow \begin{array}{l}CH_2Cl\\ |\\ CH_2Cl\\ \text{Ethylene chloride}\end{array} + 2H_2O$$

(4) *By the action of PCl_5 on aldehydes and ketones.*

$$\underset{\text{Acetaldehyde}}{CH_3CHO} + PCl_5 \longrightarrow \underset{\text{Ethylidene chloride}}{CH_3CHCl_2} + POCl_3$$

This method gives only such compounds in which the two halogen atoms are linked to the same carbon atom.

PHYSICAL CHARACTERISTICS

(1) They are colourless liquids having comparatively high boiling points. Highest members are solids.

(2) They are in general heavier than water ; methylene iodide is the densest organic liquid known, its density being 3·325.

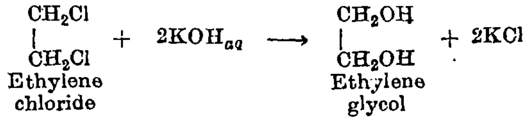
(3) They are insoluble in water but soluble in organic solvents.

CHEMICAL CHARACTERISTICS

Chemically the dihalogen derivatives are similar to monohalogen derivatives, giving all the reactions of the halogen atom in duplicate. They, however, differ from the latter in certain reactions in which both the halogen atoms are involved together. Besides the usual reactions of the alkyl halides, they give the following special reactions.

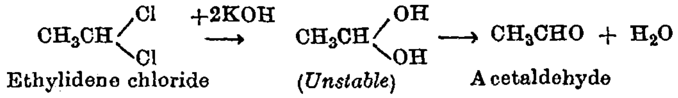
(1) ON HEATING WITH AQUEOUS POTASH, they form dihydric alcohols but when both the halogen atoms are attached to the same carbon atom they form an aldehyde.

(i)



$$\underset{\text{Ethylene chloride}}{\begin{matrix}CH_2Cl\\|\\CH_2Cl\end{matrix}} + 2KOH_{aq} \longrightarrow \underset{\text{Ethylene glycol}}{\begin{matrix}CH_2OH\\|\\CH_2OH\end{matrix}} + 2KCl$$

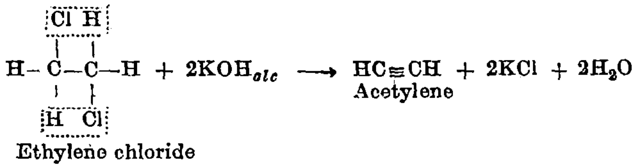
(ii)



$$\underset{\text{Ethylidene chloride}}{CH_3CH\begin{matrix}Cl\\Cl\end{matrix}} \xrightarrow{+2KOH} \underset{(\textit{Unstable})}{CH_3CH\begin{matrix}OH\\OH\end{matrix}} \longrightarrow \underset{\text{Acetaldehyde}}{CH_3CHO} + H_2O$$

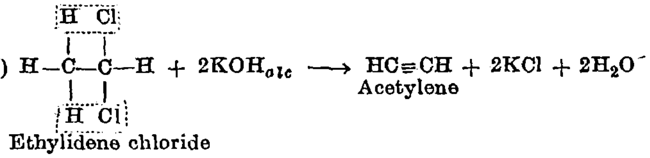
(2) ON HEATING WITH ALCOHOLIC POTASH they give alkynes.

(i)



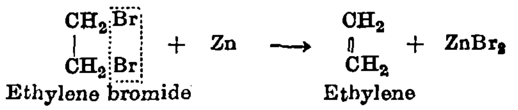
$$\underset{\text{Ethylene chloride}}{H-\overset{\overset{Cl}{|}}{\underset{\underset{H}{|}}{C}}-\overset{\overset{H}{|}}{\underset{\underset{Cl}{|}}{C}}-H} + 2KOH_{alc} \longrightarrow \underset{\text{Acetylene}}{HC\equiv CH} + 2KCl + 2H_2O$$

(ii)



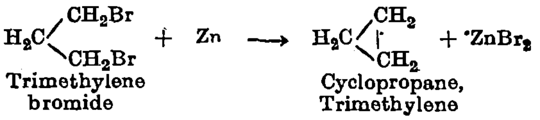
$$\underset{\text{Ethylidene chloride}}{H-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-\overset{\overset{Cl}{|}}{\underset{\underset{Cl}{|}}{C}}-H} + 2KOH_{alc} \longrightarrow \underset{\text{Acetylene}}{HC\equiv CH} + 2KCl + 2H_2O$$

(3) On treatment with zinc they are dehalogenated forming an *alkene* or *cycloalkanes* according as the halogens are on adjacent carbon atoms or at the ends of a normal chain.



$$\begin{matrix} CH_2Br \\ | \\ CH_2Br \end{matrix} + Zn \longrightarrow \begin{matrix} CH_2 \\ \| \\ CH_2 \end{matrix} + ZnBr_2$$

Ethylene bromide Ethylene



TRIHALOGEN DERIVATIVES

In these compounds three hydrogen atoms of a hydrocarbon have been replaced by halogen atoms. Thus methane forms

$CHCl_3$	Chloroform	or	Trichloromethane
$CHBr_3$	Bromoform	or	Tribromomethane
CHI_3	Iodoform	or	Triiodomethane

Chloroform and iodoform are used in medicine and are important.

CHLOROFORM, TRICHLOROMETHANE, $CHCl_3$

The name chloroform was given to this compound by Dumas who established that its molecule contained chlorine in union with 'formyl', an old name for CH ⋮ radical.

Preparation. (1) Chloroform is manufactured in U.S.A. by reduction of carbon tetrachloride with water and iron.

$$CCl_4 + H_2 \longrightarrow CHCl_3 + HCl$$

(2) It is obtained in the laboratory and also on commercial scale by boiling alcohol or acetone with bleaching powder. Alcohol is converted into chloroform by the following steps.

(i) *Oxidation of alcohol to acetaldehyde by chlorine of the bleaching powder.*

$$CH_3CH_2OH + Cl_2 \longrightarrow \underset{\text{Acetaldehyde}}{CH_3CHO} + 2HCl$$

(ii) *Chlorination of acetaldehyde to chloral.*

$$CH_3CHO + 3Cl_2 \longrightarrow \underset{\text{Chloral}}{CCl_3CHO} + 3HCl$$

(iii) *Hydrolysis of chloral by lime present in bleaching powder to form calcium formate and chloroform.*

$$CCl_3\vdots\boxed{CHO + HO}\vdots H \longrightarrow CHCl_3 + \underset{\text{Formic acid}}{HCOOH}$$

$$2HCOOH + Ca(OH)_2 \longrightarrow (HCOO)_2Ca + 2H_2O$$

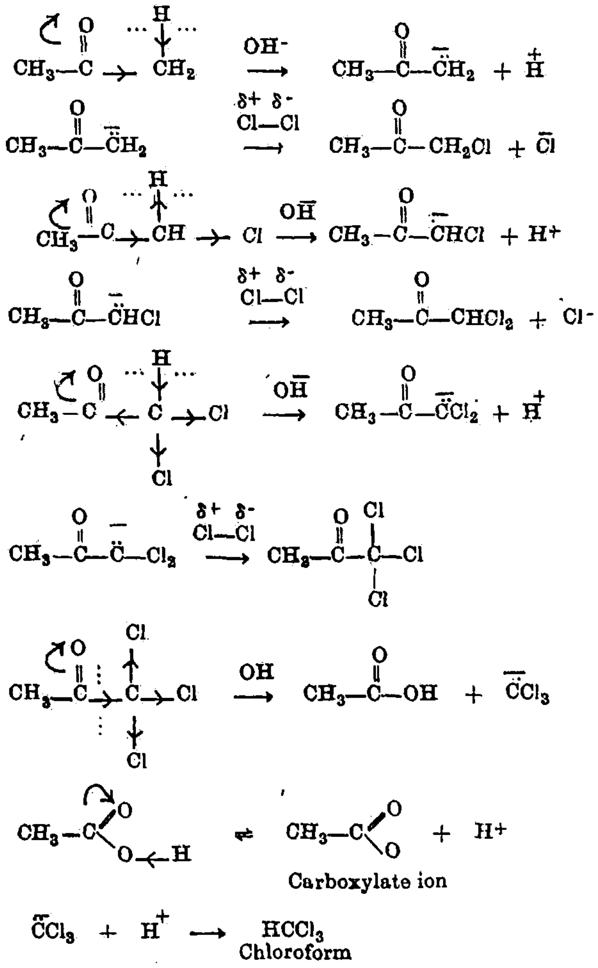
In the case of acetone, the conversion into chloroform takes place by similar steps.

$$\underset{\text{Acetone}}{CH_3COCH_3} + 3Cl_2 \longrightarrow \underset{\text{Trichloroacetone}}{CCl_3COCH_3} + 3HCl$$

$$CCl_3\vdots\boxed{COCH_3 + HO}\vdots H \longrightarrow \underset{\text{Chloroform}}{CHCl_3} + CH_3COOH$$

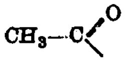
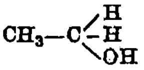
Mechanism

Formation of chloroform from acetone involves the presence of OH ions from $Ca(OH)_2$ acting as proton remover. The arrows depict the direction of electron displacement.

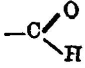


Caboxylate ion is stabilised due to resonance.

It follows from the above discussion that only compounds containing the groupings


or


can give rise to the formation of chloroform by undergoing the above changes, Ethyl alcohol, Acetaldehyde and Acetone are generally employed for this purpose. $-CH_2OH$ group of ethyl alcohol is first oxidised by Cl_2 to yield



The resulting acetaldehyde undergoes the rest of reaction in a manner comparable with that of acetone.

(3) Pure chloroform is prepared by the action of alkali on chloral hydrate.

$$\underset{\text{Chloral}}{\text{CCl}_3\boxed{\text{CHO+KO}}\text{H}} \longrightarrow \text{CHCl}_3 + \text{HCOOK}$$

Laboratory Method. Chloroform is prepared in the laboratory by heating together bleaching powder, water and acetone or alcohol. The apparatus needed for the preparation is shown in Fig. 13·3.

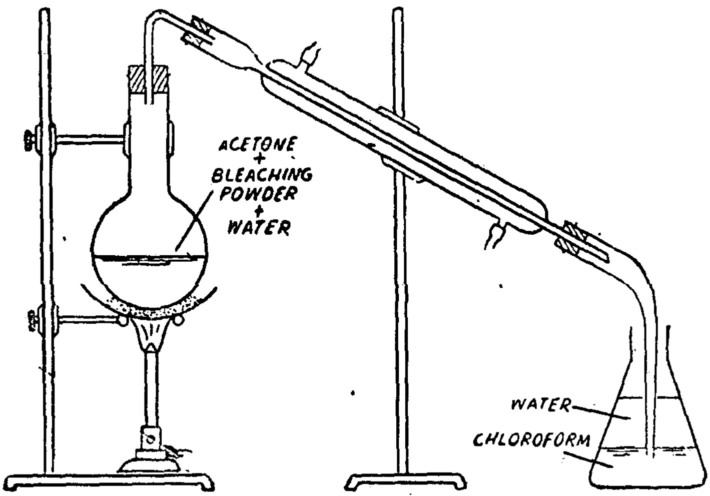


Fig. 13·3. Preparation of Chloroform.

About 100 grams of bleaching powder are mixed with 200 mls. of water to make a thin paste. This is then transferred into a one-litre round-bottomed flask. 25 mls. of acetone are now added to it and the flask heated gently. A mixture of chloroform and water is obtained as the distillate. The distillation is stopped when no more chloroform passes over. The mixture from the receiver is transferred into a separating funnel and the lower layer of chloroform separated. It is washed with a dilute solution of sodium hydroxide and then dried over anhydrous calcium chloride. It is finally purified by redistillation and collecting the fraction passing over between 50 and 60°C.

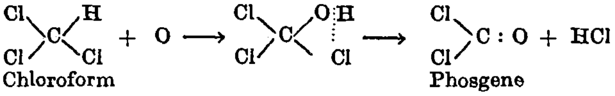
Industrial Method. Chloroform is obtained on the commercial scale by employing the reaction between acetone (for ethyl alcohol) and bleaching powder.

$$\text{CH}_3\text{COCH}_3 + 6\text{CaOCl}_2 \longrightarrow 2\text{CHCl}_3 + (\text{CH}_3\text{COO})_2\text{Ca} + 2\text{Ca(OH)}_2 + 3\text{CaCl}_2 + 6\text{H}_2\text{O}$$

The acetone is run into a cast iron still containing a suspension of the bleaching powder. The reaction mixture is maintained at 45°C, with the help of a heating coil and a stirrer provided in the still till the whole of acetone has been added. The temperature is then raised to distil off the chloroform.

Properties (*Physical*). Chloroform is a colourless mobile liquid with a peculiar sweet smell and sweetish taste. It boils at 61° and its specific gravity is 1·485 It is practically insoluble in water but dissolves readily in alcohol and ether. It acts as a solvent for many organic substances such as oils, fats and resins. Chloroform vapours when inhaled produce temporary unconsciousness and hence its use as anaesthetic.

(*Chemical*). (1) OXIDATION. When exposed to light and air, chloroform slowly decomposes into phosgene and hydrogen chloride.



Phosgene is dangerously poisonous. To avoid this decomposition in chloroform for anaesthetic purpose, it is stored in dark blue or brown bottles filled up to the stopper. The decomposition can further be retarded by the addition of about one per cent alcohol.

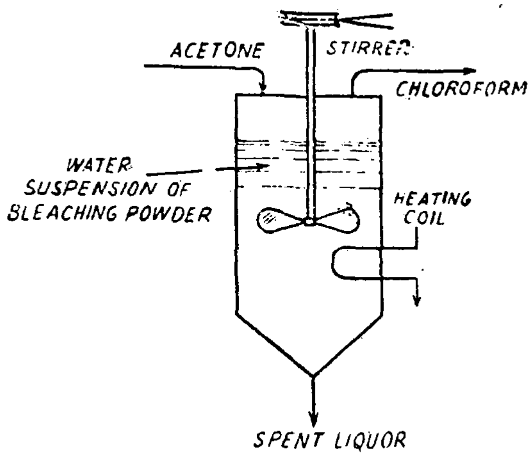
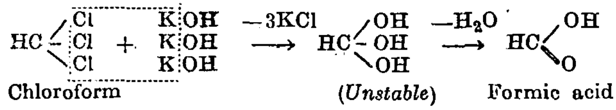


Fig. 13·4. Manufacture of Chloroform.

(2) REDUCTION. Upon reduction with zinc and hydrochloric acid, it gives methylene chloride.

$$\underset{}{CHCl_3} + 2H \longrightarrow \underset{\text{Methylene chloride}}{CH_2Cl_2} + HCl$$

(3) HYDROLYSIS. When boiled with an aqueous solution of caustic potash, chloroform is hydrolysed to potassium formate.



$$HCOOH + KOH \longrightarrow \underset{\text{Pot. formate}}{HCOOK} + H_2O$$

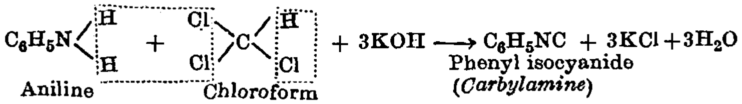
(4) CHLORINATION. Upon reaction with chlorine, it gives carbon tetra-chloride.

$$CHCl_3 + Cl_2 \longrightarrow CCl_4 + HCl$$

(5) NITRATION. It reacts with concentrated nitric acid forming *chloropicrin*.

$$\underset{\text{Chloroform}}{Cl_3C\,H} + HO\,NO_2 \longrightarrow \underset{\text{Chloropicrin}}{Cl_3C.NO_2} + H_2O$$

(6) CARBYLAMINE REACTION. When warmed with a primary amine and alcoholic potash, chloroform gives *carbylamine* which has an extremely disagreeable odour.



$$C_6H_5N\begin{smallmatrix}H\\H\end{smallmatrix} + \begin{smallmatrix}Cl\\Cl\end{smallmatrix}C\begin{smallmatrix}H\\Cl\end{smallmatrix} + 3KOH \longrightarrow C_6H_5NC + 3KCl + 3H_2O$$

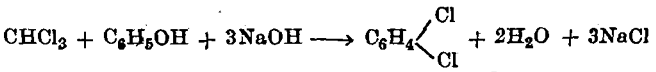
Aniline Chloroform Phenyl isocyanide (*Carbylamine*)

This is a delicate test for the presence of a primary amine.

(7) CONDENSATION WITH ACETONE. Chloroform undergoes condensation with acetone in the presence of alkali to form *Chloretone* which is used as a hypnotic.

$$\underset{\text{Acetone}}{(CH_3)_2CO} + HCCl_3 \longrightarrow \underset{\text{Chloretone}}{(CH_3)_2C(OH)CCl_3}$$

(8) ACTION WITH PHENOL AND SODIUM HYDROXIDE (*Reimer-Tiemann Reaction*). Chloroform when heated with a concentrated solution of phenol and sodium hydroxide, forms salicylaldehyde.



$$CHCl_3 + C_6H_5OH + 3NaOH \longrightarrow C_6H_4\begin{smallmatrix}Cl\\Cl\end{smallmatrix} + 2H_2O + 3NaCl$$

Salicylaldehyde

Uses. (1) Chloroform is extensively used as a general anaesthetic.

(2) It is used as a solvent for fats and iodine.

(3) It is employed as a laboratory reagent for testing the presence of primary amines.

(4) It is added to decomposable organic materials to prevent putrefaction.

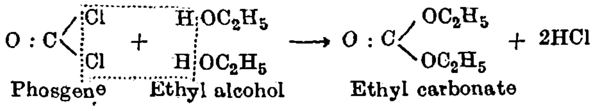
Chloroform as Anaeshetic. The anaesthetic action of chloroform was first discovered by Simpson in 1815 and since then it has been extensively used for the purpose. However, it is gradually going into disrepute owing to its deleterious action upon heart. When inhaled in sufficient quantity, it causes death on account of cardiac and respiratory failure.

PRECAUTIONS. Chloroform which is to be used as anaesthetic must be very pure and all the precautions must be observed in preventing its decomposition to phosgene by the action of air and light. Anaesthetic chloroform is prepared by the action of sodium hydroxide on pure chloral hydrate.

(1) It is stored in yellow bottles to cut away the active part of light.

(2) Bottles are filled up to the stopper so that no air is left inside.

(3) 1 to 2 per cent of alcohol is added as it retards the decomposition of chloroform into phosgene. It also converts any phosgene produced into ethyl carbonate, a harmless substance.



$$O:C\begin{smallmatrix}Cl\\Cl\end{smallmatrix} + \begin{smallmatrix}H\,OC_2H_5\\H\,OC_2H_5\end{smallmatrix} \longrightarrow O:C\begin{smallmatrix}OC_2H_5\\OC_2H_5\end{smallmatrix} + 2HCl$$

Phosgene Ethyl alcohol Ethyl carbonate

IODOFORM, TRIIODOMETHANE, CHI_3

From its structural similarity to chloroform, it was named *Iodoform* by Dumas. Its methods of preparation and properties are analogous to those of chloroform.

Preparation. (1) *By the action of iodine and alkali upon ethyl alcohol or acetone.* The mechanism of the reaction is the same as described under chloroform.

$$\underset{\text{Ethyl alcohol}}{CH_3CH_2OH} + I_2 \longrightarrow \underset{\text{Acetaldehyde}}{CH_3CHO} + 2HI$$

$$CH_3CHO + 3I_2 \longrightarrow \underset{\text{Iodal}}{I_3CCHO} + 3HI$$

$$I_3C\boxed{CHO + KO}H \longrightarrow \underset{\text{Iodoform}}{CHI_3} + HCOOK$$

(2) *By the electrolysis of a solution of alcohol, an iodide* and *sodium carbonate*. This is a cheaper method and is used for the industrial preparation of iodoform. During the electrolysis, iodine is set free at the anode and sodium hydroxide is formed at the cathode. These substances then react with alcohol or acetone to form iodoform.

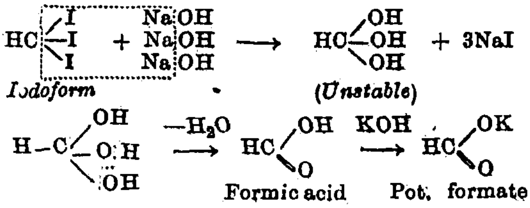
Laboratory Preparation. In the laboratory iodoform is generally prepared from alcohol or acetone by the action of iodine and sodium carbonate. The chemistry of the method is the same as already described.

Take 10 gms. of sodium carbonate in a 250 ml. round-bottomed flask and add to it 60 mls. of water. Dissolve by shaking. Add to it 15 mls. of alcohol and shake well. Now put iodine into it bit by bit by continuous shaking. Warm the flask on water-bath to about 70°C till the contents are decolorised. The yellow mass that separates is filtered, washed with water and crystallised from alcohol.

Properties (*Physical*). Iodoform is a yellow solid crystallising in hexagonal plates. M.pt. 119°. It has a characteristic smell. It is insoluble in water but dissolves readily in alcohol, chloroform and ether. Iodoform has marked antiseptic action.

In chemical properties iodoform resembles chloroform. It is, however, less stable than the latter.

When heated with alkali solutions, iodoform is hydrolysed to a formate.



Iodoform also undergoes the carbylamine reaction when warmed with a mixture of aniline and alcoholic potash solution, in a manner analogous to the corresponding reaction of chloroform.

Iodoform was extensively used as an antiseptic for dressing wounds. When it comes in contact with organic matter, iodine is set free and this explains the antiseptic action.

TETRAHALOGEN DERIVATIVES

The tetrahalogen derivatives of methane are compounds containing carbon and halogen only. They are, therefore, preferably named as *Carbon tetrahalides*.

CCl_4	CBr_4	CI_4
Tetrachloride	Tetrabromide	Tetraiodide

Of these, carbon tetrachloride is the most important.

CARBON TETRACHLORIDE, TETRACHLOROMETHANE, CCl_4

Preparation. It is obtained on the industrial scale by two methods :

(1) By chlorination of *natural gas* (methane).

$$CH_4 + 4Cl_2 \longrightarrow CCl_4 + 4HCl$$

(2) By action of chlorine on carbon disulphide using iron or antimony pentachloride as a catalyst.

$$2CS_2 + 6Cl_2 \longrightarrow 2CCl_4 + 2S_2Cl_2 \text{ (Sulphur chloride)}$$
$$CS_2 + 2S_2Cl_2 \longrightarrow CCl_4 + 6S$$

Properties. It is colourless liquid boiling at 77°C. It is insoluble in water but miscible with organic solvents. It is an excellent solvent for fats and oils. It is an inert liquid and its vapours are non-inflammable.

When heated with alcoholic caustic potash, it is decomposed to form inorganic salts.

$$CCl_4 + 6KOH \longrightarrow K_2CO_3 + 4KCl + 3H_2O$$

Its vapours when mixed with steam react at high temperature to give phosgene gas.

$$CCl_4 + H_2O \longrightarrow \underset{\text{Phosgene}}{COCl_2} + 2HCl$$

Uses. Carbon tetrachloride is used for dry-cleaning and degreasing ; an anti-worm medicine ; in fire-extinguishers ; for the industrial preparation of chloroform.

UNSATURATED HALOGEN COMPOUNDS

VINYL CHLORIDE, CHLOROETHENE, $CH_2 : CHCl$

Preparation. Commercially it is obtained by passing a mixture of acetylene and hydrogen chloride over mercury salts.

$$\underset{\text{Acetylene}}{CH{\equiv}CH} + HCl \longrightarrow \underset{\text{Vinyl chloride}}{CH_2{=}CHCl}$$

(2) Vinyl chloride is also prepared on a large scale by the reaction between ethylene chloride and dilute sodium hydroxide solution.

$$\underset{\text{Ethylene chloride}}{CH_2Cl.CH_2Cl} + NaOH \longrightarrow \underset{\text{Vinyl chloride}}{CH_2{=}CHCl} + NaCl + H_2O$$

Properties and Uses. It is a colourless gas under ordinary conditions. Liquid vinyl chloride boils at −13·9°C.

Chemically vinyl chloride gives the usual addition reactions of the double bond. Thus it reacts by addition with halogens and halogen halides just like alkenes. The halogen atom is quite unreactive and does not give any of the replacement reactions of the alkyl halides. Thus,

$$\underset{\text{Vinyl chloride}}{CH_2 : CHCl} + KOH_{aq} \longrightarrow \text{No action}$$

$$(Cf.\ \underset{\text{Ethyl chloride}}{CH_3CH_2Cl} + KOH_{aq} \longrightarrow CH_3CH_2OH + KCl + H_2O)$$

The stability of the halogen atom in vinyl chloride is comparable to that of halogen atom linked to the benzene nucleus in aromatic compounds. However, when boiled wih alcoholic caustic potash vinyl chloride forms ethylene.

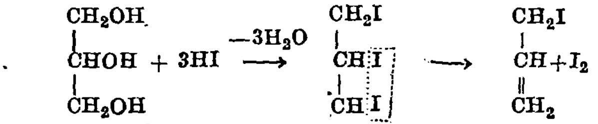
Recently vinyl chloride has gained commercial importance in the preparation of synthetic rubber, plastics and resins.

ALLYL IODIDE, 3-IODO-1-PROPENE, $CH_2{=}CHCH_2I$

Preparation. (1) It may be prepared by the action of concentrated hydriodic acid on allyl alcohol.

$$\underset{\text{Allyl alcohol}}{CH_2{=}CHCH_2OH} + HI \xrightarrow{heat} \underset{\text{Allyl iodide}}{CH_2{=}CHCH_2I} + H_2O$$

It is generally prepared by the action of a small amount of hydrogen iodide or phosphorus triodide on glycerol.



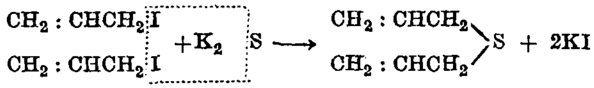
$$\begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \\ \text{Glycerol} \end{array} + 3HI \xrightarrow{-3H_2O} \begin{array}{l} CH_2I \\ | \\ CHI \\ | \\ CHI \\ \text{Glyceryl} \\ \text{tri-iodide} \end{array} \longrightarrow \begin{array}{l} CH_2I \\ | \\ CH+I_2 \\ \| \\ CH_2 \\ \text{Allyl iodide} \end{array}$$

Properties and Uses. It is a colourless liquid having a garlic odour. B.pt. 101°.

It gives all the reactions of an alkene and an alkyl halide. The halogen atom in it is more reactive than that in alkyl halides so that alkyl iodide gives the replacement reactions more readily.

Thus :

$$CH_2 : CHCH_2I + KOH_{aq} \longrightarrow \underset{\text{Allyl alcohol}}{CH_2 : CHCH_2OH} + KI$$



$$\begin{array}{l} CH_2 : CHCH_2\,I \\ CH_2 : CHCH_2\,I \end{array} + K_2S \longrightarrow \begin{array}{l} CH_2 : CHCH_2 \\ CH_2 : CHCH_2 \end{array} > S + 2KI$$

Allyl sulphide

Allyl iodide is used in organic synthesis for introducing allyl radical in other compounds.

Trichloroethylene, $CCl_2 : CHCl$. It is prepared by treating acetylene tetrachloride with lime.

$$2CHCl_2.CHCl_2 + Ca(OH)_2 \longrightarrow 2CCl_2 : CHCl + CaCl_2 + 2H_2O$$

It is used under the name **Westrosol,** as a degreasing agent and also as an anaesthetic.

Acetylene tetrachloride, $CHCl_2.CHCl_2$. It is obtained by the addition of chlorine to acetylene in the presence of catalyst.

$$CH{\equiv}CH + 2Cl_2 \longrightarrow CHCl_2.CHCl_2$$

It is a heavy, non-inflammable liquid boiling at 147°C. It is used under the technical name **Westron** as a solvent for varnishes, and also as insecticide.

Dichlorodifluoromethane, 'Freon', CCl_2F_2. This is an important mixed halide made from carbon tetrachloride and antimony fluoride.

$$3CCl_4 + 2SbF_3 \xrightarrow{SbCl_5} 2SbCl_3 + \underset{\text{Freon}}{3CCl_2F_2}$$

It is a colourless, non-toxic and non-inflammable gas, b.p.—29°C. It is widely used for refrigeration in household electrical refrigerators and in air-conditioning equipment.

Infrared spectra of Halogen derivatives. The various carbon-halogen bonds show infrared absorption bands in the regions C—F in 1000—1110 cm^{-1}, C—Cl in 650—780 cm^{-1}, C—Br in 650—750 cm^{-1}, and C—I in 500—600 cm^{-1}. Apart from absorption peaks in these regions, the Infrared spectra also have absorption peaks of various C—H and C—C bonds as shown below in case of a typical infrared spectrum of chloroform.

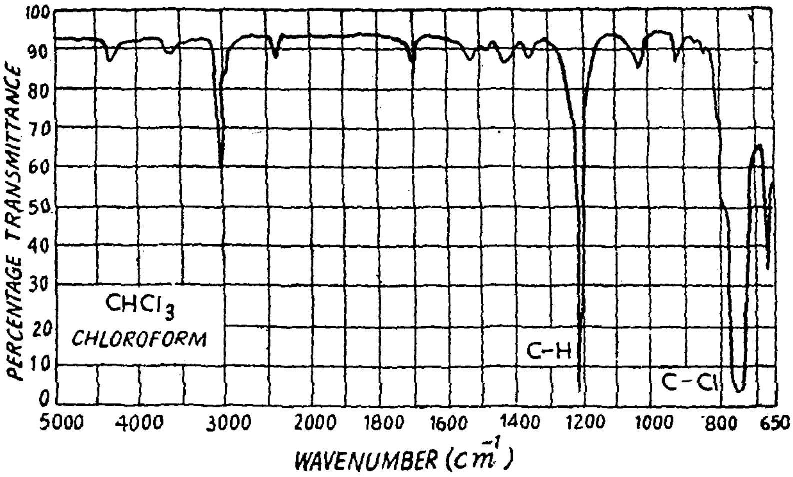


Fig. 13·5. Infrared spectrum of Chloroform.

QUESTIONS

1. What do you understand by the term alkyl halides ? How do they differ from metallic halides ?

2. Describe the general methods of formation and synthetic reactions of alkyl halides.

3. How is methyl iodide prepared in the laboratory ? Formulate the action of metallic sodium, ammonia, potassium cyanide and dilute caustic potash on it.

4. Describe in detail the preparation of ethyl bromide or ethyl iodide in the laboratory. By what reactions can one or other of three compounds be converted into (*a*) ethane, (*b*) ethylene, (*c*) acetylene ?

5. How would you prepare a pure example of ethyl bromide in the laboratory. Describe the action of the following reagents on ethyl bromide.

6. How would you obtain chloroform in the laboratory ? What are its important reactions and uses ? How would you test its presence in a liquid ?

7. Describe the preparation of (*a*) chloral hydrate, (*b*) chloroform. How does chloroform react with (*a*) alcoholic potash, (*b*) alcoholic potash and aniline, (*c*) nascent hydrogen ?

8. Describe the preparation from ethyl alcohol of (*a*) ethyl iodide, (*b*) iodoform. How and under what conditions do ethyl iodide and iodoform react wito potassium hydroxide ?

9. What are halogen derivatives of paraffins ? How is methyl chloride prepared ? Give some synthetic uses of methyl chloride.

(*Dibrugarh B.Sc., 1967*)

10. How do you account for the activity or inactivity of the halogen atom in the following compounds : Allyl chloride, Vinyl chloride, α-chloroacetone, Ethyl chloro-acetate ? (*Panjab University B.Sc. II, 1967*)

11. Give structures of the products expected from dehydrohalogenation of—

(*a*) 1-Bromohexane

(*b*) 1-Bromo-2-methylheptane

(*c*) 3-Bromo-2, 3-dimethylpentane. Predict with reasons the major product where more than one product can be formed.

(*Jadavpur B.Sc., 1969*)

12. How is chloroform prepared on a large scale ? Describe its important reactions and uses. (*Jammu & Kashmir B.Sc., 1969*)

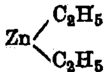
13. Give an account of the product or products formed when alkyl halides react with (*i*) sodium cyanide and (*ii*) silver cyanide. What structures would you assign to these structures ? (*Delhi B.Sc., 1969*)

14

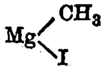
Organo-Metallic Compounds

Victor Grignard
(1871—1935)
French chemist. Nobel Prize winner in 1912 for his contributions to Synthetic Organic Chemistry. His fame rests principally on the usefulness of the reaction which takes his name.

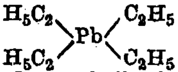
Organic compounds in which one or more hydrocarbon radicals are attached directly to a metallic atom are termed **Organo-metallic compounds**. For example,



Diethylzinc

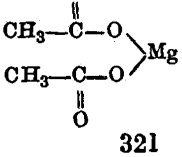


Methylmagnesium *iodide*



Tetraethyllead

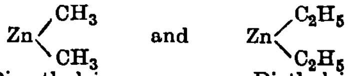
It may be noted that in all the above molecules the metallic atom is in direct union with a carbon. Compounds like magnesium acetate in which magnesium is linked to an oxygen atom are not organo metallic compounds.



Of all the organo-metallic compounds so far investigated those of zinc, magnesium and lead are important.

ORGANO-ZINC COMPOUNDS

Zinc forms two organo-metallic compounds which were first studied in detail by Frankland (1849). They are :



Dimethylzinc Diethylzinc

They are often referred to as **Dialkylzincs**.

Preparation. Dialkylzincs are obtained by the action of zinc on alkyl halides.

$$\underset{\text{Ethyl iodide}}{C_2H_5I} + Zn \longrightarrow \underset{\text{Ethylzinc iodide}}{C_2H_5ZnI}$$

$$2C_2H_5ZnI \longrightarrow \underset{\text{Diethylzinc}}{(C_2H_5)_2Zn} + ZnI_2$$

The ethylzinc iodide first formed is distilled in an inert atmosphere as Dialkylzincs are spontaneously inflammable in air.

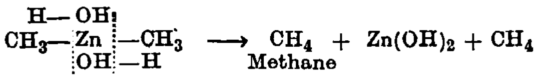
Dimethylzinc can also be prepared by a similar method.

Properties and Uses. Dialkylzincs are colourless, unpleasant smelling liquids which have comparatively low boiling points.

$Zn(CH_3)_2$ b.p. 46°C ; $Zn(C_2H_5)_2$ b.p. 118°C.

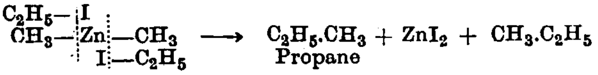
They are spontaneously inflammable and produce painful burns when brought in contact with skin. Their important *synthetic reactions* are :

(1) They react violently with water forming the corresponding *Alkanes*. Thus :



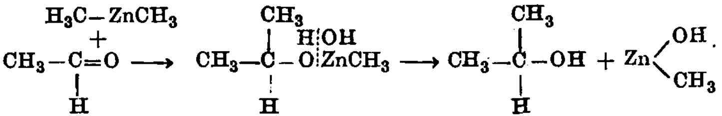
$$\begin{matrix} H-OH \\ CH_3-Zn-CH_3 \\ OH-H \end{matrix} \longrightarrow \underset{\text{Methane}}{CH_4} + Zn(OH)_2 + CH_4$$

(2) When heated with alkyl halides, they form *Higher alkanes*. Thus :



$$\begin{matrix} C_2H_5-I \\ CH_3-Zn-CH_3 \\ I-C_2H_5 \end{matrix} \longrightarrow \underset{\text{Propane}}{C_2H_5.CH_3} + ZnI_2 + CH_3.C_2H_5$$

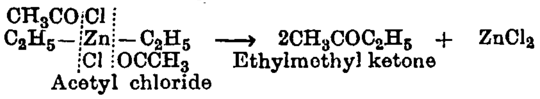
(3) With aldehydes and ketones they form *Alcohols*. Thus :



$$\underset{\text{Acetaldehyde}}{\begin{matrix} H_3C-ZnCH_3 \\ + \\ CH_3-\underset{H}{C}=O \end{matrix}} \longrightarrow CH_3-\overset{CH_3}{\underset{H}{C}}-O{:}ZnCH_3 \;(H{:}OH) \longrightarrow \underset{\text{Isopropyl alcohol}}{CH_3-\overset{CH_3}{\underset{H}{C}}-OH} + Zn\begin{matrix} OH \\ CH_3 \end{matrix}$$

Acetaldehyde Isopropyl alcohol

(4) With acid chlorides, dialkylzincs form *Ketones*. Thus :



$$\begin{matrix} CH_3CO{:}Cl \\ C_2H_5-Zn-C_2H_5 \\ Cl{:}OCCH_3 \end{matrix} \longrightarrow \underset{\text{Ethylmethyl ketone}}{2CH_3COC_2H_5} + ZnCl_2$$

Acetyl chloride

In preparative chemistry alkylzincs have gradually been replaced by Grignard reagents which are more reactive, convenient to handle, and comparatively stable.

ORGANO-MAGNESIUM HALIDES

In 1900 Victor Grignard showed that magnesium in presence of dry ether reacts with organic halides giving compounds of the general formula

$$R-Mg-X$$

where $X = Cl$, Br, or I

$R =$ Univalent hydrocarbon radical.

These alkylmagnesium halides or the **Grignard reagents**, as they are commonly called after the name of the discoverer, are exceedingly important in organic synthesis and *almost all classes of compounds can be prepared from them.*

Preparation. They are prepared in the laboratory by the action of alkyl halides on magnesium suspended in ether.

$$\underset{\text{Alkyl halide}}{RX} + Mg \xrightarrow{\text{(Ether)}} \underset{\text{Grignard reagent}}{R-Mg-X}$$

e.g.

$$CH_3I + Mg \xrightarrow{\text{(Ether)}} \underset{\text{Methylmagnesium iodide}}{CH_3-Mg-I}$$

In the preparation of Grignard reagents great care must be taken to ensure that the reactants are absolutely dry and pure, and the apparatus quite clean and dry. The slightest trace of moisture or impurity will side-track the main reaction.

(*i*) **Magnesium.** Magnesium ribbon is washed with ether to remove grease and placed in a desicator for a long time to remove moisture. The surface film of oxide is removed by rubbing with sand-paper or by treatment with dilute HCl.

(*ii*) **Ether.** It is washed with water to remove any alcohol and then allowed to stand on $CaCl_2$ (*anhydrous*) for 2-3 days when alcohol and water are removed. Then it is distilled over sodium and P_2O_5 and the last traces of alcohol and water are thus removed.

(*iii*) **Halide.** It is purified by the usual methods and finally distilled over P_2O_5.

Magnesium ribbon is cut into small pieces which are suspended in dry ether contained in a round-bottomed flask. This is then fitted with a water condenser carrying a calcium chloride tube at the upper end. The alkyl halide is gradually added through the condenser, removing the calcium chloride tube for a while. It may sometimes be necessary to start the reaction by warming or by adding a trace of iodine *catalyst*. When a little Grignard reagent is formed, it catalyses the reaction and magnesium dissolves with evolution of heat so that cooling may sometimes be necessary. When the reaction is complete, a clear solution of the Grignard reagent in ether is obtained. Those reagents are never isolated but are prepared and used in ether solution.

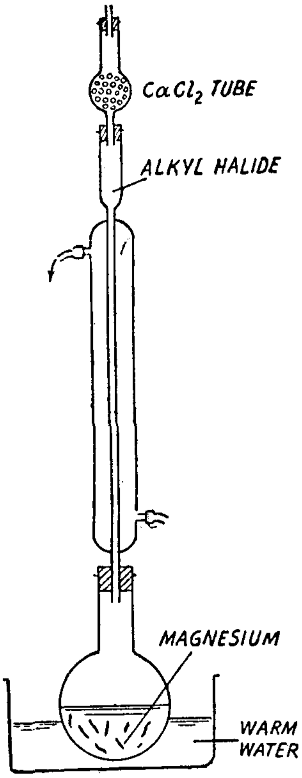
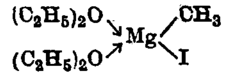


Fig. 14·1. Preparation of Grignard reagents.

Function of Ether. Although the Grignard reagent in ether reacts as if it were simply alkylmagnesium halide, ether is undoubtedly in combination with it and is not present merely as a solvent. The electronic formula of ether shows that the oxygen atom has two lone pairs of electrons out of which one is donated to the magnesium atom of alkylmagnesium halide as follows :

$H_5C_2 \times \ddot{\underset{\cdot\cdot}{O}} \times C_2H_5 \qquad CH_3 \times Mg \times \ddot{\underset{\cdot\cdot}{I}}:$

O has 2 lone pairs Mg is short of electrons



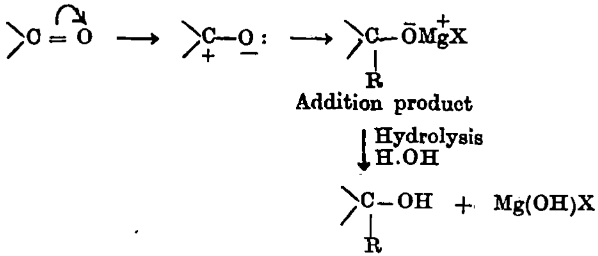
Anisole, $C_6H_5OCH_3$, and *dimethylaniline*, $C_6H_5N(CH_3)_2$ are sometimes used in place of ether. Both these possess lone pairs and are capable of co-ordination.

Formation of Grignard reagents may be represented by homolytic or heterolytic mechanisms depending upon the requirements of the reaction.

Heterolytic mechanism :

$$Mg: + R—X \longrightarrow \overset{2+}{Mg}\overset{-}{R}::\overset{-}{X} \longrightarrow R—Mg—X$$

It is evident that Grignard reagent is a convenient source of carbanions. Grignard reagent can effect ionic displacement by nucleophilic substitution and also addition to multiple bonds by heterolytic mechanism. The addition reactions include action with carbonyl compounds and carboxylic acid derivatives. The mechanism of addition is represented as



The mechanism of reactions (4), (5), (6), (7), (8) and (9) (*i*) can be explained as above.

Properties and Synthetic Applications. Grignard reagents are non-volatile, colourless solids but they are seldom prepared in the free state. For synthetic purposes they are always prepared and used in ether solution. Unlike the alkylzincs, they do not ignite spontaneously on contact with air.

Chemically Grignard reagents enter into reaction with many compounds yielding almost all types of organic derivatives. The following reactions of Grignard reagents sufficiently show their versatility as synthetic reagents. In these reactions, bromides and iodides in general react more readily than the chlorides.

(1) FORMATION OF ALKANES. Grignard reagents are decomposed by water, alcohols, ammonia, amines, etc. in each case liberat-

ing the hydrocarbon corresponding to its alkyl group. Thus :

$$\underset{\text{Methylmagnesium iodide}}{CH_3\boxed{MgI} \boxed{+ \underset{\text{Water}}{HO}}H} \longrightarrow \underset{\text{Methane}}{CH_4} + IMgOH$$

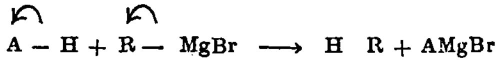
$$CH_3\boxed{MgI + \underset{\text{Ethanol}}{C_2H_5O}}H \longrightarrow CH_4 + IMgOC_2H_5$$

$$CH_3\boxed{MgI + \underset{\text{Ammonia}}{NH_2}}H \longrightarrow CH_4 + IMgNH_2$$

$$CH_3\boxed{MgI + \underset{\text{Ethylamine}}{C_2H_5NH}}H \longrightarrow CH_4 + IMgNHC_2H_5$$

Since methane evolved in the above decomposition can be measured, it gives a method for the estimation of OH, NH_2, and SH groups in organic compounds.

Mechanism. Substances containing active hydrogen undergo ionic displacements by heterolytic fission in presence of Grignard reagents.



$$A - H + R - MgBr \longrightarrow H \quad R + AMgBr$$

Water, alcohols, carboxylic acids and amines undergo this change. Indirectly the alkyl halide (R—Br) is reduced to the parent hydrocarbon.

HIGHER ALKANES can be obtained by the treatment of a Grignard reagent with an alkyl halide.

$$CH_3\boxed{MgBr + Br}\underset{\text{Ethyl bromide}}{C_2H_5} \longrightarrow \underset{\text{Propane}}{CH_3C_2H_5} + MgBr_2$$

This reaction is, in fact, an extension of Wurtz Reaction.

(2) FORMATION OF ALKENES. An alkene may be synthesised by the action of unsaturated halides on Grignard reagents.

$$CH_3\boxed{MgBr + Br}\underset{\text{Allyl bromide}}{H_2.HC{=}CH_2} \longrightarrow \underset{\text{1-Butene}}{CH_3CH_2.CH{=}CH_2}$$

Alkenes are also finally formed by the reaction between ketones and Grignard reagents. (*See reaction 5*).

$$\underset{\text{Tert. Isobutyl alcohol}}{(CH_3)_2C(OH)CH_3} \xrightarrow{heat} \underset{\text{Isobutene}}{(CH_3)_2C : CH_2} + H_2O$$

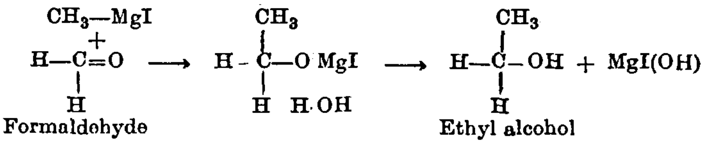
(3) FORMATION OF HIGHER ALKANES. Lower alkenes react with Grignard reagents to form derivatives which upon reaction with alkyl halides yield higher hydrocarbons.

$$\underset{\text{Propyne, Methylacetylene}}{CH_3C{\equiv}C}\boxed{H + R}MgI \longrightarrow CH_3.C{\equiv}CMgI + RH$$

$$CH_3.C{\equiv}C\boxed{MgI + I}\underset{\text{Methyl iodide}}{CH_3} \longrightarrow \underset{\text{2-Butyne, Dimethylacetylene}}{CH_3.C{\equiv}C.CH_3} + MgI_2$$

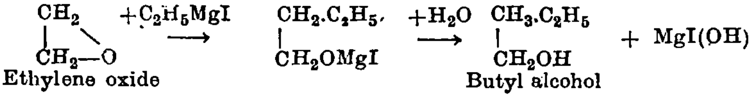
(4) FORMATION OF PRIMARY ALCOHOLS. They are formed by

the action of formaldehyde upon Grignard reagents and hydrolysis of the product with dilute hydrochloric acid.



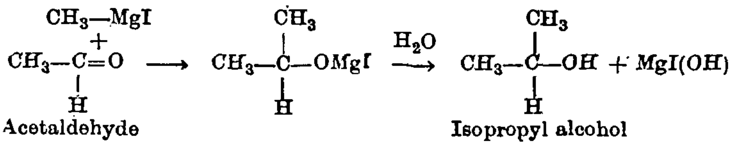
$$\begin{array}{c} CH_3{-}MgI \\ + \\ H{-}\overset{|}{C}{=}O \\ | \\ H \end{array} \longrightarrow \begin{array}{c} CH_3 \\ | \\ H{-}C{-}O\,MgI \\ | \\ H \quad H{\cdot}OH \end{array} \longrightarrow \begin{array}{c} CH_3 \\ | \\ H{-}C{-}OH \\ | \\ H \end{array} + MgI(OH)$$

A primary alcohol with two additional carbon atoms is obtained by the use of ethylene oxide.



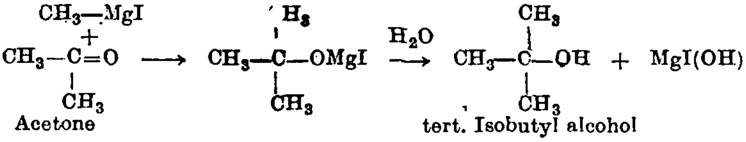
$$\begin{array}{l} CH_2 \\ |\;\diagdown \\ CH_2{-}O \end{array} + C_2H_5MgI \longrightarrow \begin{array}{l} CH_2.C_2H_5 \\ | \\ CH_2OMgI \end{array} \xrightarrow{+H_2O} \begin{array}{l} CH_3.C_2H_5 \\ | \\ CH_2OH \end{array} + MgI(OH)$$

(5) FORMATION OF SECONDARY ALCOHOLS. They are formed by the reaction of Grignard reagents with aldehydes other than formaldehyde.



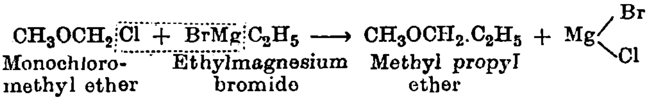
$$\begin{array}{c} CH_3{-}MgI \\ + \\ CH_3{-}C{=}O \\ | \\ H \end{array} \longrightarrow \begin{array}{c} CH_3 \\ | \\ CH_3{-}C{-}OMgI \\ | \\ H \end{array} \xrightarrow{H_2O} \begin{array}{c} CH_3 \\ | \\ CH_3{-}C{-}OH \\ | \\ H \end{array} + MgI(OH)$$

(6) FORMATION OF TERTIARY ALCOHOLS. Tertiary alcohols are easily prepared by the action of ketones on Grignard reagents.



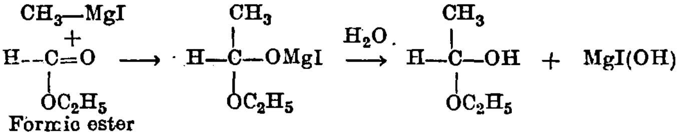
$$\begin{array}{c} CH_3{-}MgI \\ + \\ CH_3{-}C{=}O \\ | \\ CH_3 \end{array} \longrightarrow \begin{array}{c} CH_3 \\ | \\ CH_3{-}C{-}OMgI \\ | \\ CH_3 \end{array} \xrightarrow{H_2O} \begin{array}{c} CH_3 \\ | \\ CH_3{-}C{-}OH \\ | \\ CH_3 \end{array} + MgI(OH)$$

(7) FORMATION OF ETHERS. Higher ethers can be obtained by the reaction of a lower halogenated ether with the Grignard reagents.

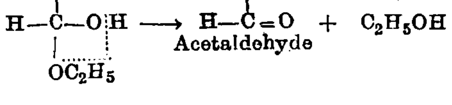


$$CH_3OCH_2\boxed{Cl + BrMg}C_2H_5 \longrightarrow CH_3OCH_2.C_2H_5 + Mg\begin{array}{l} \diagup Br \\ \diagdown Cl \end{array}$$

(8) FORMATION OF ALDEHYDES. Grignard reagents react with formic ester to form an aldehyde.



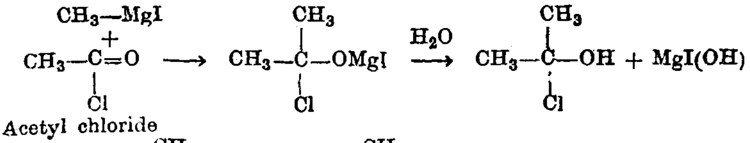
$$\begin{array}{c} CH_3{-}MgI \\ + \\ H{-}C{=}O \\ | \\ OC_2H_5 \end{array} \longrightarrow \begin{array}{c} CH_3 \\ | \\ H{-}C{-}OMgI \\ | \\ OC_2H_5 \end{array} \xrightarrow{H_2O} \begin{array}{c} CH_3 \\ | \\ H{-}C{-}OH \\ | \\ OC_2H_5 \end{array} + MgI(OH)$$



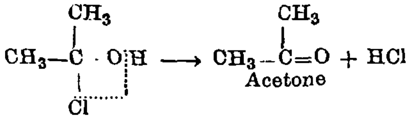
$$\begin{array}{c} CH_3 \\ | \\ H{-}C{-}O\vdots H \\ |\;\;\vdots \\ OC_2H_5 \end{array} \longrightarrow \begin{array}{c} CH_3 \\ | \\ H{-}C{=}O \end{array} + C_2H_5OH$$

(9) FORMATION OF KETONES. Ketones are formed by the action of Grignard reagents with acid chlorides and cyanides :

(i)

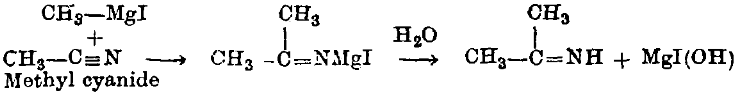


$$\begin{array}{c}CH_3-MgI\\+\\CH_3-\underset{\underset{Cl}{|}}{C}=O\\\text{Acetyl chloride}\end{array} \longrightarrow CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{Cl}{|}}{C}}-OMgI \xrightarrow{H_2O} CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{Cl}{|}}{C}}-OH + MgI(OH)$$

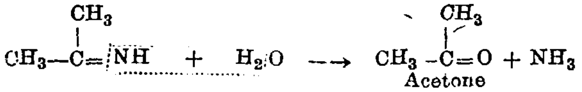


$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{Cl}{|}}{C}}-O\boxed{H} \longrightarrow \underset{\text{Acetone}}{CH_3-\overset{\overset{CH_3}{|}}{C}=O} + HCl$$

(ii)

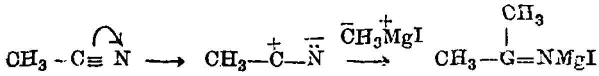


$$\begin{array}{c}CH_3-MgI\\+\\CH_3-C\equiv N\\\text{Methyl cyanide}\end{array} \longrightarrow CH_3-\overset{\overset{CH_3}{|}}{C}=NMgI \xrightarrow{H_2O} CH_3-\overset{\overset{CH_3}{|}}{C}=NH + MgI(OH)$$



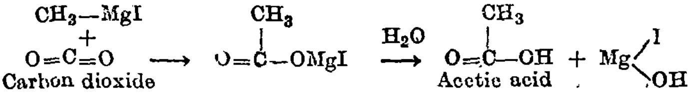
$$CH_3-\overset{\overset{CH_3}{|}}{C}=\boxed{NH + H_2}O \longrightarrow \underset{\text{Acetone}}{CH_3-\overset{\overset{CH_3}{|}}{C}=O} + NH_3$$

Mechanism :



$$CH_3-C\equiv N \longrightarrow CH_3-\overset{+}{C}-\overset{-}{\ddot{N}} \xrightarrow{\overset{-}{C}H_3\overset{+}{Mg}I} CH_3-\overset{\overset{CH_3}{|}}{C}=NMgI$$

(10) FORMATION OF CARBOXYLIC ACIDS. Grignard reagents react readily with carbon dioxide forming carboxylic acids :

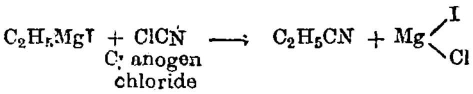


$$\begin{array}{c}CH_3-MgI\\+\\O=C=O\\\text{Carbon dioxide}\end{array} \longrightarrow O=\overset{\overset{CH_3}{|}}{C}-OMgI \xrightarrow{H_2O} \underset{\text{Acetic acid}}{O=\overset{\overset{CH_3}{|}}{C}-OH} + Mg\begin{array}{l}\diagup I\\\diagdown OH\end{array}$$

(11) FORMATION OF ESTERS. Grignard reagents react with chloroformic ester to form higher esters :

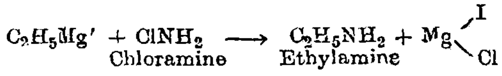
$$\underset{\text{Ethylmagnesium iodide}}{C_2H_5\boxed{MgI + Cl}}\underset{\text{Chloroformic ester}}{COOC_2H_5} \longrightarrow \underset{\text{Higher ester}}{C_2H_5COOC_2H_5} + MgI(Cl)$$

(12) FORMATION OF ALKYL CYANIDES. Alkyl cyanides are prepared by the action of cyanogen chloride with a Grignard reagent Thus :



$$C_2H_5MgI + \underset{\text{Cyanogen chloride}}{ClCN} \longrightarrow C_2H_5CN + Mg\begin{array}{l}\diagup I\\\diagdown Cl\end{array}$$

(13) FORMATION OF PRIMARY AMINES. Chloramine reacts with a Grignard reagent to form a primary amine.



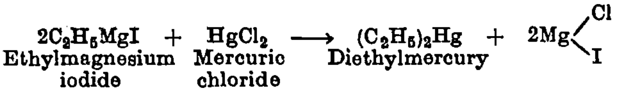
$$C_2H_5MgI + \underset{\text{Chloramine}}{ClNH_2} \longrightarrow \underset{\text{Ethylamine}}{C_2H_5NH_2} + Mg\begin{array}{l}\diagup I\\\diagdown Cl\end{array}$$

(14) FORMATION OF THIOALCOHOLS. Sulphur reacts with Grignard reagents forming thioalcohols.

$$\underset{\text{Ethylmagnesium iodide}}{C_2H_5MgI} + S \longrightarrow C_2H_5SMgI$$

$$C_2H_5S\boxed{MgI + HO}H \longrightarrow \underset{\text{Thioalcohol}}{C_2H_5SH} + MgI(OH)$$

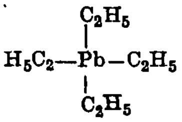
(15) Formation of Organo-metallic Compounds. Grignard reagents react with metallic halides to form other organo-metallic compounds. Thus :



$$\underset{\substack{\text{Ethylmagnesium}\\\text{iodide}}}{2C_2H_5MgI} + \underset{\substack{\text{Mercuric}\\\text{chloride}}}{HgCl_2} \longrightarrow \underset{\text{Diethylmercury}}{(C_2H_5)_2Hg} + 2Mg\begin{smallmatrix}Cl\\I\end{smallmatrix}$$

TETRAETHYLLEAD, $(C_2H_5)_4Pb$

It is a colourless liquid with a strong smell. It boils at 202°C. It is a highly poisonous substance, being absorbed both by the lungs and through the skin. It is soluble in organic liquids like gasoline but insoluble in and not decomposed by water. As indicated by its physical characters and low degree of reactivity, tetraethyllead is a purely covalent compound.



$$\begin{array}{c} C_2H_5 \\ | \\ H_5C_2-Pb-C_2H_5 \\ | \\ C_2H_5 \end{array}$$

It is conveniently obtained by the action of ethylmagnesium iodide with lead chloride.

$$2PbCl_4 + 4C_2H_5MgI \longrightarrow Pb + Pb(C_2H_5)_4 + 4MgI(Cl)$$

On industrial scale it is obtained by the reaction of ethyl chloride with sodiumlead alloy.

$$4C_2H_5Cl + 4NaPb \longrightarrow 4NaCl + 3Pb + (C_2H_5)_4Pb$$

The technical use of tetraethyllead is as '*antiknock*' for motor fuels. When mixed with petrol or gasoline, it prevents the knocking in internal combustion engines.

Theoretically, it is of interest as when passed through hot tubes at low pressure in the atmosphere of an inert gas, tetraethyllead is decomposed according to the following equation.

$$Pb(C_2H_5)_4 \longrightarrow Pb + 4C_2H_5$$

This has established the existence of free radicals, as tetramethyllead also has been shown to decompose in the same fashion forming methyl radical.

QUESTIONS

1. What are organo-metallic compounds ? Apply your definition to show that calcium oxalate is not an organo-metallic compound.

2. Describe the preparation, properties and synthetic applications of dialkylzincs. Why have they been superseded by Grignard reagents in organic synthesis ?

3. Outine the preparation of a solution of ethylmagnesium bromide. How will you prepare (*a*) ethane ; (*b*) propionic acid ; (*c*) ethyl methyl ketone and (*d*) isopropyl alcohol, from it ?

4. "Grignard's reagents have attained a position in synthetic Organic Chemistry unrivalled by any other class of compounds". Justify this statement. (*Udaipur B.Sc. II, 1967*)

5. What do you mean by organo-metallic compounds ? Give an example. Give some synthetic applications of organo-metallic compounds of magnesium. (*Dibrugarh B.Sc. II, 1967*)

6. Give examples of the uses of a Grignard's reagent in preparing (*a*) a saturated hydcoarbon, (*b*) an unsaturated hydrocarbon, (*c*) a primary alcohol (*d*) a secondary alcohol, (*e*) a tertiary alcohol, (*f*) an aldehyde, (*g*) a ketone, (*h*) a carboxylic acid. (*Banaras Hindu University B.Sc. II, 1967*)

7. How are Grignard's reagents prepared ? Discuss their important reactions and synthetic applications. (*J & K B.Sc. Suppl., 1967*)

8. What are organo-metallic compounds ? Describe the preparation of methylmagnesium iodide and show how it may be used to synthesise the following compounds :—(*a*) a primary alcohol, (*b*) an aldehyde, (*c*) a ketone, (*d*) a carboxylic acid, (*e*) a saturated hydrocarbon.
(*Shivaji University Kohlapur B.Sc. II, 1967*)

9. Write short notes on :

(*a*) Structure of Grignard's reagent. (*Aligarh B.Sc. II, 1967*)

(*b*) Synthetic uses of Grignard's reagent. (*Panjab B.Sc. II, 1967*)

(*c*) Synthesis tetramethyllead. (*Panjab B.Sc. II, 1967*)

(*d*) Synthesis of (*i*) primary, (*ii*) secondary and (*iii*) tertiary alcohols from Grignard's reagents. (*Poona B.Sc. II, 1967*)

10. How does ethylmagnesium bromide react with—

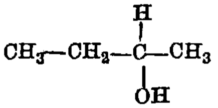
(*i*) an ester,
(*ii*) a ketone,
(*iii*) a nitrile,
(*iv*) a carboxylic acid.

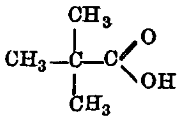
(*Panjab B.Sc. II, 1968*)

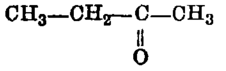
11. Give the preparation and uses of CH_3MgI. (*Bombay B.Sc.,1968*)

12. Describe a method for the preparation of methyl magnesium bromide and discuss its importance in organic synthesis. Indicate the limitations of its applications. (*Baroda B.Sc., 1968*)

13. (*a*) Show how each of the following substances can be prepared by reaction involving a Grignard reagent.

(*i*) 
$CH_3-CH_2-\overset{\overset{\large H}{|}}{\underset{\underset{\large OH}{|}}{C}}-CH_3$

(*iii*) 

(*ii*) 
$CH_3-CH_2-\underset{\underset{\large O}{\|}}{C}-CH_3$

(*iv*) $(C_2H_5)_4Pb$. (*Banaras B.Sc., 1968*)

14. Discuss briefly the Grignard reagent and its uses in Organic Chemistry. (*Ceylon B.Sc., 1968*)

15. How is methyl magnesium iodide prepared ? State its important reactions. How has its structure been determined. (*Viswa Bharati B.Sc.. 1969*)

What are organometallic compounds Give a detailed account of the preparation and synthetic applications of any one organometallic compound you have studied. (*Bangalore B.Sc., 1969*)

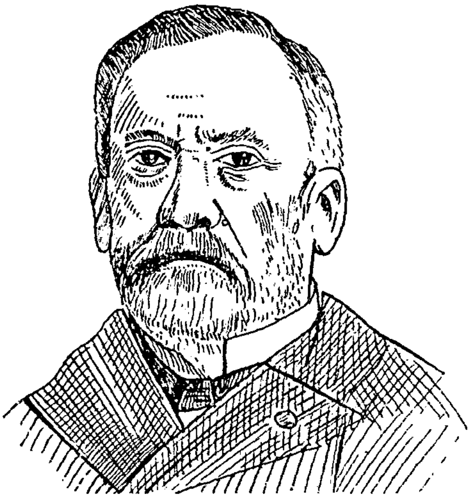
17. How is magnesium methyl iodide prepared ? How would you prepare (*a*) isopropyl alcohol (*b*) acetic acid (*c*) ethyl alcohol from it.
(*Marathwada B.Sc., 1969*)

18, How does ethylmagnesium bromide react with (*i*) ethyl formate, (*ii*) acetonitrile, (*iii*) ethylene oxide (*iv*) ethyl amine (*v*) carbon disulphide. (*Udaipur B.Sc., 1969*)

19. What are Grignard reagents ? How are they prepared ? Outline their uses in synthetic organic chemistry. (*Panjab B.Sc., 1969*)

15

Aliphatic Alcohols



LOUIS PASTEUR
(1822—1895)

French Biochemist. He is well known for his work with tartaric acid, his method for the resolution of racemic mixtures, and the elucidation of the process of fermentation.

The term alcohol is applied to all organic compounds, obtained by replacing one or more hydrogen atoms of an open-chain hydrocarbon by OH groups. The alcohols are further termed **mono-**, **di-** and **tri-hydric** according to the number of groups which they may contain. Thus :

C_2H_5OH	$CH_2OH.CH_2OH$	$CH_2OH.CHOH.CH_2OH$
Ethyl alcohol	Glycol	Glycerol
(*Monohydric*)	(*Dihydric*)	(*Trihydric*)

Alcohols could well be considered as derivatives of water obtained by the replacement of one of its hydrogen atoms by a hydrocarbon radical. Thus :

$$\underset{\text{Water}}{H\ \ O-H} \xrightarrow[+C_2H_5]{-H} \underset{\text{Ethyl alcohol}}{C_2H_5-O-H}$$

This is justified by their behaviour towards sodium metal and phosphorus pentachloride.

Analogy to Inorganic Hydroxides. Alcohol could be regarded as analogous to inorganic hydroxides.

C_2H_5OH Ethyl alcohol	$C_2H_4(OH)_2$ Glycol	$C_3H_5(OH)_3$ Glycerol
$NaOH$ Sodium hydroxide	$Ca(OH)_2$ Calcium hydroxide	$Al(OH)_3$ Aluminium hydroxide

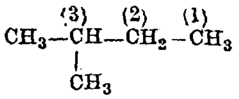
The analogy is, however, superficial and in fact entirely misleading. The two types of compounds have nothing in common except that they happen to possess hydroxyl groups. The chief difference between the organic and the inorganic hydroxides are tabulated below :

ALCOHOLS	INORGANIC HYDROXIDES
(1) Covalent compounds e.g., C_2H_5-O-H	(1) Electrovalent compounds e.g., Na^+OH^-
(2) Non-ionised.	(2) Ionised.
(3) Neutral to litmus.	(3) Alkaline to litmus.
(4) Give molecular reactions.	(4) Give ionic reactions.

It should, thus, be abundantly clear to the beginner that it is wholly absurd to consider alcohols as organic hydroxides resembling inorganic bases.

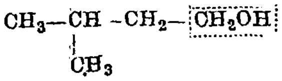
MONOHYDRIC ALCOHOLS

Alcohols containing one hydroxyl group are called *monohydroxy* or *monohydric alcohols.* They have been further classified as **primary, secondary** and **tertiary alcohols** according as the hydroxyl group may be linked to a primary, a secondary, or a tertiary carbon atom. Thus isopentane,



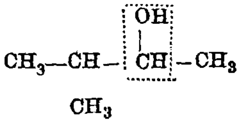
$$CH_3-\underset{\underset{\displaystyle CH_3}{|}}{\overset{(3)}{C}H}-\overset{(2)}{C}H_2-\overset{(1)}{C}H_3$$

in which the carbon atoms numbered (1), (2) and (3) are respectively primary, secondary, and tertiary-can give all the three types of alcohols.



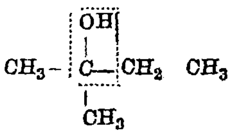
$$CH_3-\underset{\underset{\displaystyle CH_3}{|}}{CH}-CH_2-\boxed{CH_2OH}$$

Primary alcohol



$$CH_3-\underset{\displaystyle CH_3}{CH}-\boxed{\overset{\displaystyle OH}{\overset{|}{CH}}}-CH_3$$

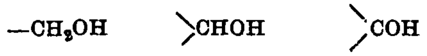
Secondary alcohol



$$CH_3-\boxed{\underset{\underset{\displaystyle CH_3}{|}}{\overset{\displaystyle OH}{\overset{|}{C}}}-}CH_2\ \ CH_3$$

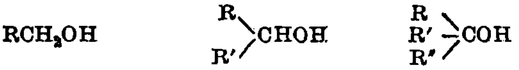
Tertiary alcohol

As indicated above by the dotted enclosures, the groups characteristic of the three types of alcohols are :



Primary Secondary Tertiary

Accordingly their symbolic or type formulas would be



Primary alcohol Secondary alcohol Tertiary alcohol

where R, R′ and R″ may represent the same or different alkyl radicals.

The general formula for monohydric alcohols is

$$C_nH_{2n+1}OH \quad \text{or} \quad C_nH_{2n+2}O$$

NOMENCLATURE

There are three ways of naming aliphatic monohydric alcohols :

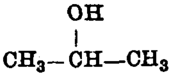
(*a*) The Common System ;

(*b*) The Carbinol System ; and

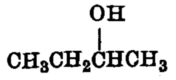
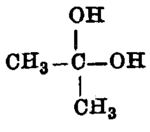
(*c*) The IUPAC System.

The Recent Chemical Abstracts favour common names for lower members while the higher and more complex alcohols are assigned by the IUPAC System.

(1) According to the COMMON SYSTEM, alcohols (R—OH) are named as Alkyl alcohols, the term alcohol designating the —OH group. Thus the common name of an individual member is obtained by naming the alkyl group linked to —OH group and adding 'alcohol' as a separate word. Such '*functional class names*' as they are called are two-word names. Thus :

CH_3OH	Methyl alcohol
CH_3CH_2OH	Ethyl alcohol
$CH_3CH_2CH_2OH$	Propyl alcohol (n-Propyl alcohol)
 $CH_3-CH(OH)-CH_3$	Isopropyl alcohol

As we go higher in the series it becomes necessary to indicate whether a particular alcohol is primary (1°), secondary (2°) or tertiary (3°).

$CH_3CH_2CH_2CH_2OH$	n-Butyl alcohol (1°)
 $CH_3CH_2CH(OH)CH_3$	sec-Butyl alcohol (2°)
 $CH_3-C(OH)(CH_3)-OH$	tert-Buryl alcohol (3°)

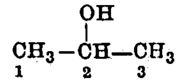
Since a n-alkyl alcohol is always a primary alcohol, it is necessary to indicate the same by a prefix.

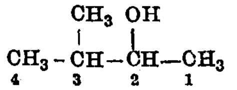
(3) The IUPAC SYSTEM names alcohols as *Alkanols*. The name of an individual alcohol is derived by dropping the final '*e*' of the name of the parent hydrocarbon and adding the suffix '*ol*'. Thus :

CH_3OH	Methanol (Methane — e + ol)
C_2H_5OH	Ethanol (Ethane — e + ol)

For naming higher alcohols, the longest carbon chain bearing the OH group is selected as the basic hydrocarbon chain. The positional numbers of the OH group and other substituents are obtained by numbering the parent chain from the end nearer the OH group. Then the systematic name of the alcohol is written as one word by the usual IUPAC conventions. Thus :

$CH_3—CH_2—CH_2OH$ 1-Propanol

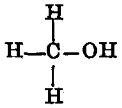

$$\underset{1}{CH_3}-\underset{2}{\overset{\overset{OH}{|}}{C}H}—\underset{3}{CH_3}$$
2-Propanol

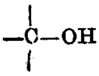

$$\underset{4}{CH_3}-\underset{3}{\overset{\overset{CH_3}{|}}{C}H}-\underset{2}{\overset{\overset{OH}{|}}{C}H}—\underset{1}{CH_3}$$
3-Methyl-2-butanol

In case the parent chain of an alcohol also contains a double bond, the locant of OH group is mentioned before the suffix '*ol*'. Thus :

$$\overset{5}{CH_3}—\overset{4}{CH}{=}\overset{3}{CH}—\overset{2}{CH_2}—\overset{1}{CH_2OH}$$
3-Penten-1-ol

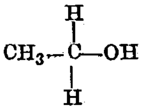
(2) The CARBINOL SYSTEM. This system which is still occasionally used names the alcohols as derivatives of methyl alcohol (CH_3OH) which is expressed as 'carbinol'. The carbon atom together with OH group is called *carbinol group*.

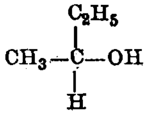

$$H—\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-OH$$
(Methyl alcohol)

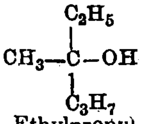

$$—\underset{|}{\overset{|}{C}}—OH$$
Carbinol group

In alcohols, each free valency of the carbinol group is assumed to carry an alkyl radical or a hydrogen atom.

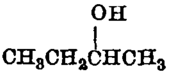
To get the name of an individual alcohol, the alkyl radicals attached to the carbinol group are named in alphabetical order and the word carbinol is added as suffix. Thus the full name of the given alcohol emerges as a continuous one-word name.


$$CH_3—\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}—OH$$
Methylcarbinol
(Ethyl alcohol)

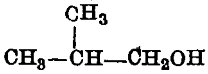

$$CH_3—\underset{\underset{H}{|}}{\overset{\overset{C_2H_5}{|}}{C}}—OH$$
Ethylmethylcarbinol


$$CH_3—\underset{\underset{C_3H_7}{|}}{\overset{\overset{C_2H_5}{|}}{C}}—OH$$
Ethylpropylcarbinol

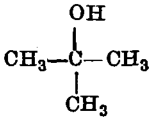
(1) $CH_3CH_2CH_2CH_2OH$ 1-Butanol ;
n-Butyl alcohol

(2) 

$CH_3CH_2CH(OH)CH_3$ 2-Butanol ; sec-Butyl alcohol

(3) 

$CH_3-CH(CH_3)-CH_2OH$ 2-Methyl-1-propanol ; Isobutyl alcohol

(4) 

$CH_3-C(OH)(CH_3)-CH_3$ 2-Methyl-2-Propanol ; tert-Butyl alcohol

ISOMERISM

Isomerism in alcohols arises from two causes : (*i*) the different structures of the carbon chain, and (*ii*) the different positions of the OH group on the carbon chain. Thus, alcohols may show chain isomerism, position isomerism, or both.

Since all the hydrogen atoms in methane and ethane are identical the replacement of any of them by (OH) group will give only one alcohol. However, propane containing two types of hydrogen atoms can form two isomeric alcohols.

$$CH_3-CH_2-CH_3$$

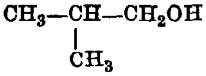
↙ Propane ↘

$CH_3CH_2CH_2OH$	$CH_3CHOHCH_3$
Propyl alcohol	Isopropyl alcohol

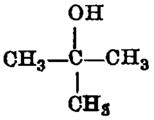
Proceeding in the same fashion, the two butanes, normal and iso, give rise to four isomeric alcohols.

(1) $CH_3CH_2CH_2CH_2OH$ n-Butyl alcohol, 1-Butanol

(2) $CH_3CH_2CHOHCH_3$ sec-Butyl alcohol, 2-Butanol

(3) 

$CH_3-CH(CH_3)-CH_2OH$ Isobutyl alcohol, 2-Methyl-1-propanol

(4) 

$CH_3-C(OH)(CH_3)-CH_3$ tert-Butyl alcohol, 2-Methyl-2-propanol

While alcohols (1) and (2), as also (3) and (5) illustrate position isomerism, the alcohols (1) and (3) are a case of chain isomerism.

Alcohols can show a third type of structural isomerism which is called *functional* or *chemical isomerism.* For example, the molecular formula C_2H_6O can represent.

CH_3CH_2OH	and	CH_3-O-CH_3
Ethyl alcohol		Dimethyl ether

Here, the two compounds belong to different classes of compounds.

Higher alcohols like amyl alcohol also exhibit optical isomerism.

METHODS OF FORMATION

Alcohols are chiefly obtained :

(*a*) *By the hydrolysis of compounds such as alkyl halides, hydrogen sulphates, amines etc., in which n-radical is linked to an atom other than carbon.*

(*b*) *By reduction of compounds such as aldehydes, ketones and acid derivatives containing a carbonyl group attached to an alkyl radical.*

(1) **Hydrolysis of Alkyl halides.** Alkyl halides when treated with aqueous potassium hydroxide, form alcohols.

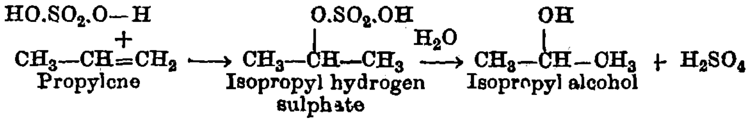
$$\underset{\text{Ethyl bromide}}{C_2H_5\boxed{Br + K}OH_{aq}} \longrightarrow \underset{\text{Ethyl alcohol}}{C_2H_5OH} + KBr$$

This method of preparing alcohols is not very satisfactory as the alkyl halides simultaneously eliminate a molecule of halogen acid giving alkenes. Therefore, we use a mild alkali like moist silver oxide or aqueous potassium carbonate instead of caustic potash. Thus :

$$\underset{\text{Ethyl iodide}}{C_2H_5\boxed{I + Ag}OH} \longrightarrow \underset{\text{Ethyl alcohol}}{C_2H_5OH} + AgI$$

The most suitable halides for use in this method are the alkyl bromides, as the chlorides are not sufficiently reactive and the iodides tend to eliminate hydrogen iodide very readily.

(2) **Hydration of Alkenes.** Alkenes when passed into sulphuric acid are absorbed by it forming alkyl hydrogen sulphates which on subsequent hydrolysis with water or steam are converted into alcohols.



$$\underset{\text{Propylene}}{\overset{\overset{\displaystyle HO.SO_2.O-H}{+}}{CH_3-CH=CH_2}} \longrightarrow \underset{\text{Isopropyl hydrogen sulphate}}{CH_3-\overset{\overset{\displaystyle O.SO_2.OH}{|}}{C}H-CH_3} \xrightarrow{H_2O} \underset{\text{Isopropyl alcohol}}{CH_3-\overset{\overset{\displaystyle OH}{|}}{C}H-CH_3} + H_2SO_4$$

This is a successful commercial method as the lower alkenes are obtained in large amounts during the cracking of petroleum.

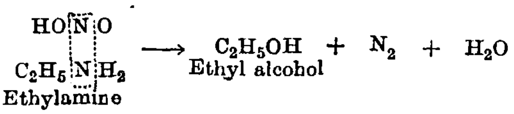
(3) **Hydrolysis of Esters.** When heated with a dilute solution of an alkali or a mineral acid, the organic esters are hydrolysed to form the parent acid and alcohol.

$$\underset{\text{Ester}}{RCOO\boxed{R' + HO}H} \longrightarrow \underset{\text{Acid}}{RCOOH} + \underset{\text{Alcohol}}{R'OH}$$

The acid or alkali used for hydrolysis accelerates the reaction by furnishing H^+ and OH' ions respectively which act as catalysts. Many higher alcohols are prepared from esters occurring in nature by this method. Thus :

$$\underset{\substack{\text{Melissyl palmitate}\\(\textit{Bees wax})}}{C_{15}H_{31}COOC_{30}H_{61}} + H_2O \longrightarrow \underset{\text{Plamitic acid}}{C_{15}H_{31}COOH} + \underset{\text{Melissyl alcohol}}{C_{20}H_{61}OH}$$

(4) **Action of Nitrous acid on Primary amines.** On treatment with sodium nitrite and dilute mineral acid, primary amines form alcohols.

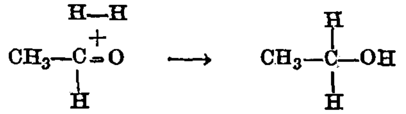


$$\underset{\text{Ethylamine}}{\begin{matrix} HO\,N\,O \\ C_2H_5\,N\,H_2 \end{matrix}} \longrightarrow \underset{\text{Ethyl alcohol}}{C_2H_5OH} + N_2 + H_2O$$

This method can be used for the preparation of higher alcohols when the corresponding acid is available in nature. The acid may be converted into the amine by the usual methods and then treated with nitrous acid.

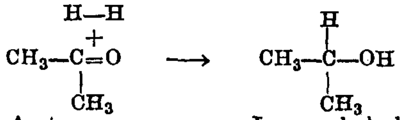
$$\underset{\text{Acid}}{\mathrm{RCOOH}} \longrightarrow \underset{\text{Amm. salt}}{\mathrm{RCOONH_4}} \longrightarrow \underset{\text{Amide}}{\mathrm{RCONH_2}} \longrightarrow \underset{\text{Amine}}{\mathrm{RNH_2}}$$

(5) **Reduction of Aldehydes and Ketones.** Aldehydes and ketones on reduction with hydrogen in presence of nickel, or with zinc and hydrochloric acid, form respectively a primary and a secondary alcohol.



$$\mathrm{CH_3{-}\overset{H-H\atop +}{\underset{\mid\atop H}{C}}{=}O} \longrightarrow \mathrm{CH_3{-}\overset{H\atop\mid}{\underset{\mid\atop H}{C}}{-}OH}$$

Acetaldehyde Ethyl alcohol



$$\mathrm{CH_3{-}\overset{H-H\atop +}{\underset{\mid\atop CH_3}{C}}{=}O} \longrightarrow \mathrm{CH_3{-}\overset{H\atop\mid}{\underset{\mid\atop CH_3}{C}}{-}OH}$$

Acetone Isopropyl alcohol

(6) **Reduction of Acid anhydrides. Acid chlorides, and Esters of fatty acids.** These compounds on reduction either with sodium and alcohol, or with hydrogen and a metal catalyst, produce alcohols. Thus :

$$\underset{\text{Anhydride}}{\mathrm{RCO.O.OCR}} + 4\mathrm{H} \longrightarrow \underset{\text{Alcohol}}{\mathrm{RCH_2OH}} + \mathrm{RCOOH}$$

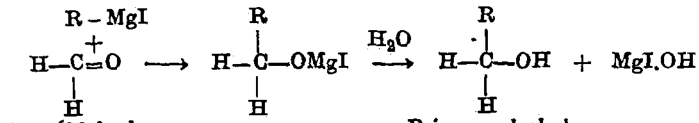
$$\underset{\text{Acid chloride}}{\mathrm{RCOCl}} + 4\mathrm{H} \longrightarrow \underset{\text{Alcohol}}{\mathrm{RCH_2OH}} + \mathrm{HCl}$$

$$\underset{\text{Ester}}{\mathrm{RCOOR}} + 4\mathrm{H} \longrightarrow \underset{\text{Alcohol}}{\mathrm{RCH_2OH}} + \mathrm{ROH}$$

The reduction of esters is particularly helpful in the preparation of higher alcohols from natural esters.

(7) **With the help of Grignard Reagents.**

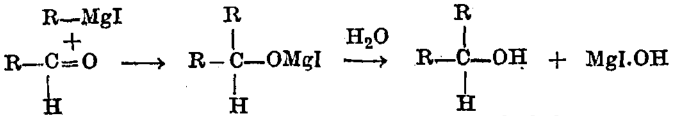
(*i*) *Primary alcohols* are obtained by treating a Grignard reagent with formaldehyde.



$$\mathrm{H{-}\overset{R-MgI\atop +}{\underset{\mid\atop H}{C}}{=}O} \longrightarrow \mathrm{H{-}\overset{R\atop\mid}{\underset{\mid\atop H}{C}}{-}OMgI} \xrightarrow{\mathrm{H_2O}} \mathrm{H{-}\overset{R\atop\mid}{\underset{\mid\atop H}{C}}{-}OH} + \mathrm{MgI.OH}$$

Formaldehyde Primary alcohol

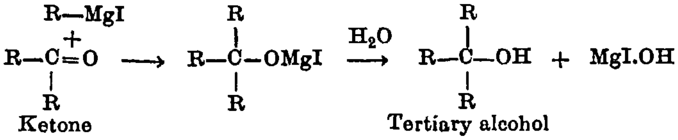
(*ii*) *Secondary alcohols* are formed by the interaction of Grignard reagents with aldehydes other than formaldehyde.



$$\mathrm{R{-}\overset{R-MgI\atop +}{\underset{\mid\atop H}{C}}{=}O} \longrightarrow \mathrm{R{-}\overset{R\atop\mid}{\underset{\mid\atop H}{C}}{-}OMgI} \xrightarrow{\mathrm{H_2O}} \mathrm{R{-}\overset{R\atop\mid}{\underset{\mid\atop H}{C}}{-}OH} + \mathrm{MgI.OH}$$

Aldehyde Secondary alcohol

(*iii*) *Tertiary alcohols* result by the reaction of Grignard reagents on ketones.



$$\underset{\text{Ketone}}{\overset{\overset{\text{R—MgI}}{+}}{\text{R—}\underset{\text{R}}{\underset{|}{\text{C}}}\text{=O}}} \longrightarrow \text{R—}\overset{\text{R}}{\overset{|}{\underset{\underset{\text{R}}{|}}{\text{C}}}}\text{—OMgI} \xrightarrow{H_2O} \underset{\text{Tertiary alcohol}}{\text{R—}\overset{\text{R}}{\overset{|}{\underset{\underset{\text{R}}{|}}{\text{C}}}}\text{—OH}} + \text{MgI.OH}$$

(3) **Fermentation of Carbohydrates.** Alcohols can be prepared by the fermentation of carbohydrates under the influence of suitable micro-organisms. Thus :

$$\underset{\text{Glucose}}{C_6H_{12}O_6} \xrightarrow{\textit{Yeast}} \underset{\text{Alcohol}}{2C_2H_5OH} + 2CO_2$$

Similarly n-primary butyl alcohol is made from starch by fermentation with *B. Clostridium acetobutylicum.*

HOW TO CONVERT A PRIMARY INTO A SECONDARY AND TERTIARY ALCOHOL.

(1) *Primary into Secondary Alcohol.* A primary alcohol may be converted into a secondary alcohol by the following steps :

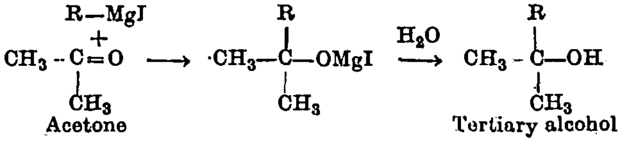
$$\underset{\text{n-Propyl alcohol}}{CH_3CH_2CH_2OH} \xrightarrow{HI} \underset{\text{Propyl iodide}}{CH_3CH_2CH_2I} \xrightarrow{\textit{Alc.}KOH} \underset{\text{Propylene}}{CH_3CH{=}CH_2}$$

$$\xrightarrow{HI} \underset{\text{Isopropyl iodide}}{CH_3CHICH_3} \xrightarrow{\textit{Aq.}KOH} \underset{\text{Isopropyl alcohol}}{CH_3CHOHCH_3}$$

(2) *Secondary into Tertiary alcohol.* A secondary alcohol may be converted into a tertiary by the aid of Grignard reagents as outlined below :

$$(i)\quad \underset{\text{Isopropyl alcohol}}{CH_3CHOHCH_3} \xrightarrow{\text{Oxid.}} \underset{\text{Acetone}}{CH_3COCH_3}$$

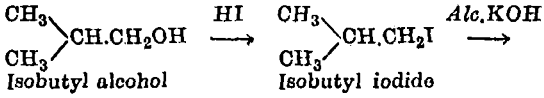
(*ii*)



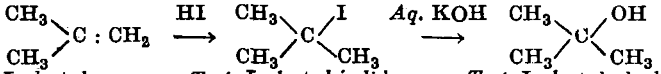
$$\underset{\text{Acetone}}{\overset{\overset{\text{R—MgI}}{+}}{CH_3\text{-}\underset{CH_3}{\underset{|}{C}}\text{=O}}} \longrightarrow CH_3\text{—}\overset{R}{\overset{|}{\underset{\underset{CH_3}{|}}{C}}}\text{—OMgI} \xrightarrow{H_2O} \underset{\text{Tertiary alcohol}}{CH_3\text{-}\overset{R}{\overset{|}{\underset{\underset{CH_3}{|}}{C}}}\text{—OH}}$$

(3) *Primary into Tertiary alcohol.* (*i*) It may be done by the methods outlined above by first converting the primary into a secondary and then to a tertiary alcohol.

(*ii*) When the given primary alcohol has a forked carbon chain attached to CH_2OH group, it can be directly converted into a tertiary alcohol as follows :



$$\underset{\text{Isobutyl alcohol}}{\begin{matrix}CH_3\diagdown\\ \quad\ \ \, CH.CH_2OH\\ CH_3\diagup\end{matrix}} \xrightarrow{HI} \underset{\text{Isobutyl iodide}}{\begin{matrix}CH_3\diagdown\\ \quad\ \ \, CH.CH_2I\\ CH_3\diagup\end{matrix}} \xrightarrow{\textit{Alc.}KOH}$$



$$(CH_3)_2C:CH_2 \xrightarrow{HI} (CH_3)_3CI \xrightarrow{Aq.\ KOH} (CH_3)_3COH$$

Isobutylene *Tert.* Isobutyl iodide *Tert.* Isobutyl alcohol

HOW TO CONVERT A HIGHER INTO A LOWER ALCOHOL AND VICE VERSA

(1) *Higher into a Lower alcohol* :

$$RCH_2OH \xrightarrow{O} RCOOH \xrightarrow{NH_3} RCOONH_4 \xrightarrow{heat}$$

$$RCONH_2 \xrightarrow{NaOH/Br_2} RNH_2 \xrightarrow{HNO_2} ROH$$

(2) *Lower into a Higher alcohol* :

$$(i)\ ROH \xrightarrow{HI} RI \xrightarrow{KCN} RCN \xrightarrow{H} RCH_2NH_2 \xrightarrow{HNO_2} RCH_2OH$$

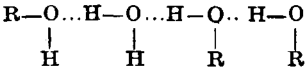
$$(ii)\ ROH \xrightarrow{HI} RI \xrightarrow{Mg} RMgI \xrightarrow{CH_2O} R.CH_2.OMgI \xrightarrow{H_2O} RCH_2OH$$

PHYSICAL CHARACTERISTICS

(1) The lower members are colourless volatile liquids which have a characteristic alcoholic smell and a burning taste. The smell and taste gradually disappears as we ascend the series.

(2) Alcohols are relatively volatile compounds but their boiling points are much higher than those of the corresponding alkanes.

The relatively high boiling points of alcohols are due to their ability to form H-bonds between themselves. Association takes place because the H-atom in alcohols is attached to a strongly electronegative element, oxygen.

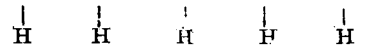


$$R—\underset{H}{O}\cdots H—\underset{H}{O}\cdots H—\underset{R}{O}\cdots H—\underset{R}{O}$$

These associated molecules will need energy for splitting up before the alcohol boils. This accounts for relatively higher boiling points of alcohols.

(3) The first three members are miscible with water but the solubility falls rapidly as we go higher in the series. The highest members are practically insoluble in water.

A compound which forms H-bonds between its own molecules can also form hydrogen bonds with water molecules. Therefore, a sort of 'co-association' between the water molecules and alcohols is expected *via* hydrogen bonding.



$$R—\underset{H}{O}\cdots H—\underset{H}{O}\cdots H—\underset{H}{O}\cdots H—\underset{H}{O}\cdots H—\underset{H}{O}\cdots$$

These alcohol-water H-bonds are the cause of relatively high solubility of alcohols in water. In higher alcohols, the size of the electron-repelling alkyl radical increases and their hydrogen bond forming character is reduced considerably. Higher alcohols have a lower tendency to form H-bonds with water and hence less soluble.

(4) The alcohols as a class are toxic substances. The toxic character of liquid alcohols increases with increasing molecular weight.

(5) The boiling points and the specific gravities increase regularly with increase of the length of the hydrocarbon chain. This will be illustrated by considering the physical constants of normal alcohols.

NAME	FORMULA	B. PT. °C	SP. GR. AT 20°
Methyl alcohol	CH_3OH	65	0·793
Ethyl alcohol	CH_3CH_2OH	78	0·789
n-Propyl alcohol	$CH_3CH_2CH_2OH$	98	0·804
n-Butyl alcohol	$CH_3(CH_2)_2CH_2OH$	118	0·810
n-Amyl alcohol	$CH_3(CH_2)_3CH_2OH$	138	0·817
n-Hexyl alcohol	$CH_3(CH_2)_4CH_2OH$	156	0·820
n-Heptyl alcohol	$CH_3(OH_2)_5CH_2OH$	176	0·818
n-Octyl alcohol	$CH_3(CH_2)_6CH_2OH$	194	0·827
n-Decyl alcohol	$CH_3(CH_3)_7CH_2OH$	231	0·830

It may be noted that from ethyl alcohol onward the boiling points increase by a regular difference of about 19°. The general rule that the physical properties of the first member of a homologous series do not fall into line with those of the rest of the series is also illustrated by alcohols.

For isomeric alcohols, a primary alcohol boils at a higher temperature than the secondary alcohol, and the latter at a higher temperature than the tertiary alcohol.

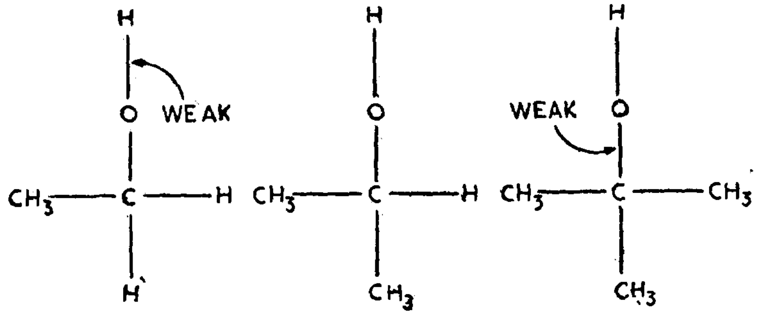
The tendency of hydrogen bond formation decreases with the increase in the number of electron-repelling alkyl groups. Hydrogen bond forming ability is more in primary alcohols than in secondary and tertiary alcohols. This explains why for isomeric alcohols, the boiling points are in the order

$$P > S > T.$$

CHEMICAL CHARACTERISTICS

The structural formulae of the three types of alcohols show that they consist of (*i*) *one or more hydrocarbon radicals* and (*ii*) *a hydroxyl group*. The chemical behaviour of alcohols is associated with the very reactive OH group. The reactions of the OH group are of two types :

(*a*) *those in which only the H-atom participates* ; *and*
(*b*) *those in which the OH group as a whole is involved.*



Primary alcohol Secondary alcohol Tertiary alcohol

In the first type of reactions, the primary alcohols are most reactive and tertiary alcohols are least so. In the second type of reactions, the order of reactivity is reversed. This is due to the fact that in primary alcohols O—to—H linkage is weak while in tertiary alcohols it is the C—to—O linkage that is weak.

The hydrocarbon radical in alcohols gives the usual reactions of the alkanes.

The general reactions of alcohols are given below :

(1) **Alcohol of Crystallisation.** The lower alcohols resemble water in the formation of addition compounds with anhydrous salts. Thus we have,

$MgCl_2.6CH_3OH$ $CaCl_2.4C_2H_5OH$
$CuSO_4.2CH_3OH$ $MgCl_2.6C_2H_5OH$

An alcohol in combination with salt is analogous to the water of crystallisation and may, therefore, be termed as the *Alcohol of Crystallisation.*

By virtue of this property, traces of methyl alcohol and ethyl alcohol can be removed from organic liquids by means of fused calcium chloride. For the same reason, calcium chloride cannot be used for drying alcohols.

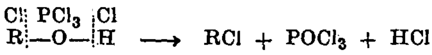
(2) **Action of Active metals.** Active metals like sodium or potassium react upon alcohols forming ALCOHOLATES OR ALKOXIDES in which the hydrogen atom of the OH group has been replaced by the metal. Thus :

$$\underset{\text{Ethyl alcohol}}{2C_2H_5OH} + 2Na \longrightarrow \underset{\text{Sodium ethoxide}}{2C_2H_5ONa} + H_2$$

In this reaction, primary alcohols are most reactive, while tertiary alcohols react upon heating.

The action of sodium on alcohol is often employed for reduction of organic compounds.

(3) **Action of Phosphorus halides.** Phosphorus halides act on alcohols when the (OH) group is replaced by a halogen atom and alkyl halide is formed.



$$\begin{array}{l} \text{Cl}\,\vdots\ \text{PCl}_3\ \vdots\,\text{Cl} \\ \text{R}\,\vdots\text{—O—}\vdots\,\text{H} \end{array} \longrightarrow \text{RCl} + \text{POCl}_3 + \text{HCl}$$

The action of phosphorus pentachloride on alcohols is an excellent method for replacing the OH group by a chlorine atom. Since the reaction is accompanied by evolution of hydrogen chloride gas, it is applied as a test for the presence of OH group in organic compounds.

Similarly, phosphorus trihalides react upon alcohols to form alkyl halides. Thus :

$$\underset{\text{Alcohol}}{3\text{ROH}} + \text{PI}_3 \longrightarrow \underset{\text{Alkyl iodide}}{3\text{RI}} + \text{P(OH)}_3$$

$$\underset{\text{Alcohol}}{3\text{ROH}} + \text{PBr}_3 \longrightarrow \underset{\text{Alkyl bromide}}{3\text{RBr}} + \text{P(OH)}_3$$

(4) **Action of Acids.** Both organic and inorganic acids react with alcohols to form ESTERS.

$$\underset{\text{Acetic acid}}{\text{CH}_3\text{CO}}\boxed{\text{OH} + \text{H}}\underset{\text{Ethyl alcohol}}{\text{OC}_2\text{H}_5} \longrightarrow \underset{\text{Ethyl acets}}{\text{CH}_3\text{COOC}_2\text{H}_5} + \text{H}_2\text{O}$$

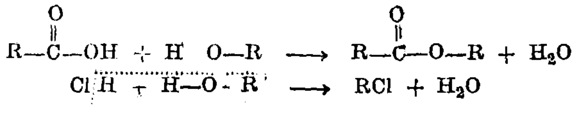
$$\text{C}_2\text{H}_5\text{OH} + \text{HNO}_3 \longrightarrow \underset{\text{Ethyl nitrate}}{\text{C}_2\text{H}_5\text{NO}_3} + \text{H}_2\text{O}$$

With halogen acids the order of reactivity of the three types of alcohols is

Tertiary > Secondary > Primary

On the other hand, the reaction rates with organic acids are in the reverse order.

As we have already explained, this is due to the fact that with organic acids the disruption of the alcohol takes place at the *oxygen-to-hydrogen* bond and with a halogen acid the whole of the OH must be knocked by a rupture at the *carbon-to-oxygen* linkage.



$$\text{R—}\overset{\overset{\displaystyle\text{O}}{\|}}{\text{C}}\text{—OH} + \text{H}\ \ \text{O—R} \longrightarrow \text{R—}\overset{\overset{\displaystyle\text{O}}{\|}}{\text{C}}\text{—O—R} + \text{H}_2\text{O}$$

$$\text{Cl}\,\boxed{\text{H} + \text{H—O}}\text{—R} \longrightarrow \text{RCl} + \text{H}_2\text{O}$$

The differences in the rate of esterification of the primary, secondary and tertiary alcohols being well marked are often used for distinguishing them from each other.

The action of sulphuric acid on alcohols is of special interest as it gives a variety of products depending upon the experimental conditions. In the first instance it gives alkyl hydrogen sulphates.

$$\underset{\text{Ethyl alcohol}}{C_2H_5OH} + H_2SO_4 \longrightarrow \underset{\text{Ethyl hydrogen sulphate}}{C_2H_5HSO_4} + H_2O$$

which are capable of reacting in three ways.

(*i*) *When heated alone* :

$$2C_2H_5HSO_4 \longrightarrow \underset{\text{Diethyl sulphate}}{(C_2H_5)_2SO_4} + H_2SO_4$$

(*ii*) *When sulphuric acid is in excess* :

$$C_2H_5HSO_4 \longrightarrow \underset{\text{Ethylene}}{C_2H_4} + H_2SO_4$$

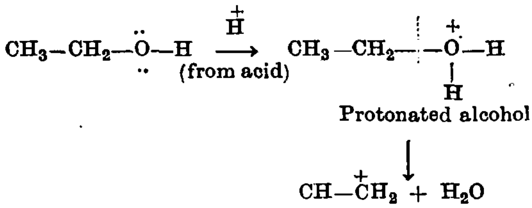
(*iii*) *When alcohol is in excess* :

$$C_2H_5\boxed{HSO_4 + H}OC_2H_5 \longrightarrow \underset{\text{Diethyl ether}}{C_2H_5OC_2H_5} + H_2SO_4$$

Mechanism

The mechanism of formation of ethylene has been discussed in the chapter on Alkenes. Methyl alcohol does not form an alkene on dehydration.

The mechanism of ether formation may be given as,



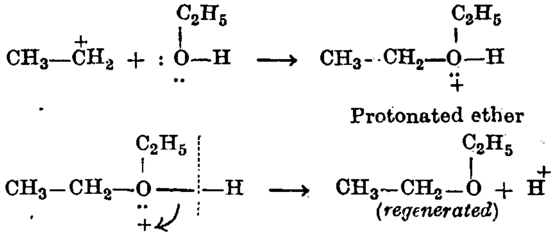
$$CH_3-CH_2-\ddot{\underset{..}{O}}-H \xrightarrow[\text{(from acid)}]{\overset{+}{H}} CH_3-CH_2-\underset{\underset{H}{|}}{\overset{+}{O}}-H$$

Protonated alcohol

$$\downarrow$$

$$CH-\overset{+}{C}H_2 + H_2O$$

Carbonium ion produced above reacts with more of alcohol (which is in excess) and gets attached to the oxygen atom (basic).



$$CH_3-\overset{+}{C}H_2 + :\underset{..}{\overset{\overset{C_2H_5}{|}}{O}}-H \longrightarrow CH_3-CH_2-\underset{\underset{+}{..}}{\overset{\overset{C_2H_5}{|}}{O}}-H$$

Protonated ether

$$CH_3-CH_2-\underset{\underset{+}{..}}{\overset{\overset{C_2H_5}{|}}{O}}-H \longrightarrow CH_3-CH_2-\overset{\overset{C_2H_5}{|}}{O} + \overset{+}{H}$$

(*regenerated*)

Similar mechanism applies to the formation of dimethyl ether $(CH_3)_2O$ from methyl alcohol and H_2SO_4.

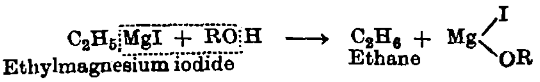
(5) **Action of Acid halides and Acid anhydrides.** Acid halides and acid anhydrides react with alcohols forming esters.

$$\underset{\text{Acetyl chloride}}{CH_3CO\boxed{Cl + H}OC_2H_5} \longrightarrow \underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + HCl$$

$$\underset{\text{Acetic anhydride}}{CH_3CO\boxed{OCOCH_3 + H}OC_2H_5} \longrightarrow \underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + CH_3COOH$$

The action of acid chlorides on alcohols is accompanied by evolution of hydrogen chloride gas and is, therefore, a convenient test for the presence of OH group in a molecule.

(6) **Action of Grignard reagents.** Alcohols react with a Grignard reagent in such a way that the hydrogen of the OH group goes with the alkyl radical forming a hydrocarbon.

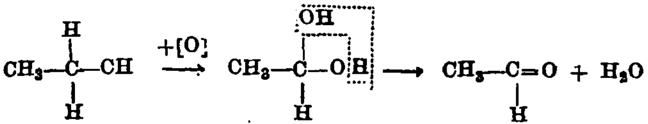


$$\underset{\text{Ethylmagnesium iodide}}{C_2H_5MgI + RO{:}H} \longrightarrow \underset{\text{Ethane}}{C_2H_6} + Mg\begin{matrix} I \\ OR \end{matrix}$$

This reaction may be used to estimate a lower alcohol present in inert solvents by collecting and measuring the volume of the gaseous hydrocarbon evolved.

(7) **Oxidation of Alcohols.** Upon oxidation with a dilute solution of sodium dichromate and sulphuric acid, primary, secondary, and tertiary alcohols give different products.

(*i*) A PRIMARY ALCOHOL is first oxidised to give an aldehyde and then an acid, each containing the same number of carbon atoms.



$$CH_3-\overset{H}{\underset{H}{C}}-OH \xrightarrow{+[O]} CH_3-\overset{OH}{\underset{H}{C}}-O{:}H \longrightarrow CH_3-\underset{H}{C}=O + H_2O$$

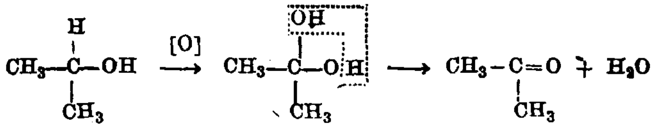
Ethyl alcohol (*Unstable*) Acetaldehyde

Acetaldehyde still possesses an oxidisable hydrogen and thus forms acetic acid.

$$CH_3-\underset{H}{C}=O \longrightarrow CH_3-\underset{OH}{C}=O$$

Acetaldehyde Acetic acid

(*ii*) A SECONDARY ALCOHOL upon oxidation gives a ketone containing as many carbon atoms as the alcohol.



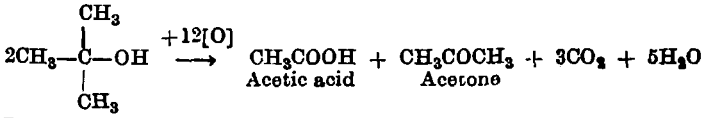
$$CH_3-\overset{H}{\underset{CH_3}{C}}-OH \xrightarrow{[O]} CH_3-\overset{OH}{\underset{CH_3}{C}}-O{:}H \longrightarrow CH_3-\underset{CH_3}{C}=O + H_2O$$

Isopropyl alcohol (*Unstable*) Acetone

The ketone has no oxidisable hydrogen and ordinarily it is not expected to undergo further oxidation. However, on vigorous oxidation it may yield a mixture of acids, each containing fewer carbon atoms than the original alcohol.

$$\underset{\text{Acetone}}{CH_3.CO.CH_3} + 3O \longrightarrow \underset{\text{Acetic acid}}{CH_3COOH} + \underset{\text{Formic acid}}{HCOOH}$$

(*iii*) A TERTIARY ALCOHOL having no oxidisable hydrogen linked to the hydroxyl-bearing carbon fails to undergo oxidation. However, on drastic oxidation a tertiary alcohol may give a mixture of products, mostly acids and ketones, each containing less carbon atoms than the alcohol.



$$2CH_3-\overset{CH_3}{\underset{CH_3}{C}}-OH \xrightarrow{+12[O]} \underset{\text{Acetic acid}}{CH_3COOH} + \underset{\text{Acetone}}{CH_3COCH_3} + 3CO_2 + 5H_2O$$

ter. Isobutyl alcohol

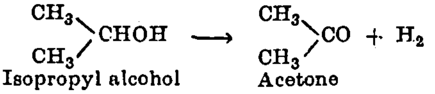
The direct behaviour of alcohols on oxidation is often used for distinguishing them from each other.

(8) **Catalytic dehydrogenation.** When the vapours of alcohols are passed over reduced copper at 300°C, primary, secondary, and tertiary alcohols offer a different behaviour.

(*i*) *Primary alcohols lose hydrogen and yield an aldehyde.*

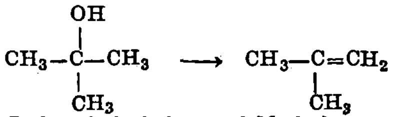
$$\underset{\text{Ethyl alcohol}}{CH_3CH_2OH} \longrightarrow \underset{\text{Acetaldehyde}}{CH_3CHO} + H_2$$

(*ii*) *Secondary alcohols lose hydrogen and yield a ketone,*



Isopropyl alcohol Acetone

(*iii*) *Tertiary alcohols are not dehydrogenated but instead lose a molecule of water upon heating, forming alkenes.* Thus :



$$CH_3-C(OH)(CH_3)-CH_3 \longrightarrow CH_3-C(CH_3)=CH_2$$

tert. Isobutyl alcohol 2-Methylpropene

This reaction can also be used for distinguishing between primary, secondary and tertiary alcohols.

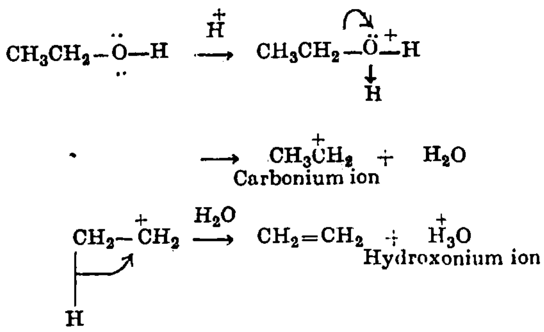
(9) **Dehydration.** Alcohols may be dehydrated by passing alcohol vapours over a suitable catalyst at appropriate temperatures, or by heating with sulphuric acid. The product of dehydration may be an alkene or an ether depending on conditions. Thus :

$$\underset{\text{Ethyl alcohol}}{2C_2H_5OH} - H_2O \longrightarrow \underset{\text{Diethyl ether}}{C_2H_5\,O.C_2H_5}$$

$$\underset{\text{Ethyl alcohol}}{C_2H_5OH} - H_2O \longrightarrow \underset{\text{Ethylene}}{C_2H_4}$$

The alkene is formed readily in tertiary alcohols, while the ease of ether formation follows the reverse order.

The acid catalysed dehydration of ethyl alcohol is believed to take place as follows through the formation of a carbonium ion.



Carbonium ion

Hydroxonium ion

Tests for an OH Group. There are three tests which may be applied to detect the presence of a hydroxyl group in an unknown organic compound. For these tests, take the liquid substance or a solution of the solid substance in an inert solvent such as dry ether or benzene.

(1) Add to it small pieces of SODIUM METAL. If bubbles of hydrogen are given off, the compound contains an OH group.

$$2ROH + 2Na \longrightarrow 2RONa + H_2$$

(2) Add to it PHOSPHORUS PENTACHLORIDE. If the mixture becomes warm with evolution of hydrogen chloride gas, the given substance is hydroxy-compound.

$$ROH + PCl_5 \longrightarrow RCl + POCl_3 + HCl\uparrow$$

(3) Add acetyl chloride or benzoyl chloride to the substance. The separation of an oily layer of the ester and evolution of HCl gas indicates the presence of an OH group. It may be noted that if the substance was taken in an organic solvent the oily ester may dissolve in it and thus limiting the test to the evolution of HCl gas only.

DIAGNOSIS OF PRIMARY, SECONDARY AND TERTIARY ALCOHOLS

The following tests may be applied for distinguishing primary, secondary, and tertiary alcohols from one another.

(1) **Oxidation Test.** The oxidation of a given alcohol and identification of the products formed leads to the clue whether the alcohol was primary, secondary or tertiary.

PRIMARY	SECONDARY	TERTIARY
CH_3CH_2OH	$(CH_3)_2CHOH$	$(CH_3)_3COH$
↓[O]	↓[O]	
CH_3CHO Aldehyde	$(CH_3)_2CO$ Ketone	↓[O]
↓[O]	↓[O]	
CH_3COOH Acid containing same number of C-atoms as original alcohol	$CH_3COOH + HCOOH$ Acids containing fewer C-atoms than original alcohol	CH_3COOH, CH_3COCH_3, etc. Products containing less C-atoms than original alcohol

(2) **Catalytic dehydrogenation.** When the vapours of an alcohol are passed over reduced copper at 300°C, the products formed are indicative of the type of the alcohol.

PRIMARY	SECONDARY	TERTIARY
CH_3CH_2OH	$(CH_3)_2CHOH$	$(CH_3)_3COH$
↓	↓	↓
$CH_3CHO + H_2$ Aldehyde	$(CH_3)_2CO + H_2$ Ketone	$(CH_3)_2C{:}CH_2 + H_2O$ Alkene

(3) **Victor Meyer's Test.** The test is based on the different behaviour of the corresponding nitroalkanes towards nitrous acid. It is carried by the following steps :

(*i*) *The alcohol is first converted into the iodide by treatment with cold hydrogen iodide.*

(*ii*) *The iodide is then treated with silver nitrite so as to form the nitroalkane.*

(*iii*) *The nitroalkane is finally treated with nitrous acid* ($NaNO_2 + H_2SO_4$) *and made alkaline.*

$C_2H_5OH + H_2SO_4 \longrightarrow$
Ethyl alcohol Eth

which are capable of reacting in

(*i*) *When heated alone*

$2C_2H$

(*ii*) *When s*

(*ii*

C_2H_6 + Mg $\langle$ I OR
Ethane

te a lower alcohol present

ting the volume of the

n with a dilute

mary, second-

hyde.

343

s a primary alcohol,
hol and if there is no

ed as follows :

TERTIARY

R_3COH
$\downarrow$ HI
R_3CI
$\downarrow AgNO_2$
R_3CNO_2
$\downarrow$ HONO
No reaction

n this test advantage is taken
formation with inorganic acids

follows the

Tertiary *dary > Primary*

while with organic acids the order is just the reverse. The difference in the rate of esterification of the primary, secondary, and tertiary alcohols is so well marked that it gives a clear indication of the type of alcohol.

(*a*) The unknown alcohol is treated with concentrated hydrochloric acid containing anhydrous zinc chloride (1 mole : 1 mole) and the time of reaction is recorded. The separation of the insoluble alkyl chloride from the solution indicates that a reaction has taken place.

(*i*) *a tertiary alcohol reacts immediately,*

(*ii*) *a secondary alcohol reacts within five minutes* ; *and*

(*iii*) *a primary alcohol does not react within five minutes.*

(*b*) The alcohol under examination is heated for one hour at 154° in sealed tubes with an equivalent quantity of acetic acid. The ester so formed is isolated and the percentage of alcohol converted into ester calculated. Approximately 47 per cent of primary, 22 per cent of secondary, and 1·5 per cent of tertiary alcohol is changed to the ester under these conditions.

(5) **Dehydration Test**. When excess of the given alcohol is treated with concentrated sulphuric acid,

a primary alcohol would give ether very easily,

a secondary alcohol won't give ether easily,

and a tertiary alcohol won't give ether at all, but alkene.

INDIVIDUAL ALCOHOLS

METHL ALCOHOL, METHANOL, CH_3OH

It occurs in nature in the form of esters. For example, *Oil of Wintergreen* is known to contain methyl salicylate. Since methyl alcohol was formerly prepared chiefly from wood by a process known as destructive distillation, it is also called *Wood Spirit* or *Wood Naphtha*.

Manufacture. Methyl alcohol can be obtained by the hydrolysis of methyl iodide or methyl ester, and by the action of nitrous acid on methylamine.

For the industrial preparation of methyl alcohol, the following methods are available.

(1) **Distillation of Wood.** Until recently the principal source of methyl alcohol was the so-called wood distillation, actually the decomposition of wood by heat. When wood is heated at temperatures between 250° and 400° in cast iron chambers, the products obtained are :

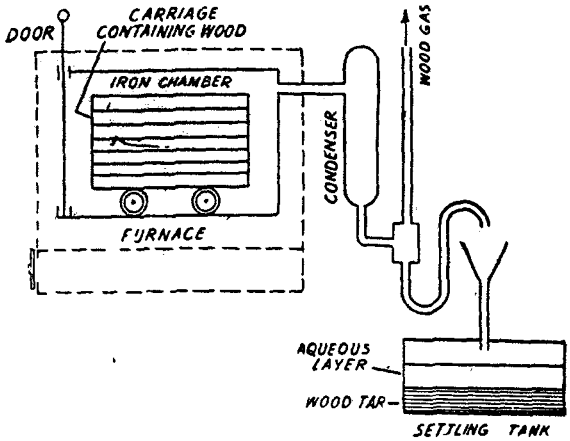


Fig. 15·1. Distillation of wood on a technical scale.

(*i*) *A gaseous mixture*, **Wood gas**, which consists of H_2, CH_4 CO, CO_2, O_2 and N_2. It is used for heating the cast-iron chambers.

(*ii*) *An aqueous distillate*, **Pyroligneous acid** (*Pyro*=*heat*, *ligneous*=of wood). It is composed of

	acetic acid	9—10 per cent
	methyl alcohol	1— 2 per cent
and	acetone	0·1—0·5 per cent

Pyroligneous acid is further treated for the recovery of these compounds.

(*iii*) *A thick black liquid*, **Wood tar**, that separates from the aqueous distillate. It contains alkanes, naphthalene, phenols, etc. Upon distillation it yields a mixture of *cresols* which is used as a preservative of wood.

(*iv*) *A solid residue*, **Wood charcoal**, left in the iron chambers. It consists chiefly of carbon and is used as a domestic fuel.

The process of wood distillation can be nicely illustrated in the laboratory by the apparatus shown in Fig. 15·2.

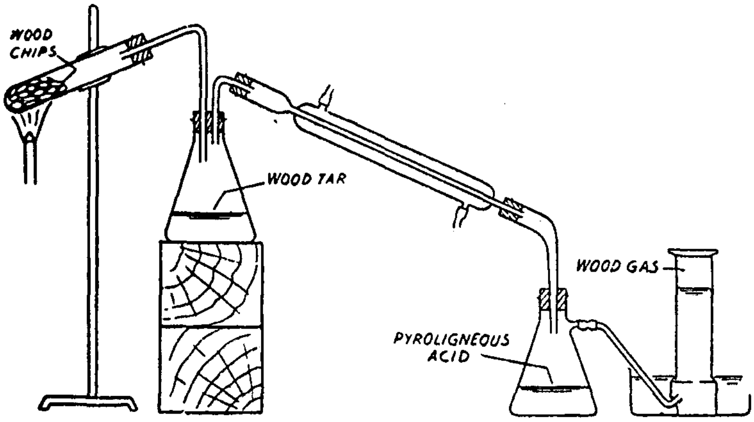


Fig. 15·2. Laboratory illustration of Wood distillation.

Recovery of Methyl alcohol from Pyroligneous acid. Pyroligneous acid is chiefly a mixture of methyl alcohol, acetic acid, and acetone along with water. It is treated for the recovery of methyl alcohol by the following steps.

(1) Removal of Acetic Acid. Acetic acid is removed by treatment of pyroligneous acid with lime and subsequent distillation.

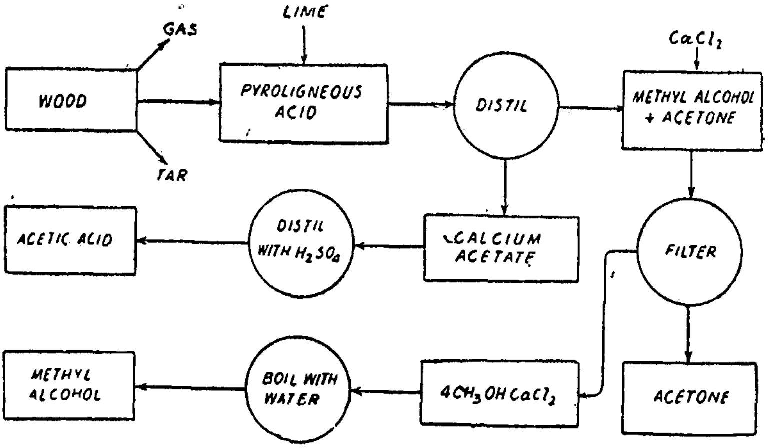


Fig. 15·3. Methyl alcohol from Wood distillation.

Methyl alcohol and acetone distil over leaving calcium acetate in the still. Solid calcium acetate is distilled with concentrated sulphuric acid when crude acetic acid is recovered.

(2) REMOVAL OF ACETONE. The distillate consisting of methyl alcohol and acetone from step (1) could be separated by fractional distillation. To get pure alcohol, the mixture is treated with calcium chloride solution when the alcohol is thrown as crystalline $CaCl_2.4CH_3OH$, leaving behind acetone. The crystals are separated and decomposed by heating with water when methyl alcohol is regenerated. This is then distilled with quick lime to remove any water which may be present.

With her vast forest resources India promises a bright future for the Wood-distillation Industry. At present the distillation is carried out on some good scale at Bhadrawati in Mysore.

(2) **From Water gas** (*Patart Process, 1923*). Most of the methyl alcohol in United States is now obtained from water gas. Water gas is a mixture of carbon monoxide and hydrogen made by passing steam over red-hot coke. The water gas is enriched with hydrogen and compressed to about 200 atmospheres pressure. It is then passed over a catalyst consisting of basic zinc chromate, $4ZnO.CrO_3$, at 300°C. The carbon monoxide of the water gas is thus reduced to form methyl alcohol.

$$CO + 2H_2 \longrightarrow CH_3OH$$

The methyl alcohol so obtained is almost pure.

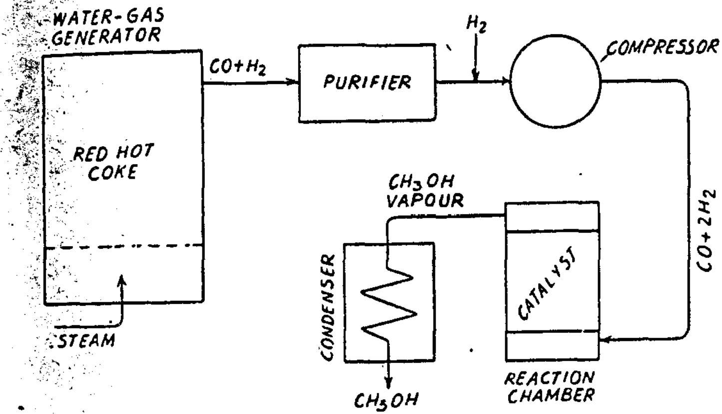


Fig. 15·4. Manufacture of methyl alcohol from Water gas (*Flow sheet*).

This method of producing methyl alcohol has a great future in our country.

(3) **From Natural gas.** Methyl alcohol is also prepared on the industrial scale from methane obtained from natural gas. Methane is mixed with oxygen and passed over a catalyst under a pressure of 100 atmospheres at 260°.

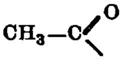
$$CH_4 + O \longrightarrow CH_3OH$$

Properties. It is a colourless mobile liquid having a specific gravity 0·793 and boiling point 65°. It has a sharp wine-like odour and a burning taste. It is miscible with water in all proportions, the mixing being attended by a contraction in volume. It is an excellent solvent for several organic substances such as oils, fats, shellac, etc.

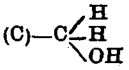
Methyl alcohol has an intoxicating effect on the human system and is extremely poisonous. When taken internally it gives rise to insanity and blindness.

Chemically it gives all the general reactions of alcohols.

Methyl alcohol differs from other members of the series in that it does not respond to the 'haloform reaction' *i.e.* it does not react with halogens in presence of alkali as it contains no such groups as



or



Tests. (1) Take about half a ml. of methyl alcohol in a test-tube, add to it a pinch of salicylic acid and a few drops of conc. H_2SO_4. Warm in a water-bath for a few minutes and note the characteristic fragrant odour of methyl salicylate.

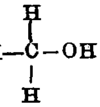
(2) Place a few drops of methyl alcohol in a wide-mouth test-tube. Heat a piece of copper gauze to redness and drop it in the test-tube. Methyl alcohol is oxidised to formaldehyde which is at once recognised by its characteristic pungent odour.

(3) Add a small quantity of methyl alcohol to some water contained in a test-tube. Heat a spiral of copper wire to redness in the flame of a Bunsen burner and plunge it into the solution. Repeat the process several times. To the cooled solution add a few drops of a dilute solution of resorcinol and pour conc. sulphuric acid down the side of the inclined tube so as to form a lower layer. At the junction of the liquids would appear a pink ring with a thick white precipitate above it.

Uses. Methyl alcohol is used as a source of formaldehyde. It is also used as an antifreeze in car radiators, as a solvent, as a petrol substitute, and for denaturing ethyl alcohol.

Constitution. (1) From combustion data and vapour density measurements it has been shown that methyl alcohol has the molecular formula CH_4O.

(2) If carbon, oxygen and hydrogen are exerting their normal covalencies of four, two and one in the molecule, the only possible structural formula of methyl alcohol is



$$\begin{array}{c} H \\ | \\ H-C-OH \\ | \\ H \end{array}$$

(3) The above structure is supported by reactions of methyl alcohol with sodium when only one of the four H-atoms is replaced by the metal.

$$CH_3OH + Na \longrightarrow CH_3ONa + H$$

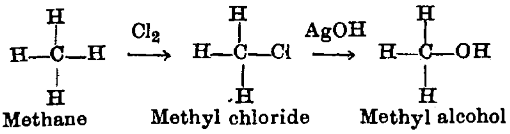
This shows that the position of one H-atom is different from the remaining three.

(4) Methy alcohol reacts with PCl_5 to form methyl chloride.

$$CH_3OH + PCl_5 \longrightarrow CH_3Cl + POCl_3 + HCl$$

This again proves that in methyl alcohol molecule one OH is linked with methyl group.

(5) The structural formula of methyl alcohol is finally confirmed by the following synthesis from methane.



$$\underset{\text{Methane}}{H-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-H} \xrightarrow{Cl_2} \underset{\text{Methyl chloride}}{H-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-Cl} \xrightarrow{AgOH} \underset{\text{Methyl alcohol}}{H-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-OH}$$

ETHYL ALCOHOL, ETHANOL, C_2H_5OH

It is the most important and the earliest known representative of the class and is popularly referred to as simply *'alcohol'*. It is the exhilarating principle of all wines and is thus named the *Spirits of wine*. Technically it is known as **Grain alcohol** since it is often manufactured from starchy grains.

Ethyl alcohol is produced in plants and animals by the fermentation of carbohydrates. Thus it can be detected in traces in plants both in the free state and in the form of esters. In animals it is found to be present in tissues, blood, and urine of diabetic persons. It is also present in human brain to the extent of ·0025 per cent.

Manufacture. (1) Ethyl alcohol has been prepared for centuries by the fermentation of sugars, particularly glucose and sucrose, in the presence of yeast.

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{\textit{Invertase}} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

$$C_6H_{12}O_6 \xrightarrow{\textit{Zymase}} 2C_2H_5OH + 2CO_2$$

Industrial alcohol is prepared from molasses and cheap starchy materials such as potatoes, maize and barley. The starch is first converted to a sugar which is then subjected to the fermentation process.

(2) In Germany large quantities of alcohol are now produced from saw dust (*cellulose*) by digesting with dilute sulphuric acid and steam at a pressure of 6 to 7 atmospheres. The cellulose is thus rapidly hydrolysed to glucose.

$$\underset{\text{Cellulose}}{(C_6H_{10}O_5)_x} + xH_2O \longrightarrow \underset{\text{Glucose}}{xC_6H_{12}O_6}$$

The resulting sugar solution is fermented by yeast neutralising with lime (*Schroller*) *process*).

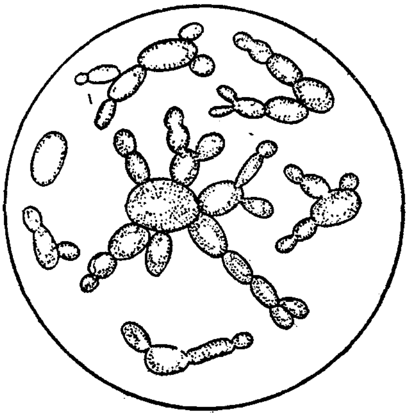


Fig. 15·5. Yeast — a single celled plant which grows and multiplies rapidly under suitable conditions.

(3) In America alcohol is made by the hydration of ethylene obtained from petroleum refineries. Ethylene is absorbed in sul-

d and the resulting ethyl hydrogen sulphate is passed into heated.

$$C_2H_4 + H_2SO_4 \longrightarrow C_2H_5HSO_4$$
$$C_2H_5HSO_4 + H_2O \longrightarrow C_2H_5OH + H_2SO_4$$

ently, the manufacture of ethyl alcohol has been achieved by direct hydration of ethylene obtained by cracking of naphtha.

(4) In Switzerland alcohol is manufactured by the hydration of acetylene to form acetaldehyde and subsequent reduction.

$$CH{\equiv}CH + H_2O \longrightarrow CH_3CHO$$
$$CH_3CHO + H_2 \longrightarrow CH_3CH_2OH$$

The acetylene required for the process is made by the action of water on calcium carbide.

From Ethylene. In U.S.A. ethylene gas is obtained in large quantities by the cracking of naphtha. This is then converted into ethyl alcohol by direct hydration in the presence of phosphoric acid catalyst.

$$CH_2{=}CH_2 + H_2O \xrightarrow[\text{Catalyst}]{H_3PO_4} CH_3CH_2OH$$

Ethylene gas and distilled water (1 : 0·6 molar ratio) are preheated to 300°C and then passed under high pressure into the reactor. The reactor is a stainless steel vessel containing phosphoric acid catalyst. The reaction products are then cooled and passed into the scrubber where ethyl alcohol is dissolved in water. The aqueous solution of alcohol is sent to the distillation unit to get pure alcohol.

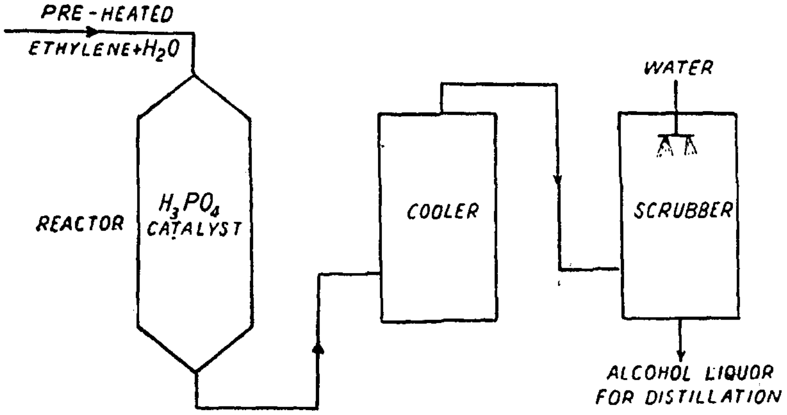


Fig. 15·6. Industrial preparation of Ethyl alcohol from ethylene.

From Molasses. In India most of the alcohol is prepared from molasses which is the mother liquor left after the crystallisation of cane sugar from concentrated juice. It is a dark coloured thick syrupy mass that still contains about fifty per cent of fermentable sugars, mostly sucrose, glucose and fructose. Thus molasses forms an excellent cheap source of industrial alcohol. Alcohol is made from molasses by the following steps :—

(1) *Dilution.* Molasses is first diluted with water to bring down the concentration of sugars to about 8 to 10 per cent. Thus the usual dilution is five volumes of water to one volume of molasses.

(2) *Addition of ammonium salts and acidification.* Molasses usually contains enough nitrogenous matter to act as food for yeast during fermentation. If the nitrogen content of the molasses is poor, it may be fortified by the addition of ammonium sulphate or ammonium phosphate.

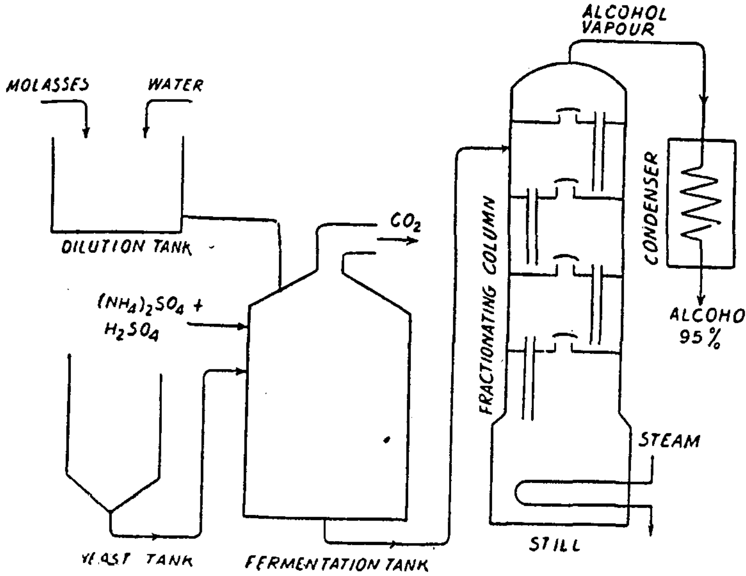


Fig. 15·7. Flow-sheet of alcohol manufacture from molasses.

The dilute solution of molasses is acidified with a small amount of sulphuric acid and warmed to 26°. Acidity is favourable to the growth of yeast but unfavourable to most other bacteria.

(3) *Addition of yeast ; fermentation.* The solution from step (2) is received in large 'fermentation tank' and yeast is added. As the yeast grows fermentation occurs, and the temperature is allowed to rise to 36°. During the process the liquor froths owing to the evolution of carbon dioxide which is collected and solidified. While the fermentation is in progress, occasionally air is bubbled through the liquor to keep the yeast alive and active. After a few days when the alcohol content rises to 15-18 per cent, the fermentation comes to a stop automatically as the yeast cells are then killed. The fermented liquor thus obtained is technically called *WASH.*

(4) ***Distillation of Wash.*** The *wash* containing 15-18 per cent alcohol and the rest water, is now subjected to fractional distillation. Since the boiling points of alcohol and water are not widely different, it becomes necessary to use a special device for the purpose. The distillation of *wash* is carried in a unit shown in Fig. 15·7. The fractionating column containing shelves fitted with baffle plates and tubes enbles the condensation and distillation to be repeated several times so as to yield almost pure alcohol. While the 'spent wash' travels down through the tubes, steam and alcohol vapours pass up. At each shelf, alcohol is vaporised from the *wash* by heating with steam which condenses. The vapours of almost pure alcohol from the head of the fractionating column are led to the condenser. Distillate containing 90-95 per cent alcohol is called *Rectified Spirit.*

The production of alcohol from molasses in India during the last five years has been almost doubled. However, there is acute shortage of industrial alcohol at present due to extreme shortage in supply of molasses.

TABLE : *Production of Alcohol in India*

YEAR	POWER ALCOHOL (*Thousand Litres*)	RECTIFIED SPIRIT (*Thousand Litres*)
1962	49,547	61,243
1963	25,318	114,415
1964	1,442	160,702
1965	815	184,654
1966	2,448	188,608

From Starch. The important raw material containing starch are potatoes, rice, maize, barley and other cereals. Of these, potatoes are employed for the manufacture of alcohol. The process involves the following steps :

(1) *Liberation of Starch.* Potatoes are cut into slices and crushed. The crushed mass is then steamed at 140-150° under pressure. In this way the cell walls containing starch particles are broken and starch brought into solution. The resulting solution is called *MASH.*

(2) *Hydrolysis of Starch into Maltose.* The enzyme *diastase* is needed to hydrolyse starch to maltose. It is present in small amounts in barley and can be developed considerably upon germination. For this purpose, barley is steeped in water at a temperature of 10-13°C for a couple of days. This is then taken out and allowed to germinate in dark at about 15°. Barley is then heated to 60° to stop germination. The dried and germinated barley is technically known as *MALT.*

To the 'mash' obtained from step (1) is now added 'malt'. Within half an hour, *diastase* present in the malt converts the starch into maltose.

$$\underset{\text{Starch}}{2(C_6H_{12}O_5)_n} + nH_2O \xrightarrow{\textit{Diastase}} \underset{\text{Maltose}}{nC_{12}H_{22}O_{11}}$$

(3) *Fermentation of Maltose to Alcohol.* To the solution of maltose obtained from the previous step is now added yeast. It furnishes the enzymes *maltase* and *zymase*. While the former converts maltose into glucose, the latter enzyme converts glucose into alcohol.

$$\underset{\text{Maltose}}{C_{12}H_{22}O_{11}} \xrightarrow{\textit{Maltase}} \underset{\text{Glucose}}{2C_6H_{12}O_6}$$

$$C_6H_{12}O_6 \xrightarrow{\textit{Zymase}} 2C_2H_5OH + 2CO_2$$

(4) *Distillation.* The formented liquor or 'wash' obtained above is then distilled in the unit described before. The product is 95 per cent alcohol or Rectified Spirit.

Alternative Method. According to another method starch may be hydrolysed to glucose by heating with dilute sulphuric acid. The excess of acid is then neutralised with lime and the resulting liquid fermented as described before. This new method eliminates the use of malt.

By-products of Alcohol Industry. The important by-products of alcohol manufactured by the fermentation processes are :

(1) *Carbon dioxide.* Large quantities of carbon dioxide are evolved during fermentation of sugars. It is stored under pressure in iron cylinders and used for making aerated waters or is sold as *dry ice*.

(2) *Acetaldehyde.* It is present in the more volatile fractions obtained during alcohol distillation. They are collected and pure acetaldehyde recovered.

(3) *Fusel Oil.* It is obtained as the last runnings between 125° and 140°. It is a bright yellow, oily liquid with nauseating odour. It consists of a mixture of amyl alcohols mainly isoamyl, $(CH_3)_2CH.CH_2,CHOH$, along with some butyl alcohol. These alcohols are not produced by the fermentation of sugars. But rather the yeast takes proteins present in the original raw material and throws out these alcohols as non-assimilate products of metabolism.

Fusel oil is used technically for the preparation of amyl acetate which is a valuable solvent for varnishes ; it is also used in confectionary and fruit essences. Thus fusel oil fetches much higher price than even ethyl alcohol.

(4) *Spent Wash.* The residual liquor from which ethyl alcohol has been removed by distillation, is called '*spent wash*'. It contains nitrogenous matter

originally present in the raw material and is used as fodder for cattle, or for watering land to increase its fertility.

(5) *Potassium acid tartarate.* Being insoluble in alcohol, it is thrown down during the fermentation of grape juice. It is used for the manufacture of tartaric acid and Rochelle salt.

Absolute alcohol. Rectified spirit obtained by the distillation of *wash* contains about 95 per cent ethyl alcohol. Since a mixture of 95·6 per cent alcohol with water boils at lower temperature (78·1°) than the boiling point of pure alcohol (78·5°), it is impossible to get an alcohol of higher concentration by fractional distillation of rectified spirit. Anhydrous or absolute alcohol can be obtained by digesting the rectified spirit over quicklime for several days and then distilling. The first and the last runnings are rejected, and the main portion of the distillate is 100 per cent or absolute alcohol.

A modern process is the *azetropic distillation* of rectified spirit with benzene. When distillation is carried after addition of a certain amount of benzene, at first *ternary* mixture of water, alcohol and benzene comes over at 65° till all the water is thus removed. Then the boiling point rises and the remaining benzene comes over as *binary* mixture with alcohol at 68°. Finally absolute alcohol distils at 78·5°.

Denatured alcohol. The manufacture and sale of ethyl alcohol is government controlled. Heavy excise duty is levied on the sale of alcoholic beverages. For industrial purposes alcohol is duty-free. Therefore, the industrial alcohol is denatured, by the addition of poisonous substances like methyl alcohol, acetone or pyridine. A common practice is to add about 4 per cent of impure methyl alcohol together with traces of pyridine and some colouring matter. The product is often sold in the market under the name *'Methylated Spirit'*. In India rectified spirit is denatured by the addition of light cautchoucine and pyridine bases. Methylated spirit is extensively used for the preparation of varnishes, and tinctures for external use.

Power alcohol. In non-petroleum countries alcohol mixed with petrol and benzene is now used as motor fuel. Alcohol thus used for the generation of power is popularly known as *'power alcohol'*. Rectified spirit alone does not mix with petrol, hence the need of the third ingredient : ether, benzene or tetraline. In a country like India with meagre petroleum resources, the use of power alcohol is a dire necessity. We can make large quantities of cheap alcohol from molasses which could be used to prepare power alcohol.

Alcoholic Beverages. When taken internally in small quantities, alcohol stimulates the human system without any apparent injurious effect, However, its continuous use leads to immoderation and induces other vices. Already the governments in the various States have schemes of prohibition in hand. Anyhow, the fact remains that alcohol is consumed in large quantities as *alcoholic liquors* or *beverages*, especially in European countries.

Alcoholic beverages are of two types : (*a*) Undistilled ; and (*b*) Distilled.

Undistilled Beverages. These are produced simply by the fermentation process from fruit-juice or grains. The beverages prepared from grape-juice or other fruit juices are called **Wines.** Wines containing 18–20 per cent alcohol and produced by natural fermentation are called *Natural Wines.* Weak natural wines are made stronger by adding pure alcohol from outside and are named as *Fortified Wines.*

Distilled Beverages. If the fermented liquids are distilled, most of the alcohol along with other volatile products *viz.*, flavours, essential oils, esters and higher alcohols, pass over as distillate. The distilled liquors have a high alcohol content which may go up to 50 per cent or even more.

The colour, flavour and taste of a particular beverage is largely determined by the materials employed and the subsequent treatment of the fermented liquor.

The description of some of the commonly used beverages is given in the table below :

BEVERAGE	SOURCE	ALCOHOL CONTENT PER CENT BY VOLUME
Undistilled Beverages :		
Claret	Grape juice	7 to 13
Port	Grape juice	15 to 24 (*fortified*)
Sherry	Grape juice	18 to 24 (*fortified*)
Champagne	Grape juice	8 to 10
Cider	Apple juice	3 to 6
Beer	Barley	3 to 5
Distilled Beverages :		
Whiskey	Barley	40 to 50
Brandy	Peeches, apples and cherries	40 to 50
Holland	Rye	40
Rum	Molasses	45 to 55
Gin	Barley	40 to 45

Alcoholometry. A heavy tax is levied on alcohol and all alcoholic preparations. Thus it is necessary to estimate the percentage of alcohol in a certain sample. Chemical methods of analysis can be employed but these take much time. A simpler method commonly used consists in determining the specific gravity of the sample by means of a hydrometer and then finding the exact percentage of alcohol from *ready reference tables*. The determination of the percentage of alcohol goes by the name of alcoholometry.

In old days, it was customary to adjudge the alcohol content by pouring the sample of alcohol on gun powder and then setting fire to it. If the liquor contained much alcohol, it burnt away leaving the gun powder dry enough to catch fire. On the contrary, if it contained much water, it damped the gun powder which now refused to catch fire. A sample of spirit which was just strong enough to fire the powder, was called **proof spirit**. Stronger spirits were called *'Over proof'* (*O.P.*) and the weaker ones 'Under proof' (*U.P.*). Proof spirit is now legally defined as an alcohol-water mixture having specific gravity 0·91976 at 15°C, and contains 57·1 per cent alcohol by weight. For excise purpose there are used special types of hydrometers graduated so as to read directly the percentage of alcohol on the scale in terms of proof spirit. The strength of any liquor is expressed as degrees *O.P.* or *U.P.*

Properties. (*Physical*). Ethyl alcohol is a colourless mobile liquid with a rather pleasant colour and burning taste. It boils at 78·5°, freezes at —114° and has specific gravity 0·789 at 20°. It mixes with water in all proportions with the evolution of heat and a contraction in volume ; the maximum contraction of 3·7 per cent takes place when 52 volumes of alcohol are mixed with 48 volumes of water. It is an excellent solvent for fats, resins and many more organic substances. It also dissolves inorganic substances like caustic soda, caustic potash, sulphur, phosphorus, etc. When taken orally in small dozes, alcohol is a good stimulant. It is directly absorbed in the blood stream and produces heat owing to oxidation, and hence its use as a medicine for contracting cold. If swallowed in large amounts, it acts as a strong poison.

(Chemical). Ethyl alcohol responds to all the general reactions of the class described before.

(1) It burns in air with a clear blue flame producing considerable heat.

$$C_2H_5OH + 7[O] \longrightarrow 2CO_2 + 3H_2O + 328 \text{ Cal.}$$

(2) Sodium and potassium react upon it forming an ethoxide and hydrogen.

$$2C_2H_5OH + 2Na \longrightarrow \underset{\text{Sod. ethoxide}}{2C_2H_5ONa} + H_2$$

(3) Alcohol reacts with phosphorus pentachloride yielding ethyl chloride.

$$C_2H_5OH + PCl_5 \longrightarrow C_2H_5Cl + POCl_3 + HCl$$

(4) With organic and inorganic acids, it gives esters.

$$C_2H_5OH + HCl \longrightarrow \underset{\text{Ethyl chloride}}{C_2H_5Cl} + H_2O$$

$$C_2H_5OH + CH_3COOH \longrightarrow \underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + H_2O$$

Its action with sulphuric acid has already been discussed under general reactions.

(5) It reacts with acid chlorides and anhydrides to form esters

$$\underset{\text{Acetyl chloride}}{CH_3COCl} + C_2H_5OH \longrightarrow \underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + HCl$$

$$\underset{\text{Acetic anhydride}}{(CH_3CO)_2O} + C_2H_5OH \longrightarrow \underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + CH_3COOH$$

(6) Upon oxidation with sod. dichromate and sulphuric acid, it first forms acetaldehyde and then acetic acid.

$$CH_3CH_2OH \xrightarrow{O} CH_3CHO \xrightarrow{O} CH_3COOH$$

(7) By the action of halogens in the presence of an alkali, alcohol is converted into chloroform. Thus :

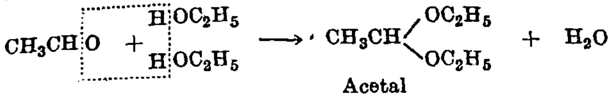
$$CH_3CH_2OH + Cl_2 \longrightarrow \underset{\text{Acetaldehyde}}{CH_3CHO} + 2HCl$$

$$CH_3CHO + 3Cl_2 \longrightarrow \underset{\text{Chloral}}{CCl_3CHO} + 3HCl$$

$$CCl_3CHO + KOH \longrightarrow \underset{\text{Chloroform}}{CHCl_3} + HCOOK$$

When treated with iodine in the presence of alkali, alcohol is converted to iodoform.

(8) In the presence of an acid, ethyl alcohol reacts with acetaldehyde to form acetal.



$$CH_3CH\boxed{O + \begin{matrix} H \\ H \end{matrix}}\begin{matrix} OC_2H_5 \\ OC_2H_5 \end{matrix} \longrightarrow \underset{\text{Acetal}}{CH_3CH\begin{matrix} \diagup OC_2H_5 \\ \diagdown OC_2H_5 \end{matrix}} + H_2O$$

(9) When the vapours of ethyl alcohol are passed over heated reduced copper, it splits out a molecule of hydrogen giving acetaldehyde.

$$CH_3CH_2OH \longrightarrow \underset{\text{Acetaldehyde}}{CH_3CHO} + H_2$$

Uses. Ethyl alcohol is used :

(1) as a fuel for lamps and stoves. For the sake of convenience in transportation, it is converted into solid state (**solid alcohol**) by dispersion in saturated calcium acetate and a little stearic acid ;

(2) as a substitute of petrol in internal combustion engines ;

(3) as a solvent for drugs, tinctures, oils, perfumes, inks, dyes, varnishes, etc. ;

(4) as a beverage ;

(5) as a preservative for biological specimens ;

(6) as an antifreeze for automobile radiators ;

(7) as a low freezing (F. Pt. —117°) and mobile fluid in scientific apparatus such as thermometers and spirit levels ;

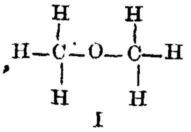
(8) as a raw material for a large number of organic compounds including ethylene, ether, acetic acid, iodoform, chloroform, chloral, etc.

Tests. (1) When warmed with anhydrous sodium acetate and concentrated sulphuric acid, ethyl alcohol forms ethyl acetate which is easily detected by its fruity smell.

(2) Upon heating gently with sodium dichromate and sulphuric acid, vapours of acetaldehyde are evolved. These vapours produce a strain of metallic silver when a paper dipped in silver nitrate solution is exposed to them.

(3) To a few drops of alcohol, add some sodium hydroxide solution and then a solution of iodine in potassium iodide till a yellow colour persists. On warming the mixture on a water bath, yellow crystals of iodoform having a characteristic odour separate out. This test can be employed for distinguishing ethyl alcohol from methyl alcohol as the latter fails to respond to it.

Structure. (1) The preliminary analysis and the vapour density determination shows that ethyl alcohol has the molecular formula C_2H_6O. Thus the two possible structures of alcohol are



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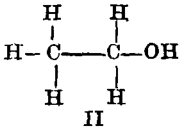


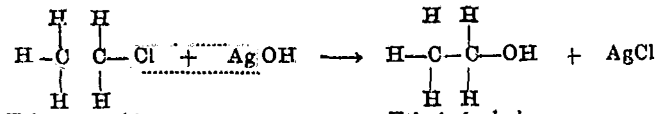
II

(2) Ethyl alcohol reacts with sodium when one of its hydrogen atoms is replaced by an atom of sodium. This shows that one of the hydrogen atoms is in a different state of combination than the rest.

(3) Ethyl alcohol also reacts with PCl_5 with the liberation of HCl gas. This shows the presence of – OH group in its molecule.

From facts (2) and (3) it is clear that formula II given above is correct for ethyl alcohol. Formula I has been shown to represent another compound, ethyl ether.

(4) The above structure of ethyl alcohol is further confirmed by its synthesis from ethyl chloride.



$$H_3C{-}CH_2{-}Cl + AgOH \longrightarrow H_3C{-}CH_2{-}OH + AgCl$$

Ethyl chloride Ethyl alcohol

PROPYL ALCOHOLS, PROPANOLS, C_3H_7OH

Both the propyl alcohols theoretically possible are known.

Propyl alcohol, 1-Propanol, $CH_3.CH_2.CH_2OH$. It occurs in fusel oil from which it is obtained by fractional distillation. It is a colourless liquid, b p. 97°, resembling ethyl alcohol in taste and odour. It is used as a solvent.

Isopropyl alcohol, 2-Propanol, $CH_3.CHOH.CH_3$. It may be made by the catalytic reduction of acetone. In U.S.A. it is prepared in large amounts from propylene obtained by cracking of petroleum during distillation. Propylene is absorbed in concentrated sulphuric acid and the isopropyl hydrogen sulphate thus produced is treated with steam.

$$CH_3CH{=}CH_2 + H_2SO_4 \longrightarrow \underset{\text{Isopropyl hydrogen sulphate}}{(CH_3)_2CH.HSO_4}$$

$$(CH_3)_2CH.HSO_4 + H_2O \longrightarrow \underset{\text{Isopropyl alcohol}}{(CH_3)_2CHOH} + H_2SO_4$$

Isopropyl alcohol is a colourless liquid with an odour somewhat like that of acetone. It is known commercially as *Petrohol*. It is also used as a solvent in the preparation of perfumes, nail polish, and lacquers. It is also used for the industrial production of acetone by catalytic dehydrogenation.

BUTYL ALCOHOLS, BUTANOLS, C_4H_9OH

There are four isomeric butyl alcohols:

(1) *n*-Butyl alcohol, 1-butanol, $CH_3CH_2CH_2CH_2OH$, b p. 117°.

(2) *Sec.* Butyl alcohol, 2-Butanol, $CH_3CH_2CHOHCH_3$, b.p. 99°.

(3) Isobutyl alcohol, 2-methyl-1-propanol, $(CH_3)_2CHCH_2OH$, 107°.

(4) *Tert.* Butyl alcohol, 2-methyl-2-propanol, $(CH_3)_3COH$, m.p. 25°.

Of all the butyl alcohols, *n*-butyl alcohol is by far the most important. It is prepared industrially by the fermentation of grain, potatoes or molasses with *Bacillus clostridium acetobutylicum.* The resulting mixture of ethyl alcohol, acetone and butyl alcohol is separated by fractional distillation. In U.S.A. butyl alcohol is produced commercially from acetaldehyde by condensation and subsequent hydrogenation.

$$2CH_3CHO \longrightarrow \underset{\text{Aldol}}{CH_3CH(OH)CH_2CHO} \xrightarrow[(-H_2O)]{\text{heat}}$$

$$\underset{\text{Crotonaldehyde}}{CH_3CH{=}CH.CHO} \xrightarrow{+2H_2} \underset{\text{Butyl alcohol}}{CH_3CH_2CH_2CH_2OH}$$

n-Butyl alcohol is a colourless liquid, b.p. 117°. It is a valuable solvent and is used for the technical production of butyl acetate and butyl phthalate both of which are employed as solvent for paints, lacquers and enamels. Butyl acetate is also in demand as a fruit essence.

AMYL ALCOHOLS, PENTANOLS, $C_5H_{11}OH$

All the eight isomeric amyl alcohols are known. A mixture of amyl alcohol is produced commercially by the chlorination of pentanes, obtained from the gaseous fraction of petroleum, and subsequent hydrolysis of the chlorides with aqueous sodium hydroxide. It is sold in the market under the name *Pentasol.* The chief ingredients of pentasol are 2-methyl-1-butanol (b.p. 128°) and 1-pentanol (b.p. 138°). Another source of amyl alcohols is fusel oil which contains mainly 3-methyl-1-butanol (b.p. 132°) and 2 methyl-1-butanol. The last named alcohol is of interest as it offers the simplest case of optical isomerism and is, therefore, also called *active amyl alcohol.*

Commercial amyl alcohol is used in the manufacture of amyl acetate which is an excellent solvent for lacquers.

UNSATURATED ALCOHOLS

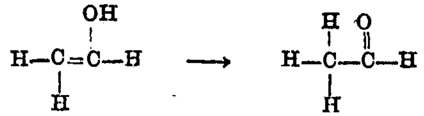
Unsaturated monohydric alcohols are of two types according as the OH is attached to a carbon which is singly or doubly-linked to another carbon. The simplest representatives of these alcohols are :

$CH_2{=}CH{-}OH$	$CH_2{=}CH{-}CH_2OH$
Vinyl alcohol	Allyl alcohol

In general, the first type of compounds resemble aromatic phenols while the second type resemble aliphatic alcohols.

VINYL ALCOHOL, $CH_2{=}CH.OH$

All attempts to prepare vinyl alcohol result in the formation of acetaldehyde. This is due to the fact that this compound shows keto-enol tautomerism. The vinyl alcohol as soon as it is produced, ketonises to form acetaldehyde.



$$\mathrm{H{-}\underset{\underset{H}{|}}{C}{=}\overset{\overset{OH}{|}}{C}{-}H \longrightarrow H{-}\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}{-}\overset{\overset{O}{\|}}{C}{-}H}$$

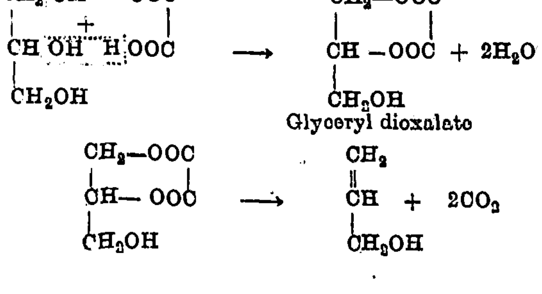
Vinyl alcohol Acetaldehyde

However, derivatives of vinyl alcohol such as vinyl bromide and vinyl acetate are quite stable.

ALLYL ALCOHOL, 3-PROPANOL, $CH_2{=}CH{-}CH_2OH$

It occurs in small quantities in pyroligneous acid.

Preparation. Allyl alcohol is prepared by heating anhydrous glycerol with about twice its weight of crystalline oxalic acid to about 230°. The glyceryl dioxalate first produced at once decomposes into carbon dioxide and allyl alcohol.



$$\begin{array}{l} CH_2OH\quad HOOC \\ |\qquad\quad + \qquad | \\ CHOH\quad\ HOOC \\ | \\ CH_2OH \end{array} \longrightarrow \begin{array}{l} CH_2{-}OOC \\ |\qquad\quad | \\ CH{-}OOC \\ | \\ CH_2OH \end{array} + 2H_2O$$

Glyceryl dioxalate

$$\begin{array}{l} CH_2{-}OOC \\ |\qquad\quad | \\ CH{-}OOC \\ | \\ CH_2OH \end{array} \longrightarrow \begin{array}{l} CH_2 \\ \| \\ CH \\ | \\ CH_2OH \end{array} + 2CO_2$$

Allyl alcohol is now manufactured by the hydrolysis of allyl chloride obtained by the chlorination of propylene.

$$CH_2{=}CHCH_2Cl + NaOH \longrightarrow CH_2{=}CHCH_2OH + NaCl$$

Properties. Allyl alcohol is a colourless, mobile liquid, b.p. 96°, with a pungent odour. It has a mild lachrymatory effect. It is completely miscible with water, alcohol and ether in all proportions.

The molecule of allyl alcohol contains an ethylenic linkage and a primary alcohol group and shows reactions characteristic of these groups.

Reactions of Ethylenic linkage

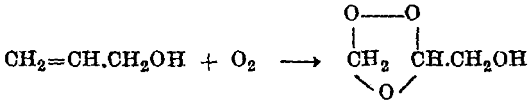
(1) Allyl alcohol forms addition compounds with hydrogen halogens and hydrogen halides.

$$CH_2{=}CH_2CH_2OH + H_2 \longrightarrow \underset{\text{1-Propanol}}{CH_3CH_2CH_2OH}$$

$$CH_2{=}CH.CH_2OH + Br_2 \longrightarrow \underset{\text{2, 3-Dibromo-1-propanol}}{CH_2Br.CHBr.CH_2OH}$$

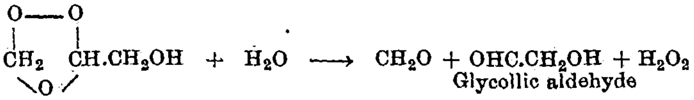
$$CH_2{=}CH.CH_2OH + HBr \longrightarrow \underset{\text{2-Bromo-1-propanol}}{CH_2CHBr.CH_2OH}$$

(2) With ozone it forms the ozonide which on hydrolysis forms glycollic aldehyde and formaldehyde.



$$CH_2{=}CH.CH_2OH + O_2 \longrightarrow \underset{\diagdown O \diagup}{\overset{O-O}{CH_2 \quad CH.CH_2OH}}$$

Ozonide



$$\underset{\diagdown O \diagup}{\overset{O-O}{CH_2 \quad CH.CH_2OH}} + H_2O \longrightarrow CH_2O + \underset{\text{Glycollic aldehyde}}{OHC.CH_2OH} + H_2O_2$$

This reaction proves the structure of allyl alcohol.

(b) On careful oxidation with permanganate solution, allyl alcohol gives glycerol.

$$CH_2{=}CHCH_2OH + H_2O + [O] \longrightarrow CH_2OH.CHOH.CH_2OH$$

Reactions of CH_2OH Group

(4) Allyl alcohol reacts with sodium giving sodium allylate.

$$CH_2{=}CHCH_2OH + Na \longrightarrow \underset{\text{Sod. allylate}}{CH_2{=}CHCH_2ONa} + \tfrac{1}{2}H_2$$

(5) It forms esters with organic and inorganic acids.

$$CH_2{=}CHCH_2OH + CH_3COOH \longrightarrow \underset{\text{Allyl acetate}}{CH_2{=}CHCH_2OOCCH_3} + H_2O$$

$$CH_2{=}CHCH_2OH + HCl \longrightarrow \underset{\text{Allyl chloride}}{CH_2{=}CHCH_2Cl} + H_2O$$

(6) On mild oxidation with ammoniacal silver oxide, allyl alcohol is oxidised to acrylic aldehyde and then acrylic acid.

$$\underset{\text{Allyl alcohol}}{CH_2 : CH.CH_2OH} \longrightarrow \underset{\text{Acrylic aldehyde}}{CH_2 : CH.CHO} \longrightarrow \underset{\text{Acrylic acid}}{CH_2 : CH.COOH}$$

Upon oxidation with sodium dichromate and sulphuric acid, a split at the double bond may result in the formation of formic acid and oxalic acid.

Infrared spectra of Alcohols. Strong infrared absorption bands of primary, secondary and tertiary alcohols occur in the regions 3200—3630 and 1000—1410 cm^{-1}. This being due to the presence of hydroxy group present in them. The complete infrared spectrum of an alcohol will also show other absorption bands due to other structural units present such as C—C and C—H bands. These are clearly seen in the infrared spectrum of ethyl alcohol given below.

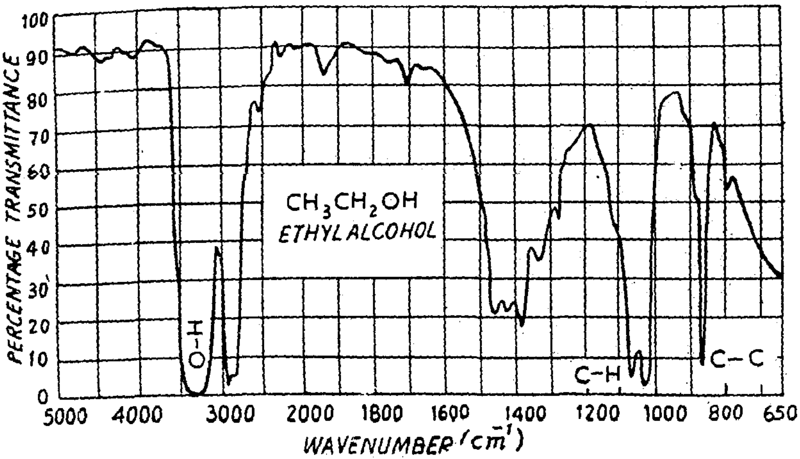


Fig. 15·8. Infrared spectrum of Ethyl alcohol.

QUESTIONS

1. What do you understand by the term alcohol ? Comment on t statement : "Any compound that contains an OH group linked to a carb atom is an alcohol."

2. Describe the general methods of formation of monohydric alcoh taking the synthesis of ethanol and propanols for illustration.

3. Write the structural formulae of the isomeric alcohols having molecular formula $C_4H_{10}O$. By what reactions can these compounds distinguished ?

4. Describe the preparation and properties of methyl alcohol. Ho it distinguished from ethyl alcohol ?

5. Describe the products of wood distillation. How are they isolated what are the uses to which they are put ? What is the scope of this indust India ?

6. Give a synthetic method for the preparation of methyl alc Why at some places it has superseded the wood distillation method ?

7. Describe the manufacture of methyl alcohol. How would you co methyl alcohol into :

(i) propyl alcohol.

(*ii*) isopropyl alcohol,

(*iii*) trimethyl carbinol.

8. Describe the manufacture of ethyl alcohol. How is the constitution of the substance established ?

9. Indicate stages by which starting from ethyl alcohol you would prepare (*a*) Ethylene glycol, (*b*) Ethylene oxide, (*c*) Isopropyl alcohol, (*d*) Methylamine, (*e*) *n*-Propylamine, and (*f*) Glycerol.

10. Give an account of the manufacture of alcohol from potatoes. Explain the terms : (*a*) Proof spirit, (*b*) Denaturant, (*c*) Power alcohol and (*d*) Absolute alcohol.

11. Name and write the formulae of the three different products that may be obtained by the action of concentrated sulphuric acid on ethyl alcohol under different experimental conditions. Describe, with a diagram, the laboratory preparation of one of the products.

12. What scheme of reactions can change methyl alcohol into ethyl alcohol and ethyl into methyl alcohol.

13. You are given two unlabelled liquids which are methanol and ethanol How will you proceed to find which is which ? How far can you rely on the iodoform test for the identification of alcohols ?

14. Give the structural formulae, the methods of preparation, and the distinctive properties of the isomeric butyl alcohols. How would you proceed to convert a primary alcohol into secondary and tertiary alcohols ?

15. Give preparation and properties of allyl alcohol. Why was it so named ?

16. Describe the manufacture of ethyl alcohol from starch. What is the action of (*a*) Chlorine, (*b*) Hydrochloric acid, and (*c*) Sodium on ethyl alcohol ? Give equations. (*Calcutta B.Sc., 1964*)

17. Starting from ethyl alcohol, give the method of preparation of (*a*) ethylene, (*b*) ethyl bromide, (*c*) acetic acid and (*d*) ethyl ether. (*Venkateswara B.Sc. II, 1964*)

18. Describe the manufacture of ethyl alcohol from molasses.
What is the action of ethyl alcohol on (*a*) concentrated sulphuric acid (*b*) Phosphorus pentachloride (*c*) acetic acid ? (*Marathwada B.Sc. II, 1964*)

19. Describe a method to estimate the number of hydroxyl groups present in an organic compound. (*Nagpur B.Sc. II, 1964*)

20. What is absolute alcohol ? How can it be prepared from rectified spirit using benzene ? How are primary, secondary and tertiary alcohols distinguished from one another ? (*Kurukshetra B.Sc. II, 1967*)

21. A saturated monohydric alcohol of the formula $C_2H_{10}O$ exists in four isomeric forms. Write the structural formulae and name each of them according to IUPAC system. What will be the expected order of reactivities of these towards HCl ? (*Allahabad B.Sc. II, 1967*)

22. What is fermentation ? Give a brief account of alcoholic fermentation. (*Dibrugarh B.Sc., 1967*)

23. Write equations to show how the following may be prepared from ethyl alcohol (*a*) ethylenic glycol (*b*) methane (*c*) acetone (*d*) propionamide. (*Osmania B.Sc., 1968*)

24. Classify the alcohols. How can you distinguish them from each other. (*Dibrugarh B.Sc., 1968*)

25. Describe, giving equations, the method you would use for the conversion of *n*-propyl alcohol into isopropyl alcohol. (*Delhi B.Sc., 1966*)

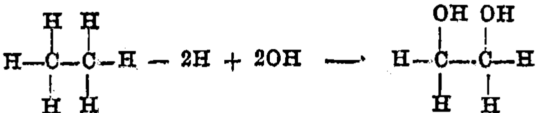
16

Aliphatic Alcohols (Continued)

JOSEPH A. LE BEL
(1847—1930)
French Chemist. Best known for his stereochemical theory of carbon compounds. Co-discoverer of the cause of optical activity with van't Hoff.

DIHYDRIC ALCOHOLS : GLYCOLS

The alcohols containing two hydroxy groups are called dihydric alcohols or *glycols* (Greek : *glycys* = sweet) since they have a sweet taste. They may be derived from alkanes by replacing two H-atoms attached to different carbon atoms, by OH groups. Thus :

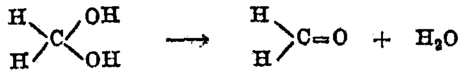


$$\mathrm{H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-H - 2H + 2OH \longrightarrow H-\underset{H}{\overset{OH}{C}}-\underset{H}{\overset{OH}{C}}-H}$$

Ethane

Ethanediol,
Ethylene glycol

As a rule dihydric alcohols containing two hydroxy groups attached to the same carbon are unstable. They at once split out a molecule of water giving an aldehyde or a ketone. That is why the glycol derived from methane is not known.



Methylene glycol
(*Unstable*)

Formaldehyde

Glycols take their names from the alkane or the polymethylene from which they are formed. Their IUPAC name is *alkanediols*. The names of some lower members are given below.

FORMULA	COMMON NAME	IUPAC NAME
$CH_2OH.CH_2OH$	Ethylene glycol	Ethanediol
$CH_2OH.CHOH.CH_3$	Propylene glycol	1, 2-Propanediol
$CH_2OH.CH_2.CH_2OH$	Trimethylene glycol	1, 3-Propanediol

They are designated as α-glycols, β-glycols, γ-glycols, etc. according as the two OH groups are linked to 1, 2, ; 1, 3- ; or 1, 4-carbon atoms.

The general methods of formation of glycols are analogous to those used for monohydric alcohols ; here we have only to develop two OH groups instead of one. They are colourless viscous liquids or solids with a sweet taste. They give all the reactions of monohydric alcohols twice over.

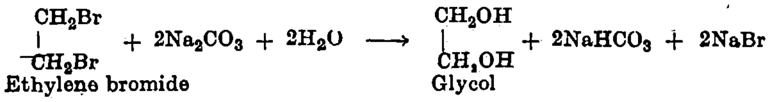
ETHYLENE GLYCOL, *1, 2-Ethanediol,* $CH_2OH.CH_2OH$

It is the simplest and the best known member of the class. It is often referred to as **glycol**.

Preparation. (1) *Oxidation of ethylene.* Glycol is formed by the oxidation of ethylene with potassium permanganate made alkaline with sodium carbonate.

$$\underset{\text{Ethylene}}{CH_2:CH_2} + H_2O + O \longrightarrow \underset{\text{Glycol}}{CH_2OH.CH_2OH}$$

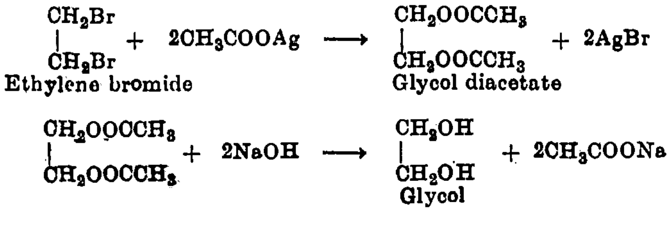
(2) *Hydrolysis of ethylene bromide.* In the laboratory glycol may be obtained by the hydrolysis of ethylene bromide with aqueous sodium carbonate solution.



$$\underset{\text{Ethylene bromide}}{\begin{array}{l}CH_2Br\\|\\CH_2Br\end{array}} + 2Na_2CO_3 + 2H_2O \longrightarrow \underset{\text{Glycol}}{\begin{array}{l}CH_2OH\\|\\CH_2OH\end{array}} + 2NaHCO_3 + 2NaBr$$

The reagents are heated for several hours in a flask fitted with a reflux condenser, until the oily drops of ethylene bromide have disappeared. The resulting solution is evaporated on a water-bath to remove most of the water. The semi-solid residue is extracted with ether-alcohol mixture, which dissolves glycol leaving behind potassium bromide. After filtration, the glycol is recovered from the solution by fractional distillation.

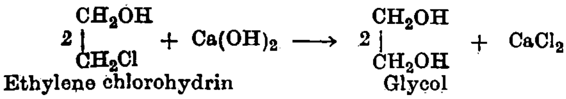
A quick laboratory method of preparing glycol is to convert ethylene bromide to diacetate which on subsequent hydrolysis with dilute sodium hydroxide solution gives glycol.



$$\underset{\text{Ethylene bromide}}{\begin{array}{l}CH_2Br\\|\\CH_2Br\end{array}} + 2CH_3COOAg \longrightarrow \underset{\text{Glycol diacetate}}{\begin{array}{l}CH_2OOCCH_3\\|\\CH_2OOCCH_3\end{array}} + 2AgBr$$

$$\begin{array}{l}CH_2OOCCH_3\\|\\CH_2OOCCH_3\end{array} + 2NaOH \longrightarrow \underset{\text{Glycol}}{\begin{array}{l}CH_2OH\\|\\CH_2OH\end{array}} + 2CH_3COONa$$

(3) *Hydrolysis of ethylene chlorohydrin.* Glycol is prepared on a technical scale by the hydrolysis of ethylene chlorohydrin with lime or sodium bicarbonate solution.

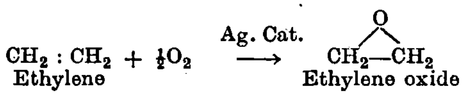


$$2\underset{\text{Ethylene chlorohydrin}}{\begin{array}{l}CH_2OH\\|\\CH_2Cl\end{array}} + Ca(OH)_2 \longrightarrow 2\underset{\text{Glycol}}{\begin{array}{l}CH_2OH\\|\\CH_2OH\end{array}} + CaCl_2$$

Ethylene chlorohydrin required in the process is made by passing ethylene, obtained by the cracking of petroleum or by the catalytic dehydration of ethyl alcohol into aqueous hypochlorous acid.

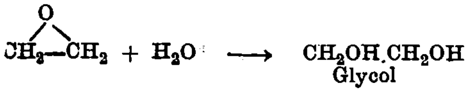
$$CH_2:CH_2 + HO.Cl \longrightarrow CH_2OH.CH_2Cl$$

(4) *Hydrolysis of ethylene oxide.* In a recent industrial method ethylene oxide is produced by the direct combination of ethylene with oxygen at high pressure and temperature in the presence of a silver catalyst.



$$\underset{\text{Ethylene}}{CH_2:CH_2} + \tfrac{1}{2}O_2 \xrightarrow{\text{Ag. Cat.}} \underset{\text{Ethylene oxide}}{\overset{O}{CH_2{-}CH_2}}$$

The ethylene oxide is then hydrolysed by warming with dilute sulphuric acid solution.

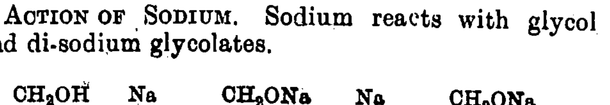


$$\overset{O}{CH_2{-}CH_2} + H_2O \longrightarrow \underset{\text{Glycol}}{CH_2OH.CH_2OH}$$

Properties. (*Physical*). Glycol is a colourless syrupy liquid, b.p. 197°, m.p. −11.5°, sp. gr. 1·111 at 20°. It has a sweetish taste. It is hygroscopic and is miscible with water and alcohol in all proportions, but dissolves sparingly in ether. It is as toxic as methyl alcohol when taken orally.

(*Chemical*). The molecule of glycol consists of two primary alcohol groups linked together and hence it shows the chemical reactions of primary alcohols twice over.

(1) ACTION OF SODIUM. Sodium reacts with glycol forming mono- and di-sodium glycolates.



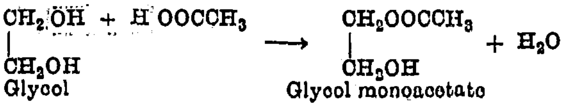
$$\underset{\text{Glycol}}{\begin{array}{l}CH_2OH\\|\\CH_2OH\end{array}} \xrightarrow[60^\circ]{Na} \underset{\text{Monosodium glycolate}}{\begin{array}{l}CH_2ONa\\|\\CH_2OH\end{array}} \xrightarrow[170^\circ]{Na} \underset{\text{Disodium glycolate}}{\begin{array}{l}CH_2ONa\\|\\CH_2ONa\end{array}}$$

(2) ACTION OF PHOSPHORUS PENTACHLORIDE. Glycol reacts with phosphorus pentachloride when one or both −OH groups may by replaced by Cl.

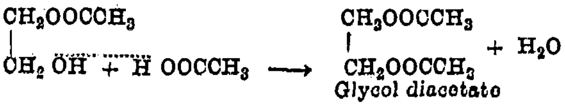
$$\underset{\text{Glycol}}{CH_2OH.CH_2OH} + PCl_5 \longrightarrow \underset{\text{Ethylene chlorohydrin}}{CH_2OH.CH_2Cl} + POCl_3 + HCl$$

$$\underset{\text{Glycol}}{CH_2OH.CH_2OH} + 2PCl_5 \longrightarrow \underset{\text{Ethylene chloride}}{CH_2Cl.CH_2Cl} + 2POCl_3 + 2HCl$$

(3) Action of Acids. Acids react upon glycol to form *'alcohol esters'* or *'diesters'* according to conditions of experiment.

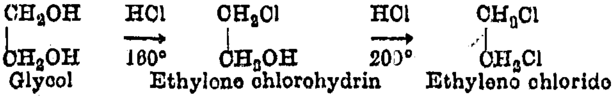


$$\underset{\text{Glycol}}{\begin{array}{l} CH_2OH \\ | \\ CH_2OH \end{array}} + HOOCCH_3 \longrightarrow \underset{\text{Glycol monoacetate}}{\begin{array}{l} CH_2OOCCH_3 \\ | \\ CH_2OH \end{array}} + H_2O$$



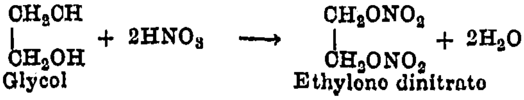
$$\begin{array}{l} CH_2OOCCH_3 \\ | \\ CH_2OH \end{array} + HOOCCH_3 \longrightarrow \underset{\text{Glycol diacetate}}{\begin{array}{l} CH_2OOCCH_3 \\ | \\ CH_2OOCCH_3 \end{array}} + H_2O$$

Similary, glycol reacts with inorganic acids in two steps.



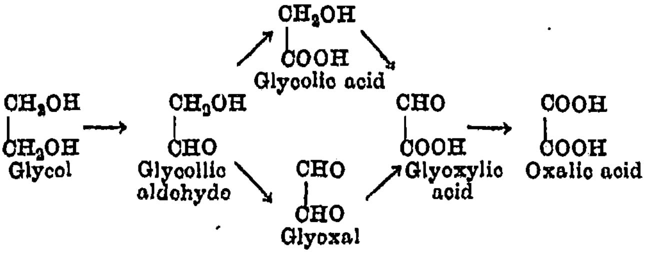
$$\underset{\text{Glycol}}{\begin{array}{l} CH_2OH \\ | \\ CH_2OH \end{array}} \xrightarrow[160°]{HCl} \underset{\text{Ethylene chlorohydrin}}{\begin{array}{l} CH_2Cl \\ | \\ CH_2OH \end{array}} \xrightarrow[200°]{HCl} \underset{\text{Ethylene chloride}}{\begin{array}{l} CH_2Cl \\ | \\ CH_2Cl \end{array}}$$

By treating glycol with a mixture of nitric acid and sulphuric acid, ethylene dinitrate is formed.

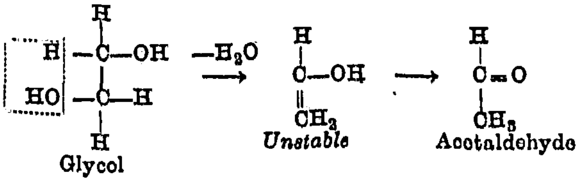


$$\underset{\text{Glycol}}{\begin{array}{l} CH_2OH \\ | \\ CH_2OH \end{array}} + 2HNO_3 \longrightarrow \underset{\text{Ethylene dinitrate}}{\begin{array}{l} CH_2ONO_2 \\ | \\ CH_2ONO_2 \end{array}} + 2H_2O$$

(4) Oxidation. The oxidation of glycol yields a number of substances as one or both primary alcohol groups may be oxidised to aldehydic or carboxyl groups. Thus :

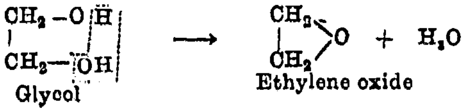


(5) Dehydration. (*i*) When heated with anhydrous zinc chloride, glycol forms acetaldehyde.



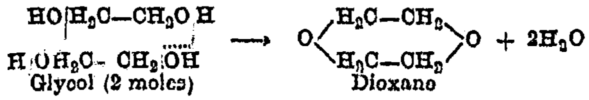
$$\underset{\text{Glycol}}{\begin{array}{c} H \\ | \\ H-C-OH \\ | \\ HO-C-H \\ | \\ H \end{array}} \xrightarrow{-H_2O} \underset{\textit{Unstable}}{\begin{array}{l} H \\ | \\ C-OH \\ \| \\ CH_2 \end{array}} \longrightarrow \underset{\text{Acetaldehyde}}{\begin{array}{l} H \\ | \\ C=O \\ | \\ CH_3 \end{array}}$$

(*ii*) When heated alone at 500°, it gives *ethylene oxide.*



$$\underset{\text{Glycol}}{\begin{array}{l} CH_2-OH \\ | \\ CH_2-OH \end{array}} \longrightarrow \underset{\text{Ethylene oxide}}{\begin{array}{l} CH_2 \\ | \quad\;\; \rangle O \\ CH_2 \end{array}} + H_2O$$

(*iii*) Upon heating with concentrated sulphuric acid, glycol is converted to dioxane which is used as an industrial solvent.



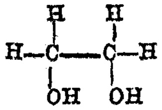
Glycol (2 mols) Dioxane

(6) DEHYDROGENATION. Glycol is dehydrogenated by lead tetra-acetate, forming formaldehyde.

$$\underset{\text{Glycol}}{CH_2OH.CH_2OH} - 2H \longrightarrow \underset{\text{Formaldehyde}}{2CH_2O}$$

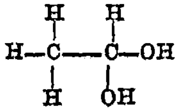
Uses. Since glycol forms low freezing mixtures with water (60 per cent solution freezing at —49°), it is sold under the name *Prestone* for use as anti-freeze for motor car radiators and as a cooling liquid in aeroplane motors. It is also used : (*i*) for preventing ice formation on aeroplane wings, (*ii*) in making low-freezing dynamite, (*iii*) as a preservative, (*iv*) as a dielectric in electrical condensers, and (*v*) as a starting material for numerous valuable compounds : 'nitroglycol', an explosive ; diglycol oleate, a rubber ; glycol stearate, a lubricant for springs ; monomethyl ether, a solvent for cellulose, etc.

Structure. Glycol has the molecular formula $C_2H_6O_2$. Since it gives mono- and di-derivatives by the action of sodium, phosphorus pentachloride etc., it contains two OH groups. Therefore, the two possible structures are :



$$\begin{array}{c} H\quad H \\ |\quad\ | \\ H-C-C-H \\ |\quad\ | \\ OH\ \ OH \end{array}$$

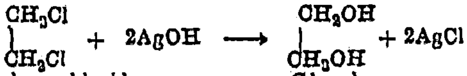
I



$$\begin{array}{c} H\quad H \\ |\quad\ | \\ H-C-C-OH \\ |\quad\ | \\ H\quad OH \end{array}$$

II

Formula II represents an unstable compound as it contains two (OH) groups attached to the same carbon. Hence formula I represents glycol. It has been further confirmed by the synthesis of the compound from ethylene chloride.



$$\underset{\text{Ethylene chloride}}{\begin{array}{l} CH_2Cl \\ | \\ CH_2Cl \end{array}} + 2AgOH \longrightarrow \underset{\text{Glycol}}{\begin{array}{l} CH_2OH \\ | \\ CH_2OH \end{array}} + 2AgCl$$

Ethylene chlorohydrin, *2-Chloroethanol*, $CH_2Cl.CH_2OH$. Ethylene chlorohydrin is made on a large scale by bubbling ethylene into aqueous solution of hypochlorous acid (chlorine water).

$$CH_2:CH_2 + HOCl \longrightarrow CH_2OH.CH_2Cl$$

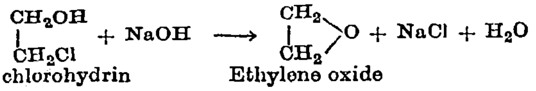
It is also obtained by the action of hydrogen chloride on glycol at 100°

Ethylene chlorohydrin is a liquid, b.p. 130°, miscible in water in all proportions. When distilled with a concentrated alkali solution, it yields ethylene oxide.

It is used as an intermediate in the technical production of glycol from ethylene.

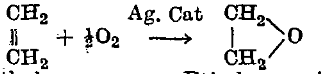
Ethylene oxide, $(CH_2)_2O$. Ethylene oxide is a cyclic ether and is isomeric with acetaldehyde.

Preparation. Ethylene oxide is prepared by distilling ethylene chlorohydrin with concentrated caustic soda solution.



Ethylene chlorohydrin Ethylene oxide

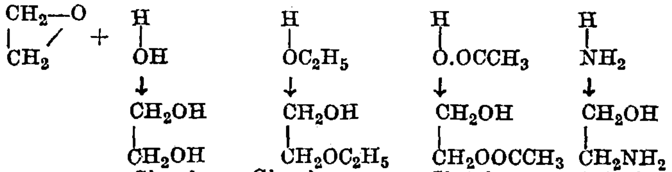
Now it is also produced on a large scale by the direct combination of ethylene with oxygen in the presence of a silver catalyst.



Ethylene Ethylene oxide

Properties. Ethylene oxide is a gas at ordinary temperature and pressure. Liquid substance boils at 13° and has ethereal smell. It is soluble in water, alcohol and ether.

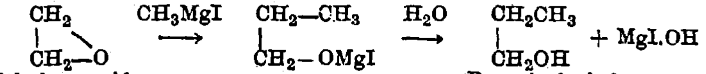
Because of the tendency of the three-membered ring to open, ethylene oxide readily unites with water, alcohols, acids and ammonia to form valuable bifunctional compounds.



Glycol Glycol mono-ethyl ether Glycol mono-acetate β-Amino-ethanol

As shown above, ethylene oxide reacts with ethyl alcohol to form glycol monoethyl ether. This is used as a solvent for cellulose nitrate under the name 'Cellosolve'. Methyl and butyl alcohols give *'methyl cellosolve'* and *'butyl cellosolve'* which are excellent solvents for making lacquers.

Ethylene oxide reacts with Grignard reagents to form addition compounds which upon hydrolysis yield primary alcohols.



Ethylene oxide Propyl alcohol

Uses. Ethylene oxide is an excellent fumigant and insecticide for grain, dried fruits and tobacco. It is used as the starting material for industrial solvents known as cellosolves. It is also used for the synthesis of primary alcohols.

Trihydric Alcohols

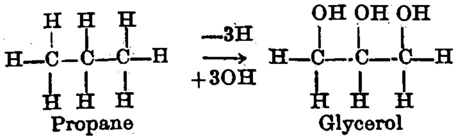
Alcohols containing three OH groups are called the trihydric alcohols. The introduction of the third OH group in the molecule raises the boiling point by about 100°, increases the viscosity, and makes the alcohol more sweet. An increase in the number of —OH groups enhances the chances of hydrogen bonding and association, thereby increasing the boiling points *e.g.*

$CH_3—CH_2OH$ b.pt. 78·5°C $CH_2OH—CH_2OH$ b. pt. 197°C $CH_2OH.CHOH.CH_2OH$ b.pt. 290°C

Chemically, trihydric alcohols give the reactions of the OH oup in triplicate. The simplest and the most important member of e class is glycerol.

YCEROL, 1, 2, 3-PROPANETRIOL, $C_3H_5(OH)_3$

Glycerol may be theoretically derived from propane by the acement of one hydrogen atom on each of the carbon atoms in molecule by a hydroxyl group.

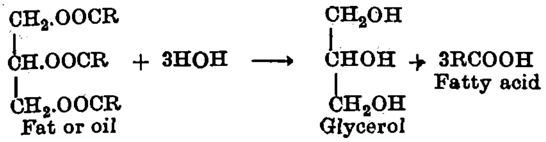


$$\underset{\text{Propane}}{CH_3-CH_2-CH_3} \xrightarrow[+3OH]{-3H} \underset{\text{Glycerol}}{CH_2OH-CHOH-CH_2OH}$$

the IUPAC name for it is *1, 2, 3-Propanetriol.* The name rol was originally derived from the word *Glyceros,* meaning It occurs in combination with higher organic acids in the of natural fats and oils.

Preparation. Glycerol is prepared industrially mainly from by three methods :

(1) *By the Hydrolysis of Fats and Oils.* Fats and oils are the rs of glycerol with organic acids (mainly palmitic, stearic and acids). On hydrolysis they form glycerol and the acids.



$$\underset{\text{Fat or oil}}{\begin{array}{l}CH_2.OOCR\\ |\\ CH.OOCR\\ |\\ CH_2.OOCR\end{array}} + 3HOH \longrightarrow \underset{\text{Glycerol}}{\begin{array}{l}CH_2OH\\ |\\ CHOH\\ |\\ CH_2OH\end{array}} + \underset{\text{Fatty acid}}{3RCOOH}$$

The hydrolysis of fats is carried originally either for soap ufacture or for the production of stearic acid needed in the industry, and glycerol is obtained as a by-product.

Glycerol from Soap Manufacture. In soap manufacture, the fat is yed by boiling with alkali solution. The free fatty acids produced by react with the alkali to form solid soap while the glycerol is left in (*Spent lye*).

$$\text{Fat + alkali solution } (lye) \longrightarrow \underbrace{\text{Glycerol + alkali left + Soap}}_{\text{Spent lye}}$$

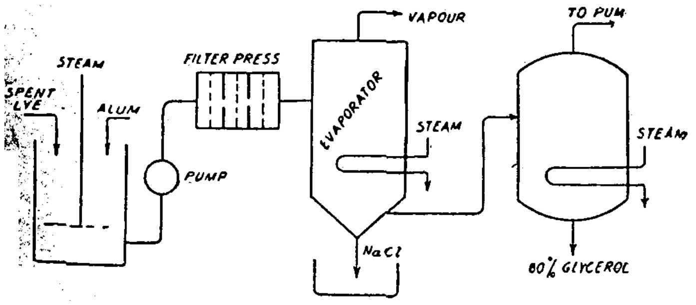


Fig. 16·1. Recovery of glycerol from spent lye.

After the removal of soap, the spent lye containing 3 to 5 per cent glycerol is treated for its recovery. The impurities present in it are precipitated by adding alum and the filtrate concentrated by evaporation. Since glycerol decomposes much below its boiling point, the evaporation is carried under vacuum. The concentrated solution which now contains about 80 per cent glycerol is treated with animal charcoal and purified by distillation with superheated steam under reduced pressure. The distillate is then evaporated *in vacuo* until the glycerol has specific gravity 1·26.

Glycerol from Candle Industry. In making candles from wax, the latter is mixed with a little stearic acid so that it may not soften on heating. The stearic acid needed for the purpose is obtained by the hydrolysis of solid fats carried by heating with water (or steam) under pressure using sulphuric acid as a catalyst. The solid stearic acid is removed and the remaining solution (*Sweet water*) after neutralisation is treated for the recovery of glycerol as described before.

(2) *By the Fermentation of Sugar.* Glycerol is also obtained by the fermentation of molasses or sugar in the presence of sodium sulphate.

$$\underset{\text{Glucose}}{C_6H_{12}O_6} \longrightarrow \underset{\text{Glycerol}}{C_3H_5(OH)_3} + \underset{\text{Acetaldehyde}}{CH_3CHO} + CO_2$$

Sodium sulphite upon hydrolysis yields an alkaline medium which favours the above course of fermentation. The yield of glycerol is as high as 20—25 per cent. This method was used by Germany during war when there was acute shortage of fats.

(3) *Synthetic Glycerol.* In America a method has been devised recently for the manufacture of glycerol from propylene obtained during the cracking of petroleum. Propylene is first chlorinated at 500° to give allyl chloride which upon treatment with hypochlorous acid and subsequent hydrolysis yields glycerol.

$$\underset{\text{Propylene}}{CH_2{=}CH{-}CH_3} + Cl_2 \longrightarrow \underset{\text{Allyl chloride}}{CH_2{=}CH{-}CH_2Cl} + HCl$$

$$\underset{\text{Allyl chloride}}{CH_2{=}CH{-}CH_2Cl} + HOCl \longrightarrow \underset{\text{Glyceryl dichlohydrin}}{CH_2Cl.CHOH.CH_2Cl}$$

$$CH_2Cl.CHOH.CH_2Cl + 2NaOH \longrightarrow \underset{\text{Glycerol}}{CH_2OH.CHOH.CH_2OH} + 2NaCl$$

In a non-petroleum country like India, the propylene required for the above synthesis may be obtained from acetone of the wood distillation industry as follows :

$$\underset{\text{Acetone}}{CH_3COCH_3} \xrightarrow{+2H} \underset{\text{Isopropyl alcohol}}{CH_3CHOHCH_3} \xrightarrow{-H_2O} \underset{\text{Propylene}}{CH_3{-}CH{=}CH_2}$$

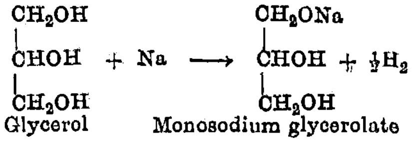
Properties. (*Physical*). Glycerol is a colourless and odourless syrupy liquid having a sweet taste. It boils at 290° with slight decomposition and has a specific gravity of 1·26. On cooling glycerol forms transparent solid crystals m.p. 17°. It is very hygroscopic. It mixes with water and alcohol in all proportions, but it is insoluble in ether. It has a sweet taste.

(*Chemical*). Glycerol molecule is made of two primary alcohol groups and one secondary alcohol group and exhibits the behaviour of these groups.

$$\underset{\text{Primary}}{CH_2OH} {-\!-\!-} \underset{\text{Secondary}}{CHOH} {-\!-\!-} \underset{\text{Primary}}{CH_2OH}$$

Thus it gives the reactions of the OH group thrice over. In general, the two *primary alcohol groups are more reactive than the secondary alcohol group.*

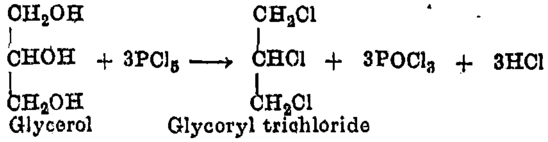
(1) REACTION WITH SODIUM. At room temperature sodium metal reacts with glycerol forming monosodium glycerolate.



$$\begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} + Na \longrightarrow \begin{array}{l} CH_2ONa \\ | \\ CHOH \\ | \\ CH_2OH \end{array} + \tfrac{1}{2}H_2$$

At higher temperatures both the primary alcohol groups are attacked yielding disodium glycerolate. The secondary alcohol group, however, refuses to react.

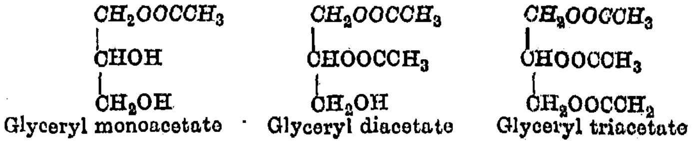
(2) REACTION WITH PHOSPHORUS PENTACHLORIDE. Glycerol reacts with phosphorus pentachloride to form glyceryl trichloride, all the three OH groups in it being replaced by Cl atoms.



$$\begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} + 3PCl_5 \longrightarrow \begin{array}{l} CH_2Cl \\ | \\ CHCl \\ | \\ CH_2Cl \end{array} + 3POCl_3 + 3HCl$$

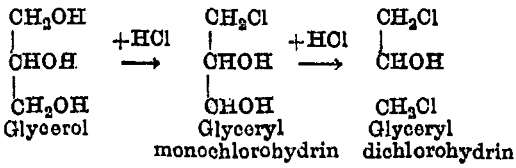
(3) REACTION WITH ACIDS GIVING ESTERS. Glycerol reacts with both organic and inorganic acids forming esters.

(*i*) With a mixture of acetic acid and acetic anhydride, it forms the three esters :



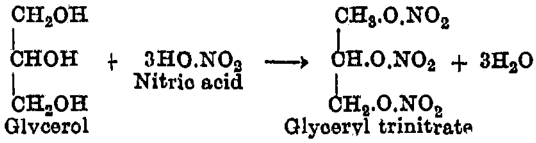
$$\begin{array}{l} CH_2OOCCH_3 \\ | \\ CHOH \\ | \\ CH_2OH \end{array} \qquad \begin{array}{l} CH_2OOCCH_3 \\ | \\ CHOOCCH_3 \\ | \\ CH_2OH \end{array} \qquad \begin{array}{l} CH_2OOCCH_3 \\ | \\ CHOOCCH_3 \\ | \\ CH_2OOCCH_2 \end{array}$$

(*ii*) With concentrated hydrochloric acid at 100°, it yields chlorohydrins.



$$\begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} \xrightarrow{+HCl} \begin{array}{l} CH_2Cl \\ | \\ CHOH \\ | \\ CHOH \end{array} \xrightarrow{+HCl} \begin{array}{l} CH_2Cl \\ | \\ CHOH \\ \\ CH_2Cl \end{array}$$

(*iii*) With nitric acid in the presence of sulphuric acid, glycerol forms glyceryl trinitrate, commonly known as *nitroglycerine.*

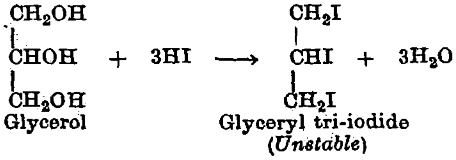


$$\begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} + \underset{\text{Nitric acid}}{3HO.NO_2} \longrightarrow \begin{array}{l} CH_3.O.NO_2 \\ | \\ CH.O.NO_2 \\ | \\ CH_2.O.NO_2 \end{array} + 3H_2O$$

(4) REACTION WITH HYDRIODIC ACID. The reaction of gly-

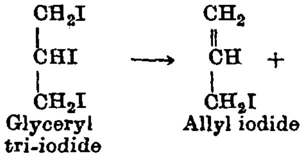
cerol with hydriodic acid proceeds in several steps forming allyl iodide, propylene and isopropyl iodide.

(*a*) Upon warming with concentrated hydriodic acid, it gives glyceryl tri-iodide.



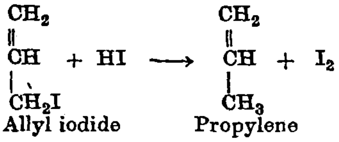
$$\begin{array}{c}CH_2OH\\ |\\ CHOH\\ |\\ CH_2OH\\ \text{Glycerol}\end{array} + 3HI \longrightarrow \begin{array}{c}CH_2I\\ |\\ CHI\\ |\\ CH_2I\\ \text{Glyceryl tri-iodide}\\ \textit{(Unstable)}\end{array} + 3H_2O$$

The tri-iodide being unstable at once splits out a molecule of iodine to form allyl iodide.



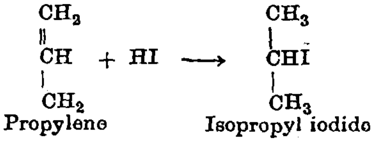
$$\begin{array}{c}CH_2I\\ |\\ CHI\\ |\\ CH_2I\\ \text{Glyceryl}\\ \text{tri-iodide}\end{array} \longrightarrow \begin{array}{c}CH_2\\ \|\\ CH\\ |\\ CH_2I\\ \text{Allyl iodide}\end{array} + I_2$$

(*b*) When heated with hydriodic acid, allyl iodide first produced is reduced to propylene.



$$\begin{array}{c}CH_2\\ \|\\ CH\\ |\\ CH_2I\\ \text{Allyl iodide}\end{array} + HI \longrightarrow \begin{array}{c}CH_2\\ \|\\ CH\\ |\\ CH_3\\ \text{Propylene}\end{array} + I_2$$

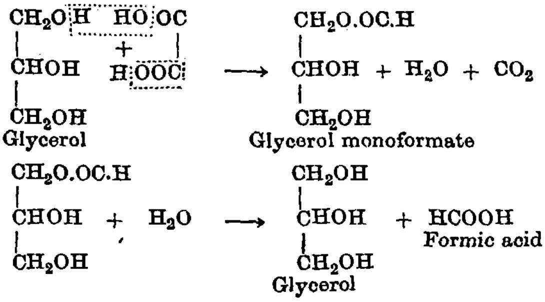
(*c*) In the presence of excess of hydriodic acid, propylene further adds a molecule of hydrogen iodid giving isopropyl iodide.



$$\begin{array}{c}CH_3\\ \|\\ CH\\ |\\ CH_2\\ \text{Propylene}\end{array} + HI \longrightarrow \begin{array}{c}CH_3\\ |\\ CHI\\ |\\ CH_3\\ \text{Isopropyl iodide}\end{array}$$

(5) REACTION WITH OXALIC ACID. Glycerol reacts with oxalic acid in two ways.

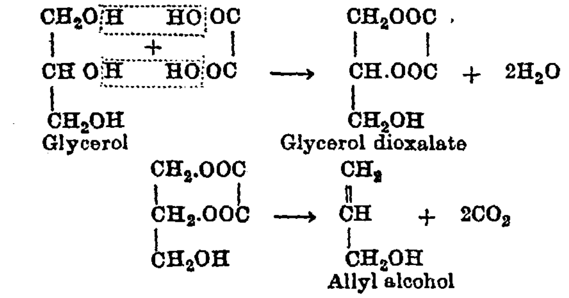
(*a*) *Formation of Formic acid.* When heated with crystalline oxalic acid to 110°, glycerol yields glycerol monoformate which upon hydrolysis forms formic acid and glycerol is regenerated.



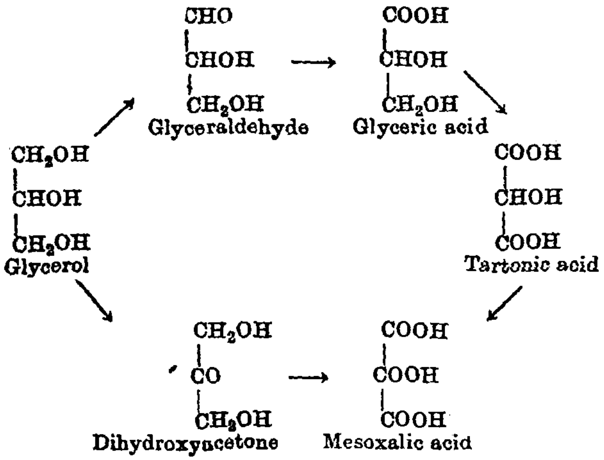
$$\begin{array}{l}CH_2O\,H \quad HO\,OC\\ | \qquad\quad + \qquad |\\ CHOH \quad H\,OOC\\ |\\ CH_2OH\\ \text{Glycerol}\end{array} \longrightarrow \begin{array}{l}CH_2O.OC.H\\ |\\ CHOH\\ |\\ CH_2OH\\ \text{Glycerol monoformate}\end{array} + H_2O + CO_2$$

$$\begin{array}{l}CH_2O.OC.H\\ |\\ CHOH\\ |\\ CH_2OH\end{array} + H_2O \longrightarrow \begin{array}{l}CH_2OH\\ |\\ CHOH\\ |\\ CH_2OH\\ \text{Glycerol}\end{array} + \begin{array}{c}HCOOH\\ \text{Formic acid}\end{array}$$

(*b*) *Formation of allyl alcohol.* When glycerol is heated with oxalic acid to 230°, glycerol dioxalate is produced. It at once decomposes into carbon dioxide and allyl alcohol.



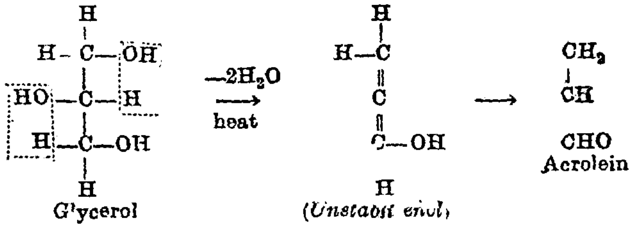
(6) OXIDATION. The two primary alcohol groups in glycerol are capable of being oxidised to the aldehyde and then the carboxyl group, while the secondary alcohol group can be oxidised to the carbonyl group. Thus glycerol gives rise to a variety of oxidation products



Thus dilute nitric acid converts glycerol into glyceric acid and tartonic acid, while strong nitric acid oxidises it to mainly glyceric acid.

When glycerol is dropped on solid potassium permanganate, it is ignited by the heat of reaction and burns with a blue flame.

(7) DEHYDRATION. When heated alone or with potassium hydrogen sulphate, glycerol eliminates two molecules of water forming acrolein.



Uses. Glycerol is used :

(*i*) as a sweetening agent in beverages and confectionary ;

(*ii*) in the preparation of high class toilet soaps and cosmetics ;

(*iii*) in preventing tobacco from drying out ;

(*iv*) as *antifreeze* in automobile radiators ;

(*v*) for lubricating fine machinery such as watches and clocks ;

(*vi*) as a preservative for fruits and other eatables which require to be kept moist ;

(*vii*) in making printing inks and inks for stamp pads ;

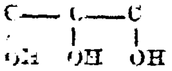
(*viii*) in the preparation of glycerol trinitrate ; and

(*ix*) as a starting material for several allyl and propyl derivatives.

Structure. (1) Elementary analysis and molecular weight determination shows that glycerol has the molecular formula $C_3H_8O_3$.

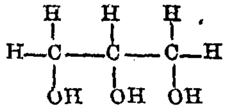
(2) With acetyl chloride it forms glycerol triacetate which shows the presence of three $-OH$ groups in the molecule. Thus, the formula of glycerol may be expressed as $C_3H_5(OH)_3$.

(3) Since two $-OH$ groups linked to the same carbon atom form an unstable structure, the three $-OH$ groups in the glycerol molecule are connected to different carbon atoms. Thus, in glycerol we have



$$\begin{array}{ccccc} C & — & C & — & C \\ | & & | & & | \\ OH & & OH & & OH \end{array}$$

(4) Supplying the necessary hydrogen atoms, the structural formula of glycerol can be written as



$$\begin{array}{ccccccc} & & H & & H & & H \\ & & | & & | & & | \\ H & — & C & — & C & — & C & — H \\ & & | & & | & & | \\ & & OH & & OH & & OH \end{array}$$

(5) This formula is supported by the fact that glycerol reacts with PCl_5 to form glycerol trichloride, $CH_2Cl.CHCl.CH_2Cl$.

(6) The above structure of glycerol is confirmed by its synthesis.

Synthesis of Glycerol. Glycerol may be synthesised from elements by the following steps :

$$2C + H_2 \xrightarrow{120°} \underset{\text{Acetylene}}{C_2H_2} \xrightarrow[HgSO_4]{H_2SO_4} \underset{\text{Acetaldehyde}}{CH_3CHO} \xrightarrow{[O]} \underset{\text{Acetic acid}}{CH_3COOH}$$

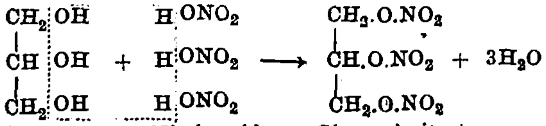
$$\xrightarrow[\textit{Ca-salt}]{\textit{Distil}} \underset{\text{Acetone}}{CH_3.CO.CH_3} \xrightarrow{\textit{Red.}} \underset{\text{Isopropyl alcohol}}{CH_3.CHOH.CH_3} \xrightarrow[\text{heat}]{H_2SO_4} \underset{\text{Propene}}{CH_2:CH.CH_3}$$

$$\xrightarrow{Cl_2} \underset{\text{Propylene chloride}}{CH_3CHCl.CH_2Cl} \xrightarrow{ICl} \underset{\text{Glyceryl trichloride}}{CH_2Cl.CHCl.CH_2Cl}$$

$$\xrightarrow{H_2O} \underset{\text{Glycerol}}{CH_2OH.CHOH.CH_2OH}$$

Nitroglycerine, Glyceryl trinitrate, $C_3H_5(ONO_2)_3$. The name 'nitroglycerine' assigned to this substance is incorrect. It is a triester of glycerol and nitric acid, and hence the proper name would be *glyceryl trinitrate* or simply *glyceryl nitrate.*

Preparation. Glycerol nitrate is manufactured by adding glycerol slowly to a mixture of nitric acid and sulphuric acid maintained at 20°.



$$\begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} + \begin{array}{l} H\,ONO_2 \\ H\,ONO_2 \\ H\,ONO_2 \end{array} \longrightarrow \begin{array}{l} CH_2.O.NO_2 \\ | \\ CH.O.NO_2 \\ | \\ CH_2.O.NO_2 \end{array} + 3H_2O$$

Glycerol Nitric acid Glyceryl nitrate

After the reaction is complete, the mixture is run into ice-cold water. The oily layer of glycerol nitrate that separates at the top is removed. It is washed with water and then with sodium carbonate solution to remove any acids. It is finally dried by passing through a mat of sponges.

Properties. Glyceryl nitrate is a colourless oily liquid (Sp. Gr. 1·6) with a sweet burning taste. Upon cooling it forms crystals, m.p. 13 2°. It is insoluble in water but dissolves readily in alcohol and ether. It is poisonous, its vapour causing violent headache and loss of consciousness.

The most important property of glyceryl nitrate is its explosive power. Its molecule having nitrogen fully loaded with oxygen is very susceptible to external shock. When struck a sharp blow, it explodes with great violence. The explosion reaction consists of internal combustion attended by splitting out of elemental nitrogen.

$$4C_3H_5(NO_3)_3 \longrightarrow 12CO_2 + 10H_2O + 6N_2 + O_2$$

The sudden liberation of the large volumes of gases in a space initially occupied by the liquid substance causes an explosion wave of enormous pressure.

Uses. As AN EXPLOSIVE. Nitroglycerine was first prepared in 1866 but its use as explosive proved to be dangerous as it exploded almost whimsically on receiving the slightest shock during transportation. In 1866 Alfred Nobel discovered that when absorbed in '*kieselguhr*', a porous earth, nitroglycerine could be transported without risk of explosion. The explosive so prepared was called **dynamite.** Now-a-days the dynamite is made by using adsorbents such as dust or starch in place of kieslguhr and ammonium nitrate (or sodium nitrate) is added to ensure complete combustion of these materials. Modern explosives such as *blasting gelatin* and *cordite* contain nitroglycerine mixed with gun-cotton (cellulose nitrate). Dynamite is used to shoot oil wells and in building roads, dams and tunnels where the removal of rock and earth is required.

(2) As A MEDICINE. Nitroglycerine is used as a medicine for treatment of heart disease, *angina pictoris,* and also for asthma as it dilates the blood vessels and thus relieves blood pressure.

QUESTIONS

1. What do you understand by the term "Polyhydric alcohol" ? Name and give the formulae of two such substances. In one case describe how the substance may be prepared in the laboratory.

2. Give the general methods of formation and properties of glycerol.

3. Give two ways in which glycol may be obtained from ethylene Describe the reaction by which the following may be obtained from glycol: (*a*) oxalic acid, (*b*) succinic acid, (*c*) acetylene, (*d*) ethylene chlorohydrin.

4. How would you prepare ethylene oxide and what are its chief chemical properties ?

5. (*a*) Describe how glycerol is recovered from spent-lye.

(*b*) How does glycerol react with the following reagents ?

(*i*) Hydrochloric acid, (*ii*) hydriodic acid, (*iii*) sulphuric acid, (*iv*) nitric acid and (*v*) phosphorus pentachloride. (*Agra B.Sc., 1960*)

6. How is glycerol obtained from oils ? How is it synthesised ? How is it converted into acrolein ? (*Andhra B.Sc., 1961*)

7. How is glycerine obtained on a large scale ? How can it be synthesised from acetone ? What are the actions of : (*a*) hydriodic acid ; (*b*) phosphorus pentachloride ; and (*c*) Potassium bisulphide on glycerine ? (*Gauhati B.Sc., 1961*)

8. Describe the manufacture of glycerol. Starting from glycerol how would you obtain (*a*) acrolein ; (*b*) nitroglycerine ; (*c*) isopropyl iodide ; and (*d*) sym-dichloroacetone ? (*Calcutta B.Sc., 1962*)

9. How is glycerol manufactured ? Outline its synthesis from acetic acid. What is the action of (*a*) phosphorus pentabromide ; (*b*) red phosphorus and iodine on glycerol. (*Annamalai B.Sc., 1962*)

10. Describe how glycerol is obtained on a large scale. Mention its important uses. What is the action of : (*i*) concentrated nitric acid ; and (*ii*) hot hydriodic acid on it ? (*Vallabhbhai Vidyapeeth B.Sc., 1962*)

11. How is glycerol recovered from spent lye ? Give the reactions of glycerol with (*a*) Hydrochloric acid ; (*b*) Hydriodic acid : (*c*) Sulphuric acid ; (*d*) Nitric acid ; and (*e*) Oxalic acid. (*Panjab B.Sc., 1962*)

12. Give an account of the total synthesis of glycerol. Starting from glycerol indicate how would you prepare (*a*) acrolein, (*b*) acrylic acid, (*c*) allyl alcohol, (*d*) allyl iodide, (*e*) glyceric acid and (*f*) glycerose. (*Peshawar B.Sc., 1962*)

13. Give the laboratory and technical method of preparation of glycerine and discuss its chemical properties. Starting from glycerine how will you prepare (*i*) acrolein, (*ii*) allyl alcohol, (*iii*) quinoline, (*iv*) dynamite ? (*Bombay B.Sc., 1963*)

14. How is glycerine obtained on a large scale ? What is the action of
   (*a*) HI
   (*b*) $KHSO_4$
   (*c*) HNO_3 and
   (*d*) Oxalic acid on glycerine ? (*Aligarh B.Sc. II, 1964*)

15. Discuss in details the constitution of glycerol and explain its reactions with hydrogen iodide and oxalic acid. (*Nagpur B.Sc. II, 1964*)

16 How is glycerol manufactured ? What are its reactions with (1) PCl_5 (2) HCl (3) $KHSO_4$ and (4) a mixture of HNO_3 and H_2SO_4 ?

How is its structure determined ? (*Marathwada B.Sc. III, 1964*)

17. Give the preparation and uses of the following (*a*) Ethylene glycol (*b*) glycerol. (*Dibrugarh B.Sc., 1967*)

18. How is glycerol manufactured ? Show by equations how the following compounds may be prepared from glycerol : (*a*) Acrolein, (*b*) Glycerol trinitrate (*c*) Formic acid, (*d*) Epichlorohydrin. (*Gorakhpur B.Sc. II, 1967*)

19. Draw a neat diagram for the manufacture of glycerol, with necessary comments. *(Kalyani B.Sc. Hons., 1967)*

20. Write an account of the manufacture of glycerol from propylene. *(Panjab B.Sc. II, 1968)*

21. How is ethylene glycol prepared in the laboratory ? Give its important properties and uses. *(Udaipur B.Sc. 1968)*

22. Outline the synthesis of glycerol starting from propylene. What happens when glycerol is heated with (*a*) oxalic acid (*b*) $KHSO_4$. *(Osmania B.Sc., 1968)*

23. Describe the manufacture of glycerol and give its important chemical properties. How is its constitution established ? *(Ujjain B.Sc., 1968)*

24. Discuss the constitution of glycerol. Starting with acetylene show how you would obtain glycerol. What is the action of the following reagents on glycerol ?

(1) Oxalic acid (2) conc. Hydriodic acid (3) Nitric acid. *(Poona B.Sc., 1968)*

25. Write a short account of the chemistry of glycerol including the method of its manufacture and synthesis. *(Kurukshetra B.Sc., 1968)*

26. Give one method for the manufacture of glycerol by synthesis.

Explain, giving equations, the action of hydrochloric acid, oxalic acid and potassium hydrogen sulphate on glycerol. *(Delhi B.Sc., 1969)*

17

Thioalcohols and Thioethers

FRANK C. WHITMORE
(1887—1947) American

Worked with aliphatic compounds rearrangements, mercury compounds, Grignard reagents, polymerisation, Silicon compounds. Author of the American Chemical Society monograph on mercury compounds and of the well-known advanced organic chemistry text-book.

The two elements oxygen and sulphur lie one above the other in the same group of the periodic classification and it is no wonder that they form similar types of compounds.

1. THIOALCOHOLS

The sulphur derivatives corresponding with monohydric alcohols are termed **thioalcohols** or simply **thiols**. They have the type formula RSH, where R stands for an alkyl radical.

While thioalcohols are truly regarded as derivatives of alcohols, they may also be looked upon as derivatives of hydrogen sulphide in which one hydrogen atom has been replaced by an alkyl radical.

$$\underset{\text{Alcohol}}{\mathrm{R{-}O{-}H}} \xrightarrow[+\mathrm{S}]{-\mathrm{O}} \underset{\text{Thioalcohol}}{\mathrm{R{-}S{-}H}} \xleftarrow[+\mathrm{R}]{-\mathrm{H}} \underset{\substack{\text{Hydrogen}\\ \text{sulphide}}}{\mathrm{H{-}S{-}H}}$$

Thus thioalcohols are often named **hydrosulphides.** Their derivation from hydrogen sulphide which is a weak acid, accounts for the feeble acid properties shown by these compounds. Like any other acid, thioalcohols react with mercuric oxide forming mercury salts and hence their name **mercaptans** (*mercurium*=mercury ; *captans*=catching).

NOMENCLATURE

The members of this class of compounds are named as *Alkyl thioalcohols* or as *Alkyl mercaptans*. Their IUPAC name is obtained by adding the suffix *-thiol* to the name of the corresponding alkane. Thus :

FORMULA	COMMON NAME	IUPAC NAME
CH_3SH	Methyl mercaptan, Methyl thioalcohol.	Methanethiol
C_2H_5SH	Ethyl mercaptan, Ethyl thioalcohol.	Ethanethiol

Ethyl thioalcohol being the most important member of the class is often referred to as simply *thioalcohol* or mercaptan.

The characteristic $-SH$ group is called thiol, mercapto, or sulphhydryl.

METHODS OF FORMATION

Mercaptans can be prepared by methods which are analogous to those used for alcohols. They can also be obtained by substitution of oxygen of alcohols by sulphur. The general methods of formation of mercaptans are :

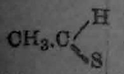
(1) *By heating potassium hydrogen sulphide with alkyl halides.*

$$\underset{\text{Ethyl iodide}}{C_2H_5I} + KSH \longrightarrow \underset{\text{Thioalcohol}}{C_2H_5SH} + KI$$

(2) *By heating alcohols with phosphorus pentasulphide.*

$$\underset{\text{Ethyl alcohol}}{5C_2H_5OH} + P_2S_5 \longrightarrow \underset{\text{Thioalcohol}}{5C_2H_5SH} + P_2O_5$$

(3) *By the biochemical reduction of the thioaldehydes with yeast.*



$$\underset{\text{Thioacetaldehyde}}{CH_3.C\begin{smallmatrix}\diagup H\\ \diagdown S\end{smallmatrix}} + 2H \longrightarrow \underset{\text{Thioalcohol}}{CH_3.CH_2.SH}$$

(4) *By passing a mixture of hydrogen sulphide and vapour of an alcohol over a heated catalyst, thorium oxide.* (COMMERCIAL).

$$\underset{\text{Ethyl alcohol}}{C_2H_5OH} + H_2S \longrightarrow \underset{\text{Thioalcohol}}{C_2H_5SH} + H_2O$$

PHYSICAL CHARACTERISTICS

(1) Excepting methyl thioalcohol which is a gas, thioalcohols [illegible] colourless volatile liquids. CH_3SH, b.p. 6° ; C_2H_5SH, b.p. 37°.

(2) They have an extremely repulsive smell recalling that of [illegible] and H_2S, which diminishes with increasing molecular weight.

(3) Their boiling points are much lower than those of the corresponding alcohols.

(4) Unlike alcohols they are insoluble in water. However, they are soluble in alcohol and ether.

Lower boiling points and lesser solubilities of thiols from those of corresponding alcohols may be attributed to a greater hydrogen bonding in the latter.

THIOLS	B.PT.	ALCOHOLS	B.PT.	DIFFERENCE
H.SH	−62°	H.OH	100°	162
CH_3SH	6°	CH_3OH	66°	60
C_2H_5SH	37°	C_2H_5OH	78°	40

Sulphur is much less electronegative than oxygen, giving S-H bonds having a much smaller ionic character than O—H bonds. Accordingly thiols form very weak H-bonds.

As the molecular weight increases the difference of b.pt. also decreases due to a lesser association in higher alcohols, the reason evidently being the greater electron repelling tendency of higher alkyl radicals.

(5) They are very feeble acids as they contain ionisable hydrogen, $C_2H_5SH \rightarrow C_2H_5S^- + H^+$.

CHEMICAL CHARACTERISTICS

Chemically thioalcohols very closely resemble with alcohols the SH group giving all the reactions analogous to those of the OH group. They, however, differ from the latter in two respects.

(*i*) ACID CHARACTER. Thioalcohols being the derivatives of the weak acid H_2S, are weakly acid in character. Thus like other acids they react with alkalis and salt solution forming metallic derivatives. Alcohols, on the other hand, are the derivatives of water and are, therefore, neutral.

(*ii*) OXIDATION REACTIONS. Sulphur in thioalcohols is bivalent but it has a tendency to extend its valency to four. Thus unlike alcohols, they can be oxidised when the sulphur atom adds up two oxygen atoms and sulphonic acids are formed.

The general reactions of thioalcohols are given below :

(1) **Action of Sodium**: Like alcohol they react with sodium with the evolution of hydrogen.

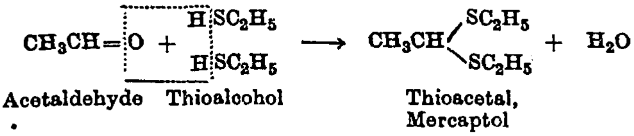
$$2C_2H_5SH + 2Na \longrightarrow \underset{\text{Sod. mercaptide}}{2C_2H_5SNa} + H_2$$

(2) **Action of Acids and Acid chlorides.** Similar to alcohols they react with acids and acid chlorides forming THIOESTERS.

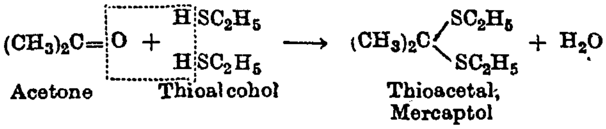
$$\underset{\text{Acetic acid}}{CH_3CO\vdots\boxed{OH + H}\vdots SC_2H_5} \longrightarrow \underset{\text{Ethyl thioacetate}}{CH_3COSC_2H_5} + H_2O$$

$$\underset{\text{Acetyl chloride}}{CH_3CO\vdots\boxed{Cl + H}\vdots SC_2H_5} \longrightarrow CH_3COSC_2H_5 + HCl$$

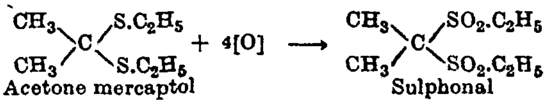
(3) **Condensation with Aldehydes and Ketones.** Like alcohols, the thioalcohols react with aldehydes to give THIOACETALS.



Thioalcohols being more reactive than alcohols, also react with ketones to give THIOACETALS.



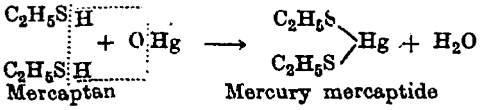
Acetone mercaptol on oxidation with potassium permanganate gives SULPHONAL which is an important hypnotic.

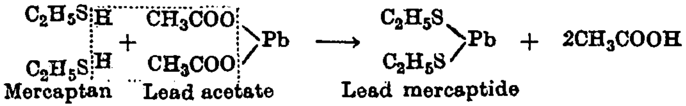


(4) **Formation of Salts.** Thioalcohols dissolve in alkalis forming salts called MERCAPTIDES.

$$\underset{\text{Thioalcohol}}{C_2H_5SH} + KOH \longrightarrow \underset{\text{Pot. mercaptide}}{C_2H_5SK} + H_2O$$

They also react with metallic salts and oxides forming mercaptides.

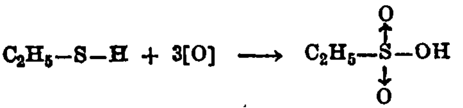




Alcohols being neutral fail to give the above reactions.

(5) **Oxidation reaction.** The behaviour of thioalcohols towards oxidising agents is radically different from that of the alcohols.

(*i*) With a strong oxidising agent like nitric acid, they form the corresponding SULPHONIC ACIDS



$$C_2H_5{-}S{-}H + 3[O] \longrightarrow C_2H_5{-}\underset{\downarrow \atop O}{\overset{O \atop \uparrow}{S}}{-}OH$$

Ethylsulphonic acid

(*ii*) Mild oxidising agents such as hydrogen peroxide or the oxygen of air oxidise thioalcohols to DISULPHIDES.

$$\underset{\text{Thioalcohol}}{C_2H_5.S{:}H} + O + H{:}S.C_2H_5 \longrightarrow \underset{\text{Diethyl disulphide}}{C_2H_5S.S.C_2H_5} + H_2O$$

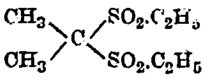
USES OF MERCAPTANS

(1) Lower mercaptans are mixed with commercial gases and refrigerating fluid to detect any leakage in pipe lines. The nose can detect one part of ethyl mercaptan in 50 billion parts of air.

(2) Very dilute solution of mercaptans aid in the healing of tissues as also appears to be function of the mercaptans present in body secretions.

(3) Mercaptans are used to prepare sulphonal and other similar hypnotics.

Sulphonal:

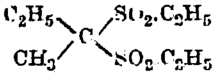


Sulphonal represents an important class of hypnotics. This is prepared by the condensation of acetone with ethyl mercaptan and the subsequent oxidation of the acetone mercaptol produced by potassium permanganate.

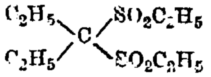
$$(CH_3)_2CO + 2C_2H_5SH \longrightarrow \underset{\text{Acetone-mercaptol}}{(CH_3)_2C(SO_2C_2H_5)_2} + H_2O$$

$$(CH_3)_2C(SC_2H_5)_2 + 4[O] \longrightarrow \underset{\text{Sulphonal}}{(CH_3)_2C(SO_2.C_2H_5)_2}$$

Properties and Uses. Sulphonal forms colourless crystals which melt at 126°. It is sparingly soluble in cold water but completely soluble in hot water. It is important as a drug for producing sleep. Homologues of sulphonal, namely TRIONAL AND TETRONAL, have been shown to be even more effective hypnotics.



Trional



Tetronal

THIOETHERS OR ALKYL SULPHIDES

As the name implies, thioethers are ethers in which the oxygen atoms has been replaced by that of sulphur.

$$\underset{\text{Diethyl ether}}{C_2H_5{-}O{-}C_2H_5} \xrightarrow[+S]{-O} \underset{\text{Ethyl thioether}}{C_2H_5{-}S{-}C_2H_5}$$

Thioethers could also be regarded as dialkyl derivatives of hydrogen sulphide just as ethers are thought of as derivatives of water.

$$H{-}S{-}H \xrightarrow[+2R]{-2H} \underset{\text{Thioether}}{R{-}S{-}R}$$

Thus thioethers resemble inorganic sulphides and are often called **Dialkyl sulphides**. However, they differ from inorganic sulphides in being non-ionised compounds.

METHODS OF PREPARATION

(1) *By the distillation of alkyl halides with potassium sulphide.*

$$2C_2H_5I + K_2S \longrightarrow (C_2H_5)_2S + 2KI$$

Ethylene iodide Ethylene sulphide

(2) *By the treatment of alkali mercaptides with alkyl halides.*

$$C_2H_5\boxed{Br + Na}SC_2H_5 \longrightarrow C_2H_5SC_2H_5 + NaBr$$

Ethyl bromide Sod. mercaptide Ethyl sulphide

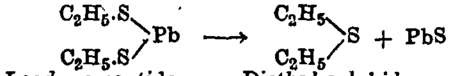
The method may also be used for the preparation of mixed thioethers.

(3) *By heating ethers with phosphorus pentasulphide.*

$$5(C_2H_5)_2O + P_2S_5 \longrightarrow 5(C_2H_5)_2S + P_2O_5$$

Diethyl ether Diethyl sulphide

(4) *By heating certain mercaptides*, when they decompose to form an alkyl sulphide.



$$(C_2H_5.S)_2Pb \longrightarrow (C_2H_5)_2S + PbS$$

Lead mercaptide Diethyl sulphide

PHYSICAL CHARACTERISTICS

(1) Thioethers are colourless and volatile liquids.

$(CH_3)_2S$, b.p. 38° ; $(C_2H_5)_2S$, b.p. 92°

Dimethyl sulphide Diethyl sulphide

(2) As ordinarily prepared they have a disagreeable odour resembling that of thioalcohols. Pure thioethers have an ethereal smell which is not unpleasant.

(3) Their boiling points are in general higher than those of the corresponding ethers.

(4) They are insoluble in water but soluble in alcohol, ethers and other organic solvents.

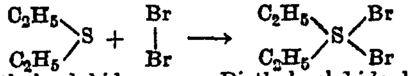
(5) They are neutral in character as they have no ionisable hydrogen.

CHEMICAL CHARACTERISTICS

Chemically, thioethers offer a great resemblance to ethers. However, the tendency to extend valency is much more prominent in sulphur than in oxygen. Thus thioethers form addition compounds more readily than do ethers.

The general reactions of thioether are given below.

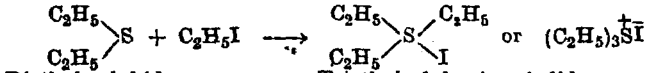
(1) **Addition of halogens.** Thioethers add halogens forming dihalogen compounds.



$$(C_2H_5)_2S + Br_2 \longrightarrow (C_2H_5)_2SBr_2$$

Diethyl sulphide Diethyl sulphide dibromide

(2) **Addition of alkyl halides.** Just as ethers add a molecule of a hydrogen halide forming oxonium derivatives, thioethers form SULPHONIUM DERIVATIVES.



$$\begin{matrix} C_2H_5 \\ C_2H_5 \end{matrix}\!\!>\!S + C_2H_5I \longrightarrow \begin{matrix} C_2H_5 \\ C_2H_5 \end{matrix}\!\!>\!S\!<\!\begin{matrix} C_2H_5 \\ I \end{matrix} \quad \text{or} \quad (C_2H_5)_3\overset{+}{S}\overset{-}{I}$$

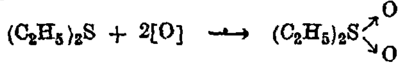
Diethyl sulphide Triethylsulphonium iodide

The sulphonium iodide reacts with moist silver oxide (AgOH) giving triethylsulphonium hydroxide which is a strong base.

(3) **Oxidation reactions.** (*a*) With a mild oxidising agent like hydrogen peroxide, thioethers form SULPHOXIDES.

$$\underset{\text{Diethyl sulphide}}{(C_2H_5)_2S} + [O] \longrightarrow \underset{\text{Diethyl sulphoxide}}{(C_2H_5)_2S{\rightarrow}O}$$

(*b*) On strong oxidation with concentrated nitric acid or permanganate, they form SULPHONES.

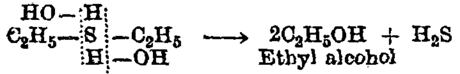


$$(C_2H_5)_2S + 2[O] \longrightarrow (C_2H_5)_2S\begin{matrix} \nearrow O \\ \searrow O \end{matrix}$$

Diethyl sulphide Diethyl sulphone

The sulphones are crystalline compounds and are often used for the characterisation of a liquid thioether.

(4) **Hydrolysis with alkalis.** When boiled with alkali solution, thioethers are hydrolysed forming the parent alcohol and hydrogen sulphide.



$$\begin{matrix} & HO-H & \\ C_2H_5- & S & -C_2H_5 \\ & H-OH & \end{matrix} \longrightarrow 2C_2H_5OH + H_2S$$

Ethyl alcohol

In this respect thioethers resemble esters. The reaction shows that *thioethers are the diesters of hydrogen sulphide*

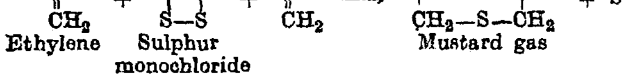
Mustard gas, ββ′- Dichlorodiethyl sulphide, $(ClCH_2.CH_2)_2S$

It was used as a 'poison gas' in the World War of 1914-18. It has a faint mustard-like odour and hence its name.

Preparation. (1) It was originally prepared by the Germans from ethylene through several steps :

$$\underset{\text{Ethylene}}{CH_2:CH_2} \xrightarrow{HOCl} CH_2OH.CH_2Cl \xrightarrow{Na_2S} (CH_2OH.CH_2)_2S \xrightarrow{HCl} \underset{\text{Mustard gas}}{(CH_2Cl.CH_2)_2S}$$

(2) The English and the Americans prepared it by a simpler method by passing ethylene into sulphur monochloride.



$$\begin{matrix} CH_2 \\ \| \\ CH_2 \end{matrix} + \begin{matrix} Cl \;\; Cl \\ |\;\;\;\; | \\ S-S \end{matrix} + \begin{matrix} CH_2 \\ \| \\ CH_2 \end{matrix} \longrightarrow \begin{matrix} CH_2Cl \qquad CH_2Cl \\ | \qquad\qquad | \\ CH_2-S-CH_2 \end{matrix} + S$$

Ethylene Sulphur monochloride Mustard gas

Properties. Mustard gas is not a gas but an oily liquid, b.p. 217°. It however, vaporises when sprinkled by means of bursting shells. It produces painful blisters on the skin and has very destructive effect on the lungs and air passages. It is generally known to have a prolonged action, causing death after about four days.

Chemically mustard gas combines the reactions of an alkyl halide and a thioether.

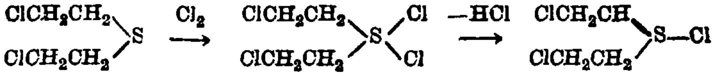
(1) HYDROLYSIS. The chlorine atoms are readily hydrolysed even in aqueous solution.

$$(ClCH_2CH_2)_2S + 2H_2O \longrightarrow (HOCH_2CH_2)_2S + 2HCl$$

(2) OXIDATION. It is easily oxidised with nitric acid and hydrogen peroxide to form the sulphoxide and finally the sulphone.

$$(ClCH_2CH_2)_2S \xrightarrow{+O} \underset{\text{Sulphoxide}}{(ClCH_2CH_2)_2SO} \xrightarrow{+O} \underset{\text{Sulphone}}{(ClCH_2CH_2)_2SO_2}$$

(3) ACTION OF CHLORINE. Chlorine adds to sulphur and then a molecule of HCl is eliminated yielding a product which has no poisonous action.



Since the products of chlorination and oxidation yield non-poisonous substances, the above reactions are employed to destroy mustard gas. The destruction of mustard gas is best accomplished by treating the affected region with free chlorine gas or bleaching powder

QUESTIONS

1. What are mercaptans ? Give their methods of preparation, properties and uses.

2. How are mercaptans prepared ? Give their physical and chemical properties. Describe the preparation of sulphonal and mention its uses.

3. Describe the preparation and reactions of ethyl mercaptan.

4. How are thioalcohols and thioethers prepared ? Illustrate the statement that the chemical behaviour of these compounds is due to the tendency of divalent sulphur to pass to the tetravalent state.

5. How would you prepare sulphonal and what are its chief chemical properties.

6. How is mustard gas prepared ? Discuss its use as a poison gas.

7. (*a*) What are thioalcohols, and how are they generally prepared.?

(*b*) What is the action of the following on thio-ethyl alcohol ?

(*i*) Mercuric chloride,

and (*ii*) Strong Nitric acid. (*Karnatak B.Sc., 1960*)

8. How does nitric acid and hydrogen peroxide respectively react with : (*a*) ethyl mercaptan and (*b*) diethyl sulphide ?

Give the synthesis of sulphonal and mustard gas. (*Gujarat B.Sc., 1960*)

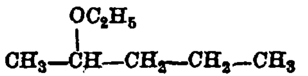
9. Discuss the properties due to — SH in mercaptans. (*Panjab B.Sc. II, 1964*)

10. What are mercaptans ? Discuss the general methods of their preparation, properties and uses. (*Nagpur B.Sc. II, 1964*)

11. What are mercaptans ? Why are they so called ? How would you prepare ethyl mercaptan ? Mention some of its characteristic properties. (*Jabalpur B.Sc., 1964*)

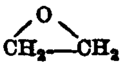
(2) The IUPAC SYSTEM allows symmetrical ethers to retain their common names because these have become too familiar. However, unsymmetrical ethers are assigned systematic names as *Alkoxy* (RO—) derivatives of hydrocarbons. To derive the name of an individual member, the larger of the two alkyl groups linked to oxygen atom determines the name of the parent hydrocarbon. Thus :

$CH_3O-CH_2-CH_2-CH_3$ 1-methoxypropane

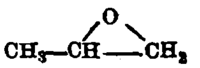


$CH_3-CH(OC_2H_5)-CH_2-CH_2-CH_3$ 2-ethoxypentane

(3) CYCLIC ETHERS formed between oxygen and two adjacent carbon atoms are known as *oxides* or *epoxy compounds*. They are either named as the oxides of the corresponding alkenes or as epoxy derivatives of the alkanes. Thus :



Epoxyethane, Ethylene oxide



1, 2-Epoxypropane, Propylene oxide

ISOMERISM

Ethers display isomerism with monohydric alcohols and also amongst themselves.

(1) **Isomerism with alcohols.** Each ether has one or more isomeric alcohols. Thus :

ETHER	ISOMERIC ALCOHOL
CH_3-O-CH_3 Dimethyl ether	CH_3CH_2OH Ethyl alcohol
$C_2H_5-O-C_2H_5$ Diethyl ether	(*i*) $CH_3CH_2CH_2OH$ 1-Propanol
	(*ii*) $CH_3CHOHCH_3$ 2-Propanol

As we go higher in the series the number of alcohols isomeric with a particular ether goes on increasing. The isomerism between ethers and alcohols is an excellent illustration of *functional isomerism.*

(2) **Isomerism amongst themselves** — *Metamerism.*

In addition to the usual chain isomerism which the ethers may exhibit, they show another type of isomerism due to the different distribution of the carbon atoms about the oxygen atom. Thus a mixed ether may be isomeric with a simple ether. For example, the formula $C_4H_{10}O$ represents the following isomeric ethers.

$C_2H_5-O-C_2H_5$	Dimethyl ether
$CH_3-O-CH_2CH_2CH_3$	Methyl propyl ether

This special type of isomerism which exists amongst the members of the same class of compounds is called **metamerism.** It is not limited to ethers but is also shown by ketones, amines, esters, etc.

METHODS OF FORMATION

Directly or indirectly ethers are always formed from alcohols. They can be obtained by the following general methods.

(1) **Dehydration of alcohols with sulphuric acid.** This method of formation of ethers is of great practical value. Alcohols upon heating with concentrated sulphuric acid lose a molecule of water as follows giving ethers.

$$\underset{\text{Ethyl alcohol}}{2C_2H_5OH} \rightleftharpoons \underset{\text{Diethyl ether}}{(C_2H_5)_2O} + H_2O$$

The H^+ ions furnished by sulphuric acid catalyse the above reaction. Also, the sulphuric acid present removes the water produced during the reactions and thus shifts the equilibrium to the right.

(2) **Passing alcohol vapour over alumina.** In lower primary alcohols the dehydration may be effected by passing the vapours of the alcohol over alumina at 240—260°.

$$\underset{\text{Ethyl alcohol}}{2C_2H_5OH} \longrightarrow \underset{\text{Diethyl ether}}{C_2H_5OC_2H_5} + H_2O$$

The application of this method to secondary and tertiary alcohols is unsatisfactory owing to the marked tendency of these substances to form alkanes under the conditions.

(3) **Action of alkyl halides on alcoholates.** Ethers can be indirectly obtained from alcohols by first converting them to alcoholate and then reacting it with an alkyl halide.

$$2C_2H_5OH + 2Na \longrightarrow \underset{\text{Sod. alcoholate}}{2C_2H_5ONa} + H_2$$

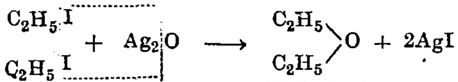
$$C_2H_5O\vdots\underset{\text{Ethyl bromide}}{Na + Br\vdots C_2H_5} \longrightarrow \underset{\text{Diethyl ether}}{C_2H_5OC_2H_5} + NaBr$$

By taking a different halide we can get a mixed ether by this method.

$$C_2H_5O\vdots Na + I\vdots CH_3 \longrightarrow \underset{\text{Ethyl methyl ether}}{C_2H_5OCH_3} + NaI$$

This method of preparing ethers first studied by Williamson is known as *Williamson's synthesis*.

(4) **Heating alkyl with silver oxide.** Simple ethers can be obtained by boiling alkyl halides with DRY silver oxide (Ag₂O). Thus :



$$\begin{matrix} C_2H_5\,I \\ C_2H_5\,I \end{matrix} + Ag_2O \longrightarrow \begin{matrix} C_2H_5 \\ C_2H_5 \end{matrix}\!\!>O + 2AgI$$

Diethyl ether

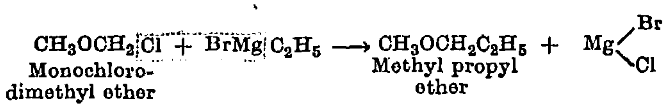
It may be considered a sort of double decomposition taking place between the alkyl halide and silver oxide.

By taking a mixture of two different alkyl halides the method can be used for the formation of mixed ethers.

(5) **Action of a lower halogenated ether with a Grignard reagent.**

This is a good method for preparing higher ethers from lower members. Thus:

$$\underset{\text{Monochloro-dimethyl ether}}{CH_3OCH_2\vdots Cl} + BrMg\vdots C_2H_5 \rightarrow \underset{\text{Methyl propyl ether}}{CH_3OCH_2C_2H_5} + Mg(Br)Cl$$



$$\underset{\text{Monochloro-dimethyl ether}}{CH_3OCH_2Cl} + BrMgC_2H_5 \longrightarrow \underset{\text{Methyl propyl ether}}{CH_3OCH_2C_2H_5} + Mg\begin{matrix} \diagup Br \\ \diagdown Cl \end{matrix}$$

PHYSICAL CHARACTERISTICS

(1) Excepting dimethyl ether and methyl ethyl ether both of which are gases, all ethers are colourless liquids with pleasant odours.

(2) In general lower members of the series are very volatile, their boiling points being considerably lower than those of the alcohols from which they are made.

(3) They are only slightly soluble in water and being lighter form the upper layer when mixed with it. They are, however, freely soluble in organic solvents like chloroform, benzene, etc

Since ethers have no hydrogen attached with oxygen atom, they have no tendency to hydrogen bonding, *Cf.* alcohols that have great tendency to associate. Also the ether molecules are unable to form hydrogen bonds with water molecules unlike alcohols. This accounts for their insolubility in water.

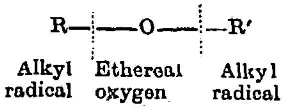
(4) The specific gravities and boiling points show a gradual increase with increase in molecular weight.

NAME OF ETHER	BOILING POINT	SPECIFIC GRAVITY
Dimethyl ether, $CH_3.O.CH_3$	24°	...
Ethyl methyl ether, $CH_3.O.C_2H_5$	7·9°	0·7260 (0°)
Diethyl ether, $C_2H_5.O.C_2H_5$	35°	0·7135 (20°)
Methyl propyl ether, $CH_3.O.C_3H_7$	39°	0·7460
Ethyl propyl ether, $C_2H_5.O.C_3H_7$	61°	0·7546 (0°)
Dipropyl ether, $C_3H_7.OC_3H_7$	91°	0·7360 (20°)

(5) Lower ethers act as anaesthetics.

CHEMICAL CHARACTERISTICS

The chemical behaviour of ethers follows from their structure. They consist of two alkyl radicals linked to an oxygen atom.



$$\underset{\substack{\text{Alkyl}\\\text{radical}}}{R}\text{—}\underset{\substack{\text{Ethereal}\\\text{oxygen}}}{\text{—O—}}\text{—}\underset{\substack{\text{Alkyl}\\\text{radical}}}{R'}$$

(*i*) At the hydrocarbon radicals ethers behave exactly like alkanes, undergoing halogenation.

(*ii*) The *ethereal* oxygen (linked to two carbons) is inert. However, by virtue of its lone pairs, the oxygen atom can extend its valency to 3 or 4, and thus ethers are capable of forming addition compounds with reagents such as mineral acids and oxygen.

(*iii*) Unlike a carbon-to-carbon linkage carbon-to-oxygen linkage is not very stable. Although unaffected under ordinary conditions, ether can be made to react with water, acids, phosphorus pentachloride, etc., when one or both the oxygen bonds are ruptured.

The general reactions of ethers are given below :

(1) **Inertness** Owing to the absence of active groups and multiple bonds from their molecules, ethers are comparatively inert substances. The reagents like ammonia, alkalis, dilute acids, and metallic sodium have no action upon them in cold. They are not readily oxidised or reduced.

(*Substitution Reactions of the Alkyl radicals*)

(2) **Halogenation.** Under suitable conditions chlorine and bromine react upon ethers to form halogenated products. Thus :

$$\underset{\text{Diethyl ether}}{CH_3CH_2OC_2H_5} + Cl_2 \longrightarrow \underset{\alpha\text{-Chlorodiethyl ether}}{CH_3CHClOC_2H_5} + HCl$$

As a rule, halogen tends to substitute first in the α-position.

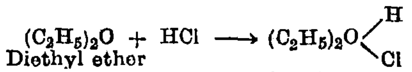
(*Addition Reactions of the O atom*)

(3) **Formation of Peroxides.** In contact with air or ozone, ethers form peroxides.

$$\underset{\text{Diethyl ether}}{(C_2H_5)_2O} + O \longrightarrow \underset{\text{Peroxide}}{(C_2H_5)_2O\rightarrow O}$$

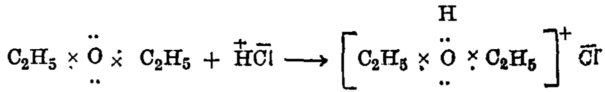
The formation of peroxides is accelerated by ultraviolet light and by the absence of moisture.

(4) **Formation of Oxonium salts.** Ethers unite with strong mineral acids forming salt-like complexes. Thus ·



Oxonium salt

The formation of these derivatives of ethers is analogous to the formation of ammonium salts from ammonia and acids and hence they have been named OXONIUM SALTS.

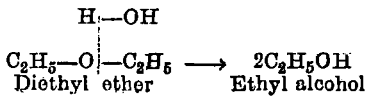


$$\underset{\text{Diethyl ether}}{C_2H_5 \times \overset{\cdot\cdot}{\underset{\cdot\cdot}{O}} \times C_2H_5} + \overset{+}{H}\overset{-}{Cl} \longrightarrow \underset{\text{Oxonium salt}}{\left[C_2H_5 \times \overset{H}{\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}} \times C_2H_5\right]^+} \overset{-}{Cl}$$

Oxonium salts are, in general, stable only at low temperature or in high concentrations of the acids. On dilution they dissociate into the original ether and halogen acid.

(*Decomposition Reactions involving rupture of C-to-O linkages*)

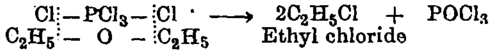
(5) **Hydrolysis**. When boiled with water or treated with steam, ethers are decomposed at one of the oxygen bonds to form alcohols.



$$\underset{\text{Diethyl ether}}{C_2H_5{-}O\overset{H-OH}{|}{-}C_2H_5} \longrightarrow \underset{\text{Ethyl alcohol}}{2C_2H_5OH}$$

The rate of hydrolysis of ethers is accelerated considerably by the presence of acids.

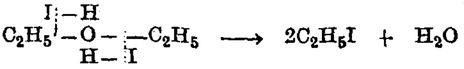
(6) **Action of Phosphorus pentachloride.** With hot phosphorus pentachloride, ethers react with cleavage at both the oxygen bonds forming alkyl chlorides.



$$\begin{array}{l} Cl\,\vdots{-}PCl_3{-}\vdots\,Cl \\ C_2H_5\,\vdots{-}\;O\;{-}\,\vdots\,C_2H_5 \end{array} \longrightarrow \underset{\text{Ethyl chloride}}{2C_2H_5Cl} + POCl_3$$

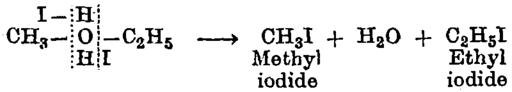
(7) **Action of Halogen acids.** When treated with hydriodic acid in the cold, ethers split to form one molecule of the alcohol and alkyl halide each. However, if the reaction is carried at high temperatures with excess of the halogen acid, simple ethers give an alkyl halide and water. Thus :

$$\underset{\text{Diethyl ether}}{C_2H_5{-}\vdots\,O{-}C_2H_5 + H\,\vdots\,I} \longrightarrow \underset{\text{Ethyl iodide}}{C_2H_5I} + \underset{\text{Ethyl alcohol}}{C_2H_5OH}$$



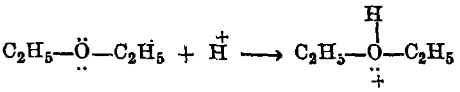
$$C_2H_5\,\vdots{-}\underset{H-\vdots I}{\overset{I\vdots-H}{O}}{-}\vdots{-}C_2H_5 \longrightarrow 2C_2H_5I + H_2O$$

Mixed ethers, on the other hand, react with hot hydriodic acid yielding mixtures of alkyl halides. Thus :



$$CH_3{-}\vdots\underset{\vdots H\vdots I}{\overset{I-\vdots H\vdots}{O}}\vdots{-}C_2H_5 \longrightarrow \underset{\text{Methyl iodide}}{CH_3I} + H_2O + \underset{\text{Ethyl iodide}}{C_2H_5I}$$

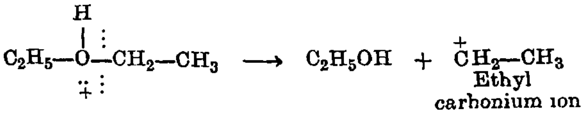
Mechanism. The reaction is believed to proceed through a carbonium ion formation as



$$C_2H_5{-}\ddot{\underset{\cdot\cdot}{O}}{-}C_2H_5 + \overset{+}{H} \longrightarrow \underset{\text{Protonated ether}}{C_2H_5{-}\underset{\overset{\cdot\cdot}{+}}{\overset{H}{\overset{|}{O}}}{-}C_2H_5}$$

Protonated ether

The positive charge on the oxygen atom of the protonated ether induces a small positive charge on the carbon adjacent to it and ultimately the bond cleavage takes place to yield a carbonium ion



$$C_2H_5{-}\underset{\overset{\cdot\cdot}{+}}{\overset{H}{\overset{|}{O}}}\vdots{-}CH_2{-}CH_3 \longrightarrow C_2H_5OH + \underset{\text{Ethyl carbonium ion}}{\overset{+}{C}H_2{-}CH_3}$$

Carbonium ion is susceptible to attack by a nucleophilic reagent ($\bar{I}$)

$$CH_3{-}\overset{+}{C}H_2 + :\overset{\cdot\cdot\,-}{\underset{\cdot\cdot}{I}}: \longrightarrow CH_3CH_2I$$

Ethyl alcohol formed above reacts with excess of HI to form Ethyl iodide.

$$C_2H_5OH + HI \longrightarrow C_2H_5I + H_2O$$

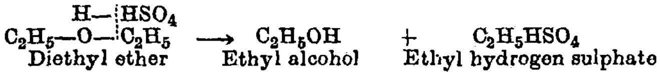
The reaction with hot hydroiodic acid and identification of the products formed, not only enables us to establish the constitution of a given ether, but also affords an excellent method (**Zelisel's method**) for the detection and estimation of alkoxy groups (—OR) in a compound. A known weight of the ether is refluxed with 57% HI (*a constant boiling mixture*). The volatile alkyl iodide thus.

formed is swept away by a stream of CO_2 and the mixture is absorbed in an alcoholic solution of $AgNO_3$. The precipitate of silver iodide formed is filtered, washed, dried and weighed. By the law of equivalents we have

$$—OR \equiv RI \equiv AgI$$

The alkoxyl content (—OR), can be calculated from gravimetric results as usual.

(8) **Action of Sulphuric acid**. Cold concentrated sulphuric acid has no action on ethers except that it dissolves them forming oxonium salts. However, if the solution is heated, the ether is decomposed to yield a molecule of the alcohol and alkyl hydrogen sulphate.



$$\underset{\text{Diethyl ether}}{\overset{H—\vdots HSO_4}{C_2H_5—O—\vdots C_2H_5}} \longrightarrow \underset{\text{Ethyl alcohol}}{C_2H_5OH} + \underset{\text{Ethyl hydrogen sulphate}}{C_2H_5HSO_4}$$

With excess of sulphuric acid, the molecule of alcohol produced also reacts to form alkyl hydrogen sulphate.

USES OF ETHERS

(1) Being characterised by their general inertness, ethers are extensively used as INDIFFERENT SOLVENTS both in the laboratory and commerce.

(2) Lower ethers are employed as GENERAL ANAESTHETICS. Since they produce intense local cooling when sprayed on skin, ethers are also used as LOCAL ANAESTHETICS for minor surgical operations.

(3) The lower ethers are volatile liquids which on evaporation produce low temperatures. They are, therefore, used as REFRIGERANTS.

DIMETHYL ETHER, $(CH_3)_2O$

This is the first member of the series.

Preparation. It may be prepared by any of the general methods already described.

(1) Dimethyl ether can be made by heating methyl alcohol with concentrated sulphuric acid at 140°.

$$\underset{\text{Methyl alcohol}}{2CH_3OH} \rightleftharpoons \underset{\text{Dimethyl ether}}{(CH_3)_2O} + H_2O$$

The equilibrium is turned to the right by volatilisation of the ether produced.

(2) It can also be made by passing vapour of methyl alcohol over a heated catalyst such as thorium oxide or aluminium oxide.

$$\underset{\text{Methyl alcohol}}{2CH_3OH} \rightarrow \underset{\text{Dimethyl ether}}{(CH_3)_2O} + H_2O$$

(3) Dimethyl ether is also formed by the reaction between sodium methylate and methyl iodide.

$$\underset{\text{Sod. methylate}}{CH_3O\vdots Na} + I\vdots CH_3 \longrightarrow \underset{\text{Dimethyl ether}}{CH_3OCH_3} + NaI$$

Properties and Uses. It is a gas at ordinary temperature and pressure. Liquid dimethyl ether boils at −24°. It is very soluble in water, 37 volumes of it dissolving in 1 volume of water at 18°.

It gives all the reactions characteristic of ethers.

Dimethyl ether is largely employed as a refrigerant. When used for the quick freezing of foodstuffs by direct contact, it leaves no taste or odour. It is also used as a low-temperature solvent.

DIETHYL ETHER, ETHER, $(C_2H_5)_2O$

This is the most important representative of this class and is often referred to as simply ETHER. From its method of formation by heating alcohol with sulphuric acid, diethyl ether was at one time named ETHER SULPHURIC.

Preparation. It is prepared in the laboratory and on a large scale by heating ethyl alcohol with concentrated sulphuric acid to 140°C.

$$\underset{\text{Ethyl alcohol}}{2C_2H_5OH} \longrightarrow \underset{\text{Diethyl ether}}{(C_2H_5)_2O} + H_2O$$

The mechanism of the reaction was given by Williamson as follows :

$$\underset{\text{Ethyl alcohol}}{C_2H_5OH} + H_2SO_4 \longrightarrow \underset{\text{Ethyl hydrogen sulphate.}}{C_2H_5HSO_4 + H_2O}$$

$$C_2H_5\underline{\vdots HSO_4 + H\vdots}OC_2H_5 \longrightarrow \underset{\text{Diethyl ether}}{C_2H_5OC_2H_5} + H_2SO_4$$

Since sulphuric acid is not used up in the process, it would appear that a small quantity of the acid is enough to convert unlimited quantity of alcohol into ether. Hence this method of preparation of ether is often referred to as the **Williamson's continuous etherification process.** In actual practice, however, it is found that the process is not continuous and the reaction comes to a stop unless fresh sulphuric acid is added from time to time. This is due to two causes : (1) the water formed during etherification dilutes the concentrated sulphuric acid and (2) a part of sulphuric acid is lost on account of its oxidising action on alcohol, the acid itself being reduced to sulphurous acid.

According to more recent views, H^+ ions furnished by sulphuric acid catalyse the formation of ether from alcohol. The original theory of Williamson postulating the formation of ethyl hydrogen sulphate as intermediate compound has been modified.

Laboratory Preparation. A 500 ml. distillation flask is fitted with a tap funnel and a thermometer. The side-tube of the flask is attached to a long water condenser, the lower end of which is fitted into a filtration flask. The side tube of the filtration flask carries a rubber tubing that leads to the floor. The receiving flask is kept dipping in ice-cold water. The entire apparatus is made leakproof.

100 ml. alcohol is taken in the distillated flask and an equal volume of conc. sulphuric acid is added gradually with shaking and cooling. The flask

is fitted up as shown in Fig. 18·1 and is heated on a sand bath or an asbestos covered wire gauze. When the temperature rises to about 140°, ether begins to distil over. Alcohol is now run in from the tap funnel at the same rate at which ether distils.

Ether obtained in the receiving flask contains alcohol, water at sulphurous acid as impurities. It is first shaken with dilute sodium hydroxide

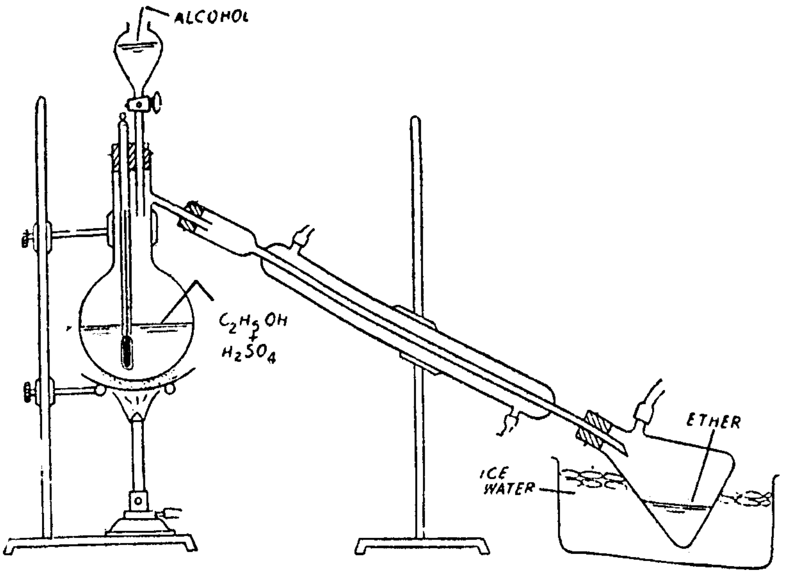


Fig. 18·1. Laboratory preparation of Diethyl ether.

solution which removes sulphurous acid. The ethereal layer is then separated and agitated with a 5% calcium chloride solution. This removes alcohol. The ethereal layer is then separated again and allowed to stand over anhydrous calcium chloride for drying and distilled.

Commercial Method. The plant used for the purpose is shown in Fig. 18·2. This equipment permits the production of an almost unlimited amount

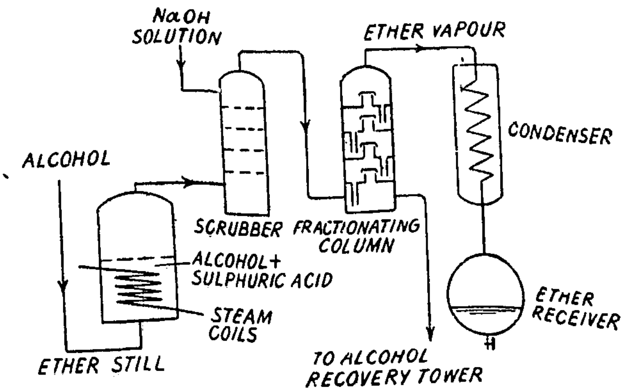


Fig. 18·2. Manufacture of Diethyl ether.

of ether from one charge of the acid. The *ether pot* is charged with conc. sulphuric acid and alcohol is then added to it. The mixture is heated by passing steam through coils. The temperature is maintained at about 140° and alcohol is slowy run into the ether pot. The vapours issuing from the pot consist of ether, alcohol, steam and acid fumes. The latter are removed by passing the vapours through a scrubber down which falls a stream of sodium hydroxide solution. The vapours then pass through a fractionating column where alcohol and water are condensed, while ether vapours escape at the top. Alcohol-water mixture is sent to the alcohol recovery tower. This plant after being charged with sulphuric acid once, can be run continuously for months together.

Properties. It is a colourless highly volatile liquid having a rather pleasant odour and a sweetish burning taste. It boils at 34·6° and has a specific gravity 0·720 at 15°. The vapour of diethyl ether is about two and a half times heavier than air. At 20°, it is soluble in water to the extent of 7 per cent while water dissolves in ether to the extent of 3 per cent at the same temperature. On inhalation its vapours produce general anaesthesia.

The chemical reactions of diethyl ether have already been discussed under the general treatment.

It is highly inflammable and its vapours form explosive mixtures with air. Ether burns with a clear flame :

$$\underset{\text{Diethyl ether}}{C_2H_5OC_2H_5} + 6O_2 \longrightarrow 4CO_2 + 5H_2O$$

Ether dissolves readily in aqueous solution of hydrogen chloride forming oxonium salt.

In contact with air ether forms the peroxide which is highly explosive. Hence, old ether that has been exposed to air for long should never be distilled without the previous removal of peroxide.

Uses. (1) When rapidly evaporated, ether produces intense cooling, and hence its use as a REFRIGERANT. A mixture of ether and dry ice gives a temperature as low as −77°

(2) Mixed with alcohol, it is used as a petrol substitute under the commercial name NATALITE.

(3) Ether is an excellent solvent and is used for extracting organic substances from aqueous solutions. Being immiscible with water the ethereal layer can be easily separated and evaporated to give back the organic substance.

(4) It is an excellent inert medium for many organic reactions such as the Wurtz-Fittig and the Grignard reactions.

(5) Ether is one of the best known anaesthetics. It is superior to chloroform in that it produces loss of consciousness without interfering much with the functions of heart and lungs.

Structure. (1) The molecular formula of ether has been found to be $C_4H_{10}O$.

(2) It does not react with sodium and phosphorus pentachloride in cold. This shows the absence of —OH group.

(3) It reacts with hydriodic acid to yield one molecule of ethyl alcohol and one molecule of ethyl iodide. This proves the presence of two ethyl radicals in its molecule.

(4) Keeping in view the above facts, ether can be represented as

$$C_2H_5-O-C_2H_5$$

(5) The above structure of ether is further supported by the following synthesis

$$\underset{\text{Sod. ethoxide}}{C_2H_5O\boxed{Na + I}} \underset{\text{Ethyl iodide}}{C_2H_5} \longrightarrow C_2H_5.O.C_2H_5 + NaI$$

Diisopropyl ether, $(CH_3)_2CH.O.CH(CH_3)_2$. It is prepared on a technical scale from propene obtained from the cracking stills of petroleum. It is brought in contact with 70 to 85 per cent sulphuric acid at 0°—50° and under pressures of 50 to 500 pounds per square inch when a molecule of water is added.

$$\underset{\text{Propene}}{2CH_3CH=CH_2} + H_2O \longrightarrow \underset{\text{Diisopropyl ether}}{(CH_3)_2CH.O.CH(CH_3)_2}$$

Diisopropyl ether is a colourless liquid boiling at 68·7°. It has a specific gravity of ·7247 at 20°. It is very slightly soluble in water only 0·2 gram per 100 grams. It is inflammable. It gives all the reactions expected of an ether.

Diisopropyl ether is used in many industrial processes in place of diethyl ether. Its higher boiling point and low solubility in water make it superior to diethyl ether as an extracting agent. Mixed with petrol in a 2 : 3 ratio it gives an excellent motor fuel.

β : β′-Dichlorodiethyl ether, $(CH_2Cl.CH_2)_2O$. It is obtained on the commercial scale by the dehydration of ethylene chlorohydrin by treatment with sulphuric acid at 100°.

$$2CH_2Cl.CH_2OH \longrightarrow (CH_2Cl.CH_2)_2O + H_2O$$

It is an excellent solvent and is used for dissolving out olefinic and aromatic impurities from lubricating oils under the name **Chlorex.**

Divinyl ether, $(CH_2=CH)_2O$. It is a typical unsaturated ether. It is prepared by the action of alkali upon dichlorodiethyl ether.

$$\underset{\text{Dichlorodiethyl ether}}{(CH_2Cl.CH_2)_2O} + 2KOH \xrightarrow{heat} \underset{\text{Divinyl ether}}{(CH_2=CH)_2O} + 2KCl + 2H_2O$$

It is highly inflammable liquid boiling at 28·3°. In chemical behaviour it bears a likeness to both ethylene and ether. It has been found to be a better anaesthetic than ether. It is more rapid in producing anaesthesia and recovery therefrom.

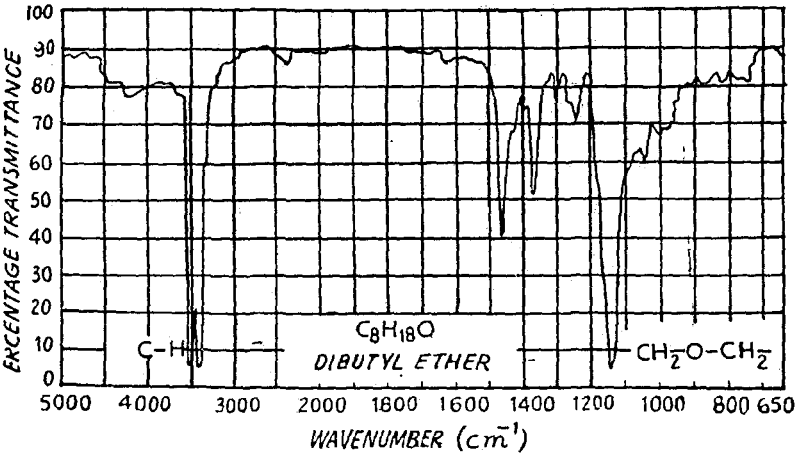


Fig. 18·3. Infrared spectrum of Dibutyl ether.

Infrared spectra of Ethers. Ethers containing $CH_2—O—CH_2$ group in their molecule absorb radiations in the region 1060—1150 cm.$^{-1}$ as is indicated in the Infrared spectrum of Dibutyl ether given above.

COMPARISON OF ETHERS AND ALCOHOLS

As stated earlier, alcohols are monoalkylwaters, while ethers are dialkylwaters,

R—O—H	Alcohol
R—O—R	Ether

Thus alcohols containing OH group react with many reagents just like water, HOH. In ethers, the reactive H atom of the alcohols is replaced by relatively stable alkyl group and thus making them chemically inert. Hence alcohols and ethers give many similar reactions, the latter doing so under more drastic conditions. This may be illustrated by taking example of ethyl alcohol and diethyl ether.

ETHYL ALCOHOL, C_2H_5OH	DIETHYL ETHER, $(C_2H_5)_2O$
Physical Properties :—	
(1) Sweet alcoholic odour.	(1) Pleasant ethereal odour.
(2) Volatile liquid, b.p. 78°.	(2) Volatile liquid, b.p. 35°.
(3) Miscible with water.	(3) Immiscible with water.
Chemical Reactions :—	
(1) Forms alkonium salts with strong acids	(1) Forms oxonium salts.
(2) Question of hydrolysis does not arise.	(2) Hydrolysed to ethanol.
(3) Reacts with *cold* HI to form C_2H_5I, and when heated reduced to ethane.	(3) Forms ethyl iodide and ethanol. When heated gives two molecules of ethyl iodide.
(4) With hot conc. H_2SO_4, gives $C_2H_5HSO_4$ and H_2O.	(4) Gives $C_2H_5HSO_4$ and C_2H_5OH.
(5) With PCl_5 it forms ethyl chloride and HCl.	(5) Forms ethyl chloride (2 molecules).
(6) Reacts with sodium to form C_2H_5ONa and H_2.	(6) No action.
(7) Reacts with acetyl chloride to form ethyl acetate.	(7) No action.
(8) On oxidation yields acetaldehyde.	(8) Not easily oxidised.
(9) Reacts with chlorine by oxidation and by substitution to form chloral.	(9) Undergoes chlorination to give polyhalogen derivatives

The physical properties of ethyl alcohol and ether, and reactions (5), (6), (7) and (8) may be used as tests for distinguishing one from the other.

QUESTIONS

1. What are ethers ? How they differ from metallic oxides ?

2. Give the general methods of formation and properties of ethers.

3. How is diethyl ether prepared ? How and under what conditions does it react with (*a*) hydriodic acid, (*b*) bromine, and (*c*) phosphorus pentachloride ?

4. Describe how diethyl ether may be prepared from ethyl alcohol. Outline the evidence which establishes the constitutional formula of this compound.

5. Ethyl alcohol and dimethyl ether have the same formula C_2H_6O. How would you ascertain structural formula of each ? Describe the action of H_2SO_4 on ethyl alcohol.

6. How is divinyl ether prepared ? Why is it considered a better anaesthetic than ether ?

7. Write the formulae of the various ethers having the empirical formula $C_5H_{12}O$. State how would you prepare only one of the isomerides and outline a method for the preparation of the necessary alcohol. (*Nagpur B.Sc., 1957*)

8. How is pure diethyl ether prepared in the laboratory ? What is its action on (*a*) sodium, (*b*) phosphorus pentachloride in the cold and in the hot, (*c*) hydriodic acid.

Two compounds *A* and *B* have the molecular formula C_3H_8O. *A* reacted with hydriodic acid to give C_3H_7I. *B* reacted with hydriodic acid to give methyl iodide as one of the products. Deduce the probable structure of *A* and *B*. (*Rangoon Univ., 1958*)

9. Describe the preparation and purification of diethyl ether by the continuous process. State its properties and uses. How has the structure of diethyl ether been ascertained ? What are mixed ethers ? Give examples. (*Calcutta B.Sc., 1963*)

10. How is diethyl ether prepared ? Give its properties and uses. (*Marthwada B.Sc. II, 1963*)

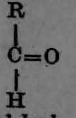
11. How is pure diethyl ether prepared ? State its important properties. How has the structure of diethyl ether been ascertained ? (*Udaipur B.Sc., 1969*)

19

Aldehydes and Ketones

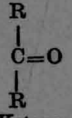
CHARLES FRIEDEL
(1832—1899, French)
Worked on aldehydes and ketones and discovered isopropyl alcohol. Performed the synthesis of glycerol from acetone. Best known in connection with the Friedel-Crafts reaction.

Aldehydes and ketones are two important classes of compounds which bear a marked structural similarity. Both types of compounds contain the carbonyl group >CO. In aldehydes the >CO group is linked to an alkyl radical and a hydrogen atom, while in ketones it is united with two alkyl radicals.



$$\begin{array}{c} R \\ | \\ C{=}O \\ | \\ H \end{array}$$

Aldehyde



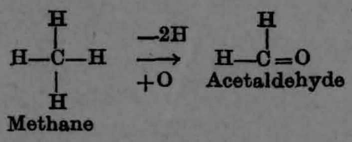
$$\begin{array}{c} R \\ | \\ C{=}O \\ | \\ R \end{array}$$

Ketone

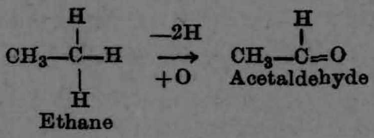
These compounds resemble greatly in their methods of formation and chemical behaviour and, therefore, have been included in the same chapter.

1. ALDEHYDES

They are derivatives of hydrocarbons in which the two hydrogen atoms linked to a carbon at the end of the chain have been replaced by a bivalent oxygen.

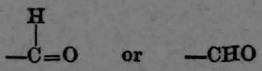


$$\underset{\text{Methane}}{\mathrm{H{-}\overset{\displaystyle H}{\underset{\displaystyle H}{C}}{-}H}} \xrightarrow[+\mathrm{O}]{-2\mathrm{H}} \underset{\text{Acetaldehyde}}{\mathrm{H{-}\overset{\displaystyle H}{C}{=}O}}$$



$$\underset{\text{Ethane}}{\mathrm{CH_3{-}\overset{\displaystyle H}{\underset{\displaystyle H}{C}}{-}H}} \xrightarrow[+\mathrm{O}]{-2\mathrm{H}} \underset{\text{Acetaldehyde}}{\mathrm{CH_3{-}\overset{\displaystyle H}{C}{=}O}}$$

Thus we get a class of compounds characterised by the presence of a



$$\mathrm{{-}\overset{\displaystyle H}{C}{=}O} \quad \text{or} \quad \mathrm{{-}CHO}$$

group which is called the *aldehyde group*. Aldehydes could also be derived from hydrocarbons by substituting a $-\mathrm{CHO}$ group for a hydrogen atom at the end of the carbon chain. Thus :

$$\underset{\text{Methane}}{\mathrm{CH_4}} \xrightarrow[+\mathrm{CHO}]{-\mathrm{H}} \underset{\text{Acetaldehyde}}{\mathrm{CH_3CHO}}$$

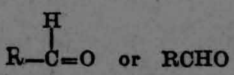
This derivation is obviously faulty as the first member of the series formaldehyde would then be a derivative of hydrogen (H_2) rather than of a hydrocarbon.

The oxidation of a primary alcohol gives an aldehyde which undergoes further oxidation to yield acids.

$$\underset{\text{Ethyl alcohol}}{\mathrm{CH_3CH_2OH}} \xrightarrow{-2\mathrm{H}} \underset{\text{Acetaldehyde}}{\mathrm{CH_3CHO}} \xrightarrow{+\mathrm{O}} \underset{\text{Acetic acid}}{\mathrm{CH_3COOH}}$$

Thus aldehydes are spoken of as the *first oxidation products of primary alcohols*. This is how the name aldehyde arose from *alcohol dehydrogenatum* which means that aldehydes are derived by the dehydrogenation of alcohols.

The general formula for the homologous series of aldehydes may be written as $C_nH_{2n}O$. The type formula for this class is



$$\mathrm{R{-}\overset{\displaystyle H}{C}{=}O} \quad \text{or} \quad \mathrm{RCHO}$$

NOMENCLATURE

(1) The COMMON NAME. Aldehydes take their common names from the carboxylic acids they form on oxidation. The portion -oic *acid* of the name of the corresponding acid is replaced by the suffix -aldehyde *e.g.*,

Acetic acid — *ic acid* + *aldehyde* ⟶ Acetaldehyde

Thus :

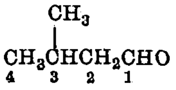
FORMULA	COMMON NAME
$HCHO$	Formaldehyde
CH_3CHO	Acetaldehyde
CH_3CH_2CHO	Propionaldehyde
$CH_3CH_2CH_2CHO$	Butyraldehyde (n-Butyraldehyde)
$CH_3CH_2CH_2CH_2CHO$	Valeraldehyde (n-Valeraldehyde)

In present practice the prefix n- formerly used in the name of normal (straight chain) aldehydes is dropped. The name of an aldehyde (without n-) implies that it is a straight chain aldehyde.

(2) According to IUPAC SYSTEM the name of an individual aldehydes is derived by dropping the terminal '*e*' of the name of the corresponding alkane (containing same number of C—atoms) and adding the suffix '*al*'. Thus :

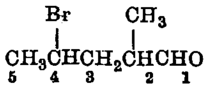
FORMULA	IUPAC NAME
$HCHO$	Methanal, Formaldehyde
CH_3CHO	Ethanal, Acetaldehyde
CH_3CH_2CHO	Propanal
$CH_3CH_2CH_2CHO$	Butanal

While naming complex aldehydes the longest carbon chain including the —CH=O (formyl group) is selected as the parent chain. The carbon atom of the formyl group is numbered 1, and other substituents on the chain are assigned positions and named in the usual fashion. Since the —CHO group is always at the end of the chain at C1, it is unnecessary to specify its position in the systematic name. Thus :



$$\underset{4}{CH_3}\underset{3}{\overset{\overset{CH_3}{|}}{C}H}\underset{2}{CH_2}\underset{1}{CHO}$$

3-Methylbutanal



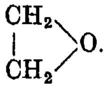
$$\underset{5}{CH_3}\underset{4}{\overset{\overset{Br}{|}}{C}H}\underset{3}{CH_2}\underset{2}{\overset{\overset{CH_3}{|}}{C}H}\underset{1}{CHO}$$

4-Bromo-2-methylpentanal

ISOMERISM

Aldehydes exhibit chain isomerism. They also show functional isomerism with ketones. Thus propanal, CH_3CH_2CHO, is isomeric with acetone, CH_3COCH_3.

Aldehydes exhibit functional isomerism with cyclic ethers.

Thus acetaldehyde is isomeric with ethylene oxide .

METHODS OF FORMATION

The following general methods are available for the preparation of aldehydes.

(1) **Direct oxidation of primary alcohols.** Primary alcohols on oxidation by heating with sodium dichromate and sulphuric acid form the corresponding aldehydes.

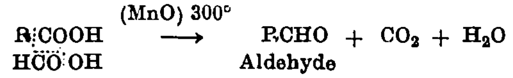
$$\underset{\text{Alcohol}}{CH_3CH_2OH} + O \longrightarrow \underset{\text{Acetaldehyde}}{CH_3CHO} + H_2O$$

Since aldehydes have lower boiling points than the corresponding alcohols, they escape from the hot oxidising mixture and are thus saved from further oxidation. The above reaction is also carried by passing the vapours of an aldehyde mixed with air over a heated silver catalyst.

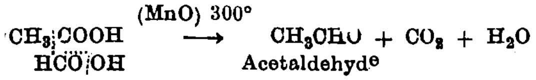
(2) **Catalytic dehydrogenation of primary alcohols.** When vapours of a primary alcohol are passed over a suitable catalyst like reduced copper or silver at high temperature, the alcohol is dehydrogenated to form an aldehyde.

$$\underset{\text{Ethyl alcohol}}{CH_3CH_2OH} \xrightarrow[250^\circ]{\text{Cat.}} \underset{\text{Acetaldehyde}}{CH_3CHO} + H_2$$

(3) By passing vapours of a mixture of formic acid with another fatty acid, over manganous oxide at 300°.

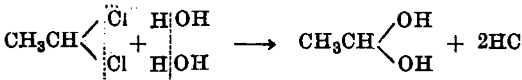


$$\begin{matrix} R\vdots COOH \\ HCO\vdots OH \end{matrix} \xrightarrow{(MnO)\ 300^\circ} \underset{\text{Aldehyde}}{RCHO} + CO_2 + H_2O$$



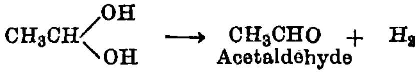
$$\begin{matrix} CH_3\vdots COOH \\ HCO\vdots OH \end{matrix} \xrightarrow{(MnO)\ 300^\circ} \underset{\text{Acetaldehyde}}{CH_3CHO} + CO_2 + H_2O$$

(4) **Hydrolysis of dihalogen derivatives.** The dihalogen derivatives containing the groups $—CHCl_2$ or $—CHBr_2$ upon hydrolysis with a mild alkali (*baryta*, or aqueous suspension of lead monoxide) yield aldehydes. Thus :



$$CH_3CH\begin{matrix} Cl \\ Cl \end{matrix} + \begin{matrix} H\vdots OH \\ H\vdots OH \end{matrix} \longrightarrow CH_3CH\begin{matrix} OH \\ OH \end{matrix} + 2HCl$$

Ethylidene chloride (*Unstable*)



$$CH_3CH\begin{matrix} OH \\ OH \end{matrix} \longrightarrow \underset{\text{Acetaldehyde}}{CH_3CHO} + H_2O$$

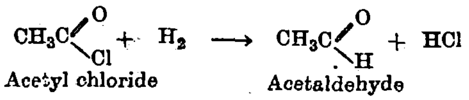
This method is not very useful in as much as these dihalides are generally prepared from the aldehydes themselves.

(5) **Distillation of the calcium salt of a fatty acid with calcium formate.** Aldehydes can be prepared by the dry distillation of equimolecular mixture of the calcium salt of a carboxylic acid with calcium formate.

$$\underset{\text{Calcium acetate}}{CH_3COOCa/2} + \underset{\text{Calcium formate}}{HCOOCa/2} \longrightarrow \underset{\text{Acetaldehyde}}{CH_3CHO} + CaCO_3$$

This method permits the preparation of aldehydes from carboxylic acids which cannot be reduced directly.

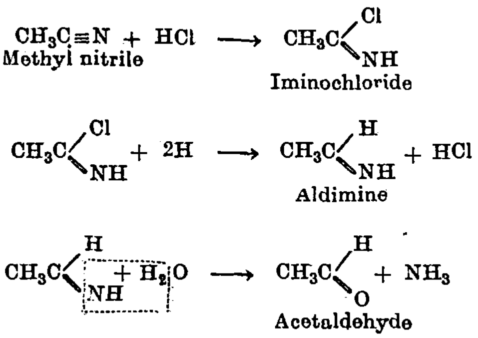
(6) **Reduction of acid chlorides.** Acid chlorides can be reduced with hydrogen in the presence of palladium or platinum as catalyst (*Rosenmund's method*).



$$\underset{\text{Acetyl chloride}}{CH_3C\begin{smallmatrix}\diagup O\\ \diagdown Cl\end{smallmatrix}} + H_2 \longrightarrow \underset{\text{Acetaldehyde}}{CH_3C\begin{smallmatrix}\diagup O\\ \diagdown H\end{smallmatrix}} + HCl$$

This method is quite useful since carboxylic acids are readily accessible compounds.

(7) **From nitriles by Stephen's Reaction.** When an alkyl nitrile is treated with hydrochloric acid gas an iminochloride is formed which on reduction with stannous chloride and subsequent hydrolysis forms an aldehyde.

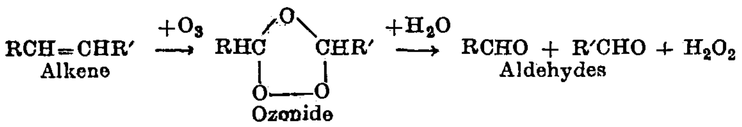


$$\underset{\text{Methyl nitrile}}{CH_3C{\equiv}N} + HCl \longrightarrow \underset{\text{Iminochloride}}{CH_3C\begin{smallmatrix}\diagup Cl\\ \diagdown NH\end{smallmatrix}}$$

$$CH_3C\begin{smallmatrix}\diagup Cl\\ \diagdown NH\end{smallmatrix} + 2H \longrightarrow \underset{\text{Aldimine}}{CH_3C\begin{smallmatrix}\diagup H\\ \diagdown NH\end{smallmatrix}} + HCl$$

$$CH_3C\begin{smallmatrix}\diagup H\\ \diagdown NH\end{smallmatrix} + H_2O \longrightarrow \underset{\text{Acetaldehyde}}{CH_3C\begin{smallmatrix}\diagup H\\ \diagdown O\end{smallmatrix}} + NH_3$$

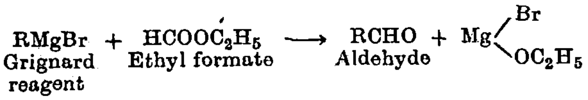
(8) **Ozonolysis of alkene compounds.** Alkene compounds containing the grouping RCH : combine with ozone to form the ozonide which on subsequent hydrolysis yields aldehydes. Thus :



$$\underset{\text{Alkene}}{RCH{=}CHR'} \xrightarrow{+O_3} \underset{\text{Ozonide}}{RHC\overset{O}{\frown}CHR' \;(O{-}O)} \xrightarrow{+H_2O} \underset{\text{Aldehydes}}{RCHO + R'CHO} + H_2O_2$$

Zinc dust is added to destroy H_2O_2 and thus prevent further oxidation of the aldehydes formed.

(9) **From Grignard reagents.** Aldehydes may be prepared by allowing an excess of formic ester to interact with a Grignard reagent.



$$\underset{\text{Grignard reagent}}{RMgBr} + \underset{\text{Ethyl formate}}{HCOOC_2H_5} \longrightarrow \underset{\text{Aldehyde}}{RCHO} + Mg\begin{smallmatrix}\diagup Br\\ \diagdown OC_2H_5\end{smallmatrix}$$

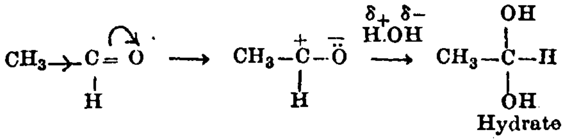
PHYSICAL CHARACTERISTICS

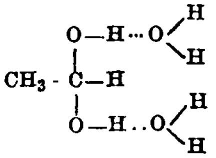
(1) Formaldehyde the first member of the aldehyde series, is gas at ordinary temperature while acetaldehyde boils at 21°. The next nine members of the straight-chain series are liquids and the higher members are solids.

(2) As a rule, aldehydes possess an unpleasant odour but as we go up the series the smell becomes more and more fruity so much so that the compounds containing 8 to 13 carbon atoms are used in perfumery.

(3) The first few members are freely miscible with water, solubility falls rapidly with increase of molecular weight and the higher aldehydes are completely insoluble.

Solubility of acetaldehyde in water is explained by saying that it forms an unstable hydrate with water which in turn forms hydrogen bonds with more water molecules. The mechanism is as follows :



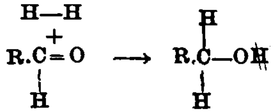


(4) Their boiling points and specific gravities show a regular increase as we ascend the series.

ALDEHYDE	B.P. °C	SP. GR.
Formaldehyde, HCHO	-21	0·815 at —20°
Acetaldehyde, CH_3CHO	$+20·3$	0·783 at 18°
Propionaldehyde, C_2H_5CHO	49·3	0·807 at 20°
n-Butyraldehyde, C_3H_7CHO	75·7	0·817 at 20°
n-Valeraldehyde, C_4H_9CHO	103·4	0·819 at 11°
n-Caproic aldehyde, $C_5H_{11}CHO$	130	0·819 at 15°

CHEMICAL CHARACTERISTICS

Chemically, aldehydes form one of the most reactive classes of organic compounds. As indicated by the type formula

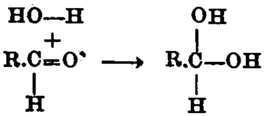


$$\begin{array}{c}H-H\\+\\R.C=O\\|\\H\end{array}\longrightarrow\begin{array}{c}H\\|\\R.C-OH\\|\\H\end{array}$$

Aldehyde Primary alcohol

Aldehydes may also be reduced with chemical reducing agents such as sodium amalgam and dilute acids, or a metal and acid.

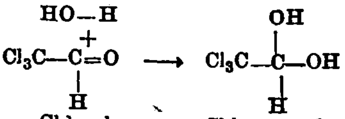
(*ii*) ADDITION OF WATER.



$$\begin{array}{c}HO-H\\+\\R.C=O\\|\\H\end{array}\longrightarrow\begin{array}{c}OH\\|\\R.C-OH\\|\\H\end{array}$$

Aldehyde Hydrate

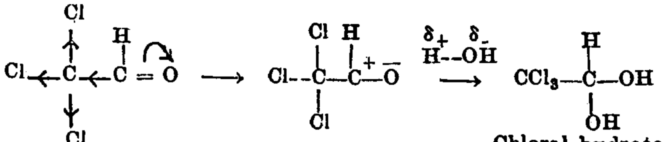
In most cases, the dihydroxy compound is too unstable to be isolated. However, the aldehydes which contain at least two halogen atoms linked to the carbon adjacent to the CHO group yield stable hydrates.



$$\begin{array}{c}HO-H\\+\\Cl_3C-C=O\\|\\H\end{array}\longrightarrow\begin{array}{c}OH\\|\\Cl_3C-C-OH\\|\\H\end{array}$$

Chloral Chloral hydrate

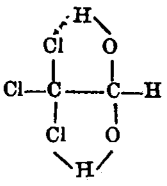
Chloral hydrate, though having two —OH groups on C-atom, is unusually stable owing to the electron withdrawing properties of the three chlorine atoms. This makes possible for the formation of intramolecular hydrogen bonding and hence the molecule becomes quite stable.



$$\begin{array}{c}Cl\\\uparrow\\Cl\leftarrow C\leftarrow\overset{H}{\overset{|}{C}}=O\\\downarrow\\Cl\end{array}\longrightarrow\begin{array}{c}Cl\quad H\\|\quad\ |\\Cl-C-\overset{+}{C}-\overset{-}{O}\\|\\Cl\end{array}\xrightarrow{\overset{\delta+\ \ \delta-}{H--OH}}\begin{array}{c}H\\|\\CCl_3-C-OH\\|\\OH\end{array}$$

I II Chloral hydrate III

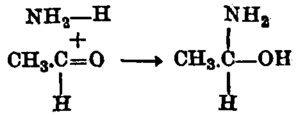
The -atom in compound II is highly positive.



(Intramolecular H-Bonding)

Aldehydes add alcohols much in the same way as they do in water.

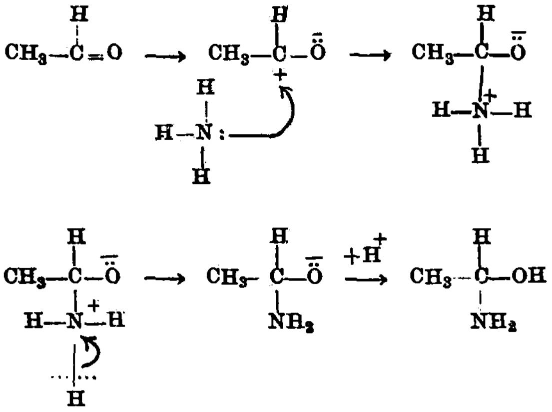
(*iii*) ADDITION OF AMMONIA. When an aldehyde dissolved in ether is treated with gaseous ammonia, addition compound known as **aldehyde ammonia** is precipitated.



$$\mathrm{CH_3.}\underset{\mathrm{H}}{\underset{|}{\mathrm{C}}}\mathrm{{=}O} + \mathrm{NH_2{-}H} \longrightarrow \mathrm{CH_3.}\overset{\mathrm{NH_2}}{\overset{|}{\underset{\mathrm{H}}{\underset{|}{\mathrm{C}}}}}\mathrm{{-}OH}$$

Acetaldehyde Acetaldehyde ammonia

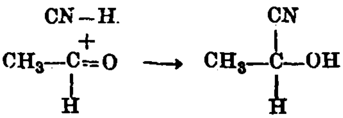
Mechanism :



Formaldehyde, however, does not form an aldehyde ammonia.

The aldehyde ammonias when heated with dilute acids, regenerate the aldehydes. Thus the formation and decomposition of these compounds is used for the isolation of aldehydes.

(*iv*) ADDITION OF HYDROGEN CYANIDE. Hydrogen cyanide in the presence of a trace of KCN reacts with aldehydes to form addition compounds containing a cyanogen radical and a hydroxy group. These are named **cyanohydrins** or HYDROXYNITRILES.



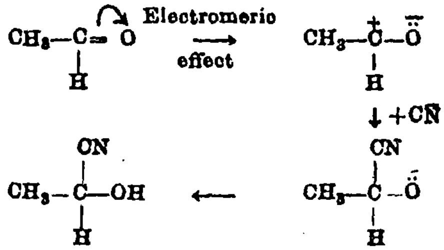
$$\mathrm{CH_3{-}}\underset{\mathrm{H}}{\underset{|}{\mathrm{C}}}\mathrm{{=}O} + \mathrm{CN{-}H} \longrightarrow \mathrm{CH_3{-}}\overset{\mathrm{CN}}{\overset{|}{\underset{\mathrm{H}}{\underset{|}{\mathrm{C}}}}}\mathrm{{-}OH}$$

Acetaldehyde Acetaldehyde cyanohydrin

Mechanism. The reaction is initiated by the electrophilic cyanide ions (CN^-) furnished by the HCN which is a weak acid.

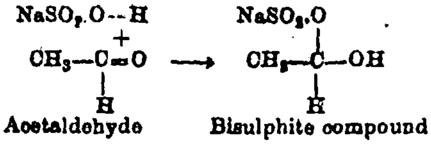
$$HCN \rightleftharpoons H^+ + CN^-$$

The forward reaction is catalysed by a base and thus the concentration of cyanide ions is increased.



On hydrolysis with dilute acids the CN group is converted to COOH group and hence it affords a convenient method for the preparation of hydroxy acids.

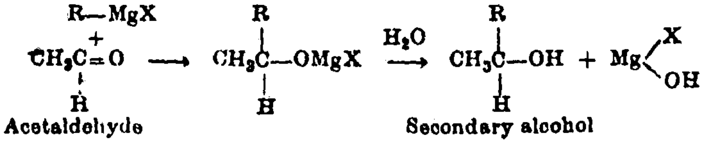
(*v*) ADDITION OF SODIUM BISULPHITE. Aldehydes react with sodium bisulphite, $NaHSO_3$, to form crystalline compounds known as the **bisulphite compounds**



These compounds are soluble in water but insoluble in saturated solution of sodium bisulphite. Thus, the reaction is carried by shaking the aldehyde with a saturated sodium bisulphite solution when the *aldehyde bisulphite compound* is thrown out.

Since the bisulphite compounds are decomposed by warming with dilute alkalis or acids to give back the original aldehydes, the reaction may be used for the separation and purification of aldehydes.

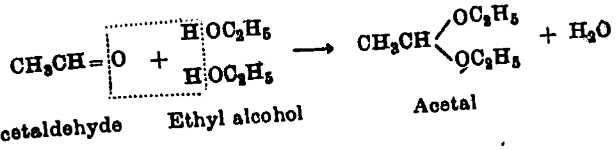
(*vi*) ADDITION OF GRIGNARD REAGENTS. Aldehydes form addition compounds with alkyl magnesium halides which upon hydrolysis yield secondary alcohols.



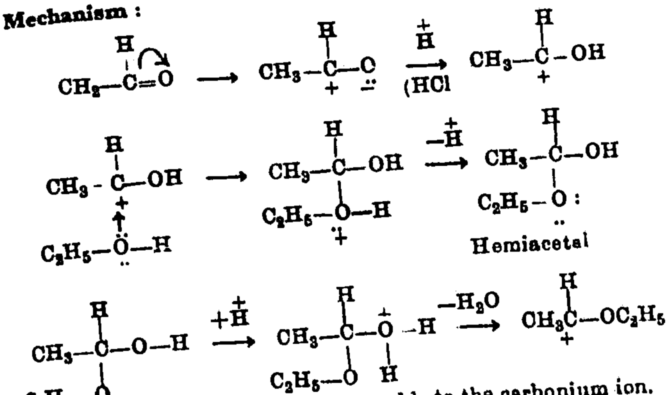
Formaldehyde reacts with a Grignard reagent to form a primary alcohol

(3) **Replacement reactions of the carbonyl group.** Aldehydes react with many reagents to form products in which the oxygen of the carbonyl group is replaced by a bivalent group or two monovalent atoms. These reactions are most often accompanied by the elimination of a molecule of water.

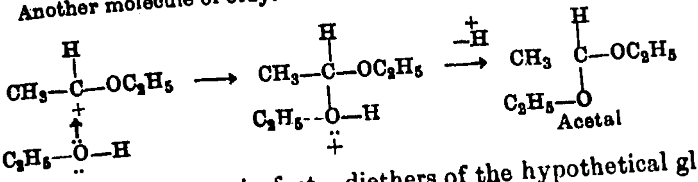
(*i*) REACTION WITH ALCOHOLS. Aldehydes react with alcohols in the presence of hydrogen chloride gas forming **acetals**.



Mechanism :



Another molecule of ethyl alcohol adds to the carbonium ion.



The acetals are, in fact, diethers of the hypothetical glycols having two OH groups linked to the same carbon.

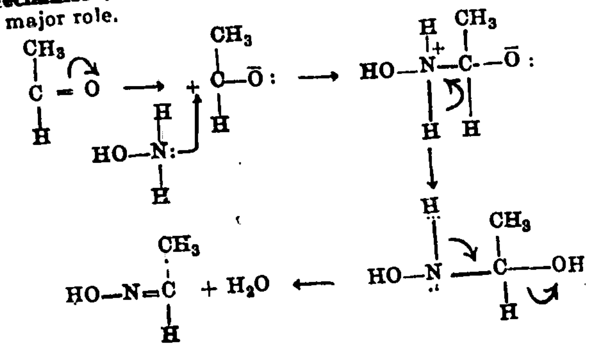
(*ii*) REACTION WITH HYDROXYLAMINE. Aldehydes react readily with hydroxylamine, NH_2OH, to form products called **Aldoximes**.

$$CH_3CH{=}O + H_2NOH \longrightarrow CH_3CH{=}NOH + H_2O$$

Acetaldehyde Acetaldoxime

Since the oximes are well-defined crystalline substances, their formation affords a good method of identifying aldehydes.

Mechanism. In this reaction the basic N-atom (having a long pair) plays the major role.



Acetaldoxime

This mechanism can also be applied to reactions (*ii*), (*iii*) and (*iv*) given below :

(*iii*) REACTION WITH PHENYLHYDRAZINE. Aldehydes react with phenylhydrazine. $H_2N.NHPh$, yielding crystalline **phenylhydrazones.**

$$CH_3CH{=}O + H_2N.NHPh \longrightarrow CH_3CH{=}N.NHPh + H_2O$$

Acetaldehyde Phenylhydrazine Acetaldehyde phenylhydrazone

Phenylhydrazones are crystalline compounds with characteristic melting points. Thus the formation of these compounds is usually employed for the identification of aldehydes.

(*iv*) REACTION WITH SEMICARBAZIDE. Like phenylhydrazine, semicarbazide, $NH_2.CO.NH.NH_2$ reacts with an aldehyde giving a well defined crystalline compound called **semicarbazone.** Thus :

$$CH_3CH{=}O + H_2N.NH.CO.NH_2 \longrightarrow CH_3CH{:}N.NH.CO.NH_2 + H_2O$$

Acetaldehyde Semicarbazide Acetaldehyde semicarbazone

Semicarbazide is a valuable analytical reagent for the identification of aldehydes.

(*v*) REACTION WITH PHOSPHORUS PENTACHLORIDE. Aldehydes react with phosphorus pentachloride forming dichloro derivatives, the oxygen of the carbonyl group having been replaced by two chloride atoms. Thus :

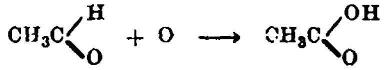
$$CH_3CH{=}O + Cl_3PCl_2 \longrightarrow CH_3CHCl_2 + POCl_3$$

Acetaldehyde Ethylidene chloride

This is a useful method for preparing halogen compounds in which both the halogen atoms are united to the same carbon.

(4) **Reactions due to the H atom of CHO group** The solitary hydrogen in aldehydes is extremely reactive and is easily changed to OH group. Thus, while aldehydes are capable of oxidation, they can extract oxygen from the reagents which would be consequently reduced.

(*i*) OXIDATION OF ALDEHYDES. Aldehydes can be readily oxidised to an acid containing the same number of carbon atoms.

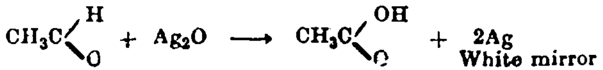


$$CH_3C\begin{matrix}\diagup H\\ \diagdown O\end{matrix} + O \longrightarrow CH_3C\begin{matrix}\diagup OH\\ \diagdown O\end{matrix}$$

Acetaldehyde Acetic acid

The oxidising agent commonly used is sodium dichromate and sulphuric acid.

(*ii*) REACTION WITH AMMONIACAL SILVER NITRATE. Silver oxide (Ag_2O) dissolved in ammonia (*ammoniacal silver nitrate*) is a mild oxidising agent When warmed with an aldehyde it is reduced to metallic silver which is precipitated as a mirror on the walls of the containing vessel.



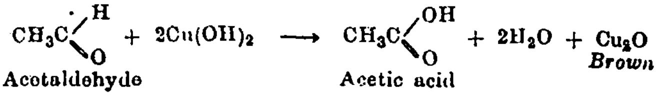
$$CH_3C\begin{matrix}\diagup H\\ \diagdown O\end{matrix} + Ag_2O \longrightarrow CH_3C\begin{matrix}\diagup OH\\ \diagdown O\end{matrix} + 2Ag$$

White mirror

Acetaldehyde Acetic acid

This is one of the tests commonly used for the detection of aldehyde group in organic compounds.

(*iii*) REACTION WITH FEHLING'S SOLUTION. Aldehydes also reduce cupric to cuprous salts. Thus an alkaline solution of copper hydroxide which contains sodium potassium tartarate to prevent its precipitation (*Fehling Solution*), when warmed with an aldehyde forms a reddish brown precipitate of cuprous oxide.



$$CH_3C{\overset{H}{\underset{O}{\lessgtr}}} + 2Cu(OH)_2 \longrightarrow CH_3C{\overset{OH}{\underset{O}{\lessgtr}}} + 2H_2O + Cu_2O$$

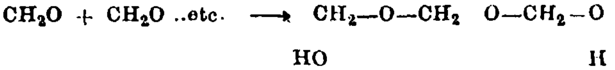
Acetaldehyde Acetic acid *Brown*

This is an excellent test to detect the presence of an aldehyde

(5) **Other reactions of aldehydes :**

(*i*) POLYMERISATION. The lower aldehydes show a marked tendency to polymerise forming compounds in which several molecules are linked together through oxygen. Thus:

(*a*) Formaldehyde on evaporation forms *paraformaldehyde*

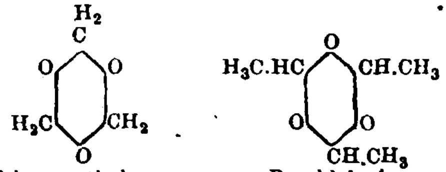


$$CH_2O + CH_2O \text{ ..etc.} \longrightarrow \underset{HO}{CH_2}{-}O{-}CH_2\ \ O{-}CH_2{-}\underset{H}{O}$$

Paraformaldehyde

In paraformaldehyde the number of formaldehyde units that have combined varies between 6 and 100, and the end valencies are probably hydrated as shown.

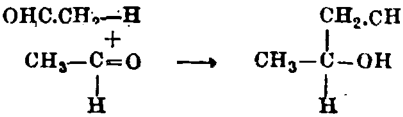
(*b*) Formaldehyde and acetaldehyde in contact with sulphuric acid yield cyclic *trimers*.



Trioxymethylene Paraldehyde

When any of the polymers described above is treated with a trace of acid and distilled, it depolymerises back to the original aldehyde.

(*ii*) ALDOL CONDENSATION. In the presence of a mild alkali, two molecules of an aldehyde unite to produce a molecule of **aldol**, which is both an aldehyde and an alcohol. Thus :

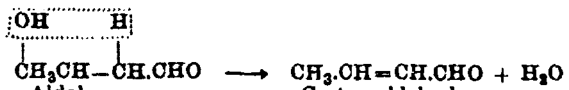


$$\begin{matrix} OHC.CH_2{-}H \\ + \\ CH_3{-}\underset{H}{\underset{|}{C}}{=}O \end{matrix} \longrightarrow CH_3{-}\overset{CH_2.CHO}{\overset{|}{\underset{H}{\underset{|}{C}}}}{-}OH$$

Acetaldehyde Aldol

This special type of condensation encountered in aldehydes is called

Aldol condensation. If heated with a dehydrating agent, the aldol molecule loses a molecule of water yielding an alkene-aldehyde.



$$CH_3\overset{OH}{CH}-\overset{H}{CH}.CHO \longrightarrow CH_3.CH{=}CH.CHO + H_2O$$

Aldol Crotomaldehyde

'Mixed aldols' are produced by the condensation of one aldehyde with another aldehyde. Thus :

$$\underset{\text{Formaldehyde}}{CH_2O} + \underset{\text{Acetaldehyde}}{CH_3CHO} \longrightarrow \underset{\text{Mixed aldol}}{CH_2(OH)CH_2CHO}$$

The mechanism of aldol condensation has already been discussed under 'Condensation'.

(*iii*) RESINIFICATION. When heated with a concentrated alkali-solution, aldehydes form dark coloured resinous products called **aldehyde resins** Thus :

$$\underset{\text{Acetaldehyde}}{nCH_3CHO} \longrightarrow \underset{\text{Resin}}{(CH_3CHO)_n}$$

where n is very large. This reaction is given by all aliphatic aldehydes except formaldehyde.

(*iv*) SCHIFF'S REACTION. The red dye *magenta* when treated with sulphur dioxide is converted to a colourless substance. The decolorised solution of the dye is called *Schiff's reagent*. When an aldehyde is added to Schiff's reagent, it restores the intense red colour of the original dye. This constitutes the well-known **Schiff's test** for the detection of aldehydes.

TESTS FOR ALDEHYDES

(1) *Aldehyde resin test.* Aldehydes when warmed with a concentrated alkali solution form dark coloured resins which rise to the surface. Formaldehyde fails to give this test.

(2) *Schiff's test.* When a dilute solution of aldehyde is added to magenta solution decolorised by sulphur dioxide, the intense red colour of the original dye is restored.

(3) *Formation of Bisulphite Compounds.* On adding 1-2 ml. of a cold saturated solution of sodium bisulphite to about the same volume of aldehyde and shaking a crystalline aldehyde sodium bisulphite compound separates.

(4) *Formation of Phenylhydrazone.* The calculated quantities of the aldehyde (0·5 ml.), phenylhydrazine hydrochloride (0·2 gm.), and sodium acetate (0·5 gm.) are dissolved in water (10 mls.) and warmed on water bath. An oily substance is produced.

(5) *Silver mirror test.* Ammonium hydroxide is added dropwise to a ten per cent solution of silver nitrate. When the precipitate first formed has dissolved, the solution is warmed with a little aldehyde solution A shining silver mirror is deposited on the inner wall of the test-tube.

(6) *Fehling's solution test.* A little dilute solution of the aldehyde is added to Fehling's solution taken in a test tube. A reddish brown precipitate of cuprous oxide is thrown down.

(7) *Nitroprusside test.* Aldehydes produce a red colour with an alkaline nitroprusside solution. This test is given by formaldehyde.

INDIVIDUAL ALDEHYDES

FORMALDEHYDE, METHANAL, H.CH:O

It is the first member of the homologous series of aldehydes. Traces of formaldehyde are produced by the incomplete combustion of coal, wood, sugar, etc.

Preparation. (1) *By reduction of carbon monoxide.* Formaldehyde is produced from carbon monoxide and hydrogen when a mixture of these gases (*water gas*) is passed at low pressure through an electric discharge of low intensity.

$$CO + H_2O \longrightarrow CH_2O$$

(2) *By oxidation of methyl alcohol.* Large quantities of formaldehyde are prepared by passing a mixture of methyl alcohol vapour and air over heated copper or silver.

$$2CH_3OH + \tfrac{1}{2}O_2 \longrightarrow \underset{\text{Formaldehyde}}{2CH_2O} + H_2O$$

A catalyst composed of molybdenum trioxide and ferric oxide converts 95 per cent of methyl alcohol to formaldehyde.

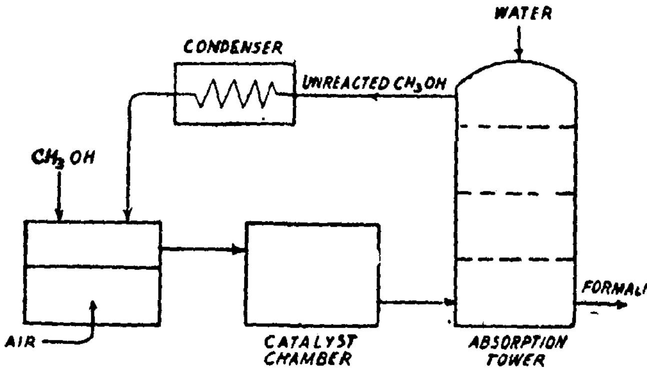
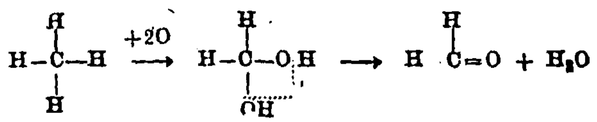


Fig. 19·1. Manufacture of formalin.

Since formaldehyde is a gas, the product is sold in the market as 40 per cent aqueous solution under the name FORMALIN.

(3) It is also manufactured in U.S.A. by the controlled oxidation of methane under pressure.



$$H-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-H \xrightarrow{+2O} H-\overset{\overset{H}{|}}{\underset{\underset{OH}{|}}{C}}-O.H \longrightarrow H\overset{\overset{H}{|}}{C}=O + H_2O$$

Laboratory Method. Formaldehyde is prepared in the laboratory by the oxidation of methyl alcohol in the presence of platinum. The apparatus required is shown in Fig. 19·1.

A round-bottom flask is fitted with a cork through which pass two tubes bent at right angles. One of these tubes reaches the bottom of the flask and the other ends just below the cork. The second tube connects the flask to the combustion tube. The other end of the combustion tube is fitted with a tube leading into a filtration flask which is attached to an aspirator or filter pump. About 50 ml. of methyl alcohol is put in the round-bottom flask which is then placed in warm water. In the meantime the combustion tube is heated. When air is sucked in, it is mixed with methyl alcohol vapours and the mixture then passes over heated platinised asbestos. Here, the alcohol is oxidised to formaldehyde gas which is dissolved in water contained in the filtration flask.

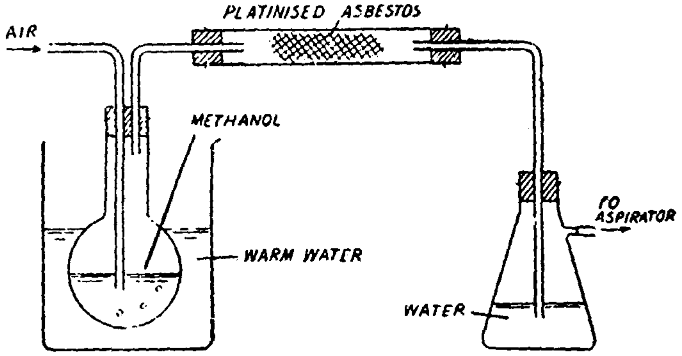
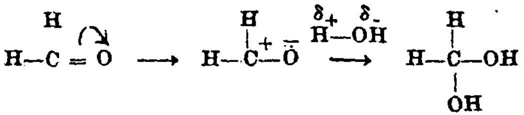


Fig. 19·2. Preparation of formalin by catalytic oxidation of methyl alcohol.

Properties. (*Physical*). Formaldeyde is a colourless gas at ordinary temperature and pressure. It is easily condensed to a liquid which boils at −21° It has a very pungent and penetrating odour. It is readily soluble in water In the gaseous state or when dissolved in water, formaldehyde is a powerful disinfectant.

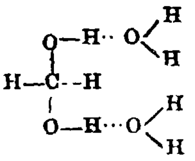
Formaldehyde forms an unstable hydrate with water. It is decidedly more stable than the hydrate of acetaldehyde, the latter being unstable owing to the presence of the electron repelling methyl group. Mechanism of hydrate formation may be depicted as



$$\underset{\text{I}}{\mathrm{H{-}\overset{H}{C}{=}O}} \longrightarrow \underset{\text{II}}{\mathrm{H{-}\overset{H}{\overset{|}{C}}{}^{+}{-}\overset{-}{O}}} \quad \overset{\delta+\ \ \delta-}{\mathrm{H{-}OH}} \longrightarrow \underset{\text{III}}{\mathrm{H{-}\overset{H}{\overset{|}{C}}{-}OH \atop \quad\ \ \overset{|}{OH}}}$$

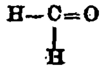
The presence of a methyl group in place of H-atom would exert its inductive effect (*electron repelling*) and reduce the magnitude of positive charge on C-atom in formula II. (*See acetaldehyde*).

Its solubility in water may be attributed to hydrogen bonding between water and molecules of formaldehyde hydrate.



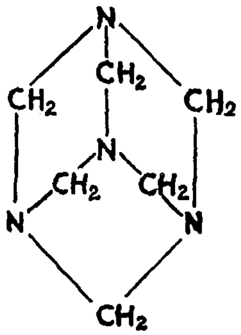
$$\mathrm{H{-}C{-}H} \text{ with } \mathrm{O{-}H\cdots O{<}^{H}_{H}} \text{ above and } \mathrm{O{-}H\cdots O{<}^{H}_{H}} \text{ below}$$

(*Chemical*). Structurally, formaldehyde differs from other aldehydes in that it has a hydrogen linked to the —CHO group instead of the alkyl radical.



$$\underset{\substack{|\\ H}}{H-C}=O$$

Consequently it does not duplicate all of the general reactions of the higher aldehydes and is actually more reactive. The following reactions of formaldehyde are noteworthy.



Hexamethylenetetramine

(1) Reaction with Ammonia. Unlike other aldehydes, it does not form aldehyde-ammonia but instead gives a white crystalline compound HEXAMETHYLENETETRAMINE.

$$6CH_2O + 4NH_3 \longrightarrow \underset{\substack{\text{Hexamethylene}\\ \text{tetramine}}}{(CH_2)_6N_4} + 6H_2O$$

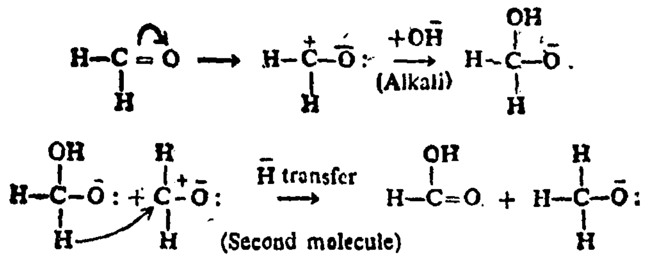
The proposed structural formula for the compound is indicated. It is used in medicine as a urinary antiseptic under the name **urotropine.**

(2) Reaction with Sodium Hydroxide. Formaldehyde differs from other aldehydes as it does not form a resin with dilute sodium hydroxide solution. However, when treated with a concentrated alkali solution, it undergoes *Cannizzaro reaction.*

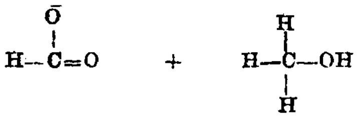
$$\begin{array}{c} HCHO \\ \\ HCHO \end{array} + H_2O \longrightarrow \begin{array}{c} HCOOH \\ + \\ CH_3OH \end{array}$$

Actually the free formic acid produced in the reaction as shown above would react with sodium hydroxide to form sodium formate.

Mechanism :

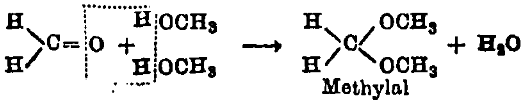


Now a proton transfer from HCOOH molecule takes place, giving formate ion and methyl alcohol—



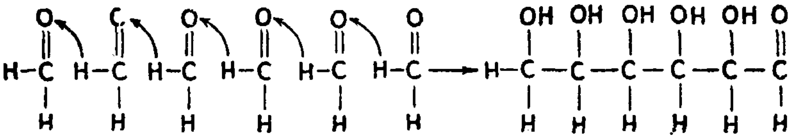
$$H-\overset{\substack{\bar{O}\\ |}}{C}=O \quad + \quad H-\overset{\substack{H\\ |}}{\underset{\substack{|\\ H}}{C}}-OH$$

(3) REACTION WITH ALCOHOLS. Like other aldehydes, it reacts with alcohols forming acetals. Thus in the presence of hydrogen chloride and fused calcium chloride, formaldehyde reacts with methyl alcohol to form **methylal.**



Methylal

(4) POLYMERISATION TO SUGARS. When a dilute solution of formaldehyde containing a weak alkali (baryta or lime) is allowed to stand, there is formed a mixture of sugars, called FORMOSE. The sugars are produced through a chain of aldol condensations. Thus :

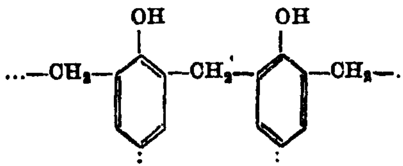


Formaldehyde (6 molecules)　　Glucose

This demonstrates beautifully how formaldehyde formed by the reduction of carbon dioxide, $CO_2 + H_2O \rightarrow CH_2O + O_2$ in plants further combines to give sugars by photosynthesis.

(5) CONDENSATION WITH PHENOL. Formaldehyde on condensation with phenol gives artificial resins and plastics which are used for making electric equipment under the name BAKELITE.

When phenol is refluxed with 40% formaldehyde in presence of 0·88 ammonia (catalyst), an oily liquid separates. This upon heating and finally cooling by dropping in water, gives a hard and brittle mass known as *Bakelite*.



(Bakelite)

Uses. Formaldehyde is placed in the market as 40 per cent aqueous solution under the name '*formalin*' and is used as such for most purposes.

(1) The vapour of formaldehyde, produced by the action of heat on formalin is used as a disinfectant. Formalin is used for sterilising surgical instruments.

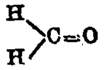
(2) Formalin is used for preserving biological and anatomical specimens, since it makes the tissues hard and insoluble.

(3) On account of its hardening effect on hide-proteins formalin is used for tanning.

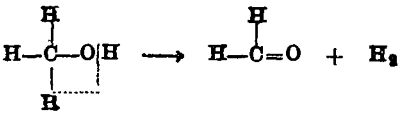
(4) Formalin is used in the production of plastics including well-known '*Bakelite*' which is obtained by heating phenol with formalin.

(5) Formalin is used as reducing agent for decolorising of *vat dyes* and also for making mirrors.

Structure. The molecular formula of formaldehyde is CH_2O. If the constituting atoms have their normal valencies, the structural formula can be written in one way only,



The structural formula is supported by the reactions of formaldehyde. It is confirmed by the formation of formaldehyde by the dehydrogenation of methyl alcohol.



$$H-\overset{H}{\underset{H}{C}}-O-H \longrightarrow H-\overset{H}{C}=O + H_2$$

Tests. Formaldehyde gives all the general reactions of aldehydes excepting No. 1 and 5 (*iii*). It also gives the following specific test. A freshly prepared solution of pyrogallol is mixed with the solution of formaldehyde and excess of concentrated hydrochloric acid is added. In a few minutes a white precipitate is formed which rapidly turns pink and then deep red. This test is not shown by acetaldehyde.

ACETALDEHYDE, ETHANAL, $CH_3.CH : O$

This is the second member of the series. Being the most important and typical member of the class, it is often referred to as simply *aldehyde*. It is formed as an intermediate compound in the alcoholic fermentation of glucose and is present in wines.

Preparation. (1) *By oxidation of Ethyl alcohol.* Acetaldehyde is obtained by passing ethyl alcohol vapour mixed with air, over a silver catalyst at a suitable temperature.

$$\underset{\text{Ethyl alcohol}}{2CH_3CH_2OH} + O_2 \longrightarrow \underset{\text{Acetaldehyde}}{2CH_3CHO} + 2H_2O$$

It may also be prepared by the oxidation of ethyl alcohol with sodium dichromate and sulphuric acid.

(2) By passing ethyl alcohol vapour over reduced copper at 250°—300°.

$$\underset{\text{Ethyl alcohol}}{CH_3CH_2OH} \longrightarrow \underset{\text{Acetaldehyde}}{2CH_3CHO} + H_2$$

(3) By distilling a mixture of calcium acetate and calcium formate in a hard glass test-tube.

$$\underset{\text{Ca-acetate}}{CH_3COO.Ca/2} + \underset{\text{Ca-formate}}{HCOO.Ca/2} \longrightarrow \underset{\text{Acetaldehyde}}{CH_3CHO} + CaCO_3$$

(4) By passing acetylene into warm dilute sulphuric acid con-

taining about 1 per cent of mercuric sulphate (together with a little ferric sulphate) as a catalyst.

$$\underset{\text{Acetylene}}{CH\equiv CH} + H_2O \longrightarrow \underset{\text{Acetaldehyde}}{CH_3CHO}$$

Laboratory Preparation. Acetaldehyde is prepared in the laboratory by the oxidation of ethyl alcohol using a mixture of aqueous sodium dichromate solution and sulphuric acid in the oxidising agent. The apparatus used for the purpose is fitted as shown. Fig 19·3.

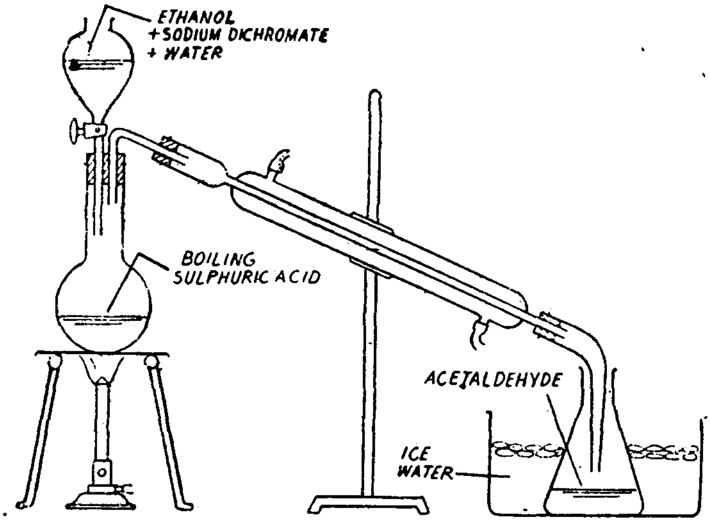


Fig. 19·3. Preparation of acetaldehyde.

A mixture of 50 mls. of water and 17 mls. of concentrated sulphuric acid is placed in a distilling flask fitted with a tap-funnel and connected to a condenser and adapter. 50 gms. of coarsely powdered sodium dichromate are dissolven in a mixture of 50 mls. of water and 40 mls. of ethyl alcohol; the solution is put in the flask and heated gently to boil. The burner is now put out and the solution from the tap-funnel allowed to fall dropwise. A vigorous action takes place, and the solution in the flask turns green owing to the formation of chromium sulphate. A mixture of acetaldehyde, water and a little alcohol distils over. The distillate collects in a conical flask placed in ice-cold water. The alcohol and most of water is removed by standing over calcium chloride and redistillation.

Pure acetaldehyde may be obtained by receiving the distillate in ether and then treating the ether solution with ammonia. The crystals of aldehyde-ammonia which separate are dried with filter paper and then distilled with dilute sulphuric acid. The aldehyde passing over at 21° is collected in ice-cold receiver as described before.

Industrial Preparation. Acetaldehyde is prepared industrially (*i*) by the oxidation of ethyl alcohol with air in the presence of silver, (*ii*) by the catalytic dehydrogenation of ethyl alcohol, and (*iii*) by the hydrasion of acetylene under the influence of mercury salts.

Properties (*Physical*). Acetaldehyde is a colourless volatile liquid, b.p. 21°. It has a characteristic pungent odour. It is readily soluble in water, alcohol, and ether. Its solutions in water, have an agreeable fruity odour.

(Chemical). The chemical reactions of acetaldehyde have been discussed under the general characteristics of aldehydes. A brief survey of the same is given below by way of recapitulation.

(1) CHLORINATION. Acetaldehyde reacts with moist chlorine to form *chloral.*

$$\underset{\text{Acetaldehyde}}{CH_3CHO} + 3Cl_2 \longrightarrow \underset{\text{Chloral}}{CCl_3CHO} + 3HCl$$

If the chlorination is carried in the presence of an alkali, chloral decomposes to give chloroform.

$$\underset{\text{Chloral}}{CCl_3CHO} + NaOH \longrightarrow \underset{\text{Chloroform}}{CHCl_3} + HCOONa$$

(2) ADDITION REACTIONS. Acetaldehyde reacts with hydrogen, ammonia, hydrogen cyanide, sodium bisulphite and a Grignard reagent by addition at the double bond of the carbonyl group.

$$CH_3.CH{=}O$$

$$+$$

$$H{-}H \longrightarrow \underset{\text{Ethyl alcohol}}{CH_3CH_2OH}$$

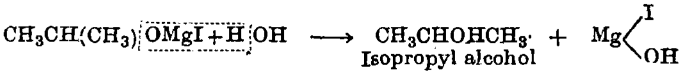
$$NH_2{-}H \longrightarrow \underset{\text{Acetaldehyde ammonia}}{CH_3CH(NH_2)OH}$$

$$NC{-}H \longrightarrow \underset{\text{Acetaldehyde cyanohydrin}}{CH_2CH(CN)OH}$$

$$NaO_3S{-}H \longrightarrow \underset{\text{Acetaldehyde bisulphite compound}}{CH_3CH(SO_3Na)OH}$$

$$CH_3{-}MgI \longrightarrow CH_3CH(CH_3)OMgI$$

The addition compound obtained from Grignard reagent upon hydrolysis gives a secondary alcohol.



$$CH_3CH(CH_3)\boxed{OMgI + H}OH \longrightarrow \underset{\text{Isopropyl alcohol}}{CH_3CHOHCH_3} + Mg\begin{matrix} \diagup I \\ \diagdown OH \end{matrix}$$

(3) REPLACEMENT REACTIONS. Acetaldehyde enters into reactions with alcohol, hydroxylamine, phenylhydrazine, semicarbazide and phosphorus pentachloride giving products in which the O atom of the CHO group has been replaced by a bivalent or two monovalent groups.

$$CH_3CH{=}\boxed{O + 2H}OC_2H_5 \longrightarrow \underset{\text{Acetal}}{CH_3CH(OC_2H_5)_2} + H_2O$$

$$+ H_2NaOH \longrightarrow \underset{\text{Acetaldoxime}}{CHCH:NOH} + H_2O$$

$$+ H_2NNHPh \longrightarrow \underset{\text{Phenylhydrazone}}{CH_3CH:N\,NH.Ph} + H_2O$$

$$+ H_2N.NHCONH_2 \longrightarrow \underset{\text{Semicarbazone}}{CH_3CH:N.NHCONH_2} + H_2O$$

$$\boxed{+ Cl_3PO}Cl_3 \longrightarrow \underset{\text{Ethylidene chloride}}{CH_3CHCl_2} + POCl_3$$

(4) OXIDATION. When the vapours of acetaldehyde are mixed

with air and passed over vanadium pentoxide, acetaldehyde is oxidised to acetic acid.

$$\underset{\text{Acetaldehyde}}{CH_3CHO} + \tfrac{1}{2}O_2 \longrightarrow \underset{\text{Acetic acid}}{CH_3COOH}$$

This can also be effected in aqueous solution by sodium dichromate and dilute sulphuric acid.

While acetaldehyde itself is easily oxidised to acetic acid, it reduces Fehling's solution and ammoniacal silver oxide to cuprous oxide (*red*) and silver (*mirror*) respectively.

(5) POLYMERISATION. Acetaldehyde has a marked tendency to polymerise.

(*i*) With a drop of concentrated sulphuric acid, it polymerises with explosive violence to form *paraldehyde.*

$$\underset{\text{Acetaldehyde}}{CH_3CHO} \longrightarrow \underset{\text{Paraldehyde}}{(CH_3CHO)_3}$$

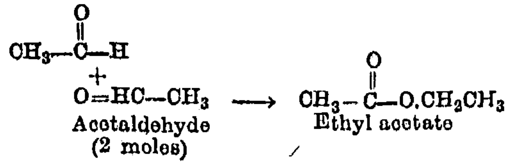
(*ii*) If hydrogen chloride is passed through acetaldehyde cooled in a freezing mixture, a white precipitate of the metaldehyde is produced which like paraldehyde has a cyclic structure.

$$\underset{\text{Acetaldehyde}}{4CH_3CHO} \longrightarrow \underset{\text{Metaldehyde}}{(CH_3CHO)_4}$$

(*iii*) Upon boiling with dilute sodium or potassium hydroxide solution, a yellow insoluble solid (acetaldehyde resin) is deposited. It has a smell of bad apples but its composition is not clear.

$$nCH_3CHO \longrightarrow \underset{\text{Resin}}{(CH_3CHO)_n}$$

(*iv*) In the presence of aluminium ethylate, $Al(OC_2H_5)_3$ acetaldehyde polymerises to form ethyl acetate *Tischenko Reaction*).



$$CH_3-\overset{O}{\overset{\|}{C}}-H + O{=}HC-CH_3 \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-O.CH_2CH_3$$

Acetaldehyde (2 moles) Ethyl acetate

(6) ALDOL CONDENSATION. In contact with a catalyst like sodium carbonate or zinc chloride acetaldehyde forms an aldol.

$$CH_3CHO + CH_3CHO \longrightarrow \underset{\text{Aldol}}{CH_3CH(OH)CH_2CHO}$$

Upon heating, the aldol loses a molecule of water to form crotonaldehyde.

$$CH_3CH(OH)CH_2CHO \longrightarrow CH_3CH : CH.CHO + H_2O$$

(7) SCHIFF'S REAGENT. Acetaldehyde restores the red colour of decolorised magenta solution.

Uses. (1) Acetaldehyde is used in the technical preparation of a number of organic compounds including acetic acid, ethyl acetate and n-butyl alcohol.

(2) It has also been used for the silvering of mirrors.

(3) Paraldehyde is used in medicine as a hypnotic.

(4) Metaldehyde, under the name '*meta*' is used as a solid fuel in small lamps.

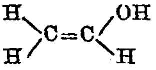
Tests (*See* Tests of aldehydes). (1) Rosin test; (2) Schiff's test; (3) Silver mirror test; (4) Fehling's solution test; (5) Nitro-prusside test; and (6) *Iodoform test*: Yellow crystals of iodoform are obtained by adding a few mls. of 10 per cent KI solution and a few mls. of sodium hypochlorite solution to aqueous acetaldehyde solution in a test-tube.

Tests 1, 5 and 6 are not given by formaldehyde.

Structure. (1) As shown by elementary analysis and molecular weight determination, the molecular formula of acetaldehyde is C_2H_4O.

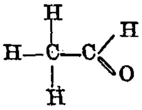
(2) The reduction of acetaldehyde to ethyl alcohol and then ethane shows that the two carbon atoms in its molecule are linked to each other directly.

(3) Retaining the normal valencies of carbon, oxygen and hydrogen (4, 2 and 1 respectively), we can write the structural formula of acetaldehyde as



I

or



II

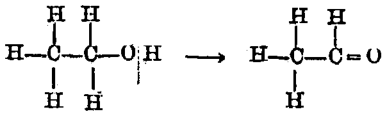
(4) The structure I is ruled out straightway as acetaldehyde does not give the usual addition reactions of an olefinic linkage.

(5) The structure II is supported by the following reactions :

(*a*) The action of phosphorus pentachloride upon acetaldehyde yields ethylidene chloride, CH_3CHCl_2. This indicates the absence of OH group in the molecule and confirms the presence of O linked to carbon alone.

(*b*) The action of chlorine on acetaldehyde forms chloral, $CCl_3.CHO$. This shows that three H atoms are linked to one carbon, while the fourth one is attached to the second carbon atom which also carries the O atom.

(*c*) Acetaldehyde is produced by the catalytic dehydrogenation of ethyl alcohol.



$$\mathrm{H{-}\overset{H}{\underset{H}{C}}{-}\overset{H}{\underset{H}{C}}{-}O{\vdots}H \longrightarrow H{-}\overset{H}{\underset{H}{C}}{-}\overset{H}{C}{=}O}$$

Ethyl alcohol Acetaldehyde

Chloral, *Trichloroacetaldehyde*, CCl_3CHO

Its systematic name would be TRICHLOROETHANAL.

Preparation. BY DIRECT CHLORINATION OF ACETALDEHYDE. Chloral can be prepared from acetaldehyde by direct chlorination in the presence of calcium carbonate.

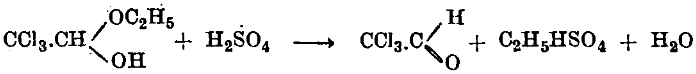
$$\underset{\text{Acetaldehyde}}{CH_3CHO} + 3Cl_2 \longrightarrow \underset{\text{Chloral}}{CCl_3CHO} + 3HCl$$

Calcium carbonate is needed to neutralise the hydrogen chloride produced which would otherwise cause the polymerisation of chloral.

(2) BY THE ACTION OF CHLORINE ON ALCOHOL. Chloral is manufactured on a large scale by passing chlorine into absolute alcohol containing ferric chloride as a catalyst. The alcohol is oxidised to aldehyde and simultaneously chlorinated.

$$CH_3CH_2OH + 4Cl_2 \longrightarrow \underset{\text{Chloral}}{CCl_3CHO} + 5HCl$$

The product of the reaction is, in fact, the crystalline alconollate which on distillation with sulphuric acid yields free chloral.



$$\mathrm{CCl_3.CH\overset{OC_2H_5}{\underset{OH}{\langle}} + H_2SO_4 \longrightarrow CCl_3.C\overset{H}{\underset{O}{\langle}} + C_2H_5HSO_4 + H_2O}$$

Chloral alcoholate · Chloral

Properties. Chloral is a colourless, oily liquid with a pungent odour and a sweetish taste, b.p. 98°. It is insoluble in water. When taken internally it induces sleep and hence its use as a hypnotic.

Chloral undergoes the usual reactions of aldehydes.

(1) ADDITION REACTIONS. Chloral combines with ammonia to give chloral-ammonia, $CCl_3.CH(OH)NH_2$; with hydrogen cyanide to form chloral cyanohydrin, $CCl_3.CH(OH)CN$; and with sodium bisulphite to give bisulphite compound, $CCl_3CH(OH)SO_3Na$.

(2) OXIDATION. Chloral reduces Fehling's solution to cuprous oxide, and ammoniacal solution of silver oxide to silver. In these reactions, chloral is oxidised to trichloroacetic acid.

$$CCl_3.CHO + O \longrightarrow CCl_3.COOH$$

Fuming nitric acid also affects the above change.

(3) REDUCTION. When reduced with zinc and hydrochloric acid, chloral is converted to acetaldehyde.

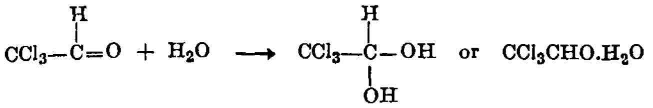
$$CCl_3.CHO + 6H \longrightarrow CH_3CHO + 3HCl$$

It can also be reduced at the – CHO group giving trichloroethanol

(4) REDUCTION WITH ALKALIS Chloral is hydrolysed by boiling with aqueous alkali solution to form chloroform and a metal formate:

$$CCl_3CHO + NaOH \longrightarrow CHCl_3 + HCOONa$$

(5) FORMATION OF HYDRATE. If a small quantity of water is added to chloral, colourless crystals of chloral hydrate (m.p. 52°) are formed.



$$CCl_3\text{—}\overset{H}{\overset{|}{C}}\text{=}O + H_2O \longrightarrow CCl_3\text{—}\underset{OH}{\underset{|}{\overset{H}{\overset{|}{C}}}}\text{—}OH \text{ or } CCl_3CHO.H_2O$$

Chloral hydrate is used as a hypnotic and is a rare example of a stable compound in which two hydroxyl groups are attached to the same carbon atom.

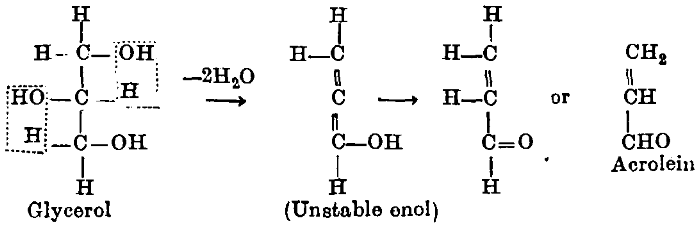
(6) POLYMERISATION. In the presence of an acid, chloral readily polymerises to a white amorphous solid known as *matachloral.*

UNSATURATED ALDEHYDES

Acrolein, *Propenal, Acrylic aldehyde,* $CH_2 : CH.CHO$.

This is the simplest and the best known unsaturated aldehyde. It is formed in small amounts when fats are over-heated.

Preparation. Acrolein is prepared by dehydration of glycerol by heating with potassium hydrogen sulphate.



Properties. Acrolein is a colourless liquid, b.p. 53°. It has an extremely pungent and penetrating odour, and hence its name (*acer*=sharp ; *oleum*=oil). It has a strong irritating action upon the eyes and nose, causing watering.

Acrolein molecule contains an alkene linkage and also a CHO group. Thus it behaves both as an alkene and as an aldehyde.

(1) *Reactions of the Double bond.* Acrolein gives the usual addition reactions at the double bond. Thus :

$$CH_2{=}CH.CHO + Br_2 \longrightarrow CH_2Br\,CHBr.CHO$$

αβ-Dibromopropanal

$$CH_2{=}CH.CHO + HCl \longrightarrow CH_2Cl.CH_2CHO$$

β-Choloropropanal

The addition of halogen acid to acrolein defies Markownikoff's rule.

(2) *Reactions of the* – CHO *group.* Acrolein gives the usual reactions of an aldehyde *e.g.* reduction, oxidation, polymerisation resinification, etc Thus :

$$CH_2{=}CH.CHO + 2H \longrightarrow \underset{\text{Allyl alcohol}}{CH_2{=}CH.CH_2OH}$$

$$CH_2{=}CH.CHO + O \longrightarrow \underset{\text{Acrylic acid}}{CH_2{=}CH.COOH}$$

It readily polymerises to a white solid DISACRYL.

Uses. Acrolein is used as a WARNING AGENT for any leakage in refrigeration with methyl chloride. It was also used as a TEAR GAS during the WORLD WAR I.

Crotonaldehyde, 2-Butenal, $CH_3.CH{:}CH.CHO$. It is prepared by heating aldol with a little iodine.

$$\underset{\text{Aldol}}{CH_3.CH(OH).CH_2.CHO} \longrightarrow CH_3CH{:}CH.CHO + H_2O$$

Crotonaldehyde is a pungent smelling liquid, b.p. 102·2°. It shows the reactions of an alkene and an aldehyde.

Crotonaldehyde is used as a solvent, insecticide and denaturant for more alcohol.

2. KETONES

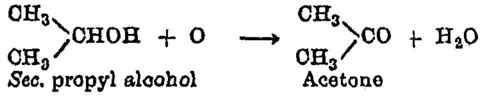
Ketones are the derivatives of hydrocarbons in which the two hydrogen atoms on a carbon in the middle of the chain have been replaced by a bivalent oxygen atom.

$$\underset{\text{Propane}}{CH_3.CH_2.CH_3} \xrightarrow[+O]{-2H} \underset{\text{Acetone}}{CH_3.CO.CH_3}$$

$$CH_3.CH_2.CH_2.CH_3 \longrightarrow \underset{\text{Ethyl methyl ketone}}{CH_3.CO.CH_2\,CH_3}$$

Thus ketones constitute a glass of compounds which are characterised by the presence of a carbonyl group (C=O) united to two carbon atoms. Such a carbonyl group is called a **Ketonic group**.

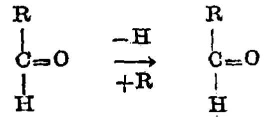
Just as aldehydes are the first oxidation products of primary alcohols, ketones are the *first oxidation products of secondary alcohols*



$$(CH_3)_2CHOH + O \longrightarrow (CH_3)_2CO + H_2O$$

Sec. propyl alcohol Acetone

Ketones have a close structural similarity to aldehydes and in fact they could aptly be regarded as *alkyl aldehydes.*



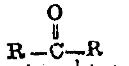
$$R{-}\overset{}{C}(=O){-}H \xrightarrow[+R]{-H} R{-}C(=O){-}H$$

Aldehyde Ketone (Alkyl aldehyde)

The structural similarity between the two types of compounds is reflected in their chemical behaviour.

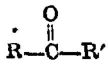
NOMENCLATURE

Ketones may be represented by the formula,


$R-\overset{\overset{O}{\|}}{C}-R$

Symmetrical ketone

or


$R-\overset{\overset{O}{\|}}{C}-R'$

Unsymmetrical ketone

They are designated as *symmetrical ketone* (simple ketone) or *unsymmetrical ketone* (mixed ketone) according as the two alkyl groups attached to the carbonyl group (C=O) are identical or different.

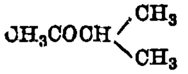
Ketones are named by two systems :

(1) According to the COMMON SYSTEM, symmetrical ketones are named as *dialkyl* ketones *e.g.*,

CH_3COCH_3	*Dimethyl ketone (acetone)*
$C_2H_5COC_2H_5$	Diethyl ketone

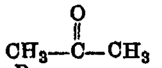
The common names of unsymmetrical or mixed ketones are derived by naming the two alkyl groups attached to the CO-group as separate words in alphabetic order and adding the third word 'ketone'. Thus :

$CH_3COC_2H_5$ Ethyl methyl ketone

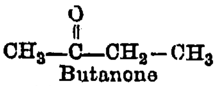

$CH_3COCH\genfrac{}{}{0pt}{}{\diagup CH_3}{\diagdown CH_3}$

Isopropyl methyl ketone

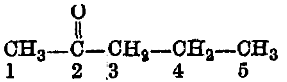
(2) According to IUPAC SYSTEM, the name of a ketone is derived by dropping the final 'e' of the name of the parent hydrocarbon and adding the suffix '*one*'. In case of ambiguity, the position of the carbonyl group (C=O) is indicated by numbering the carbon chain from the end nearest to it. Thus :


$CH_3-\overset{\overset{O}{\|}}{C}-CH_3$

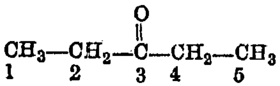
Propanone,
Acetone


$CH_3-\overset{\overset{O}{\|}}{C}-CH_2-CH_3$

Butanone
(No ambiguity)

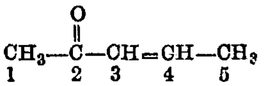

$\underset{1}{CH_3}-\underset{2}{\overset{\overset{O}{\|}}{C}}-\underset{3}{CH_2}-\underset{4}{CH_2}-\underset{5}{CH_3}$

2-Pentanone


$\underset{1}{CH_3}-\underset{2}{CH_2}-\underset{3}{\overset{\overset{O}{\|}}{C}}-\underset{4}{CH_2}-\underset{5}{CH_3}$

3-Pentanone

In complex compounds, where prefixing of the positional number to the ketone name gives rise to confusion it is inserted before the suffix *-one*. Thus :


$\underset{1}{CH_3}-\underset{2}{\overset{\overset{O}{\|}}{C}}-\underset{3}{CH}=\underset{4}{CH}-\underset{5}{CH_3}$

3-Penten-2-one

ISOMERISM

In addition to chain isomerism, ketones also show *metamerism*. Thus the formula $C_4H_{10}CO$ represents the metamers

$CH_3.CO.C_3H_7$	$C_2H_5.CO.C_2H_5$
Methyl propyl ketone	Diethyl ketone

Ketones also show functional isomerism with aldehydes and unsaturated alcohols. Thus, the formula C_3H_6O represents the following compounds.

$CH_3.CO.CH_3$	Acetone
$CH_3.CH_2.CHO$	Propionaldehyde
$CH_2{=}CH.CH_2OH$	Allyl alcohol

METHODS OF FORMATION

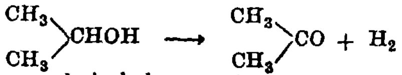
The methods of formation of ketones are analogous to those used for aldehydes.

(1) ***Direct oxidation of secondary alcohols.*** *Just as* aldehydes are produced by the oxidation of primary alcohols, ketones are obtained by the oxidation of secondary alcohols.

$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>CHOH + O \longrightarrow \begin{matrix}CH_3\\CH_3\end{matrix}\!\!>CO + H_2O$$

Isopropyl alcohol Acetone

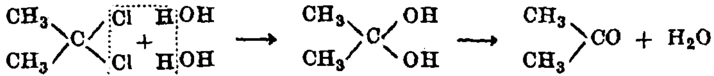
(2) **Catalytic dehydrogenation of secondary alcohols.** The vapours of secondary alcohols when passed over a hot metal catalyst such as copper or silver at high temperatures, yield ketones.



$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>CHOH \longrightarrow \begin{matrix}CH_3\\CH_3\end{matrix}\!\!>CO + H_2$$

Isopropyl alcohol Acetone

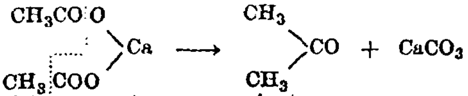
(3) **Hydrolysis of dihalogen derivatives.** The dihalogen derivatives in which both the halogen atoms are linked to the same carbon in the middle of the chain, on hydrolysis gives ketones.



$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C<\begin{matrix}Cl & & H\,OH\\ & + & \\ Cl & & H\,OH\end{matrix} \longrightarrow \begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C<\begin{matrix}OH\\OH\end{matrix} \longrightarrow \begin{matrix}CH_3\\CH_3\end{matrix}\!\!>CO + H_2O$$

2, 2-Dichloropropane (*Unstable*) Acetone

(4) **Distillation of calcium salts of fatty acids.** When the calcium salt of a fatty acid other than formic acid is heated, the corresponding ketone is formed.



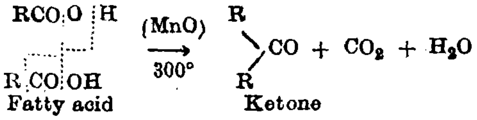
$$\begin{matrix}CH_3CO\,O\\CH_3\,COO\end{matrix}\!\!>Ca \longrightarrow \begin{matrix}CH_3\\CH_3\end{matrix}\!\!>CO + CaCO_3$$

Calcium acetate Acetone

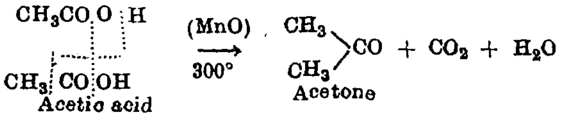
By taking mixture of calcium salts of two different acids this method could also be employed for the production of mixed ketones.

$$\underset{\text{Cal. acetate}}{CH_3COOCa/2} + \underset{\text{Cal. propionate}}{C_2H_5COOCa/2} \longrightarrow \underset{\text{Ethyl methyl ketone}}{CH_3.CO.C_2H_5} + CaCO_3$$

(5) **Catalyic decomposition of fatty acids** *by passing the vapours over manganous oxide heated to 300°.*

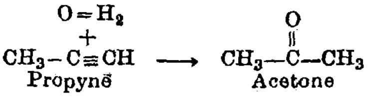


$$\underset{\text{Fatty acid}}{\begin{matrix} RCO.O\,\vdots\,H \\ R.CO.OH \end{matrix}} \xrightarrow[300^\circ]{(MnO)} \underset{\text{Ketone}}{R_2CO} + CO_2 + H_2O$$



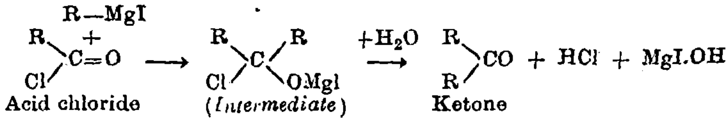
$$\underset{\text{Acetic acid}}{\begin{matrix} CH_3CO.O\,\vdots\,H \\ CH_3\,\vdots\,CO.OH \end{matrix}} \xrightarrow[300^\circ]{(MnO)} \underset{\text{Acetone}}{(CH_3)_2CO} + CO_2 + H_2O$$

(6) **Hydration of higher alkynes.** In the presence of sulphuric acid and mercury salts, homologues of acetylene add a molecule of water forming ketones.



$$\underset{\text{Propyne}}{CH_3-C\equiv CH} + O{=}H_2 \longrightarrow \underset{\text{Acetone}}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3}$$

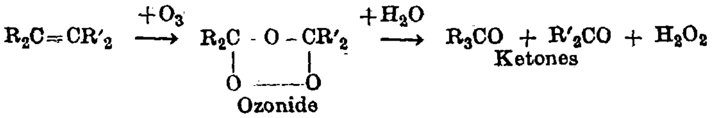
(7) **Action of Grignard reagents with acid chlorides.** Ketones can be synthesised by the addition of Grignard reagents to acid chlorides and subsequent hydrolysis of the product.



$$\underset{\text{Acid chloride}}{R(Cl)C{=}O} + R{-}MgI \longrightarrow \underset{(\textit{Intermediate})}{R_2C(Cl)OMgI} \xrightarrow{+H_2O} \underset{\text{Ketone}}{R_2CO} + HCl + MgI.OH$$

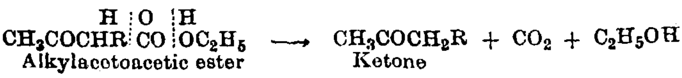
Obviously, by taking a suitable Grignard reagent, the method can also yield a mixed ketone.

(8) **Ozonolysis of alkenes of the type $R_2C{=}CR'_2$.**



$$R_2C{=}CR'_2 \xrightarrow{+O_3} \underset{\text{Ozonide}}{R_2C\underset{O-O}{-O-}CR'_2} \xrightarrow{+H_2O} \underset{\text{Ketones}}{R_2CO + R'_2CO} + H_2O_2$$

(9) **Hydrolysis of substituted acetoacetic esters.** Alkyl derivatives of acetoacetic ester, $CH_3COCH_2COOC_2H_5$, upon hydrolysis with a dilute alkali produce the corresponding ketones. Thus :



$$\underset{\text{Alkylacetoacetic ester}}{CH_3COCHR\,\vdots\,CO\,\vdots\,OC_2H_5} \;(+\,H\,\vdots\,O\,\vdots\,H) \longrightarrow \underset{\text{Ketone}}{CH_3COCH_2R} + CO_2 + C_2H_5OH$$

By taking a suitable ester, almost any ketone could be prepared by this method.

PHYSICAL CHARACTERISTICS

(1) The lower ketones are colourless mobile liquids with an ethereal, pleasant odour. Higher members are colourless solids that are practically odourless

(2) In volatility ketones lie in-between the corresponding aldehydes and the alcohols, their boiling point being in that order.

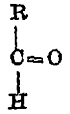
(3) The first few members are freely soluble in water, and the middle ones are quite insoluble. These are, however, soluble in alcohol and ether.

(4) The boiling points and specific gravities rise with increase in molecular weight. The physical constants of some of the ketones are given below :

KETONE	B.P C°	SP. G. 20/4°
Dimethyl ketone, CH_3COCH_3	56·5	0·792
Ethyl methyl ketone, $CH_3COC_2H_5$	79·6	0·805
Diethyl ketone, $(C_2H_5)_2CO$	102·7	0·816
Methyl propyl ketone, $CH_3COC_3H_7$	101·7	0·812
n-Butyl methyl ketone, $CH_3COC_4H_9$	127·5	0·830
Diamyl ketone, $(C_5H_{11})_2CO$	226·3	0·826

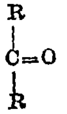
CHEMICAL CHARACTERISTICS

Owing to their close structural similarity, ketones behave like aldehydes in most respects.



$R-C(=O)-H$

Aldehyde



$R-C(=O)-R$

Ketone

Thus both types of compounds give the reactions of one hydrocarbon radical and the carbonyl group. The ketones differ from the aldehydes as the very reactive hydrogen atom in the latter has been replaced by a comparatively inert hydrocarbon radical. Therefore, the reducing properties of aldehydes and their ability to polymerise are altogether missing in ketones. The general reactions of ketones are described below.

(1) **Reactions of the alkyl radicals :**

(*i*) HALOGENATION · HALOFORM REACTION. The two hydro carbon radicals in ketones undergo the usual substitution with chlorine and bromine, the halogenation proceeding in the α-position. Thus :

$$\underset{\text{Ketone}}{RCH_2COR'} + Cl_2 \longrightarrow \underset{\text{Monochloroketone}}{RCHCl.CO.R'} + HCl$$

One or more hydrogen atoms are substituted depending upon conditions.

The halogenation proceeds especially rapidly in alkaline solution, but under these conditions decomposition follows. Thus :

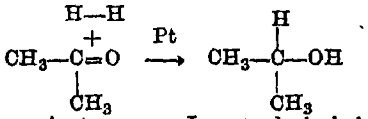
$$\underset{\text{Trichloroacetone}}{CCl_3\vdots CO.CH_3 + NaO\vdots H} \longrightarrow \underset{\text{Chloroform}}{CHCl_3} + CH_3COONa$$

In alkaline solutions iodine also substitutes readily yielding iodoform.

The action of halogens on a ketone in the presence of alkali, resulting in the formation of chloroform, bromoform and iodoform (*Haloform Reaction*), is given by all methyl ketones.

(2) **Addition reactions of the carbonyl group.** These reactions are in most respects similar to those of the aldehydes.

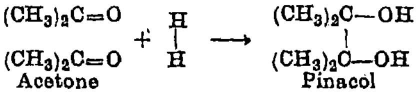
(*i*) ADDITION OF HYDROGEN. In the presence of a metal catalyst like nickel or platinum, ketones are reduced with hydrogen producing secondary alcohols.



$$\underset{\text{Acetone}}{CH_3-\overset{\overset{H-H}{+}}{\underset{CH_3}{C}}=O} \xrightarrow{Pt} \underset{\substack{\text{Isopropyl alcohol}\\(\textit{Sec. alcohol})}}{CH_3-\overset{H}{\underset{CH_3}{C}}-OH}$$

Acetone Isopropyl alcohol (*Sec. alcohol*)

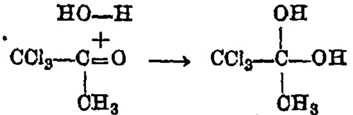
Reduction of ketones in neutral or alkaline solution also yields ditertiary alcohols known as PINACOLS.



$$\begin{matrix}(CH_3)_2C=O \\ (CH_3)_2C=O\end{matrix} + \begin{matrix}H\\|\\H\end{matrix} \longrightarrow \begin{matrix}(CH_3)_2C-OH\\|\\(CH_3)_2C-OH\end{matrix}$$

Acetone Pinacol

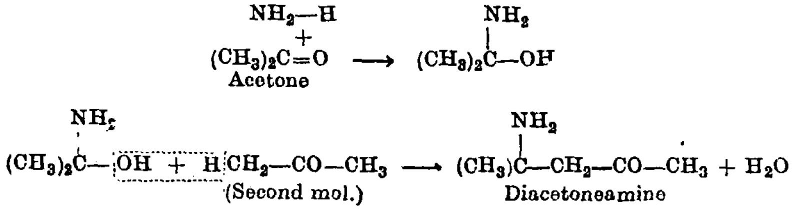
(*ii*) ADDITION OF WATER. Just like aldehydes, they form dihydroxy compounds with water, which are stable in the case of certain halogenated ketones. Thus :



$$CCl_3-\overset{\overset{HO-H}{+}}{\underset{CH_3}{C}}=O \longrightarrow CCl_3-\overset{OH}{\underset{CH_3}{C}}-OH$$

Trichloroacetone Hydrate

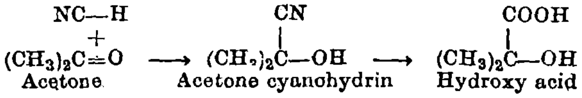
(*iii*) ADDITION OF AMMONIA. They react with ammonia forming complex compounds which are not comparable with aldehyde-ammonias.



$$\underset{\text{Acetone}}{(CH_3)_2C{=}O} + NH_2{-}H \longrightarrow (CH_3)_2\overset{\overset{NH_2}{|}}{C}{-}OH$$

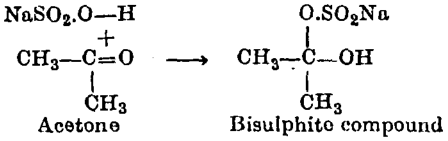
$$(CH_3)_2\overset{\overset{NH_2}{|}}{C}{-}\boxed{OH + H}\underset{\text{(Second mol.)}}{CH_2{-}CO{-}CH_3} \longrightarrow \underset{\text{Diacetoneamine}}{(CH_3)_2\overset{\overset{NH_2}{|}}{C}{-}CH_2{-}CO{-}CH_3} + H_2O$$

(*iv*) ADDITION OF HYDROGEN CYANIDE. Like aldehydes, ketones add a molecule of hydrogen cyanide forming CYANOHYDRINS which upon hydrolysis by heating with concentrated hydrochloric acid yield the HYDROXY ACIDS.



$$\underset{\text{Acetone}}{(CH_3)_2C{=}O} + NC{-}H \longrightarrow \underset{\text{Acetone cyanohydrin}}{(CH_3)_2\overset{\overset{CN}{|}}{C}{-}OH} \longrightarrow \underset{\text{Hydroxy acid}}{(CH_3)_2\overset{\overset{COOH}{|}}{C}{-}OH}$$

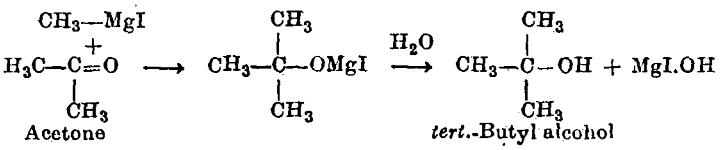
(*v*) ADDITION OF SODIUM BISULPHITE. Ketones react with sodium bisulphite giving crystalline BISULPHITE COMPOUNDS from which the original compounds can be regenerated by the action of *dilute acids or alkalis.*



$$\underset{\text{Acetone}}{CH_3{-}\underset{\underset{CH_3}{|}}{C}{=}O} + NaSO_2.O{-}H \longrightarrow \underset{\text{Bisulphite compound}}{CH_3{-}\overset{\overset{O.SO_2Na}{|}}{\underset{\underset{CH_3}{|}}{C}}{-}OH}$$

Formation of these bisulphite compounds and their subsequent decomposition is a good method of purifying ketones.

(*vi*) ADDITION OF GRIGNARD REAGENTS. They react with Grignard reagents to form addition products which upon hydrolysis yield tertiary alcohols. Thus :

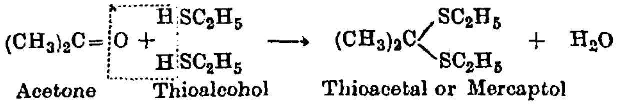


$$\underset{\text{Acetone}}{H_3C{-}\underset{\underset{CH_3}{|}}{C}{=}O} + CH_3{-}MgI \longrightarrow CH_3{-}\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}{-}OMgI \xrightarrow{H_2O} \underset{\textit{tert.}\text{-Butyl alcohol}}{CH_3{-}\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}{-}OH} + MgI.OH$$

Mechanism of addition reactions of ketones is similar to that of aldehydes.

(3) **Replacement reactions of the carbonyl group** :

(*i*) REACTION WITH THIOALCOHOLS. Unlike aldehydes, ketones do not react with alcohols but they undergo condensation with alcohols forming THIOACETALS.



$$\underset{\text{Acetone}}{(CH_3)_2C{=}O} + \underset{\text{Thioalcohol}}{\begin{matrix} H\,SC_2H_5 \\ H\,SC_2H_5 \end{matrix}} \longrightarrow \underset{\text{Thioacetal or Mercaptol}}{(CH_3)_2C\begin{matrix} SC_2H_5 \\ SC_2H_5 \end{matrix}} + H_2O$$

(*ii*) REACTION WITH HYDROXYLAMINE. Ketones react with hydroxylamine forming **ketoximes**.

$$\underset{\text{Acetone}}{(CH_3)_2C=}\boxed{O + H_2}\underset{\text{Hydroxylamine}}{NOH} \longrightarrow \underset{\text{Ketoxime}}{(CH_3)_2C=NOH} + H_2O$$

(*iii*) REACTION WITH PHENYLHYDRAZINE. They react with phenylhydrazine in a manner similar to aldehydes, giving PHENYLHYDRAZONES.

$$\underset{\text{Acetone}}{(CH_3)_2C=}\boxed{O + H_2}\underset{\text{Phenylhydrazine}}{N.NHPh} \longrightarrow \underset{\text{Phenylhydrazone}}{(CH_3)_2C=N.NHPh} + H_2O$$

(*iv*) REACTION WITH SEMICARBAZIDE. With semicarbazide, ketones react to form KETONE SEMICARBAZONES.

$$\underset{\text{Acetone}}{(CH_3)_2C=}\boxed{O + H_2}N.NHCONH_2 \longrightarrow \underset{\text{Semicarbazone}}{(CH_3)_2C:N.NHCONH_2} + H_2O$$

Just as in the case of aldehydes. the formation of oxime, phenylhydrazone and semicarbazone is very helpful in the identification of ketones.

(*v*) REACTION WITH PHOSPHORUS PENTACHLORIDE. Ketones react with phosphorus pentachloride forming derivatives in which the oxygen atom is replaced by two halogen atoms.

$$\underset{\text{Acetone}}{(CH_3)_2C=}\boxed{O + Cl_3P}Cl_2 \longrightarrow \underset{\text{2,2-Dichloropropane}}{(CH_3)_2CCl_2} + POCl_3$$

(4) **Other reactions of ketones.** Unlike aldehydes ketones do not undergo polymerisation at all.

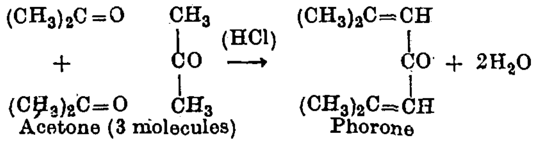
(*i*) CONDENSATION. Ketones give condensation reactions in which two or more molecules may react together, often by the elimination of water molecules. Thus :

(*a*) On treatment with strong alkali, two molecules of acetone react to form DIACETONYL ALCOHOL. (*Cf.* aldol condensation).

$$\underset{\text{Acetone (2 molecules)}}{(CH_3)_2C=O + CH_3COCH_3} \longrightarrow \underset{\text{Diacetonyl alcohol}}{(CH_3)_2C(OH)CH_2COCH_3}$$

(*b*) When saturated with hydrogen chloride gas, acetone yields unsaturated ketones

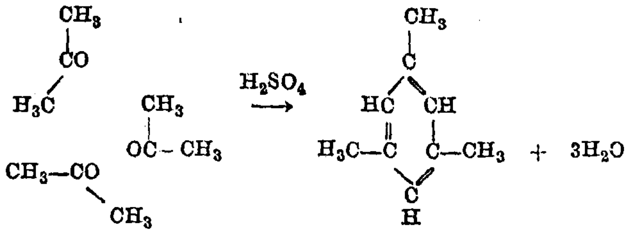
$$\underset{\text{Acetone (2 molecules)}}{(CH_3)_2C=\boxed{O + H}CH.CO.CH_3} \xrightarrow{(HCl)} \underset{\text{Mesityl oxide}}{(CH_3)_2C=CH.CO.CH_3} + H_2O$$



$$\begin{array}{ccc} (CH_3)_2C=O & CH_3 & (CH_3)_2C=CH \\ + & | \\ & CO & \xrightarrow{(HCl)} & CO + 2H_2O \\ & | & & | \\ (CH_3)_2C=O & CH_3 & (CH_3)_2C=CH \end{array}$$

Acetone (3 molecules) Phorone

(*c*) In the presence of concentrated sulphuric acid, three molecules of acetone condense together to form MESITYLENE (tri-methyl benzene)



Mesitylene

This reaction provides a method of passing from aliphatic to aromatic series.

(*ii*) Oxidation. While the aldehydes are oxidised to give acids without any rupture of the molecule, ketones yield acids by decomposition at one of the hydrocarbon radicals. Thus :

$$\underset{\text{Acetone}}{CH_3.CO.CH_3} + 3O \longrightarrow \underset{\text{Acetic acid}}{CH_3COOH} + \underset{\text{Formic acid}}{HCOOH}$$

In a mixed methyl ketone, the oxidation takes place at the carbon atom adjacent to CO group which is poorer in hydrogen, (*Popoff's Rule*). Thus :

$$\underset{\text{Ethyl methyl ketone}}{CH_3COCH_2CH_3} + 3O \longrightarrow CH_3COOH + CH_3COOH$$

This reaction serves to distinguish ketones from aldehydes as the former substances are not oxidised by Fehling's solution or ammoniacal silver nitrate solution. The oxidation of ketones can only be effected by strong oxidising agents such as chromic acid.

TESTS FOR KETONES

(1) Ketones do not form resins on warming with sodium hydroxide.

(2) They do not give Schiff's test.

(3) They do not reduce Fehling's solution or ammoniacal silver nitrate solution.

(4) Ketones form bisulphite compounds.

(5) Like aldehydes they form phenylhydrazones, oximes, and semicarbazones.

The first three negative tests are, however, given by aldehydes and are used for distinguishing them from ketones. Tests (4) and (5) are shown both by aldehydes and ketones but the melting points of the products are characteristic.

Acetone, *Dimethyl ketone, Propanone,* $CH_3.CO.CH_3$

It is the first and the best known member of the homologous series of ketones. Acetone is present in traces in normal urine but in conditions such as diabetes or starvation the amount is largely increased. It is a product of decomposition of cellulose, and is found in *wood spirit* obtained by the *dry* distillation of wood.

Preparation. (1) By the oxidation of isopropyl alcohol with sodium dichromate and sulphuric acid.

$$CH_3.CHOH.CH_3 + O \longrightarrow CH_3.CO.CH_3 + H_2O$$

This is also achieved by passing the vapours of alcohol mixed with oxygen over zinc oxide at 320°.

Isopropyl alcohol is also converted to acetone on industrial scale by the catalytic dehydrogenation.

(2) By the distillation of calcium acetate.

$$(CH_3COO)_2Ca \longrightarrow (CH_3)_2CO + CaCO_3$$

This method is used for the preparation of acetone in the laboratory and also in industry.

(3) By passing acetic acid vapour over a copper catalyst at 300—400°.

$$2CH_3COOH \longrightarrow (CH_3)_2CO + CO_2 + H_2$$

(4) By passing a mixture of acetylene and steam over a catalyst (zinc and magnesium vanadates) at 420°.

$$2CH \vdots CH \longrightarrow \underset{\text{Propylene}}{CH_3.C \vdots CH} + C$$

$$CH_3C \vdots CH + H_2O \longrightarrow \underset{\text{Acetone}}{CH_3.CO.CH_3}$$

(5) By fermentation of starch or molasses by the bacterium *Chostridium acetobutylicum* (Weizmann). The starch is converted to sugars which undergo further decomposition giving acetone

$$\underset{\text{Glucose}}{3C_6H_{12}O_6} \longrightarrow \underset{\text{Butyl alcohol}}{2C_4H_9OH} + \underset{\text{Acetone}}{(CH_3)_2CO} + 7CO_2 + 4H_2 + H_2O$$

LABORATORY PREPARATION

Acetone may be made in the laboratory by heating calcium acetate. Place a well ground mixture of 10 grams of each calcium acetate and anhydrous sodium acetate (*flux*) in a dry hard glass test-tube. Fit up the test-tube with a water condenser as shown in Fig. 19·4. To the other end of the condenser is attached an adapter which goes into the receiving flask. The mixture in the tube is then heated very carefully at first to avoid cracking, moving the flame all the while. Finally heat strongly with full flame until all the liquid has come over. The distillate is shaken with a saturated solution of sodium bisulphite. Acetone bisulphite compound that separates is removed and then decomposed by distilling with sodium carbonate solution. The distillate obtained at 45—56·5° is dried over anhydrous chloride.

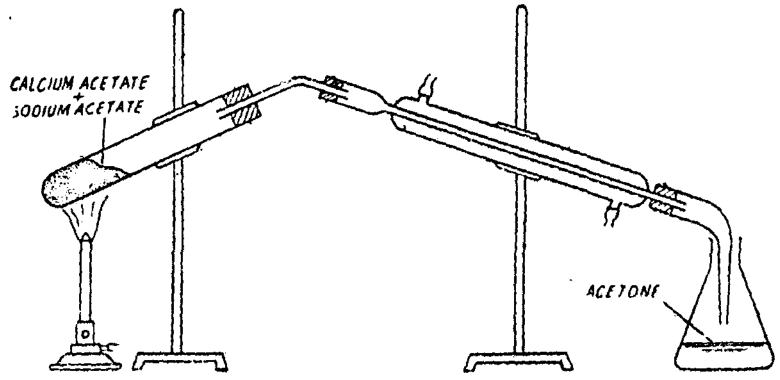
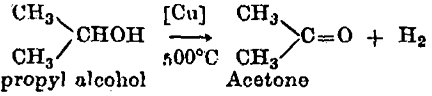


Fig. 19·4. Preparation of acetone.

INDUSTRIAL PREPARATION

Acetone is prepared on an industrial scale by (1) Catalytic dehydrogenation of isopropyl alcohol obtained from propylene in gases formed during the cracking of petroleum ; (2) Interaction of acetylene and steam ; (3) Fermentation of starch and molasses ; (4) Wood distillation, separation from pyroligneous acid, and by heating calcium acetate (*see methyl alcohol*).

By Dehydrogenation of Isopropyl Alcohol. Most of the acetone at present is manufactured from isopropyl alcohol obtained from propene of cracked petroleum. It is dehydrogenated by passing its vapours over heated copper catalyst at 500°C.



$$\begin{matrix}CH_3\diagdown \\ CH_3\diagup\end{matrix}CHOH \xrightarrow[500^\circ C]{[Cu]} \begin{matrix}CH_3\diagdown \\ CH_3\diagup\end{matrix}C{=}O + H_2$$

Isopropyl alcohol Acetone

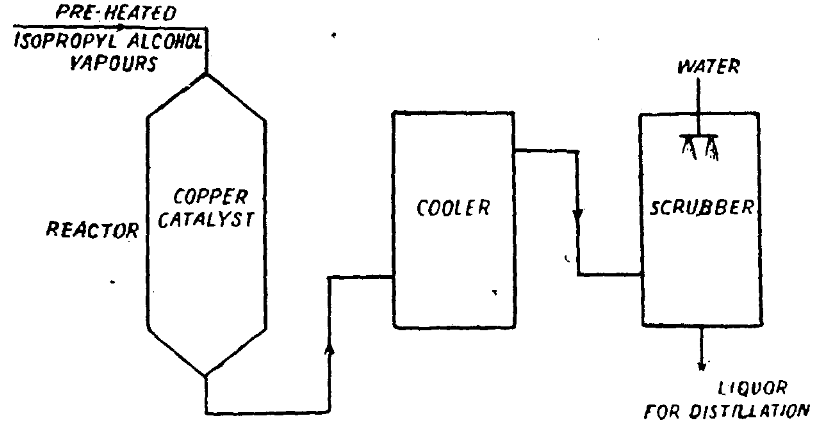


Fig. 19·5. Industrial preparation of acetone.

Isopropyl alcohol vapour is preheated and passed into a reactor packed with a copper catalyst. The reaction being endothermic the temperature is maintained at 500°C. The gaseous products from the reactor are passed through a cooler to a water scrubber for the complete recovery of acetone. The liquor obtained from the scrubber is fractionated to give pure acetone.

Properties (*Physical*). Acetone is a colourless liquid, b.p. 56·5°. It has a characteristic pleasant odour and a pungent sweet taste. It mixes with water, alcohol and ether in all proportions. It is very volatile and inflammable. It has a specific gravity 0·792 at 20°.

Chemical. Acetone gives *all the general reactions of ketones* described before.

(1) **Halogenation.** Chlorine reacts with acetone giving first monochloroacetone, $CH_2Cl.CO.CH_3$, and ultimately hexachloroacetone, $CCl_3.CO.CCl_3$. Bromine and iodine react to form ultimately $CHBr_2.CO.CHBr_2$ and $CH_2I.CO.CH_2I$ respectively.

(2) **Chloroform Reaction.** When acetone is distilled with bleaching powder ($CaOCl_2 \rightleftharpoons CaO + Cl_2$), which supplies both chlorine and alkali, it first forms trichloroacetone which upon hydrolysis yields chloroform.

$$\underset{\text{Acetone}}{CH_3.CO.CH_3} + 3Cl_2 \longrightarrow \underset{\text{Trichloroacetone}}{CCl_3.CO.CH_3} + 3HCl$$

$$CCl_3.CO.CH_3 + Ca(OH)_2 \longrightarrow \underset{\text{Chloroform}}{CHCl_3} + CH_3COOH$$

This reaction is used for the preparation of chloroform. A similar reaction with iodine and alkali gives iodoform.

(3) **Addition Reactions.** Acetone reacts with H_2, HCN, $NaHSO_3$ and NH_3, by addition at the carbonyl group.

$$\begin{array}{rcl}
(CH_3)_2C{=}O & & \\
+ & & \\
H{-}H & \longrightarrow & \underset{\text{Isopropyl alcohol}}{(CH_3)_2CHOH} \\
NC{-}H & \longrightarrow & \underset{\text{Acetone cyanohydrin}}{(CH_3)_2C(CN)OH} \\
NaSO_2.O{-}H & \longrightarrow & \underset{\text{Bisulphite compound}}{(CH_3)_2C(O.SO_2Na)OH} \\
H_2N{-}H & \longrightarrow & \underset{\text{Acetone ammonia}}{(CH_3)_2C(NH_2).OH} \\
CH_3{-}MgBr & \longrightarrow & (CH_3)_2C(CH_3).OMgBr
\end{array}$$

Acetone-ammonia is formed at −65°, while at room temperature acetone reacts with ammonia giving diacetoneamine, $(CH_3)_2C(NH_2)CH_2.COCH_3$. The addition compound of a Grignard reagent upon hydrolysis yields a tertiary alcohol.

$$(CH_3)_2C(CH_3).OMgBr + H_2O \longrightarrow \underset{\textit{tert.}\text{ Butyl alcohol}}{(CH_3)_3C.OH} + MgOH.Br$$

(4) **Replacement Reactions.** Acetone reacts with NH_2OH, $NH_2.NHPh$, $NH_2.NHCONH_2$ and PCl_5 whereby the O-atom of CO group is replaced. Thus :

$$\begin{array}{lll}
(CH_3)_2C{=}O + H_2NOH & \longrightarrow & \underset{\text{Oxime}}{(CH_3)_2C{:}NOH} + H_2O \\
\phantom{(CH_3)_2C{=}O} + H_2N.NHPh & \longrightarrow & \underset{\text{Phenylhydrazone}}{(CH_3)_2C{:}N.NHPh} + H_2O \\
\phantom{(CH_3)_2C{=}O} + H_2N.NHCONH_2 & \longrightarrow & \underset{\text{Semicarbazone}}{(CH_3)_2C{:}N.NHCONH_2} + H_2O \\
\phantom{(CH_3)_2C{=}O} + PCl_3Cl_2 & \longrightarrow & \underset{\text{2, 2-Dichloropropane}}{(CH_3)_2CCl_2} + POCl_3
\end{array}$$

When reduced with amalgamated zinc and conc. hydrochloric acid, acetone is reduced to propane (*Clemmensen Reaction*).

$$\underset{\text{Acetone}}{CH_3.CO.CH_3} + 2H_2 \longrightarrow \underset{\text{Propane}}{CH_3.CH_2.CH_3} + H_2O$$

(5) OXIDATION. Acetone upon oxidation with a powerful oxidising agent such as sodium dichromate and sulphuric acid, gives acetic acid and carbon dioxide.

$$\underset{\text{Acetone}}{CH_3.CO.CH_3} + 2O_2 \longrightarrow \underset{\text{Acetic acid}}{CH_3COOH} + CO_2 + H_2O$$

Acetone, however, is not a reducing agent. Thus it neither reduces Fehling's solution nor an ammoniacal solution of silver nitrate.

(6) CONDENSATION. (*a*) In the presence of an alkali two molecules of acetone combine to form *diacetonyl alcohol*. (*b*) When saturated with dry HCl gas, it *gives mesityl oxide* and *phorone*. (*c*) With conc. sulphuric acid three molecules of acetone condense to form *mesitylene*. (For details *see the general reactions of ketones*).

Uses. (1) It is employed as a SOLVENT in the manufacture of smokeless powders (*Cordite*), celluloid, collodion, paints and varnish removers, etc. It is an ingredient of liquid nail polish.

(2) Acetone is stored in solution in acetylene under pressure.

(3) It is used as a RAW MATERIAL for the production of iodoform, chloroform and sulphonal.

(4) It is a possible ingredient of motor fuel because it has high antinock value.

Tests. Acetone gives negative tests with sodium hydroxide, ammoniacal silver nitrate, Fehling's solution, and Schiff's reagent.

(1) *Iodoform Test.* If iodine solution be added drop by drop to a solution of acetone and ammonia (3 to 5 drops) a black precipitate of nitrogen iodide is formed. On warming it disappears and iodoform is obtained. Alcohol does not form iodoform in this way.

(2) *Nitroprusside or* **Legal's Test.** Freshly prepared solution of sodium nitroprusside (5 drops) is added to dilute acetone (5 mls.) and sodium hydroxide (1 ml.). A ruby red colour is produced which fades to yellow on standing.

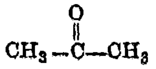
(3) *Indigo Test.* A little *o*-nitrobenzaldehyde is dissolved in 2 mls. of acetone and the solution stirred into 200 mls. of water containing a little potassium hydroxide. A blue colour of *Indigotin* is produced.

Structure. (1) The molecular formula of acetone is C_3H_6O.

(2) Unlike alcohols, it does not react with sodium, hence the absence of OH group in the molecule.

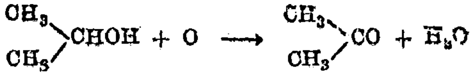
(3) Acetone reacts with phosphorus pentachloride to form 2-dichloropropane, $CH_3CCl_2.CH_3$ without the evolution of hydrogen chloride gas. This again shows the absence of OH group and the presence of CO group, since the O atom of acetone has been replaced by two Cl atoms.

(4) From the above considerations, the formula for acetone can be written as



$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$$

(5) The structure of acetone is confirmed by its mode of formation by the oxidation of isopropyl alcohol.



$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!CHOH + O \longrightarrow \begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!CO + H_2O$$

Infrared spectra of aldehydes and ketones. The carbonyl groups in saturated aliphatic aldehydes and ketones show strong absorption bands in the regions 1720—1740 cm^{-1} and 1700—1725 cm^{-1} respectively. Infrared spectrum of acetone given below indicates the various absorption bands.

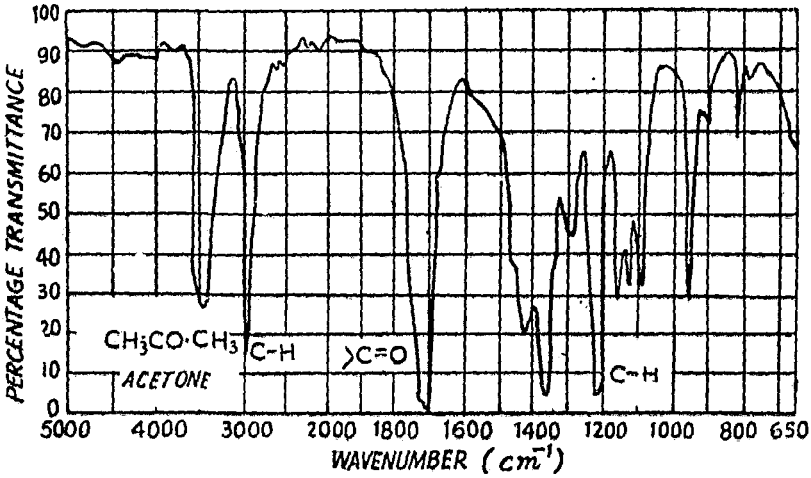


Fig. 19·6. Infrared spectrum of Acetone.

COMPARISON OF ALDEHYDES AND KETONES

As pointed out before, aldehydes and ketones bear a marked structural similarity

R—CO—R′	Ketones
R—CO—H	Aldehydes

They have R—CO — in common and thus both classes give the reactions of the hydrocarbon radical R and >CO group. Aldehydes, however, are more reactive and possess reducing properties which are missing in ketones. The difference in behaviour is obviously due to the fact that the very active hydrogen linked to CO in aldehydes has been replaced by a comparatively inert alkyl group R in ketones.

ALDEHYDES	KETONES
Points of Resemblance :	
(1) Undergo halogenation in the hydrocarbon radical.	(1) Undergo halogenation like aldehydes.
(2) On reduction give primary alcohols.	(2) On reduction give secondary alcohols.
(3) React with HCN forming cyanohydrins.	(3) Form cyanohydrins like aldohydes.
(4) React with $NaHSO_3$ giving sodium bisulphite compounds.	(4) Give sodium bisulphite compounds like aldehydes.
(5) Give dihalogen derivatives with PCl_5, O being replaced by two Cl atoms.	(5) Give dihalogen derivatives similar to those obtained from aldehydes.
(6) React with NH_2OH by elimination of a water molecule to form *Aldoximes.*	(6) Form *Ketoximes* under similar conditions.
(7) React with $Ph.NH.NH_2$ by elimination of a water molecule to form *Phenylhydrazones.*	(7) React similarly to form *Phenyl hydrazones.*
Points of Difference :	
(1) React with ammonia to form *aldehyde-ammonias.*	(1) Give *complex compounds* instead of aldehydes ammonias.
(2) React with alcohols to form *acetals.*	(2) No action.
(3) Upon oxidation give fatty acids containing the same number of carbon atoms.	(3) Oxidised with difficulty giving fatty acids containing smaller number of carbon atoms than the original ketones.
(4) Reduce ammoniacal silver nitrate solution with the formation of mirror.	(4) Do not reduce ammoniacal silver nitrate.
(5) Reduce Fehling's solution with the formation of red cuprous oxide.	(5) Do not reduce Fehling's solution
(6) Polymerise readily.	(6) Do not polymerise.
(7) Form brown resinous mass with NaOH solution.	(7) Do not form resins with NaOH solution.
(8) Restore pink colour of Schiff's reagent.	(8) Do not restore the colour of Schiff's reagent.

QUESTIONS

1. What are aldehydes and ketones ? Point out the structural relationship between the two types of compounds.

2. Describe the general methods of formation and properties of aldehydes.

3. *Describe the preparation of acetaldehyde. Give its properties and* how it reacts with Caustic potash, Ammonia and Potassium cyanide ?

4. How is acetone manufactured ? State its properties and uses.

5. Give the evidence on which the structural formula of acetaldehyde is based. Make a brief survey, comparing the reactions of acetaldehyde with those of acetone.

6. Compare and contrast the chemical properties of aliphatic aldehydes and ketones.

7. How is acetone obtained ? Give an account of its physical properties, and enumerate as many reactions as you can in which it takes part. In what respects does a ketone differ from an aldehyde ?

8. "The behaviour of the first member of the series is usually somewhat different from the behaviour of the subsequent members of the series."

Illustrate this with reference to formaldehyde and formic acid.

(Udaipur B.Sc., 1967)

9. (*a*) Describe the laboratory method of preparation of pure acetaldehyde.
   (*b*) *In what respects does it differ from* formaldehyde ?
   (*c*) Write with examples, what you know about the reducing character of acetaldehyde. *(Kurukshetra B.Sc., 1968)*

10. (*a*) How would you distinguish between a Ketone and an Aldehyde ?
    (*b*) Write an account of the uses of ethyl acetoacetate in organic synthesis. *(Kurukshetra B.Sc., 1968)*

11. Describe two general methods of preparation of aliphatic aldehydes. Give the reactions of acetaldehyde with (*a*) phenyl hydrazine (*b*) Ammonia (*c*) Solution of sodium bisulphide (*d*) Moist silver oxide. Give also the mechanism of the above mentioned reactions as far as possible.

(Jadavpur B.Sc., 1969)

12. What are the three organic compounds which may be prepared from the calcium salts of the fatty acids. Give the distinguishing properties of the compounds prepared. *(Bangalore B.Sc., 1969)*

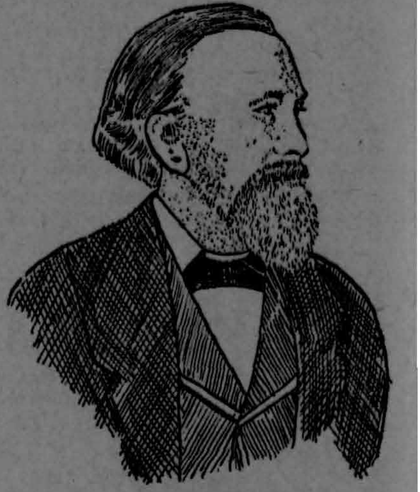
13. Cite experimental facts and give explanation in support of the statement that formaldehyde differs more from the rest of the fatty aldehydes than they differ among each other. *(Udaipur B.Sc., 1969)*

14. Describe the general methods for the preparation of aldehydes. Give those reactions in which acetone differs from acetaldehyde.

(Jammu & Kashmir B.Sc., 1969)

20

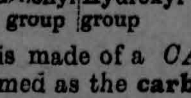
Carboxylic Acids



E. FRANKLAND
(1825—1899)

English Scientist. He collaborated with Kolbe in obtaining acetic acid by heating methyl cyanide with potash. The organo-metallic compounds of zinc were first studied by Frankland in 1849.

Many organic acids are characterised by the presence of the grouping.



$$\underbrace{-\overset{\overset{\displaystyle O}{\|}}{C}-}_{\text{Carbonyl group}}\Big|\underbrace{-OH}_{\text{Hydroxyl group}}$$

Since the structure is made of a *CARB*onyl group and hydr*OXYL* group, it has been named as the **carboxyl group**, and the compounds containing it are called *carboxylic acids*. They are further classed as *mono*, *di* and *tricarboxylic acids* according to the number of carboxyl groups which they contain.

MONOCARBOXYLIC ACIDS

The saturated monocarboxylic acids are popularly referred to as the **Fatty acids** since many of them are formed by the hydrolysis of natural fats.

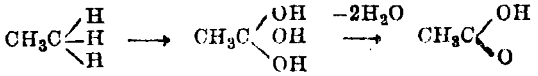
The monocarboxylic acids may be regarded as the ***derivatives of alkanes*** in which a hydrogen atom has been replaced by a carboxyl group. Thus :

$$\underset{\text{Methane}}{CH_4} \xrightarrow[+COOH]{-H} \underset{\text{Acetic acid}}{CH_3COOH}$$

$$\underset{\text{Ethane}}{CH_3CH_3} \xrightarrow[+COOH]{-H} \underset{\text{Propionic acid}}{CH_3CH_2COOH}$$

In this way, formic acid, the first member of the homologous series, would be derived from hydrogen H_2

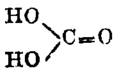
Better still, the fatty acids could be considered as the *third oxidation products of alkanes* in which the CH_3 group has been ultimately converted to carboxyl group.



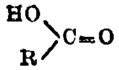
Ethane *(Unstable)* Acetic acid

This view shows correctly that formic acid is a derivative of methane.

The carboxylic acids may also be regarded as the ***derivatives of carbonic acid*** in which one (OH) group has been exchanged for an alkyl radical.



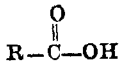
Carbonic acid



Carboxylic acid

This view is supported by the fact that both carbonic acid and carboxylic acids split out carbon dioxide readily.

The general formula for fatty acids is $C_nH_{2n+1}COOH$ or $C_nH_{2n}O_2$. The type formula of these compounds is



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-OH$$

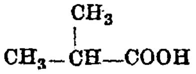
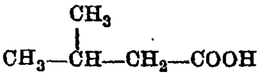
but it is usually written as RCOOH or RCO_2H in order to use but one line of space.

NOMENCLATURE

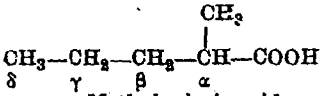
The aliphatic monocarboxylic acids are named in three ways :

(1) The COMMON SYSTEM. Being the earliest known organic substances, quite a number of them have common or trivial names. Such names reflect the natural sources from which the acids were first isolated, and do not follow any rule except that they end in *–ic acid*. The common names are now recommended for the first few members but the traditional names die hard and are still used

for certain higher acids for convenience. The common names of some carboxylic acids are listed below :

$HCOOH$	Formic acid
CH_3COOH	Acetic acid
CH_3CH_2COOH	Propionic acid
$CH_3CH_2CH_2COOH$	Butyric acid
 $CH_3-\overset{\overset{CH_3}{\mid}}{C}H-COOH$	Isobutyric acid
$CH_3CH_2CH_2CH_2COOH$	Valeric acid
 $CH_3-\overset{\overset{CH_3}{\mid}}{C}H-CH_2-COOH$	Isovaleric acid

In the common system, Greek letters (α, β, γ, δ etc.) are used to indicate the position of substituents. The first carbon after the COOH group is designated as α, the next β, and so on. The carbon atom in the COOH group is not assigned a letter Thus :



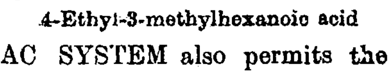
$$\underset{\delta}{CH_3}-\underset{\gamma}{CH_2}-\underset{\beta}{CH_2}-\underset{\alpha}{\overset{\overset{CH_3}{\mid}}{C}H}-COOH$$

α-Methylvaleric acid

(2) According to the IUPAC SYSTEM, the carboxylic acids are named as *Alkanoic acids* (alkane — *e* + *oic* acid). The systematic name of an individual acid is derived by deleting the terminal '*e*' from the name of the parent alkane (having same No. of C atoms) and adding '—*oic* acid'. Thus the systematic names of the first few members are given below although IUPAC preferred names are the common names.

$HCOOH$	Methanoic acid (Methane — *e* + *oic* acid)
CH_3COOH	Ethanoic acid
CH_3CH_2COOH	Propanoic acid
$CH_3CH_2CH_2COOH$	Butanoic acid

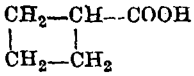
For naming higher members, we look for the longest carbon chain containing the —COOH group. The number of carbon atoms (including that of COOH group) constituting this chain gives the name of the parent alkane. The positions of substituents are assigned by numbering the selected chain starting from the carbon of the COOH group but it is unnecessary to indicate its position which is always 1. Thus :



$$\underset{6}{CH_3}-\underset{5}{CH_2}-\underset{4}{\overset{\overset{C_2H_5}{\mid}}{C}H}-\underset{3}{\overset{\overset{CH_3}{\mid}}{C}H}-\underset{2}{CH_2}-\underset{1}{COOH}$$

4-Ethyl-3-methylhexanoic acid

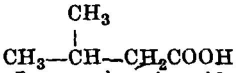
The IUPAC SYSTEM also permits the naming of complex members particularly the cyclic acids as 'Alkanecarboxylic acids'. In this scheme, the parent hydrocarbon is first named as if COOH group is absent and then the '—carboxylic acid' is added to it. Thus :



$$\begin{array}{l}CH_2-CH-COOH\\ |\quad\quad\ \ |\\ CH_2-CH_2\end{array}$$

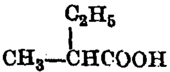
Cyclobutanecarboxylic acid

(3) The SUBSTITUTED-ACETIC ACID SYSTEM. The carboxylic acids particularly those with branched chains are sometimes named as alkyl substituted acetic acids in the same fashion as alcohols are named as derivatives of carbinol. Thus the derived name of a complex acid will be given by naming the names of alkyl radicals attached to the COOH bearing carbon and adding the suffix '—acetic acid'. Thus, the names of the substituent alkyl groups are written as a part of the single word which precedes 'acid' in the full name.



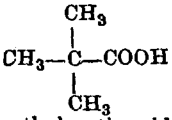
$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{C}H-CH_2COOH$$

Isopropylacetic acid



$$CH_3-\overset{\overset{\displaystyle C_2H_5}{|}}{C}HCOOH$$

Ethyl methyl acetic acid



$$CH_3-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-COOH$$

Trimethylacetic acid

ISOMERISM

Like the alkyl halides and the alcohols, fatty acids show both position and chain isomerism.

The fatty acids are also isomeric with esters containing the same number of carbon atoms. For example, the formula $C_3H_6O_2$ represents

CH_3CH_2COOH and CH_3COOCH_3

Propionic acid — Methyl acetate

METHODS OF FORMATION

Fatty acids can be obtained by the following methods :

(1) **Oxidation of alcohols and aldehydes.** Primary alcohols or aldehydes upon oxidation yield fatty acids. Thus :

$$\underset{\text{Ethyl alcohol}}{CH_3CH_2OH} + 2O \longrightarrow \underset{\text{Acetic acid}}{CH_3COOH} + H_2O$$

$$\underset{\text{Acetaldehyde}}{CH_3CHO} + O \longrightarrow CH_3COOH$$

The oxidation is best done with sodium dichromate and sulphuric acid.

(2) **Hydrolysis of esters.** Fatty acids are produced by the hydrolysis of esters in the presence of a mineral acid.

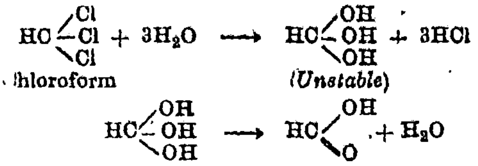
$$\underset{\text{Ester}}{RCOOR'} + HOH \longrightarrow \underset{\text{Acid}}{RCOOH} + \underset{\text{Alcohol}}{R'OH}$$

This method is particularly useful for the preparation of higher acids from fats, which are the triesters of glycerol.

(3) **Hydrolysis of alkyl cyanides.** Alkyl cyanides when hydrolysed with mineral acids form monocarboxylic acids.

$$\underset{\text{Alkyl nitrile}}{RC \vdots N} + 2H_2O + HCl \longrightarrow \underset{\text{Acid}}{RCOOH} + NH_4Cl$$

(4) **Hydrolysis of trihalogen derivatives**. Trihalogen derivatives of alkanes in which the three halogen atoms are linked to the same carbon atom upon hydrolysis with an alkali yield fatty acids. Thus,



$$\underset{\text{Chloroform}}{HC\begin{array}{l}\diagup Cl\\ -Cl\\ \diagdown Cl\end{array}} + 3H_2O \longrightarrow \underset{(Unstable)}{HC\begin{array}{l}\diagup OH\\ -OH\\ \diagdown OH\end{array}} + 3HCl$$

$$HC\begin{array}{l}\diagup OH\\ -OH\\ \diagdown OH\end{array} \longrightarrow HC\begin{array}{l}\diagup OH\\ \diagdown O\end{array} + H_2O$$

(5) **Reaction between an alkyl halide and the ester of a lower halogenated acid.** Higher fatty acids can be obtained by the action of sodium on a mixture of an alkyl halide and the ester of a lower halogenated acid. Thus,

$$\underset{\text{Ethyl chloride}}{C_2H_5Cl} + 2Na + \underset{\text{Ethyl chloroacetate}}{ClCH_2COOC_2H_5} \longrightarrow \underset{\text{Ethyl butyrate}}{C_2H_5CH_2COOC_2H_5} + 2NaCl$$

$$C_2H_5CH_2COOC_2H_5 + H_2O \longrightarrow \underset{\text{Butyric acid}}{C_2H_5CH_2COOH} + \underset{\text{Ethyl alcohol}}{C_2H_5OH}$$

The resulting ester upon hydrolysis liberates the free higher acid. This reaction can also be carried with silver in place of sodium.

(6) **Reaction of a Grignard reagent with carbon dioxide.** The ethereal solution of a Grignard reagent absorbs carbon dioxide gas forming an addition product which upon treatment with a dilute mineral acid gives a fatty acid.

$$\underset{\text{Grignard reagent}}{RMgBr} + CO_2 \longrightarrow \underset{\text{Intermediate}}{RCOOMgBr}$$

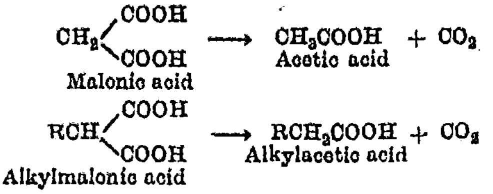
$$RCOO\,MgBr + HO\,H \longrightarrow \underset{\text{Acid}}{RCOOH} + MgBr.OH$$

(7) **Reaction of carbon monoxide with alcoholates.** At high temperature carbon monoxide reacts with alkali alcoholates iving salt of fatty acids.

$$\underset{\text{Sod. alcoholate}}{C_2H_5ONa} + CO \longrightarrow \underset{\text{Sod. propionate}}{C_2H_5COONa}$$

The acid is liberated by reaction with a mineral acid.

(8) **Action of heat on dicarboxylic acids.** The dicarboxylic acids of the malonic acid series, in which the two COOH groups are linked to the same carbon, upon heating split out a molecule of carbon dioxide giving fatty acids. Thus :



$$\underset{\text{Malonic acid}}{CH_2\begin{array}{l}\diagup COOH\\ \diagdown COOH\end{array}} \longrightarrow \underset{\text{Acetic acid}}{CH_3COOH} + CO_2$$

$$\underset{\text{Alkylmalonic acid}}{RCH\begin{array}{l}\diagup COOH\\ \diagdown COOH\end{array}} \longrightarrow \underset{\text{Alkylacetic acid}}{RCH_2COOH} + CO_2$$

(9) **Hydrolysis of alkyl-acetoacetic esters.** A variety of monocarboxylic acids can be synthesised by the hydrolysis of suitable alkyl-acetoacetic esters with a concentrated solution of alcoholic potash. Thus :

$$\underset{\text{Alkylacetoacetic ester}}{CH_3CO\overset{HO|H}{|}CHR.COO\overset{H|OH}{|}C_2H_5} \longrightarrow \underset{\text{Acetic acid}}{CH_3COOH} + \underset{\text{Alkylacetic acid}}{RCH_2COOH} + C_2H_5OH$$

PHYSICAL CHARACTERISTICS

(1) The lower fatty acids up to C_{10} are colourless liquids. The higher ones are colourless waxy solids.

(2) The first three members have a sharp pungent odour. The middle ones, C_4 to C_9, have an odour of rancid butter. The higher members are colourless

(3) The lower members are very soluble in water but the solubility falls rapidly with rise of molecular weight, the acids from C_{10} onward being insoluble. Fatty acids are readily soluble in alcohol and ether.

(4) They dissolve in water giving weakly acid solutions, turning blue litmus red.

$$RCOOH \rightleftharpoons RCOO^- + \overset{+}{H}$$

As we ascend the series, the value of dissociation constant (K_a) decreases which signifies that acid character weakens. The higher members hardly affect litmus.

(5) The boiling points of fatty acids show a regular increase with increase of molecular weight. Their melting points are, however, irregular, the even members melting at a higher temperature than the odd members which follow them.

The physical constants of some of the normal acids are given in the table below :

ACID	M.PT. °C	B.PT. °C	$K_a \times 10^5$
Formic acid, $HCOOH$	8 6	100·8	17·7
Acetic acid, CH_3COOH	16·7	118	1·8
Propionic acid, C_2H_5COOH	−22	141	1·3
Butyric acid, C_3H_7COOH	—4·7	16·5	1·5
Valeric acid, C_4H_9COOH	—34·5	187	1·4
Caproic acid, $C_5H_{11}COOH$	—1·5	202	1·32
Heptonic acid, $C_6H_{13}COOH$	10	222	0·3
Palmitic acid, $C_{15}H_{31}COOH$	62	268	
Stearic acid, $C_{17}H_{35}COOH$	69·3	287	

CHEMICAL CHARACTERISTICS

The molecule of a fatty acid, R.CO.OH, is made of

(*i*) *a hydrocarbon radical R,*

(*ii*) *a carbonyl group CO* ⎤ *Carboxyl group.*
and (*iii*) *a hydroxyl group OH* ⎦

Thus, the reactions of fatty acids consist of :

(*a*) those *due to the alkyl radical* which undergoes halogenation like the alkanes.

(*b*) those *due to the carbonyl group* which is relatively inert and does not show the usual aldehyde and ketone reactions. It can, however be reduced to $-CH_2-$ group with difficulty.

(*c*) *those due to the hydroxyl group* which is very reactive and can be replaced by other atoms or groups. The presence of the carbonyl group activates the hydroxyl group so that unlike alcohols, fatty acids react with alkalis to form salts.

(*d*) those *due to the carboxyl group as a whole i.e.*, the reactions in which both the CO and OH groups are involved simultaneously.

Reactions due to the Alkyl Radical

(1) **Halogenation.** In the presence of a catalyst such as iodine or phosphorus, chlorine and bromine attack the hydrocarbon radical forming substituted acids. Thus :

$$\underset{\text{Acetic acid}}{CH_3COOH} + Cl_2 \longrightarrow \underset{\text{Monochloroacetic acid}}{CH_2Cl.COOH} + HCl$$

In higher acids, halogenation takes place first in the α-position and continues till all the hydrogen atoms are replaced by halogen atoms.

$$\underset{\text{Propionic acid}}{CH_3CH_2COOH} + Cl_2 \longrightarrow \underset{\alpha\text{-Chloropropionic acid}}{CH_3CHCl.COOH} + HCl$$

(2) **Oxidation.** With a mild oxidising agent such as hydrogen peroxide, the alkyl radical is oxidised in the β-position.

$$\underset{\text{Butyric acid}}{CH_3CH_2CH_2COOH} + O \longrightarrow \underset{\beta\text{-Hydroxybutyric acid}}{CH_3CHOHCH_2COOH}$$

Reactions due to the Carbonyl Group

(3) **Reduction.** The lower fatty acids cannot be reduced easily. The higher acids on prolonged heating with hydriodic acid, or with hydrogen at high temperature in the presence of a catalyst, form primary alcohols. Thus :

$$\underset{\text{Acid}}{RCOOH} + 2H_2 \longrightarrow \underset{\text{Alcohol}}{RCH_2OH} + H_2O$$

Reactions due to the Hydroxyl Group

(4) **Formation of Salts.** The fatty acids react with alkalis to form salts. Thus :

$$\underset{\text{Acid}}{RCOOH} + NaOH \longrightarrow \underset{\text{Salt}}{RCOONa} + H_2O$$

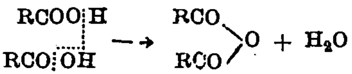
$$\underset{\text{Acid}}{2RCOOH} + Na_2CO_3 \longrightarrow \underset{\text{Salt}}{2RCOONa} + H_2O + CO_2$$

The reaction with sodium carbonate or sodium bicarbonate is attended by effervescence due to the evolution of carbon dioxide gas, and is used as a test for the presence of COOH group.

(5) **Formation of Esters.** When heated with alcohols in the presence of a dehydrating agent such as sulphuric acid, the hydrogen of the OH group is replaced by an alkyl radical resulting in the formation of an ester. Thus :

$$\underset{\text{Acid}}{RCOOH} + \underset{\text{Alcohol}}{R'OH} \longrightarrow \underset{\text{Ester}}{RCOOR'} + H_2O$$

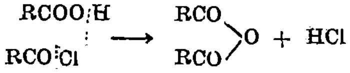
(6) **Formation of Anhydrides.** Fatty acids when treated with a strong dehydrating agent such as phosphorus pentoxide, split out one molecule of water from two molecules of acid forming *acid anhydrides*.



$$\begin{matrix} RCOO\vdots H \\ RCO\vdots OH \end{matrix} \longrightarrow \begin{matrix} RCO \\ RCO \end{matrix}\!\!>\!O + H_2O$$

Acid Acid anhydride

Acid anhydrides are also obtained by the reaction of a fatty acid with acid chloride.



$$\begin{matrix} RCOO\vdots H \\ RCO\vdots Cl \end{matrix} \longrightarrow \begin{matrix} RCO \\ RCO \end{matrix}\!\!>\!O + HCl$$

(7) **Formation of Acid chlorides.** Fatty acids react with phosphorus pentachloride and thionyl chloride, $SOCl_2$, to form acid chlorides, the OH group being replaced by Cl atom.

$$\underset{\text{Acid}}{RCOOH} + PCl_5 \longrightarrow \underset{\text{Acid chloride}}{RCOCl} + POCl_3 + HCl$$

$$\underset{\text{Acid}}{RCOOH} + SOCl_2 \longrightarrow \underset{\text{Acid chloride}}{RCOCl} + SO_2 + HCl$$

(8) **Formation of Amides and Nitriles.** When treated with ammonia, fatty acids first form the ammonium salts which upon heating split out a molecule of water giving acid amides. The OH group of the acid is thus replaced by $—NH_2$ group.

$$\underset{\text{Amm. salt}}{RCOONH_4} \longrightarrow \underset{\text{Amide}}{RCONH_2} + H_2O$$

If the ammonium salt is heated with phosphorus pentoxide, it eliminates two molecules of water forming a *nitrile*.

$$\underset{\text{Amm. salt}}{RCOONH_4} \longrightarrow \underset{\text{Alkyl nitrile}}{RCN} + 2H_2O$$

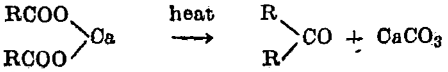
Reactions due to the COOH group as a whole

(9) **Decarboxylation.** When the sodium salt of a fatty acid is heated with sodalime, it yields an alkane.

$$\underset{\text{Sod. salt}}{RCOONa} + NaOH \longrightarrow \underset{\text{Alkane}}{RH} + Na_2CO_3$$

This amounts to the knocking of the carboxyl group by splitting out a molecule of carbon dioxide from the acid molecule. Hence, the term 'decarboxylation'.

(10) **Formation of Aldehydes and Ketones.** The dry distillation of calcium salts of fatty acids, except formic acid, yields ketones.



$$\begin{matrix} RCOO \\ RCOO \end{matrix}\!\!>\!Ca \xrightarrow{heat} \begin{matrix} R \\ R \end{matrix}\!\!>\!CO + CaCO_3$$

Cal. salt Ketone

The dry-distillation of a mixture of the calcium salt of a fatty acid with calcium formate, gives an aldehyde.

$$\underset{\text{Cal. salt}}{(RCOO)_2Ca} + \underset{\text{Cal. formate}}{(HCOO)_2Ca} \longrightarrow \underset{\text{Aldehyde}}{RCHO} + CaCO_3$$

It has been shown recently that the above reactions can be carried with free fatty acids in the vapour state in the presence of a heated catalyst such as manganous oxide

$$2RCOOH \longrightarrow R_2CO + H_2O + CO_2$$
$$RCOOH + HCOOH \longrightarrow RCHO + H_2O + CO_2$$

(11) **Electrolysis.** The solutions of alkali salts of fatty acids upon electrolysis yield alkanes.

$$2RCOONa \longrightarrow \underset{\text{Alkane}}{R.R} + 2CO_2 + 2Na$$

$$2Na + 2H_2O \longrightarrow 2NaOH + H_2$$

The overall reaction implies the decomposition of two molecules of acid as follows.

$$2RCOOH \longrightarrow \underset{\textit{Alkane}}{R.R} + 2CO_2 + H_2$$

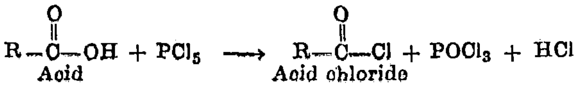
STRUCTURE OF CARBOXYLIC ACIDS

(1) Fatty acids when heated with soda-lime are deprived of a molecule of carbon dioxide forming an alkane.

$$\underset{\text{Acid}}{RCOOH} \longrightarrow \underset{\text{Alkane}}{RH} + CO_2$$

It is clear that the hydrocarbon radical R must have been present in the original acid.

(2) They react with phosphorus pentachloride giving acid chloride and hydrogen chloride.



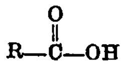
$$\underset{\text{Acid}}{R-\overset{\overset{O}{\|}}{C}-OH} + PCl_5 \longrightarrow \underset{\text{Acid chloride}}{R-\overset{\overset{O}{\|}}{C}-Cl} + POCl_3 + HCl$$

Comparing this reaction with that of PCl_5 on alcohols, we argue that fatty acids also contain a hydroxyl group.

(3) Fatty acids are obtained from aldehydes by oxidation.

$$\underset{\text{Aldehyde}}{R-\overset{\overset{O}{\|}}{C}-H} + O \longrightarrow \underset{\text{Fatty acid}}{R-\overset{\overset{O}{\|}}{C}-OH}$$

The reaction takes place as indicated above since we know that an aldehyde does not give a test of OH while an acid does so. Hence a carboxylic acid has the structural formula



$$R-\overset{\overset{\large O}{\|}}{C}-OH$$

ACIDITY AND RESONANCE

Fatty acids are believed to dissociate to a slight extent in aqueous solution.

$$RCOOH \rightleftharpoons RCOO^- + H^+$$

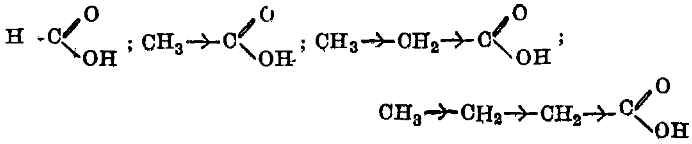
The strength of an acid depends on the extent of such an ionisation process. This is measured by the dissociation constant K_a of the given acid :

$$K_a = \frac{[R.COO^-][H^+]}{[R.COOH]}$$

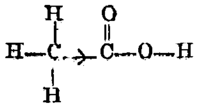
Dissociation constants of some of the carboxylic acids and their derivatives are given below.

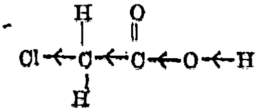
ACID	$K_a \times 10^5$	ACID DERIVATIVES	$K_a \times 10^5$
$H-COOH$	17·7	$F-CH_2-COOH$	220
CH_3-COOH	1·85	$Cl-CH_2-COOH$	150
C_2H_5-COOH	1·62	$Cl_2-CH-COOH$	5,000
C_3H_7-COOH	1·50	$Cl_3-C-COOH$	20,000

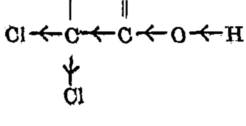
It is clear from the above table that formic acid is stronger than all acids as the size of alkyl radical increases the strength of the acid decreases. The presence of electron-donating groups makes the loss of proton (H^+) more difficult and the strength of acids decreases progressively :

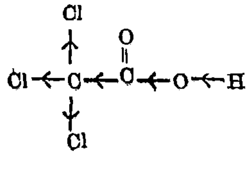


On the other hand, if an electron withdrawing group is linked with the carboxyl group, it facilitates the loss of a proton and therefore the acid strength increases. Fluoroacetic acid is stronger than chloroacetic acid since F being more electronegative exerts greater inductive effect. *Di-* and *Tri*-chloroacetic acids are more acidic than *mono*-chloroderivative because they possess more electron withdrawing Cl atoms, thus enhancing the removal of proton (H^+).



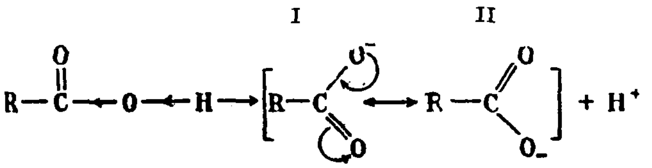






The relative strength of acids can, therefore, be examined by an inductive mechanism.

As appears from the structure of acids $R-\overset{O}{\overset{/\!\!/}{C}}-OH$, they must possess properties of the carbonyl group $\left(>C=O\right)$ and behave like aldehydes and ketones. It is not so. The presence of $-OH$ group modifies the properties of $>CO$ group which leads to a resonance structure.



Thus in the resonance hybrid both C—to—O bonds in —COOH are similar and stronger than a double bond. The resonance hybrid of I and II possesses lower energy contents ('is more stable') than either of I and II forms. The stability of this ion (carboxylate) due to resonance encourages the loss of a proton.

TESTS OF CARBOXYL GROUP

A fatty acid or any other compound containing a carboxyl group can be detected by the following tests :—

(1) In aqueous solution it turns blue litmus red.

(2) Upon distillation with soda-lime it will give the inflammable vapour of a hydrocarbon. The residue in the test-tube will produce effervescence when treated with dilute hydrochloric acid.

(3) With sodium bicarbonate solution, a carboxyl group causes effervescence due to the evolution of carbon dioxide.

(4) When warmed with alcohol and conc. sulphuric acid, a fatty acid forms an ester which is at once detected by its fruity odour.

(5) The action of phosphorus pentachloride upon acids yields acyl chlorides and hydrochloric acid gas. This test is also given by other hydroxy compounds.

INDIVIDUAL MONOCARBOXYLIC ACIDS

FORMIC ACID, METHANOIC ACID, HCOOH

Formic acid was first obtained in 1670 by the distillation of red ants and hence its name (Latin : *formicus*=ant). It is present in stings of bees and wasps, as also in bristles of nettles. The acid is found in traces in urine and perspiration

Preparation. Formic acid may be obtained by the following methods .

(1) By the oxidation of methyl alcohol or of formaldehyde using platinum black as a catalyst.

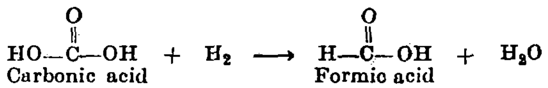
$$\underset{\text{Methyl alcohol}}{CH_3OH} + O \longrightarrow \underset{\text{Formaldehyde}}{HCHO} + H_2O$$

$$\underset{}{HCHO} + O \longrightarrow \underset{\text{Formic acid}}{HCOOH}$$

(2) By the hydrolysis of hydrogen cyanide with hydrochloric acid

$$\underset{\text{Hydrogen cyanide}}{H.C{\equiv}N} + 2H_2O + HCl \longrightarrow \underset{\text{Formic acid}}{H.COOH} + NH_4Cl$$

(3) By the reduction of carbon dioxide in aqueous solution with hydrogen in the presence of palladium black as a catalyst.



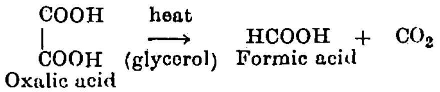
$$\underset{\text{Carbonic acid}}{HO{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OH} + H_2 \longrightarrow \underset{\text{Formic acid}}{H{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OH} + H_2O$$

(4) By passing carbon monoxide over sodalime under 8 atmospheres pressure at 200°. (*Industrial*)

$$NaOH + CO \longrightarrow \underset{\text{Sod. formate}}{HCOONa}$$

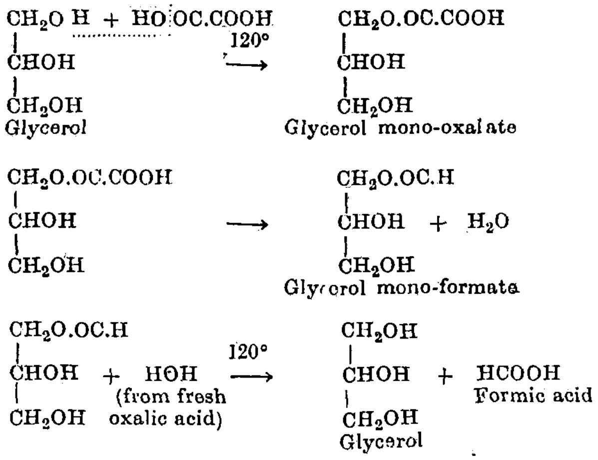
The resulting sodium formate yields free formic acid when treated with dilute sulphuric acid.

(5) By heating crystalline oxalic acid with glycerol (*catalyst*) to 120°



$$\underset{\text{Oxalic acid}}{\begin{array}{l}COOH\\ |\\ COOH\end{array}} \xrightarrow[\text{(glycerol)}]{\text{heat}} \underset{\text{Formic acid}}{HCOOH} + CO_2$$

This method is used for the laboratory preparation of formic acid. In actual practice, glycerol is first heated at 120°. Then a further quantity of hydrated oxalic acid $(COOH)_2.2H_2O$, is added and the temperature is again raised to 120°. The decomposition of oxalic acid takes place as follows :



$$\underset{\text{Glycerol}}{\begin{array}{l}CH_2O\,H + HO\,OC.COOH\\ |\\ CHOH\\ |\\ CH_2OH\end{array}} \xrightarrow{120^\circ} \underset{\text{Glycerol mono-oxalate}}{\begin{array}{l}CH_2O.OC.COOH\\ |\\ CHOH\\ |\\ CH_2OH\end{array}}$$

$$\begin{array}{l}CH_2O.OC.COOH\\ |\\ CHOH\\ |\\ CH_2OH\end{array} \longrightarrow \underset{\text{Glycerol mono-formate}}{\begin{array}{l}CH_2O.OC.H\\ |\\ CHOH\\ |\\ CH_2OH\end{array}} + H_2O$$

$$\begin{array}{l}CH_2O.OC.H\\ |\\ CHOH\\ |\\ CH_2OH\end{array} + \underset{\text{(from fresh oxalic acid)}}{HOH} \xrightarrow{120^\circ} \underset{\text{Glycerol}}{\begin{array}{l}CH_2OH\\ |\\ CHOH\\ |\\ CH_2OH\end{array}} + \underset{\text{Formic acid}}{HCOOH}$$

The glycerol set free is used over again.

Laboratory Preparation. Formic acid is prepared in the laboratory by means of the reaction between glycerol and oxalic acid, as described above.

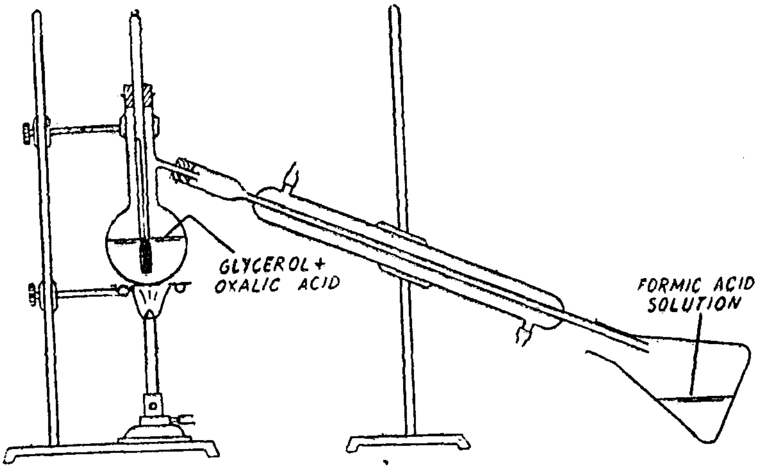


Fig. 20·1. Preparation of aqueous formic acid.

50 ml. of anhydrous glycerol and 40 gms. of powdered crystalline oxalic acid are placed in a distillation flask which is then fitted with a thermometer and water-condenser. The bulb of the thermometer is dipping in the mixture. The flask is heated until the thermometer reads 120° and this temperature is maintained till the evolution of carbon dioxide, marked by effervescence, slackens. Now the flask is cooled and another 40 gms. of oxalic acid are added. The mixture is again heated at 120° when an aqueous solution of formic acid collects in the receiver.

Anhydrous formic acid. The aqueous formic acid obtained above is neutralised with lead carbonate. The solution of lead formate thus produced is filtered and concentrated to yield crystals. The crystals of lead formate are then charged in the inner tube of a water-condenser. One end of the condenser is connected to a hydrogen sulphide generator and the other end is fitted with a Buchner flask guarded with a calcium chloride tube. Hydrogen sulphide is allowed to pass through the condenser while steam is passed through its outer jacket.

$$\underset{\text{Lead formate}}{(HCOO)_2Pb} + H_2S \longrightarrow \underset{\text{Formic acid}}{2HCOOH} + PbS$$

The anhydrous formic acid collecting in the Buchner flask is finally freed from dissolved hydrogen sulphide by distilling over fresh lead formate.

Anhydrous formic acid may also be made by distilling a mixture of sodium formate and sodium hydrogen sulphate.

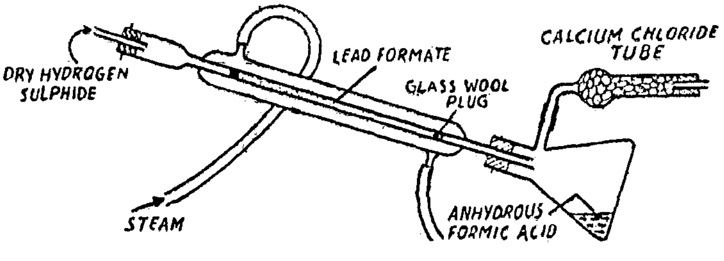


Fig. 20·2. Preparation of anhydrous formic acid.

Properties. *Physical.* Formic acid is a colourless, hygroscopic liquid, b.p. 100·8°. It has a pungent, penetrating odour like that of sulphur dioxide. It is miscible in all proportions with water, alcohol and ether. It is very poisonous and raises blisters when brought in contact with skin. It has a strong antiseptic action.

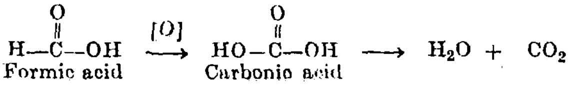
Chemical. Formic acid differs considerably in chemical behaviour from the typical fatty acid since its molecule contains a lone H atom in place of the alkyl radical. Because of this unique feature, formic acid has the structure of both an acid and an aldehyde.

$$\underset{\text{acid}}{H\!-\!\overset{\overset{O}{\|}}{C}\!-\!OH} \qquad \underset{\text{Aldehyde}}{H\!-\!\overset{\overset{O}{\|}}{C}\!-\!OH}$$

The chemical reactions of formic acid are in keeping with the above structures.

Reactions due to lone H atom

(1) OXIDATION. Formic acid can be readily oxidised to form carbon dioxide water.

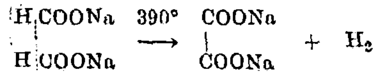


$$\underset{\text{Formic acid}}{H\!-\!\overset{\overset{O}{\|}}{C}\!-\!OH} \xrightarrow{[O]} \underset{\substack{\text{Carbonic acid}\\(\textit{Unstable})}}{HO\!-\!\overset{\overset{O}{\|}}{C}\!-\!OH} \longrightarrow H_2O + CO_2$$

Thus like aldehydes, it reduces Fehling's solution, ammoniacal silver nitrate solution and potassium permanganate solution. Also, it reduces mercuric salts to mercurous salts. Thus :

$$2HgCl_2 + HCOOH \longrightarrow Hg_2Cl_2 + 2HCl + CO_2$$

(2) CONVERSION TO OXALIC ACID. *Sodium formate when heated at about 390°, two molecules of it split out the lone H atoms* as hydrogen gas giving sodium oxalate.



$$\underset{\text{Sod. formate}}{\begin{matrix}H\,COONa\\ H\,COONa\end{matrix}} \xrightarrow{390^\circ} \underset{\text{Sod. oxalate}}{\begin{matrix}COONa\\ |\\ COONa\end{matrix}} + H_2$$

The free oxalic acid is obtained by treatment of the product with a dilute mineral acid.

Reactions due to OH group

(3) FORMATION OF SALTS. Formic acid is the strongest of all fatty acids It forms salts in the usual way.

$$\underset{\textit{Formic acid}}{HCOOH} + NaOH \longrightarrow \underset{\text{Sod. formate}}{HCOONa} + H_2O$$

(4) FORMATION OF ESTERS. Formic acid reacts with alcohols to form esters on simple heating. Thus :

$$HCOOH + \underset{\substack{\text{Methyl}\\ \text{alcohol}}}{CH_3OH} \rightleftharpoons \underset{\substack{\text{Methyl}\\ \textit{formate}}}{HCOOCH_3} + H_2O$$

The addition of mineral acid is unnecessary since formic acid itself acts as its own catalyst.

(5) DECOMPOSITION WITH SULPHURIC ACID. When warmed with concentrated sulphuric acid, formic acid decomposes to form carbon monoxide and water.

$$\underset{\text{Formic acid}}{HCOOH} \longrightarrow H_2O + CO$$

(6) REACTION WITH PCl_5. Formic acid reacts with phosphorus pentachloride forming *formyl chloride* which being unstable at once decomposes into hydrogen chloride and carbon monoxide.

$$\underset{\text{Formic acid}}{HCOOH} + PCl_5 \longrightarrow \underset{\text{Formyl chloride}}{H.CO.Cl} + POCl_3 + HCl$$

$$H.CO.Cl \longrightarrow HCl + CO$$

(7) REACTION WITH AMMONIA. Ammonia combines with formic acid to form ammonium formate which decomposes on heating to yield *formamide.*

$$\underset{\text{Formic acid}}{HCOOH} + NH_3 \longrightarrow \underset{\text{Amm. formate}}{HCOONH_4}$$

$$HCOONH_4 \xrightarrow{\text{Heat}} \underset{\text{Formamide}}{HCONH_2} + H_2O$$

Reactions of COOH Group as a whole

(8) DECARBOXYLATION. When heated above 160°, formic acid splits out a molecule of carbon dioxide giving hydrogen gas.

$$\underset{\text{Formic acid}}{HCOOH} \longrightarrow H_2 + CO_2$$

The decarboxylation can also be effected as usual by heating a mixture of sodium formate and sodium hydroxide.

(9) FORMATION OF ALDEHYDES. Calcium formate when heated alone yields formaldehyde. However, when heated with the calcium salts of other fatty acids it gives higher aldehydes. Thus :

$$\underset{\text{Cal. formate}}{(HCOO)_2Ca} + \underset{\text{Cal. acetate}}{(CH_3COO)_2Ca} \longrightarrow \underset{\text{Acetaldehyde}}{CH_3CHO} + CaCO_3$$

Uses. Formic acid is used :

(1) for the dehydration of hides,

(2) as a coagulating agent for rubber latex,

(3) in medicine as a remedy for gout and neuritis, and

(4) as an acid for dye-baths in textile industry.

Tests. (1) Formic acid can be detected by its characteristic pungent odour.

(2) When warmed with ethyl alcohol a sweet smell of ethyl formate noticed.

(3) It reduces ammoniacal silver nitrate forming a mirror. (*Distinctio from acetic acid*).

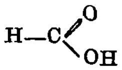
(4) It reduces Fehling's solution to a red precipitate of cuprous oxide. (*Distinction from acetic acid*).

(5) *Nitroprusside test.* If a solution of formic acid is warmed with sodium bisulphite and then treated with sodium nitroprusside, a greenish blue colour is produced. (*Distinction from acetic acid*).

(6) If aqueous solution of formic acid is neutralised with ammonia, it reacts with neutral ferric chloride solution to give a red coloration. On boiling, a brown precipitate of basic ferric formate is obtained.

Structure. (1) Formic acid has been found to possess the molecular formula, CH_2O_2.

(2) The two possible structural formulas which can be constructed according to the valency requirements of the carbon, hydrogen and oxygen atoms are



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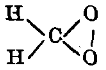


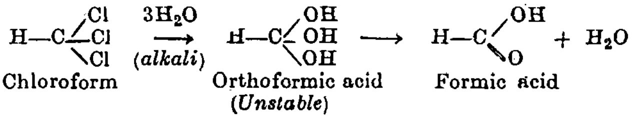
II

(3) Formula I is supported by experimental evidence and represents the structure of formic acid correctly.

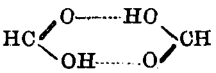
(*a*) Formic acid reacts with PCl_5 giving hydrogen chloride gas, which shows the presence of a hydroxy group.

(*b*) It reduces Fehling's solution and ammoniacal silver nitrate solution thus showing the existence of an aldehyde group.

(4) The structure of formic acid is confirmed by its synthesis from chloroform.



(5) Physical methods have shown further that the formula of formic acid is as follows :



The association of two molecules is probably responsible for the high boiling point of the acid. The chemistry of the acid, however, remains unaffected.

ACETIC ACID, ETHANOIC ACID, CH_3COOH

This is the oldest known fatty acid. It occurs in the free and the combined state in certain biological fluids and plant extracts. It is found in fruit juices which have become sour by fermentation. It is the chief constituent of vinegar and hence its name (Latin : *acetum*=vinegar).

Preparation. Acetic acid can be produced by any of the general methods described before. The technical methods of preparation are the fermentation of alcoholic liquors, from wood distiltion industry, and the modern synthetic processes.

(1) ORLEANS PROCESS. In France, this method is very prevalent and is considered to be the easiest and most effective means of converting wine into vinegar. Acetic bacteria are allowed to grow on the surface of wine in a partly filled cask. In due course wine gets converted into vinegar owing to oxidation with air.

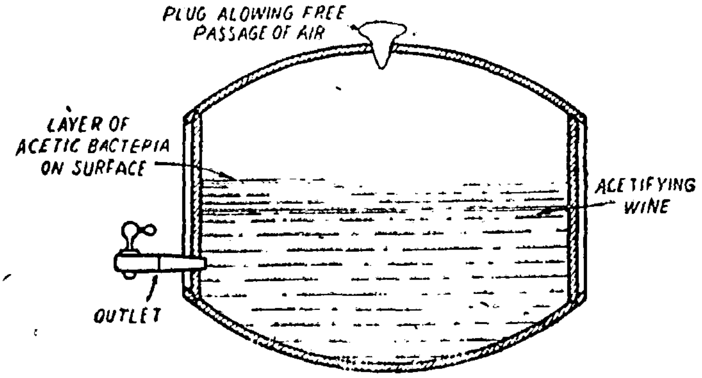


Fig. 20·3. Orlean's Process.

$$\underset{\text{Ethyl alcohol}}{CH_3CH_2OH} + O_2 \longrightarrow \underset{\text{Acetic acid}}{CH_3COOH} + H_2O$$

Vinegar is taken out from the bottom. The cask is again charged with fresh wine and the process is repeated over and over again. The reaction being extremely slow, the out-put of this process is very low but the vinegar produced is of high grade.

(2) QUICK VINEGAR FERMENTATION PROCESS. Large quantities of vinegar, which is in reality 4—6 per cent acetic acid, are obtained from fermented liquors containing 12 15 per cent alcohol. The aqueous solution of alcohol in contact with air and under the influence of *Bacterium aceti* produces acetic acid.

In the *Quick Vinegar process*, large wooden vats filled with basket-work or wood shavings impregnated with old vinegar (*Bacterium aceti*) are used in series. The vats are fitted with a perforated cover and the alcoholic solution is introduced at the top of the first vat and allowed to trickle down the shavings. Air is drawn in through the holes in the lower walls of the vessel and passes up in the opposite direction to the trickling liquid. The heat generated in the oxidation of alcohol to acetic acid maintains the temperature at about 35° which is favourable to the growth and activity of bacteria. The liquor leaving the bottom of each vat is introduced at the top of the next vat. The maximum concentration of acetic acid obtained by this method is 10 per cent. The process requires 8 to 10 days for completion.

(3) FROM WOOD DISTILLATION INDUSTRY. Formerly the chief source to produce glacial or pure acetic acid was *pyroligneous acid* obtained from the dry distillation of wood. It is a dilute aqueous solution containing about 10 per cent of acetic acid along with a little methyl alcohol and acetone. Acetic acid is removed from it by treatment with lime and distilling off methyl alcohol and acetone. The aqueous solution of calcium acetate left behind is evaporated in iron pans and the residue distilled with concentrated sulphuric acid. The distillate consists of 70-75 per cent acetic acid. To get pure or glacial acetic acid, the strong acetic acid solution is neutralised with sodium hydroxide and evaporated. The crystals of sodium acetate thus obtained are heated to expel the water. The anhydrous sodium acetate is finally distilled with concentrated sulphuric acid to yield pure acetic acid.

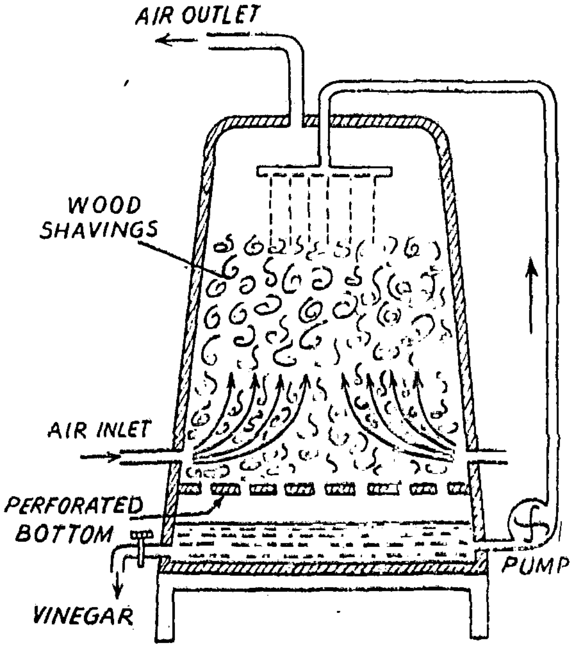


Fig. 20·4. Preparation of vinegar.

(4) MODERN SYNTHETIC METHODS. Most acetic acid is now manufactured from acetylene. Acetylene is bubbled through a dilute solution of sulphuric acid containing mercuric sulphate, when acetaldehyde is obtained. The vapours of acetaldehyde are then mixed with air and passed over manganese acetate at about 60°C.

$$\underset{\text{Acetylene}}{CH{\equiv}CH} + H_2O \longrightarrow \underset{\text{Acetaldehyde}}{CH_3CHO}$$

$$2CH_3CHO + O_2 \longrightarrow \underset{\text{Acetic acid}}{2CH_3COOH}$$

Synthetic acetic acid is also made from ethyl alcohol by the oxidation of its vapours with air over a metal catalyst.

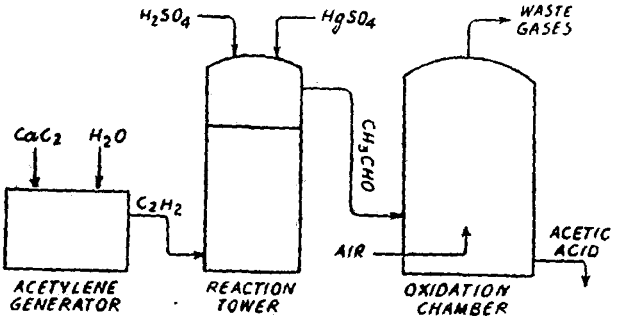


Fig. 20·5. Manufacture of acetic acid from acetylene.

Properties. *Physical.* Acetic acid is a colourless liquid with a sharp 'vinegar odour' and sour taste, b.p. 118·1°, sp. gr. 1·08 at 0°C. When cooled sufficiently, it forms 'ice-like' crystals which melt at 16·7°. Hence the pure anhydrous acid is usually called *glacial acetic acid* (*Glacial* = of ice). It has a corrosive action on the skin and causes blisters. It is miscible with water, alcohol and ether in all proportions, the solution in water being attended by a contraction of volume and liberation of heat. It dissolves sulphur, iodine, and many organic substances.

Chemical. Acetic acid is a typical fatty acid and gives all the general reactions of the class.

(8) *Action of chlorine.* Chlorine reacts with acetic acid in the presence of a catalyst (I, S or P) giving mono-, di-, and trichloroacetic acid.

$$CH_3CO_2H \xrightarrow{Cl_2} CH_2ClCO_2H \xrightarrow{Cl} CHCl_2CO_2H \xrightarrow{Cl_2} CCl_3CO_2H$$

(2) *Formation of salts.* It reacts with oxides, hydroxides and carbonates to form acetates.

$$CH_3COOH + NaOH \longrightarrow \underset{\text{Sod. acetate}}{CH_3COONa} + H_2O$$

$$2CH_3COOH + (NH_4)_2CO_3 \longrightarrow \underset{\text{Amm. acetate}}{2CH_3COONH_4} + H_2O + CO_2$$

(3) *Formation of esters.* It reacts with alcohols to form esters. Thus :

$$CH_3COOH + \underset{\text{Ethyl alcohol}}{C_2H_5OH} \rightleftharpoons \underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + H_2O$$

The reaction is reversible and is catalysed by strong mineral acids.

(4) *Formation of anhydride.* When the vapours of acetic acid are passed over a heated phosphate catalyst, it yields acetic anhydride

$$2CH_3COOH \longrightarrow (CH_3CO)_2O + H_2O$$

(5) *Action with PCl_5*. It reacts with phosphorus pentachloride vigorously forming acetyl chloride with the evolution of HCl gas.

$$CH_3COOH + PCl_5 \longrightarrow \underset{\text{Acetyl chloride}}{CH_3COCl} + POCl_3 + HCl$$

(6) *Formation of amide.* Ammonium acetate decomposes on heating to form acetamide.

$$CH_3COONH_4 \longrightarrow \underset{\text{Acetamide}}{CH_3CONH_2} + H_2O$$

(7) *Decomposition of Na-salt.* Sodium acetate when heated with soda-lime yields methane.

$$CH_3COONa + NaOH \longrightarrow \underset{\text{Methane}}{CH_4} + Na_2CO_3$$

(8) *Decomposition of Ca-salt.* Calcium acetate decomposes upon heating giving acetone.

$$(CH_3COO)_2Ca \longrightarrow \underset{\text{Acetone}}{(CH_3)_2CO} + CaCO_3$$

(9) *Electrolysis.* The electrolysis of a solution of potassium acetate forms ethane.

$$2CH_3COONa \longrightarrow \underset{\text{Ethane}}{C_2H_6} + 2CO_2 + 2Na$$

Uses. Acetic acid is used :

(1) as a laboratory reagent, and as a solvent for carrying reactions since it remains unattacked by oxidising and reducing agents ;

(2) as a table vinegar, and also in the preparation of condiments ;

(3) for coagulating rubber latex ;

(4) for curing meat and fish ;

(5) in medicines as a local irritant ;

(6) for the production of cellulose acetate required for making photographic film and the rayon known as *Celanese* .

(7) for the manufacture of acetates, acetone, and esters ; ethyl acetate and amyl acetate being used as solvents in lacquer industry.

Tests. (1) The free acid has a characteristic odour.

(2) If ferric chloride solution is added to a solution of acetic acid neutralised by ammonia, or by sodium hydroxide, a deep red coloration appears. On boiling the solution the red colour is replaced by a brown precipitate of basic ferric acetate.

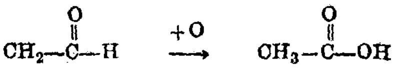
(3) If a little acetic acid is warmed with a small quantity of alcohol and a few drops of sulphuric acid for a minute, the fruity odour of ethyl acetate is noticed.

(4) *Cacodyl test.* If a little acetic acid is neutralised with potassium hydroxide solution and evaporated to dryness and the residue heated with a small quantity of arsenious oxide, an extremely nauseating odour of cacodyl oxide, $(CH_3.As.CH_3)_2O$, is produced. (*Distinction from formic acid*).

(5) Acetic acid does not reduce ammoniacal silver oxide or Fehling's solution. (*Distinction from formic acid*).

Structure. (1) The empirical formula of acetic acid as determined by elementary analysis is CH_2O. The molecular weight based on the silver salt method is 60. Then molecular formula is, therefore, $C_2H_4O_2$.

(2) Acetic acid is produced easily by the direct oxidation of acetaldehyde. The change can be visualised to take place as follows:



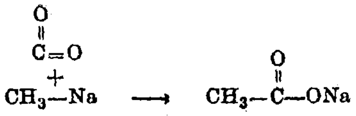
$$CH_2{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}H \xrightarrow{+O} CH_3{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OH$$

It shows that the molecule of the acid contains a carbonyl group on one band and a hydroxyl group on the other. This is supported by the reactions given below :—

(*i*) The reaction of the acid with sodium hydroxide forming sodium formate in which one H atom has been replaced by a sodium atom, indicates that the H atom of OH group is ionisable and hence different than the other three H atoms in the molecule.

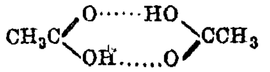
(*ii*) Prolonged action of acetic acid with chlorine gives trichloroacetic acid in which three H atoms of the methyl group have been replaced by Cl atoms while the fourth H atom remains intact.

(3) The structure of acetic acid is finally confirmed by its synthesis from sodium methide and carbon dioxide.



$$\begin{matrix} O \\ \| \\ C{=}O \\ + \\ CH_3{-}Na \end{matrix} \longrightarrow CH_3{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}ONa$$

(4) Recent investigations have shown that acetic acid is bimeric owing to association as follows:



In a solvent like benzene the association is complete when the acid has been shown to have molecular weight 60.

PROPIONIC ACID, PROPANOIC ACID, C_2H_5COOH

Propionic acid occurs in small amounts in acetic acid obtained from the wood distillation industry.

Preparation. Propionic acid may be prepared : (1) by the hydrolysis of ethyl cyanide, (2) by the oxidation of n-propyl alcohol with sodium dichromate and sulphuric acid, and (3) by the reduction of lactic acid with concentrated hydriodic acid. It is made on a large scale by heating carbon monoxide and ethyl alcohol in the presence of a catalyst.

$$\underset{\text{Ethyl alcohol}}{C_2H_5OH} + CO \longrightarrow \underset{\text{Propionic acid}}{C_2H_5COOH}$$

Properties. Propionic acid is an oily liquid, b.p. 151°. It resembles acetic acid in properties. Chlorination of propionic acid gives α-chloropropionic acid, $CH_3CHCl.COOH$.

BUTYRIC ACID, $CH_3.(CH_2)_2.COOH$

Butyric acid occurs in butter as glyceryl ester. The free acid is present in rancid butter and in perspiration.

Preparation. Butyric acid is made on a large scale (1) by the oxidation of n-butyl alcohol and (2) by the fermentation of lactic acid, glucose or starch. The fermentation of glucose may be carried by adding rancid cheese to its aqueous solution. The ferments *butyric bacilli* and *lactic bacilli* present in cheese, bring about the following changes :

$$\underset{\text{Glucose}}{C_6H_{12}O_6} \longrightarrow \underset{\text{Lactic acid}}{2C_3H_6O_3}$$

$$2C_3H_6O_3 \longrightarrow \underset{\text{Butyric acid}}{CH_3CH_2CH_2COOH} + 2CO_2 + 2H_2$$

Sour milk contains lactic acid which can be converted to butyric acid by this method.

Properties. Butyric acid is a rancid-smelling liquid, b.p. 163·5°. It shows the usual reactions of the fatty acids. It is sometimes used in the tanning industry for deliming of hides.

ISOBUTYRIC ACID, $(CH_3)_2CH.COOH$

Isobutyric acid occurs in the free state in locust bean and as methyl ester in croton oil.

Preparation. Isobutyric acid is prepared : (1) by the oxidation of isobutyl alcohol, and (2) from isopropyl alcohol by the following steps.

$$\underset{\text{Isopropyl alcohol}}{(CH_3)_2CHOH} \xrightarrow{HI} (CH_3)_2CHI \xrightarrow{KCN} (CH_3)_2CH.CN \xrightarrow{H_2O} \underset{\text{Isobutyric acid}}{(CH_3)_2CHCOOH}$$

Properties. Isobutyric acid is a colourless oily liquid, b.p. 154·5° It is sparingly soluble in water. Unlike the normal acid, it is easily oxidised to acetone, or acetic acid and carbonic acid.

HIGHER FATTY ACIDS

PALMITIC ACID, $C_{15}H_{31}COOH$, AND STEARIC ACID, $C_{17}H_{35}COOH$

These acids occur as glycerol esters in natural fats from which they are prepared by hydrolysis with superheated-steam. Palmitic acid takes its name from *Palm oil* and stearic acid from *Stear*, meaning tallow.

Palmitic acid and stearic acid are colourless waxy solids which melt at 62° and 69·3° respectively. They are insoluble in water and soluble in alcohol and ether. Their salts are soaps. The acids are mixed with wax used for making candles.

Both acids have normal structure.

UNSATURATED MONOCARBOXYLIC ACIDS

Unsaturated monocarboxylic acids are the carboxy derivatives of alkenes. Thus :

$$\underset{\text{Ethylene}}{CH_2{=}CH_2} \xrightarrow[+CO_2]{-H} \underset{\text{Acrylic acid}}{CH_2{=}CH.COOH}$$

$$\underset{\text{Propylene}}{CH_3CH{=}CH_2} \longrightarrow \underset{\text{Crotonic acid}}{CH_3CH{=}CH.COOH}$$

The earliest known member of this class is oleic acid,

$$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$$

ACRYLIC ACID, CH_2:HC.COOH

Acrylic acid is carboxyethylene and is the simplest member of the class. Its name is derived from *acrolein*, the corresponding aldehyde.

Preparation. Acrylic acid may be prepared :

(1) By heating bromopropionic acid with alcoholic potash,

$$\underset{\beta\text{-Bromopropionic acid}}{CH_2BrCH_2COOH} + KOH_{alc} \longrightarrow CH_2{:}CHCOOH + KBr + H_2O$$

(2) By treating α, β-dibromopropionic acid with zinc,

$$CH_2BrCHBrCOOH + Zn \longrightarrow CH_2{:}CHCOOH + ZnBr_2$$

(3) By *distilling β-hydroxypropionic acid*,

$$CH_2OHCH_2COOH \longrightarrow CH_2{:}CHCOOH + H_2O$$

(4) By oxidation of acrolein with silver oxide,

$$CH_2{:}CH.CHO + O \longrightarrow CH_2{:}CHCOOH$$

(5) From ethylene chlorohydrin by the following steps :

$$HO.CH_2CH_2Cl \xrightarrow{KCN} HO.CH_2CH_2CN \xrightarrow{H_2O} CH_2{:}CH{\cdot}COOH$$

Properties. Acrylic acid is a colourless liquid, b.p. 142°, having a pungent odour like that of acetic acid. It is miscible with water in all proportions. It is a stronger acid than acetic acid.

Acrylic acid behaves both as an alkene and as a fatty acid.

(1) With nascent hydrogen it is reduced to propionic acid,

$$CH_2{:}CH.COOH + 2H \longrightarrow \underset{\text{Propionic acid}}{CH_3CH_2COOH}$$

(2) With chlorine and bromine it forms addition products. Thus :

$$CH_2{:}CHCOOH + Br_2 \longrightarrow \underset{\alpha,\ \beta\text{-dibromopropionic acid}}{CH_2Br.CHBr.COOH}$$

(3) With halogen acids, it yields β-halogen acid. Thus :

$$CH_2{:}CHCOOH + HI \longrightarrow \underset{\beta\text{-iodopropionic acid}}{CH_2ICH_2COOH}$$

The addition defies Markownikoff's rule, the halogen linking with the β-carbon.

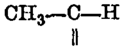
(4) Upon oxidation with dilute potassium permanganate solution, it gives glyceric acid which on vigorous oxidation decomposes to oxalic acid.

$$CH_2{:}CHCOOH + H_2O + O \longrightarrow \underset{\text{Glyceric acid}}{CH_2OH.CHOH.COOH}$$

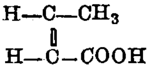
(5) On standing it at once polymerises to a solid.

(6) At the carboxyl group it forms salts, esters and acid halides.

Crotonic acid, $CH_3CH{:}CH.COOH$. Crotonic acids exists in two forms which are geometrical isomers.

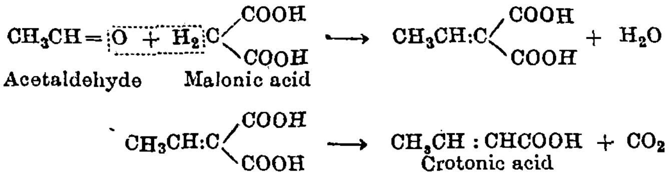


Crotonic acid
(*trans form*)



Isocrotonic acid
(*cis form*)

Ordinary crotonic acid is the trans isomer. It occurs as glyceryl esters in *croton oil* from which it takes its name. It is best prepared by heating malonic acid with paraldehyde and acetic anhydride.



It is a colourless, crystalline solid, m.p. 72°. Upon reduction with zinc dust and sulphuric acid, it is converted to n-butyric acid. When carefully oxidised with nitric acid, it forms oxalic acid and acetic acid.

Isocrotonic acid is prepared by heating β-hydroxyglutaric acid under reduced pressure. It is a colourless liquid, b.p. 172°. It is transformed to crotonic acid when heated to 10° in a sealed tube.

OLEIC ACID, $CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$

It occurs abundantly as glyceryl esters in many natural oils and fats. Olive oil, cocoanut oil, almond oil, linseed oil, etc. also contain oleic acid.

Preparation. Oleic acid is prepared by the hydrolysis of fatty oils with an alkali. These oils upon hydrolysis yield a mixture of the sodium salts of oleic acid, palmitic acid and stearic acid. These are converted into lead salts which are then treated with ether. Ether dissolves lead oleate only leaving behind lead palmitate and lead stearate. Lead oleate so obtained is decomposed by the action of a mineral acid when free oleic acid is produced.

Properties. Oleic acid is a colourless and odourless liquid which boils at 286°. When cooled it solidifies to form crystals melting at 14°. It is insoluble in water. In air it rapidly becomes yellow due to oxidation and becomes rancid.

Oleic acid gives all the reactions of an unsaturated acid. It undergoes an interesting transformation when treated with nitrous acid, a crystalline compound Elaidic acid (m.p. 44 2°) being formed. This compound is a geometrical isomer of oleic acid.

The following reactions prove the **Constitution of Oleic acid :**

(1) It adds a molecule of bromine forming dibromostearic acid.

$$C_{17}H_{33}COOH + Br_2 \longrightarrow C_{17}H_{33}Br_2COOH$$

This indicates the presence of a double bond in the molecule.

(2) With nascent hydrogen, oleic acid is converted into stearic acid which is known to have a straight-chain structure.

$$\underset{\text{Oleic acid}}{C_{17}H_{33}COOH} + 2H \longrightarrow \underset{\text{Stearic acid}}{CH_3(CH_2)_{16}COOH}$$

This reaction confirms the presence of a double bond and also shows that like stearic acid, oleic acid contains a normal chain of carbon atoms.

(3) On careful oxidation with dilute permanganate, oleic acid yields a mixture of two acids,

$$\underset{\text{Pelargonic acid}}{CH_3(CH_2)_7COOH} \quad \text{and} \quad \underset{\text{Azelaic acid}}{HOOC(CH_2)_7COOH}$$

each of which contains nine carbon atoms. As unsaturated compounds break by oxidation at the double bond, it is obvious that oleic acid contains the double union in the middle of the chain. Hence, the structural formula of oleic acid would be

$$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$$

(4) The structure of oleic acid is further confirmed by treatment with ozone. The ozonide of the acid yields the following aldehydes when decomposed with water and zinc.

$$\underset{\text{Pelargonic aldehyde}}{CH_3(CH_2)_7CHO} \qquad \underset{\text{Azelaic aldehyde}}{OHC(CH_2)_7CHO}$$

Oleic acid is used in the manufacture of soaps and for oiling wool before *spinning.*

QUESTIONS

1. What are fatty acids ? Justify their derivation from water, hydrocarbons and carbonic acid.

2. Describe the general methods of preparation and properties of monocarboxylic acid.

3. On what grounds has the conclusion been drawn that the molecular formula of the fatty acids contain the grouping —COOH ? Summarise the methods by which the grouping can be introduced into aliphatic hydrocarbons.

4. "Formic acid behaves both as an aldehyde and as an acid." Illustrate and explain.

5. How would you prepare a specimen of formic acid in the laboratory ? State the chemical properties of the acid and show that they agree with the formula usually assigned to it.

6. How is formic acid prepared in the laboratory as well as on a large scale ? Give its important reactions and tests.

7. Formic acid differs more from the rest of the fatty acids than they differ from each other. What facts can you cite in support of this statement ? What explanation of it can be given ?

8. How is acetic acid prepared commercially ? How would you prepare acetic acid from (*a*) ethyl alcohol (*b*) methyl alcohol, and (*c*) acetyl chloride ? How would you decide the structure of acetic acid ?

9. Write the structural formula of oleic acid. Describe the reactions which lead to its adoption. How is this acid prepared commercially ?

10. Indicate how propionic acid could be converted into :

(*a*) propionyl chloride, (*b*) propionic anhydride, (*c*) α-chloropropionic acid, (*d*) propionaldehyde, (*e*) lactic acid (*f*) diethyl ketone, (*g*) *n*-butyric acid and (*h*) acetaldehyde. (*Agra B.Sc., 1960*)

11. (*a*) What are the general methods of obtaining carboxylic acids ?

(*b*) State how acetic acid may be converted into (*i*) acetaldehyde, (*ii*) malonic acid, (*iii*) aminoacetic acid, (*iv*) nitromethane.

(*Panjab B.Sc., 1961*)

12. What are fatty acids ? Give an example. How is acetic acid prepared ? Starting from the acetic acid how can you prepare (*a*) acetyl chloride, (*b*) acetic anhydride, (*c*) acetamide. (*Dibrugarh B.Sc., 1967*)

13. Write a note on 'Relative' strength of acetic acid and trichloracetic acid in terms of inductive effect (explanation is required).

(*Panjab B.Sc. II, 1968*)

14. Give two different methods for the preparation of aliphatic monocarboxylic acids starting from an alkyl halide. How the acid amides and esters are prepared ? (*Jadavpur B.Sc., 1968*)

15. Describe the preparation of pure formic acid and state its properties. How does it differ from acetic acid ? (*Ujjain B.Sc., 1968*)

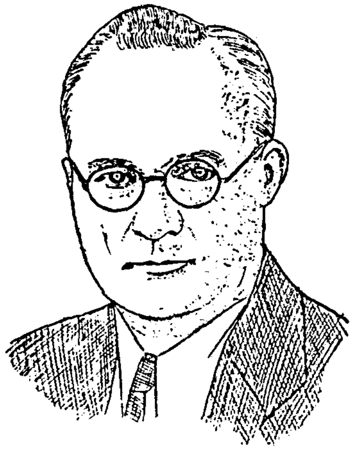
16. How is acetic acid obtained on a large scale ? How can it be converted into (*a*) monochloroacetic acid (*b*) acetyl chloride (*c*) acetic anhydride (*d*) acetamide (*e*) methylamine and (*f*) ethyl acetate. (*Madurai B.Sc., 1968*)

17. How is formic acid obtained in the laboratory ? Mention its important reactions. In what respects formic acid differs from acetic acid ?

(*Jammu & Kashmir B.Sc.; 1969*)

21

Dicarboxylic Acids



THOMAS MIDGLEY, JR.
(1889—1944)
American : known for his studies in various types of fuels and for the development of anti-knock agents including tetraethyllead. Midgley produced the organic chloro-fluoride compounds, widely used as refrigerants.

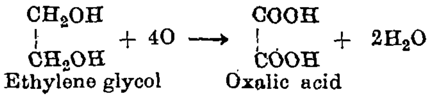
As the name implies, the dicarboxylic acids contain two carboxylic groups in their molecules. Of these most important are the straight-chain acids with the COOH groups at the terminal carbon atoms. The general formula for the series of normal dicarboxylic acids may be written as $(CH_2)_2(COOH)_2$, where *n* for the first member is zero. The acids are generally known by their common names which are derived from the origin or method of formation.

ACID	FORMULA	M.P. °C
Oxalic acid	$HOOC.COOH$	187
Malonic acid	$HOOC(CH_2)COOH$	135
Succinic acid	$HOOC(CH_2)_2COOH$	185
Glutaric acid	$HOOC(CH_2)_3COOH$	97·5
Adipic acid	$HOOC(CH_2)_4COOH$	151
Primelic acid	$HOOC(CH_2)_5COOH$	105
Suberic acid	$HOOC(CH_2)_6COOH$	142
Azelaic acid	$HOOC(CH_2)_7COOH$	106
Sebacic acid	$HOOC(CH_2)_8COOH$	134

METHODS OF PREPARATION

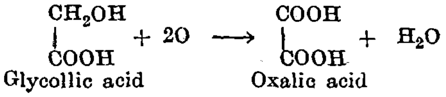
The methods of preparation of dicarboxylic acids are analogous to those used for fatty acids, only we have to develop two COOH groups instead of one.

(1) By the oxidation of diprimary glycols or hydroxy acids. Thus :



$$\begin{array}{c}CH_2OH\\|\\CH_2OH\end{array} + 4O \longrightarrow \begin{array}{c}COOH\\|\\COOH\end{array} + 2H_2O$$

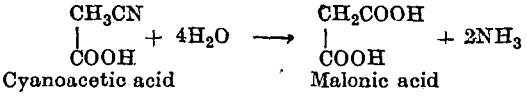
Ethylene glycol Oxalic acid



$$\begin{array}{c}CH_2OH\\|\\COOH\end{array} + 2O \longrightarrow \begin{array}{c}COOH\\|\\COOH\end{array} + H_2O$$

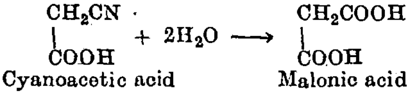
Glycollic acid Oxalic acid

(2) By the hydrolysis of dicyanides or cyano-fatty acids.



$$\begin{array}{c}CH_3CN\\|\\COOH\end{array} + 4H_2O \longrightarrow \begin{array}{c}CH_2COOH\\|\\COOH\end{array} + 2NH_3$$

Cyanoacetic acid Malonic acid



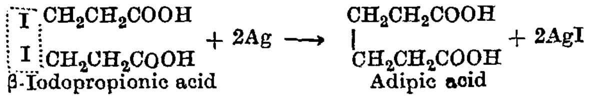
$$\begin{array}{c}CH_2CN\\|\\COOH\end{array} + 2H_2O \longrightarrow \begin{array}{c}CH_2COOH\\|\\COOH\end{array}$$

Cyanoacetic acid Malonic acid

This provides a method of obtaining dicarboxylic acids from alkenes as follows. Thus :

$$\underset{\text{Ethylene}}{C_2H_4} \xrightarrow{Br_2} \underset{\text{Dibromide}}{C_2H_4Br_2} \xrightarrow{KCN} \underset{\text{Dicyanide}}{C_2H_4(CN)_2} \xrightarrow{\text{Hydrol.}} \underset{\text{Succinic acid}}{C_2H_4(CO_2H)_2}$$

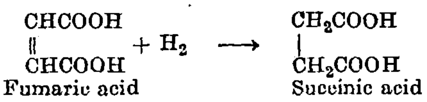
(3) By the action of precipitated silver on halogen-substituted fatty acids.



$$\begin{array}{l}I\ CH_2CH_2COOH\\ \\I\ CH_2CH_2COOH\end{array} + 2Ag \longrightarrow \begin{array}{c}CH_2CH_2COOH\\|\\CH_2CH_2COOH\end{array} + 2AgI$$

β-Iodopropionic acid Adipic acid

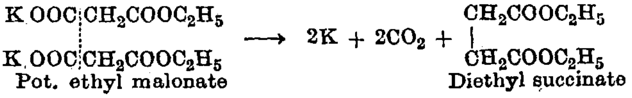
(4) By the reduction of unsaturated dicarboxylic acids.



$$\begin{array}{c}CHCOOH\\\|\\CHCOOH\end{array} + H_2 \longrightarrow \begin{array}{c}CH_2COOH\\|\\CH_2COOH\end{array}$$

Fumaric acid Succinic acid

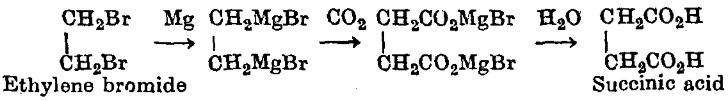
(5) By the electrolysis of salts of acid-esters of lower dicarboxylic acids.



$$\begin{array}{l}K\,OOC\,CH_2COOC_2H_5\\ \\K\,OOC\,CH_2COOC_2H_5\end{array} \longrightarrow 2K + 2CO_2 + \begin{array}{c}CH_2COOC_2H_5\\|\\CH_2COOC_2H_5\end{array}$$

Pot. ethyl malonate Diethyl succinate

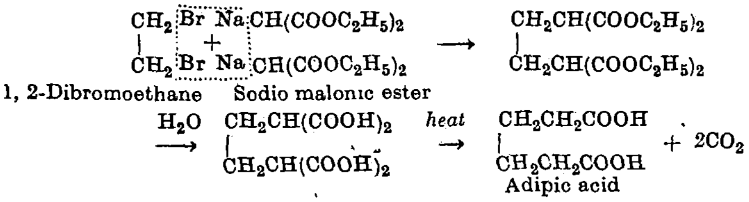
(6) From Grignard reagents of dihalo-alkanes by reaction with carbon dioxide and subsequent hydrolysis.



$$\begin{array}{c}CH_2Br\\|\\CH_2Br\end{array} \xrightarrow{Mg} \begin{array}{c}CH_2MgBr\\|\\CH_2MgBr\end{array} \xrightarrow{CO_2} \begin{array}{c}CH_2CO_2MgBr\\|\\CH_2CO_2MgBr\end{array} \xrightarrow{H_2O} \begin{array}{c}CH_2CO_2H\\|\\CH_2CO_2H\end{array}$$

Ethylene bromide Succinic acid

(7) By the action of dihalo-alkanes with sodio malonic ester and subsequent hydrolysis.



$$\underset{\text{1, 2-Dibromoethane}}{\begin{array}{l}CH_2\,Br\\ |\\ CH_2\,Br\end{array}} + \underset{\text{Sodio malonic ester}}{\begin{array}{l}Na\,CH(COOC_2H_5)_2\\ \\ Na\,CH(COOC_2H_5)_2\end{array}} \longrightarrow \begin{array}{l}CH_2CH(COOC_2H_5)_2\\ |\\ CH_2CH(COOC_2H_5)_2\end{array}$$

$$\xrightarrow{H_2O} \begin{array}{l}CH_2CH(COOH)_2\\ |\\ CH_2CH(COOH)_2\end{array} \xrightarrow{heat} \underset{\text{Adipic acid}}{\begin{array}{l}CH_2CH_2COOH\\ |\\ CH_2CH_2COOH\end{array}} + 2CO_2$$

PHYSICAL CHARACTERISTICS

(1) The dicarboxylic acids are crystalline solids, their melting points being much higher than the corresponding fatty acids.

(2) They dissolve readily in water but the solubility falls appreciably with rise of molecular weight

(3) Their solubilities and melting points show an interesting alternation. An acid with an even number of C atoms invariably has a much higher melting point and is much more soluble than the following acid containing an odd number. This is attributed to the fact that the carbon chains are arranged in zig-zag fashion (Fig. 21 1) and the COOH groups at the ends lie on the same side in odd-numbered acids and on the opposite sides in even-numbered acids.

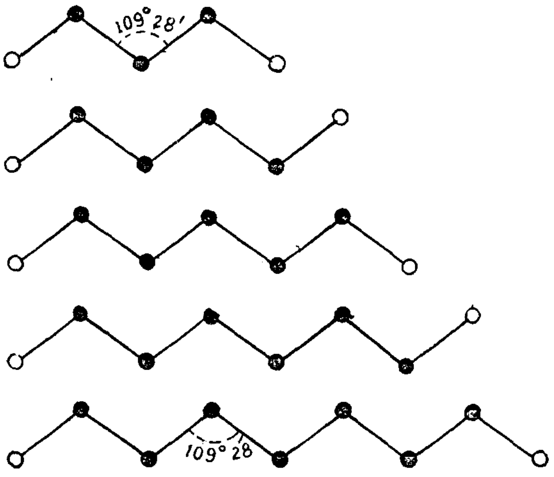


Fig. 21·1. Arrangement of carbon chains in odd and even numbered acids.

(4) They ionise in two steps and are much stronger than the fatty acids. Thus :

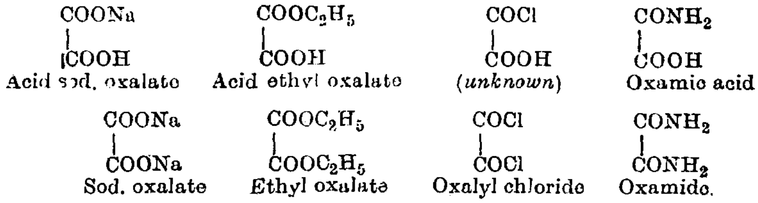
$$\underset{\text{Malonic acid}}{HOOC.CH_2.COOH} \longrightarrow HOOC\,CH_2.CO\bar{O} + \overset{+}{H}$$

$$HOOC.CH_2.CO\bar{O} \longrightarrow \underset{\text{Malonate ion}}{\bar{O}OC.CH_2CO\bar{O}} + \overset{+}{H}$$

CHEMICAL CHARACTERISTICS

The chemical reactions of dicarboxylic acids are mainly governed by the reactivity of the carboxyl groups. The behaviour of oxalic acid differs from that of the rest of the members in certain respects since its molecule has no hydrocarbon chain and consists of two COOH groups only.

(1) **Replacement reactions of COOH group.** The dicarboxylic acids show the usual reactions of the carboxylic group twice over. Thus, they form two series of derivatives according as one or both carboxyl groups react. For illustration, oxalic acid forms the following derivatives :



$\begin{array}{l}COONa\\ \vert\\ COOH\end{array}$	$\begin{array}{l}COOC_2H_5\\ \vert\\ COOH\end{array}$	$\begin{array}{l}COCl\\ \vert\\ COOH\end{array}$	$\begin{array}{l}CONH_2\\ \vert\\ COOH\end{array}$
Acid sod. oxalate	Acid ethyl oxalate	(*unknown*)	Oxamic acid
$\begin{array}{l}COONa\\ \vert\\ COONa\end{array}$	$\begin{array}{l}COOC_2H_5\\ \vert\\ COOC_2H_5\end{array}$	$\begin{array}{l}COCl\\ \vert\\ COCl\end{array}$	$\begin{array}{l}CONH_2\\ \vert\\ CONH_2\end{array}$
Sod. oxalate	Ethyl oxalate	Oxalyl chloride	Oxamide.

(2) **Action of heat.** The action of heat on dicarboxylic acids is particularly interesting.

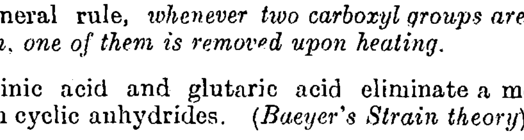
(*i*) Oxalic acid and malonic acid split out a molecule of carbon dioxide yielding fatty acids.

$$\underset{\text{Oxalic acid}}{H\,OOC.COOH} \xrightarrow{\text{heat}} \underset{\text{Formic acid}}{HCOOH} + CO_2$$

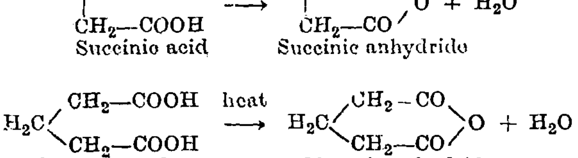
$$\underset{\text{Malonic acid}}{H\,OOC\,CH_2COOH} \xrightarrow{\text{heat}} \underset{\text{Acetic acid}}{CH_3COOH} + CO_2$$

As a general rule, *whenever two carboxyl groups are linked to the same carbon, one of them is removed upon heating.*

(*ii*) Succinic acid and glutaric acid eliminate a molecule of water and form cyclic anhydrides. (*Baeyer's Strain theory*).



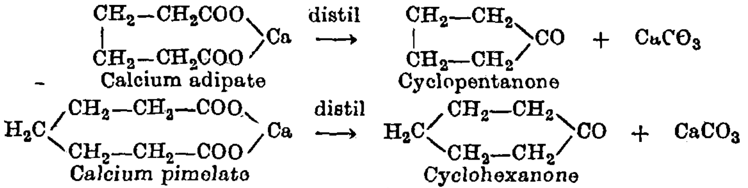
Succinic acid Succinic anhydride



Glutaric acid Glutaric anhydride

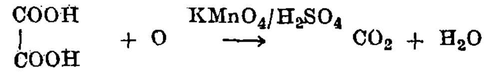
(*iii*) The action of heat on higher members from adipic acid onward does not cause any decomposition.

(3) **Decomposition of Ca-salts.** The calcium salts of higher carboxylic acids when distilled yield cyclic ketones



The calcium salts of sebacic and azelaic acids also form cycli ketones but the yield is poor.

(4) **Oxidation.** In general, the dicarboxylic acids are stabl to oxidising agents. Oxalic acid is, however, oxidised with acidifie potassium permanganate solution.



$$\begin{matrix}COOH\\ |\\ COOH\end{matrix} + O \xrightarrow{KMnO_4/H_2SO_4} CO_2 + H_2O$$

Oxalic acid

Individual Members

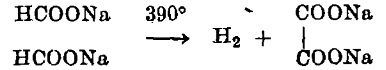
OXALIC ACID, $(COOH)_2.2H_2O$

The acid has long been known, as it is widely distributed i the plant kingdom. It occurs as potassium hydrogen oxalate in th wood sorrel (*Oxalis ocetosella*). rhubarb and tobacco. Calciu oxalate has been found in lichens and ferns. Ammonium oxalate i present in urine.

Preparation. Oxalic acid may be produced by the oxidatio of glycol and also by the hydrolysis of cyanogen. The followin methods are commonly employed for its preparation

(1) In the laboratory oxalic acid is made conveniently by th oxidation of cane sugar (*sucrose*) with nitric acid. Th —CHOH.CHOH— units present in sucrose molecule are split out and oxidised to oxalic acid. The reaction is accompanied by copiou nitrous fumes and the preparation is, therefore, carried in a fum chamber.

(2) Oxalic acid is now obtained on a large scale by heating sodium formate to 390°



$$\begin{matrix}HCOONa\\ \\ HCOONa\end{matrix} \xrightarrow{390^\circ} H_2 + \begin{matrix}COONa\\ |\\ COONa\end{matrix}$$

Sod. formate Sod. oxalate

The sodium oxalate thus formed is dissolved in water and calcium chloride solution is added to it. Calcium oxalate which is thrown out of solution is filtered and heated with a requisite quantity of dilute sulphuric acid. The calcium sulphate thus precipitated is filtered out leaving oxalic acid in solution. The solution is concentrated by evaporation to form crystals of oxalic acid.

(3) Oxalic acid is also obtained by the direct combination of carbon dioxide with metallic sodium at 360°

$$2CO_2 + 2Na \rightarrow Na_2C_2O_4$$

Sod. oxalate

(4) Formerly the acid was prepared commercially by heating saw dust (*cellulose*) at 240—245° with a concentrated solution of sodium hydroxide. The sodium oxalate thus produced was extracted with water and lime added to it. The precipitated calcium oxalate was finally treated with sulphuric acid in order to obtain oxalic acid. This method is now obsolete

Laboratory Preparation. 30 gm. of coarsely powdered cane sugar are placed in a flat-bottom flask. 150 ml. of concentrated nitric acid is added to it and the flask is warmed on a water-bath. As soon as reaction starts (marked by evolution of brown fumes), the flask is moved to a wooden block. When the evolution of brown fumes has ceased, the contents of the flask are transferred to a china dish. The dish is heated on a water-bath until the bulk of the solution is reduced to 25 ml. The concentrated solution is now cooled in ice water when crystals of oxalic acid separate. These are removed at the pump and recrystallised from hot water, and finally dried between pads of filter paper.

Properties. *Physical.* Oxalic acid forms colourless prismatic crystals with two molecules of water of crystallisation. The melting point of the hydrated acid is 101·5° ; that of the anhydrous acid is 189 5°. The crystals of oxalic acid show efflorescence in air and the hydrated acid becomes anhydrous when carefully heated at 150°. It is soluble in water and alcohol but almost insoluble in ether. It is an active poison

Chemical. Oxalic acid consists of two COOH groups in direct union. It gives the usual replacement reactions of carboxyl group twice over. Also, the acid gives some peculiar reaction which involves the rupture of the weakened linkage between the two highly oxidised carbon atoms.

(1) *Replacement reactions.* Oxalic acid forms two series of salts, esters, chlorides and amides according as one or both COOH groups react. (*See* general reactions).

(2) *Action of heat.* When heated alone, oxalic acid decomposes above its melting point, giving formic acid and carbon dioxide.

$$\underset{\text{Oxalic acid}}{\text{HOOC.COOH}} \xrightarrow{\text{heat}} \underset{\text{Formic acid}}{\text{HCOOH}} + CO_2$$

(3) *Action with glycerol.* Oxalic acid reacts with glycerol to form formic acid or allyl alcohol depending upon experimental conditions. (*See* glycerol).

(4) *Action with* H_2SO_4. When heated with concentrated sulphuric acid, it gives a mixture of carbon dioxide, carbon monoxide and steam.

$$\underset{\text{Oxalic acid}}{\text{HOOC.COOH}} \longrightarrow H_2O + CO_2 + CO$$

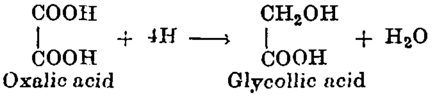
This reaction may be used to prepare carbon monoxide in the laboratory.

(5) *Oxidation.* In aqueous solution at 60° in the presence of dilute sulphuric acid, oxalic acid is oxidised by potassium permanganate to carbon dioxide and water.

$$2KMnO_4 + \underset{\text{Oxalic acid}}{5H_2C_2O_4} + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 10CO_2 + 8H_2O$$

Since this reaction is quantitative and oxalic acid is an easily purified solid, the substance is used in volumetric analysis for standardizing potassium permanganate solutions.

(6) *Reduction.* Oxalic acid is reduced by nascent hydrogen to glycollic acid.



$$\underset{\text{Oxalic acid}}{\begin{matrix}COOH\\|\\COOH\end{matrix}} + 4H \longrightarrow \underset{\text{Glycollic acid}}{\begin{matrix}CH_2OH\\|\\COOH\end{matrix}} + H_2O$$

It is a rare instance where COOH is reduced easily.

Uses Oxalic acid is used :

(1) for removing ink stains and for bleaching straw for hats, since it reduces ferric compounds to more soluble ferrous salts ;

(2) as a mordant in dyeing and calico printing ;

(3) as a standard substance in volumetric titrations ;

(4) as ferrous oxalate in photographic developers ;

(5) as potassium ferri oxalate, $K_3Fe(C_2O_4)_3$, for platinum prints in photography ; and

(6) for the preparation of allyl alcohol and formic acid in the laboratory.

Tests for Oxalic acid. (1) Warm a little oxalic acid in a test-tube with concentrated sulphuric acid ; carbon monoxide and carbon dioxide is evolved without any charring. (*Distinction from tartaric acid*).

(2) Add dropwise potassium permanganate solution of oxalic acid acidified with sulphuric acid ; the pink colour is discharged with the evolution of carbon dioxide gas.

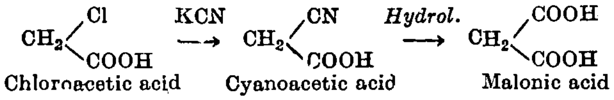
(3) Add calcium chloride solution to *neutral* solution of oxalic acid ; a white precipitate of calcium oxalate is obtained which is insoluble in acetic acid.

(4) Add ammoniacal solution of silver nitrate to a *neutral* solution of oxalic acid, no mirror is formed on warming. (*Distinction from tartaric acid* .

MALONIC ACID, $CH_2(COOH)_2$

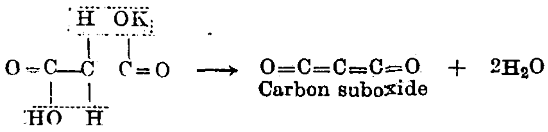
The acid occurs as calcium salt in sugar beet.

Preparation. Malonic acid is prepared from chloroacetic acid by treating with potassium cyanide to give cyanoacetic acid, and subsequent hydrolysis.



$$\underset{\text{Chloroacetic acid}}{CH_2(Cl)COOH} \xrightarrow{KCN} \underset{\text{Cyanoacetic acid}}{CH_2(CN)COOH} \xrightarrow{\textit{Hydrol.}} \underset{\text{Malonic acid}}{CH_2(COOH)_2}$$

Properties Malonic acid crystallises in large plates melting at 130-135° with decomposition. Upon heating it splits out a molecule of carbon dioxide, forming acetic acid. When heated with phosphorus pentoxide, it eliminates two molecules of water giving a highly unsaturated and very reactive substance, carbon suboxide.



$$O{=}C{-}C(H)(HO){-}C(H)(OH){=}O \longrightarrow O{=}C{=}C{=}C{=}O + 2H_2O$$

Carbon suboxide

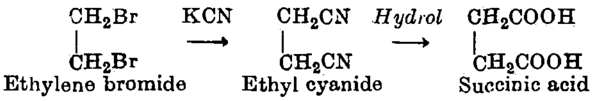
The carbon suboxide readily combines with water to give back malonic acid, and with ethyl alcohol to form diethyl malonate.

Malonic acid exhibits the normal behaviour of dicarboxylic acids in forming salts and esters. Its diethyl ester (*malonic ester*) is a valuable reagent in organic synthesis.

SUCCINIC ACID, $HOOC.CH_2.CH_2.COOH$

Succinic acid was first obtained as a product of the distillation of the fossil resin amber and hence its name (Latin : *succinum* = amber). It occurs widely in nature in numerous plants and unripe fruits. It is produced in small amount during the alcoholic fermentation of sugar.

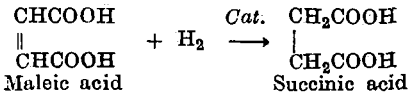
Preparation. (1) Succinic acid is prepared from ethylene bromide by treating with potassium cyanide and subsequent hydrolysis of the resulting ethylene cyanide.



$$\begin{matrix} CH_2Br \\ | \\ CH_2Br \end{matrix} \xrightarrow{KCN} \begin{matrix} CH_2CN \\ | \\ CH_2CN \end{matrix} \xrightarrow{Hydrol} \begin{matrix} CH_2COOH \\ | \\ CH_2COOH \end{matrix}$$

Ethylene bromide Ethyl cyanide Succinic acid

(2) It is obtained industrially by the catalytic reduction of maleic acid.



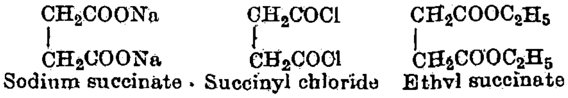
$$\begin{matrix} CHCOOH \\ \| \\ CHCOOH \end{matrix} + H_2 \xrightarrow{Cat.} \begin{matrix} CH_2COOH \\ | \\ CH_2COOH \end{matrix}$$

Maleic acid Succinic acid

Succinic acid can also be synthesised with the help of *malonic ester synthesis*. (*See* malonic acid).

Properties. Succinic acid forms white monoclinic prisms, m.p. 115°. Its solubility in water is lower than that of oxalic acid, one part of the acid dissolving in 20 parts of water.

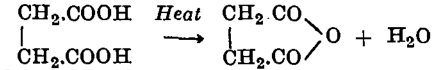
(1) It reacts with alkalis to form salts, with phosphorus pentachloride to form succinyl chloride, and with alcohol to form esters.



$$\begin{matrix} CH_2COONa \\ | \\ CH_2COONa \end{matrix} \qquad \begin{matrix} CH_2COCl \\ | \\ CH_2COCl \end{matrix} \qquad \begin{matrix} CH_2COOC_2H_5 \\ | \\ CH_2COOC_2H_5 \end{matrix}$$

Sodium succinate · Succinyl chloride Ethyl succinate

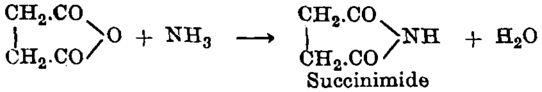
(2) When heated above the melting point, it forms succinic anhydride.



$$\begin{matrix} CH_2.COOH \\ | \\ CH_2.COOH \end{matrix} \xrightarrow{Heat} \begin{matrix} CH_2.CO \\ | \\ CH_2.CO \end{matrix}\!\!>O + H_2O$$

Succinic acid Succinic anhydride

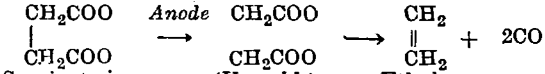
The anhydride reacts with ammonia to form succinimide,



$$\begin{matrix} CH_2.CO \\ | \\ CH_2.CO \end{matrix}\!\!>O + NH_3 \longrightarrow \begin{matrix} CH_2.CO \\ | \\ CH_2.CO \end{matrix}\!\!>NH + H_2O$$

Succinimide

(3) The electrolysis of a strong solution of its potassium salt gives ethylene. The succinate ions furnished by the salt are discharged on the anode with consequent decomposition as follows :



$$\begin{matrix} CH_2COO \\ | \\ CH_2COO \end{matrix} \xrightarrow{Anode} \begin{matrix} CH_2COO \\ \\ CH_2COO \end{matrix} \longrightarrow \begin{matrix} CH_2 \\ \| \\ CH_2 \end{matrix} + 2CO$$

Succinate ion (*Unstable*) Ethylene

Uses. Succinic acid is used in the perfume and dye industries, and also in medicine. It is employed as a standard substance in volumetric analysis.

UNSATURATED DICARBOXYLIC ACIDS

The two simplest and the most important unsaturated dicarboxylic acids are

$$\begin{matrix} H-C-COOH \\ \| \\ HOOC-C-H \end{matrix} \qquad \begin{matrix} H-C-COOH \\ \| \\ H-C-COOH \end{matrix}$$

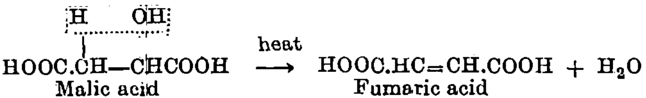
Fumaric acid Maleic acid

They form the best known case of geometrical isomerism (*see* page 114). Fumaric acid is the *trans* isomer, while maleic acid is the *cis* isomer.

FUMARIC ACID

Fumaric acid occurs in many moulds and the sap of a plant *Fumaria officinalis*, whence its name.

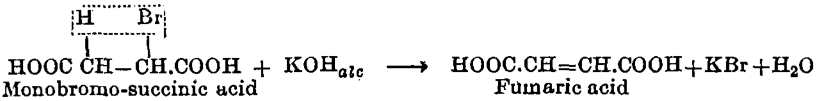
Preparation. (1) It is formed by heating malic acid at 150° for a long time.



$$HOOC.\overset{H}{C}H-\overset{OH}{C}HCOOH \xrightarrow{heat} HOOC.HC{=}CH.COOH + H_2O$$

Malic acid Fumaric acid

(2) It is also obtained by the treatment of monobromosuccinic acid with alcoholic potash.



$$HOOC\,\overset{H}{C}H-\overset{Br}{C}H.COOH + KOH_{alc} \longrightarrow HOOC.CH{=}CH.COOH + KBr + H_2O$$

Monobromo-succinic acid Fumaric acid

Properties. When crystallised from hot water, fumaric acid forms small colourless prisms, m.p. 287°. It is sparingly soluble in cold water.

Chemically fumaric acid gives the reactions of an alkene and also of a dibasic acid.

(1) On reduction with sodium amalgam, it forms succinic acid.

$$\underset{\text{Fumaric acid}}{HOOC.CH{=}CH.COOH} + H_2 \longrightarrow \underset{\text{Succinic acid}}{HOOC.CH_2{-}CH_2COOH}$$

It also forms addition products with Br_2, HBr, etc.

(2) On mild oxidation with potassium permanganate, it yields racemic tartaric acid.

$$\underset{\text{Fumaric acid}}{HOOC.CH{=}CH.COOH} + H_2O + O \longrightarrow \underset{dl\text{-tartaric acid}}{HOOC.CH(OH).CH(OH)COOH}$$

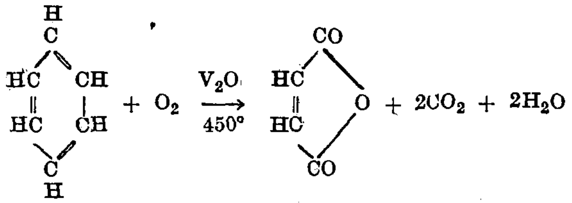
(3) At the carboxylic groups it forms salts and esters.

$$\underset{\text{Sodium fumarate}}{\begin{array}{c}CHCOONa\\ \\ CHCOONa\end{array}} \qquad \underset{\text{Ethyl fumarate}}{\begin{array}{c}CHCOOC_2H_5\\ \\ CHCOOC_2H_5\end{array}}$$

(4) When heated at 200°, it yields maleic anhydride.

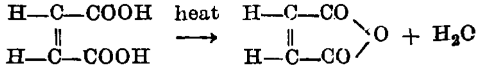
MALEIC ACID

It does not occur in nature. It is obtained from malic acid by rapid heating to 200° and subsequent treatment of the resulting maleic anhydride with water. It is produced commercially by the oxidation of benzene with air at 450° using vanadium pentoxide as a catalyst.



Benzene Maleic anhydride

Properties. Maleic acid crystallises in large prisms, m.p. 135° It is freely soluble in cold water. The chemical properties of the acid are parallel to those of fumaric acid. It forms salts and esters ; sodium maleate and ethyl maleate. Upon reduction it yields succinic acid. When oxidised with dilute potassium permanganate, it forms *meso*-tartaric acid (*Cf.* fumaric acid). When heated alone (or with acetyl chloride) above 200°, it gives maleic anhydride.



$$\begin{array}{c}H{-}C{-}COOH\\ \| \\ H{-}C{-}COOH\end{array} \xrightarrow{\text{heat}} \begin{array}{c}H{-}C{-}CO\\ \| \\ H{-}C{-}CO\end{array}\!\!>O + H_2O$$

Maleic acid is converted to fumaric acid by heating at 200° in a sealed tube, or by treatment with cold mineral acids.

QUESTIONS

1. Name the first nine normal chain dicarboxylic acids. What conventions are followed in naming substituted acids of this series ?

2. Describe the general methods of preparation and properties of aliphatic dicarboxylic acids. How do you explain the alternation in some of their physical constants ?

3. Write notes on the action of heat on dicarboxylic acids and on their calcium salts.

4. How does oxalic acid occur in nature ? How is it prepared on a large scale ? Deduce its constitutional formula.

5. How is oxalic acid obtained from carbon monoxide ? How may oxalic acid be converted into formic acid, carbon monoxide, cyanogen, and dimethyl oxalate ?

6. How is malonic acid synthesised ? Describe the action of heat on the acid.

7. Describe the preparation and properties of succinic acid. How are succinic, malic and tartaric acids related to one another ?

8. How is oxalic acid prepared from (*a*) saw dust and (*b*) carbon monoxide ? State the action of (*i*) heat, (*ii*) concentrated sulphuric acid, (*iii*) acidified potassium permanganate and (*iv*) glycerol.

(*Panjab B.Sc. II, 1965*)

9. Describe briefly the preparation of maleic and fumaric acids. Discuss their isomerism. (*Aligarh B.Sc. II, 1967*)

10. Give the general methods of the preparation of aliphatic saturated dicarboxylic acids. What is the action of heat on the dicarboxylic acids where the two carboxylic groups are separated by none, one, two and three carbon atoms ? Give the industrial methods of preparation of and the chemical reactions of oxalic acid. (*Marathwada B.Sc., 1968*)

11. Discuss the chemistry of simple dicarboxylic acids.

(*Viswa Bharati B.Sc., 1969*)

12. How is oxalic acid prepared on a commercial scale ? What is the action of—

(*a*) urea (*b*) acidified $KMnO_4$ (*c*) PCl_5 on oxalic acid.

(*Kurukshetra B.Sc., 1969*)

22

Substituted Acids

MICHAEL FARADAY
(1791—1867)

English. Although best known as a Physicist, he did important work in the field of organic chemistry. He prepared ethylene iodide, organic chlorides ; proved the isomerism of ethylene and butylene ; extracted benzene from oil gas.

They are the derivatives of organic acids in which one or more H-atoms of the alkyl radical have been substituted by other atoms or groups such as Cl, OH, NH_2, etc. Thus acetic acid forms the following substituted acids.

$Cl.CH_2COOH$	Chloroacetic acid
$HO.CH_2COOH$	Hydroxyacetic acid
$H_2N.CH_2COOH$	Aminoacetic acid, etc.

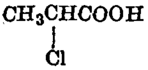
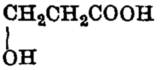
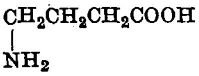
The substituted acids are called Chloro, Hydroxy-, Amino-acids, etc. after the name of the substituent. According to the **Greek letter system** the higher members are designated as α, β, γ or δ according to the position of the substituent on the carbon chain.

$$\overset{\delta}{C}-\overset{\gamma}{C}-\overset{\beta}{C}-\overset{\alpha}{C}-COOH$$

Thus, the three mono-hydroxy butyric acids are named as follows :

$CH_3CH_2CHOH.COOH$	α-Hydroxybutyric acid
$CH_3CHOH.CH_2.COOH$	β-Hydroxybutyric acid
$CH_2OH.CH_2.CH_2.COOH$	γ-Hydroxybutyric acid

The **IUPAC names** of substituted carboxylic acids are derived by prefixing the number of the carbon carrying the substituent group, the carbon of the COOH being designated as No. 1. Thus :

	IUPAC NAME
$ClCH_2COOH$	Chloroacetic acid, or Chloroethanoic acid
 $CH_3\underset{\underset{Cl}{\vert}}{C}HCOOH$	2-chloropropionic acid, or 2-chloropropanoic acid
 $\underset{\underset{OH}{\vert}}{CH_2}CH_2COOH$	3-hydroxypropionic acid 3-hydroxypropanoic acid
 $\underset{\underset{NH_2}{\vert}}{CH_2}CH_2CH_2COOH$	4-aminobutanoic acid

1. HALOGEN-SUBSTITUTED ACIDS

They are derived from acids by substituting one or more H-atoms of the hydrocarbon radical by Cl, Br or I atoms. Thus acetic acid forms three chloro-derivatives

$CH_2Cl.COOH$	$CHCl_2.COOH$	$CCl_3.COOH$
Monochloroacetic acid ,	Dichloroacetic acid	Trichloroacetic acid

Methods of Preparation. (1) *Direct Halogenation.* The α-chloro and bromo acids can be obtained directly by the action of halogens on acids. Thus :

$$\underset{\text{Acetic acid}}{CH_3COOH} + Cl_2 \longrightarrow \underset{\text{Chloroacetic acid}}{CH_2ClCOOH} + HCl$$

$$\underset{\text{Propionic acid}}{CH_3CH_2COOH} + Cl_2 \longrightarrow \underset{\text{2-Chloropropionic acid}}{CH_3CHCl.COOH} + HCl$$

The reaction is facilitated by heat or by addition of a catalyst (I or P).

Iodo acids are generally obtained by the reaction of a chloro or bromo acid with potassium iodide

$$\underset{\text{Chloroacetic acid}}{CH_2Cl.COOH} + KI \longrightarrow \underset{\text{Iodoacetic acid}}{CH_2I.COOH} + KCl$$

Acids above acetic acid are halogenated with great difficulty. Therefore, the acid is first converted to acid halide which is readily halogenated and then the COOH group is restored by hydrolysis. (**Hell-Volhard-Zelinsky Method**).

Thus :

$$\underset{\text{Butyric acid}}{C_3H_7COOH} \xrightarrow{PBr_3} C_3H_7.COBr \xrightarrow{Br_2} \underset{\text{2-Bromobutyric acid}}{C_2H_5CHBrCOBr} \xrightarrow{H_2O} \underset{\text{α-Bromobutyric acid}}{C_2H_5.CHBr.COOH}$$

(2) *Action of hydrogen halide or phosphorus halide on a hydroxy acid.*

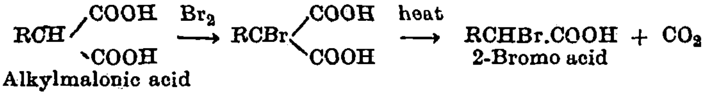
$$\underset{\text{Lactic acid}}{CH_3.CHOH.COOH} + HBr \longrightarrow \underset{\text{2-Bromopropionic acid}}{CH_3.CHBr.COOH} + H_2O$$

(3) *Direct addition of hydrogen halides to unsaturated acids.*

$$\underset{\text{Acrylic acid}}{CH_2{=}CH.COOH} + HBr \longrightarrow \underset{\text{3-Bromopropionic acid}}{CH_2Br.CH_2COOH}$$

This method yields β and γ halogenated acids.

(4) *Halogenation of monoalkyl malonic acids.* The α-chloro and α-bromo acids can be prepared conveniently by the halogenation of a monoalkyl acid and subsequent heating.



$$\underset{\text{Alkylmalonic acid}}{RCH(COOH)_2} \xrightarrow{Br_2} RCBr(COOH)_2 \xrightarrow{\text{heat}} \underset{\text{2-Bromo acid}}{RCHBr.COOH} + CO_2$$

General Properties. *Physical.* Halogen-substituted acids are colourless liquids or solids at room temperature. They dissolve in water giving strongly acidic solutions. They are very much stronger acids than the parent fatty acids. The influence of halogens in regard to the strength of the substituted acid is in the order Cl>Br>I and it also depends on the number and position of halogen atoms present. The trichloroacetic acid is about 20 times as strong as dichloroacetic acid and the latter is five times as strong as monochloroacetic acid.

Chemical. The halogen-substituted acids give reactions of alkyl halides on one hand and of the carboxylic acids on the other. Thus at the COOH group they form salts, esters, chlorides and anhydrides ; while the halogen atom can easily be exchanged for OH, NH_2, CN and other groups.

The behaviour of halogenated acids on treatment with aqueous alkalis is particularly interesting inasmuch as it depends upon the position of the halogen in the molecule.

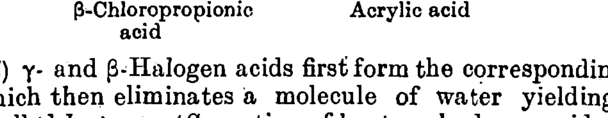
(*i*) α-Halogen acids hydrolyse to form hydroxy acids.

$$\underset{\text{Chloroacetic acid}}{CH_2Cl.COOH} + H_2O \longrightarrow \underset{\text{Glycollic acid}}{CH_2OH.COOH} + HCl$$

(*ii*) β-Halogen acids split out a molecule of halogen halide giving unsaturated acids.

$$\underset{\text{β-Chloropropionic acid}}{CH_2Cl.CH_2COOH} \longrightarrow \underset{\text{Acrylic acid}}{CH_2.CH.COOH} + HCl$$

(*iii*) γ- and β-Halogen acids first form the corresponding hydroxy acid which then eliminates a molecule of water yielding internal es ter called *lactone*. (*See* action of heat on hydroxy acids.)



$$\underset{\text{γ-Chlorobutyric acid}}{ClCH_2.CH_2.CH_2.COOH} \longrightarrow \underset{\text{Lactone}}{CH_2.CH_2.CH_2.CO\text{—}O} + HCl$$

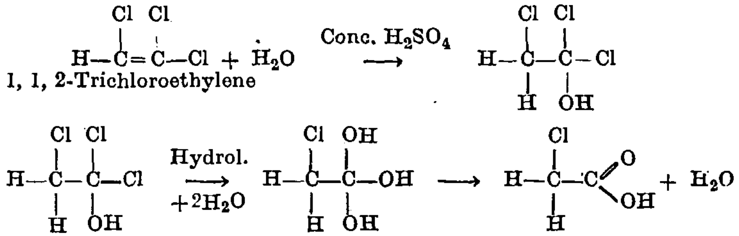
The higher halogen acids form hydroxy acids.

MONOCHLOROACETIC ACID, $CH_2Cl.COOH$

Preparation. (1) Monochloroacetic acid is prepared on a technical scale by passing chlorine into glacial acetic acid at 100° in the presence of red phosphorus.

$$\underset{\text{Acetic acid}}{CH_3COOH} + Cl_2 \xrightarrow[100^\circ]{\text{(Red P)}} \underset{\text{Chloroacetic acid}}{CH_2Cl.COOH} + HCl$$

(2) It is also prepared industrially by the hydrolysis of trichloroethylene (which is obtained by warming 'Westron' with milk of lime), by agitating it with 90 per cent conc. sulphuric acid.



Chloacetic acid

Properties. Monochloroacetic acid is a crystalline solid, m.p. 62°. It is soluble in water and has corrosive action on the skin. Upon hydrolysis with aqueous alkalis, it yields glycollic acid.

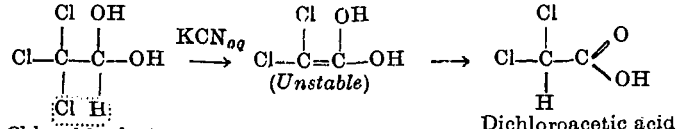
$$\underset{\text{Chloroacetic acid}}{CH_2Cl.COOH} + H_2O \longrightarrow \underset{\text{Glycollic acid}}{CH_2OH.COOH} + HCl$$

It reacts with a concentrated aqueous solution of ammonia to form aminoacetic acid.

$$\underset{\text{Chloroacetic acid}}{CH_2Cl.COOH} + 2NH_3 \longrightarrow \underset{\text{Aminoacetic acid}}{CH_2NH_2.COOH} + NH_4Cl$$

Monochloroacetic acid is used in the synthesis of indigo.

Dichloroacetic acid, $CHCl_2.COOH$. It is best prepared by heating chloral hydrate with potassium cyanide in aqueous solution. The potassium cyanide helps in splitting out HCl from the molecule of chloral hydrate yielding the unstable enol which readily ketonises to dichloroacetic acid.



Chloral hydrate

Dichloroacetic acid

Dichloroacetic acid is a colourless liquid, b.p. 194° It is soluble in water and upon hydrolysis by boiling with water it gives glyoxylic acid.

$$CHCl_2COOH \xrightarrow{\text{Hydrol.}} \underset{(\textit{Unstable})}{CH(OH)_2.COOH} \longrightarrow \underset{\text{Glyoxylic acid}}{CHO.COOH} + H_2O$$

Trichloroacetic acid, $CCl_3.COOH$. It is prepared by oxidising chloral with concentrated nitric acid.

$$\underset{\text{Trichloroacetaldehyde}}{CCl_3.CHO} + O \longrightarrow \underset{\text{Trichloroacetic acid}}{CCl_3.COOH}$$

Trichloroacetic acid is a colourless crystalline solid, m.p. 57°. When boiled with water, it decomposes into chloroform and carbon dioxide.

$$\underset{\text{Trichloroacetic acid}}{CCl_3COOH} \longrightarrow \underset{\text{Chloroform}}{CHCl_3} + CO_2$$

The ease with which C-to-C linkage is broken here is due to the fact that it is weakened being heavily loaded with electronegative atoms.

2. HYDROXY-FATTY ACIDS

They are derived from the fatty acids by replacing a hydrogen of the hydrocarbon radical by a hydroxy group. They are named by prefixing 'hydroxy' to the name of the parent acid. The position of the OH group is denoted by the letters α, β, γ and δ as described before. Thus :

$CH_2OH.COOH$	Hydroxyacetic acid (*glycollic acid*)
$CH_3.CHOH.COOH$	α-Hydroxypropionic acid (*lactic acid*)
$CH_2OH.CH_2.COOH$	β-Hydroxypropionic acid (*hydracrylic acid*)

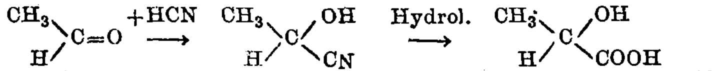
Methods of preparation. (1) By heating halogen substituted acids with water.

$$\underset{\text{Chloroacetic acid}}{CH_2Cl.COOH} + H_2O \longrightarrow \underset{\text{Glycollic acid}}{CH_2OH.COOH} + HCl$$

(2) By the action of nitrous acid (sodium nitrite and dilute mineral acid) on amino acids.

$$\underset{\text{Aminoacetic acid}}{CH_2NH_2.COOH} + HNO_2 \longrightarrow CH_2OH.COOH + N_2 + H_2O$$

(3) By reactions of hydrogen cyanide with an aldehyde or a ketone forming a cyanohydrin and subsequent hydrolysis.



Acetaldehyde α-Hydroxypropionic acid

(4) By the oxidation of glycols containing one primary alcohol grouping.

$$\underset{\text{Glycol}}{CH_2OH.CH_2OH} + 2O \longrightarrow \underset{\text{Glycollic acid}}{CH_2OH.COOH} + H_2O$$

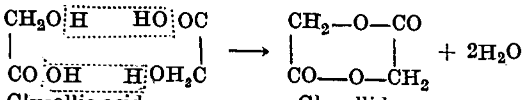
(5) By the reduction of aldehydic or ketonic acids.

$$\underset{\text{Pyruvic acid}}{CH_3.CO.COOH} + 2H \longrightarrow \underset{\text{α-Hydroxypropionic acid}}{CH_3CHOH.COOH}$$

General Properties. (*Physical*). The hydroxy acids are colourless crystalline solids or syrupy liquids. Their melting and boiling points are much higher than those of the parent fatty acids. They are extremely soluble in water but less so in alcohol and ether. They are stronger acids than the corresponding fatty acids.

(*Chemical*). The hydroxy-fatty acids respond to the usual reactions of the carboxyl group and the alcoholic OH group. Thus, at the COOH group they react to form salts, esters, amides and acid chlorides ; while at the OH group they undergo oxidation, form metallic derivatives, esters, and chlorides. The OH and COOH groups may also react together to form esters. The **action of heat** upon hydroxy acids is of special interest as it yields different products depending upon the relative positions of the two functional groups in the molecule.

(1) α-Hydroxy acids form cyclic diesters by reaction between COOH and OH groups of two different molecules.

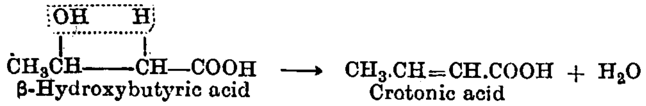


$$\begin{array}{l} CH_2O\,H \quad HO\,OC \\ | \qquad\qquad\quad | \\ CO\,OH \quad H\,OH_2C \end{array} \longrightarrow \begin{array}{l} CH_2-O-CO \\ | \qquad\qquad | \\ CO-O-CH_2 \end{array} + 2H_2O$$

Glycollic acid Glycollide

Lactic acid yields an analogous cyclic diester, *lactide.*

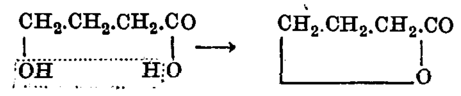
(2) β-Hydroxy acids undergo dehydration by splitting out OH and H from adjacent carbon atoms, giving unsaturated acids.



$$\begin{array}{l} \quad OH \quad\ H \\ \quad | \qquad\ | \\ CH_3CH—CH—COOH \end{array} \longrightarrow CH_3.CH{=}CH.COOH + H_2O$$

β-Hydroxybutyric acid Crotonic acid

(3) γ- and δ-Hydroxy acids form cyclic esters or '*lactones*' by losing a water molecule between the COOH and OH groups of the same molecule.



$$\begin{array}{l} CH_2.CH_2.CH_2.CO \\ | \qquad\qquad\quad | \\ OH \qquad\quad H\,O \end{array} \longrightarrow \begin{array}{l} CH_2.CH_2.CH_2.CO \\ | \qquad\qquad\quad | \\ \rule{0pt}{0pt}\_\_\_\_\_\_\_\_\_\_\ O \end{array}$$

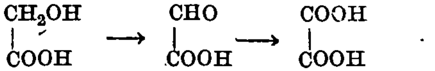
γ-Hydroxybutyric acid Butyrolactone

GLYCOLLIC ACID, HYDROXYACETIC ACID, $CH_2OH.COOH$

It is the simplest hydroxy acid known and occurs in unripe grapes, sugarcane and tomato. It is generally made by heating the aqueous solution of chloroacetic acid with barium carbonate. Technically it is prepared by the electrolytic reduction of oxalic acid.

$$\underset{\text{Oxalic acid}}{HOOC.COOH} + 4H \longrightarrow \underset{\text{Hydroxyacetic acid}}{CH_2OH.COOH} + H_2O$$

Properties. When crystallised from water, it forms colourless needles, m.p. 79°. It is readily soluble in water, alcohol and ether. It gives the reactions of a primary alcohol and of an acid. Upon oxidation it first forms glyoxalic acid and then oxalic acid.



$$\begin{array}{l} CH_2OH \\ | \\ COOH \end{array} \longrightarrow \begin{array}{l} CHO \\ | \\ COOH \end{array} \longrightarrow \begin{array}{l} COOH \\ | \\ COOH \end{array}$$

Glycollic acid Glyoxalic acid Oxalic acid

When heated above its melting point, it yields glycollide.

LACTIC ACID, α-HYDROXYPROPIONIC ACID, $CH_3.CHOH.COOH$

Lactic acid is the main constituent of milk that has gone sour and hence its name (Latin, *lac*=milk). It is found in blood and muscle tissue of human body, where it is formed by the decomposition of glycogen, $(C_6H_{10}O_5)_n$. This reaction furnishes energy needed for muscular work. The latic acid produced in muscles is then reconverted into glycogen during rest.

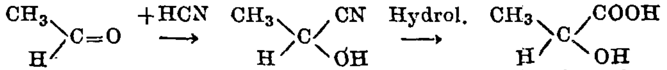
Lactic acid molecule contains an asymmetric carbon atom and exhibits optical isomerism. Ordinary lactic acid is the racemic mixture. Dextro-lactic acid or Sarcolactic acid (Sarx meaning flesh) is obtained from fatigued muscles by extraction with solvents. Laevolactic acid is prepared by the fermentation of lactose, glucose or sucrose under the influence of *B. acid ilaevolatici.*

Preparation. Lactic acid may be obtained :

(1) By hydrolysis of α chloropropionic acid.

$$\underset{\alpha\text{-Chloropropionic acid}}{CH_3.CHCl.COOH} + HOH \longrightarrow \underset{\alpha\text{-Hydroxypropionic acid}}{CH_3.CHOH.COOH} + HCl$$

(2) By hydrolysis of acetaldehyde-cyanohydrin.



$$\underset{\text{Acetaldehyde}}{\begin{matrix}CH_3\\H\end{matrix}\!\!>C=O} \xrightarrow{+HCN} \underset{\text{Cyanohydrin}}{\begin{matrix}CH_3\\H\end{matrix}\!\!>C<\!\!\begin{matrix}CN\\OH\end{matrix}} \xrightarrow{\text{Hydrol.}} \underset{\text{Lactic acid}}{\begin{matrix}CH_3\\H\end{matrix}\!\!>C<\!\!\begin{matrix}COOH\\OH\end{matrix}}$$

(3) By oxidation of propylene glycol.

$$\underset{\text{Propylene}}{CH_3.CH{=}CH_2} \xrightarrow{(H_2O+O)} \underset{\text{Propylene glycol}}{CH_3.CHOH.CH_2OH} \xrightarrow{O} \underset{\text{Lactic acid}}{CH_3.CHOH.COOH}$$

(4) *By lactic fermentation of sugar.* Lactic acid is obtained on the technical scale by the fermentation of sugars (molasses) on treatment with sour milk which contains *B. acidi laevalactici.* The fermentation proceeds best in neutral solution at 37°.

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \longrightarrow \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

$$C_6H_{12}O_6 \longrightarrow \underset{\text{Lactic acid}}{2CH_3.CHOH.COOH}$$

In actual practice a dilute solution of molasses is treated with sour milk in the presence of powdered chalk (calcium carbonate). The lactic acid as soon as it is produced combines with calcium carbonate forming sparingly soluble calcium lactate. This is filtered off and treated with dilute sulphuric acid. The lactic acid set free in aqueous solution is recovered by distillation *in vacuo.*

Lactic acid is also made from starch by first hydrolysing it to sugars and then carrying on fermentation as described above.

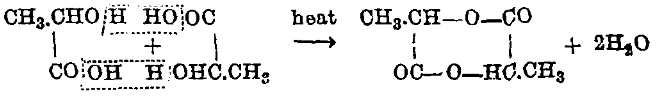
Properties. (*Physical*). Pure lactic acid is a colourless, crystalline solid, m.p. 18°. At ordinary temperature it is a syrupy liquid. It has a sour taste and is miscible in all proportions with water, alcohol and ether.

(*Chemical*). Lactic acid is at once a fatty acid and a secondary alcohol. Thus it gives the following reactions :

(1) FORMATION OF SALTS AND ESTERS. Lactic acid is a monobasic acid and thus forms metallic salts and esters.

$$\underset{\text{Sodium lactate}}{CH_3.CHOH.COONa} \qquad \underset{\text{Ethyl lactate}}{CH_3.CHOH.COOC_2H_5}$$

(2) ACTION OF HEAT. When the acid is heated under ordinary pressure, it forms a lactide.



Lactic acid
(2 molecules)

Lactide

(3) ACTION WITH H_2SO_4. When heated to 130° with dilute sulphuric acid, lactic acid decomposes to yield acetaldehyde and formic acid.

$$\underset{\text{Lactic acid}}{CH_3.CHOH.COOH} \xrightarrow{130^\circ} \underset{\text{Acetaldehyde}}{CH_3CHO} + \underset{\text{Formic acid}}{HCOOH}$$

If heated with concentrated sulphuric acid, the decomposition takes place as above but the formic acid is decomposed further to CO and H_2O. (*Test*).

(4) ACTION WITH PCl_5. Both the OH and COOH groups are attacked by phosphorus pentachloride forming lactyl chloride.

$$\underset{\text{Lactic acid}}{CH_3.CHOH.COOH} + 2PCl_5 \longrightarrow \underset{\text{Lactyl chloride}}{CH_3CHCl.COCl} + 2POCl_3 + 2HCl$$

(5) OXIDATION. Upon oxidation with potassium permanganate solution, lactic acid yields pyruvic acid.

$$\underset{\text{Lactic acid}}{CH_3.CHOH.COOH} + O \longrightarrow \underset{\text{Pyruvic acid}}{CH_3.CO.COOH} + H_2O$$

(6) ACTION WITH HI. When lactic acid is boiled with concentrated aqueous solution of hydrogen iodide, it is reduced to propionic acid.

$$\underset{\text{Lactic acid}}{CH_3.CHOH.COOH} + HI \longrightarrow \underset{\alpha\text{-Iodopropionic acid}}{CH_3.CHI.COOH} + H_2O$$

$$CH_3.CHI.COOH + HI \longrightarrow \underset{\text{Propionic acid}}{CH_3.CH_2.COOH} + I_2$$

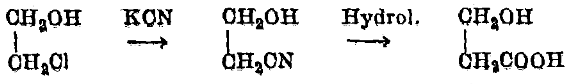
(7) IODOFORM REACTION. Like other organic compounds containing the group $CH_3.CHOH$—, lactic acid also forms iodoform when treated with iodine and alkali. (*Test*).

Uses. Lactic acid is used as a mordant for dyeing wool; for deliming of hides in tanning; and as acidulant in candles. Its salts: calcium lactate and iron lactate are used in medicine to make up the deficiency of calcium and iron in the body. Its esters—ethyl and butyl lactate—are employed as solvents in the plastic industry.

Hydracrylic acid, β-*Hydroxypropionic acid*, $CH_2OH.CH_2.COOH$. It may be prepared by the hydrolysis of β-chloropropionic acid with moist silver oxide,

$$\underset{\beta\text{-chloropropionic acid}}{CH_2Cl.CH_2.COOH} + AgOH \longrightarrow CH_2OH.CH_2.COOH + AgCl$$

or by the action of potassium cyanide on ethylene chlorohydrin and subsequent hydrolysis.



$$\begin{array}{l} CH_2OH \\ | \\ CH_2Cl \end{array} \xrightarrow{KCN} \begin{array}{l} CH_2OH \\ | \\ CH_2CN \end{array} \xrightarrow{\text{Hydrol.}} \begin{array}{l} CH_2OH \\ | \\ CH_2COOH \end{array}$$

Properties. Hydracrylic acid is a thick syrupy liquid and gives the usual reactions of OH and COOH groups. When heated alone, or with dilute sulphuric acid, it splits out a molecule of water giving acrylic acid.

$$CH_2OH.CH_2.COOH \longrightarrow \underset{\text{Acrylic acid}}{CH_2{=}CH.COOH} + H_2O$$

Upon oxidation with chromic acid, hydracrylic acid yields malonic acid.

$$CH_2OH.CH_2.COOH + 2[O] \longrightarrow \underset{\text{Malonic acid}}{HOOC.CH_2.COOH} + H_2O$$

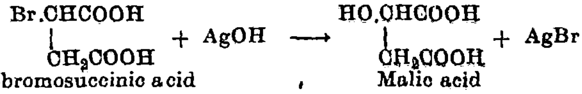
SOME HYDROXY-POLYBASIC ACIDS

MALIC ACID, MONOHYDROXYSUCCINIC ACID

Malic acid was first isolated by Scheele (1785) from unripe apples and hence its name (Latin, *maulum*=apple). It also occurs in grapes and berries of the mountain ash.

Preparation. (1) Malic acid is best prepared from unripe mountain-ash berries by extraction with boiling water.

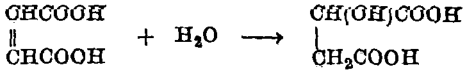
(2) It may be obtained by the treatment of bromosuccinic acid with moist silver oxide.



$$\begin{array}{l} Br.CHCOOH \\ | \\ CH_2COOH \end{array} + AgOH \longrightarrow \begin{array}{l} HO.CHCOOH \\ | \\ CH_2COOH \end{array} + AgBr$$

Monobromosuccinic acid , Malic acid

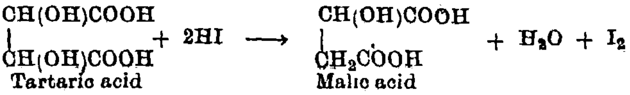
(3) It is prepared technically by heating maleic acid (obtained from benzene) with dilute sulphuric acid or caustic soda solution.



$$\begin{array}{l} CHCOOH \\ \| \\ CHCOOH \end{array} + H_2O \longrightarrow \begin{array}{l} CH(OH)COOH \\ | \\ CH_2COOH \end{array}$$

Maleic acid Malic acid

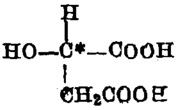
(4) It may also be made by the partial reduction of tartaric acid with hydriodic acid.



$$\begin{array}{l} CH(OH)COOH \\ | \\ CH(OH)COOH \end{array} + 2HI \longrightarrow \begin{array}{l} CH(OH)COOH \\ | \\ CH_2COOH \end{array} + H_2O + I_2$$

Tartaric acid Malic acid

Properties. *(Physical).* Owing to the presence of an asymmetric carbon atom in the molecule, malic acid exhibits optical isomerism.



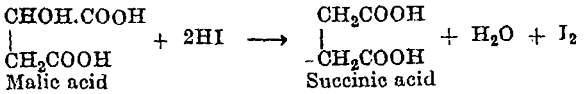
$$HO-\overset{\displaystyle H \atop |}{\underset{\displaystyle | \atop CH_2COOH}{C^*}}-COOH$$

The acid obtained from natural sources is laevo-rotatory ; the acid prepared by synthetic methods is racemic mixture while the acid made by reduction of *d*-tartaric acid with hydriodic acid is dextrorotatory.

Both dextro and laevo malic acids form colourless crystals melting at 100°. The *dl*-acid melts at 130°. Malic acid is soluble in water and alcohol.

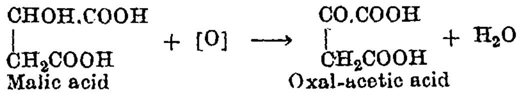
(Chemical). Malic acid is at once a secondary alcohol and a dicarboxylic acid.

(1) When reduced with hydriodic acid, it yields succinic acid



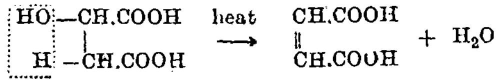
$$\begin{array}{l}\text{CHOH.COOH}\\ |\\ \text{CH}_2\text{COOH}\\ \text{Malic acid}\end{array} + 2\text{HI} \longrightarrow \begin{array}{l}\text{CH}_2\text{COOH}\\ |\\ \text{CH}_2\text{COOH}\\ \text{Succinic acid}\end{array} + H_2O + I_2$$

(2) On regulated oxidation it is converted into oxal-acetic acid.



$$\begin{array}{l}\text{CHOH.COOH}\\ |\\ \text{CH}_2\text{COOH}\\ \text{Malic acid}\end{array} + [O] \longrightarrow \begin{array}{l}\text{CO.COOH}\\ |\\ \text{CH}_2\text{COOH}\\ \text{Oxal-acetic acid}\end{array} + H_2O$$

(3) When heated, malic acid splits out a molecule of water forming fumaric acid and maleic acid.



$$\begin{array}{l}\text{HO}-\text{CH.COOH}\\ \quad\;\; |\\ \text{H}\;-\text{CH.COOH}\end{array} \xrightarrow{\text{heat}} \begin{array}{l}\text{CH.COOH}\\ \|\\ \text{CH.COOH}\end{array} + H_2O$$

Uses. Malic acid is used as a purgative in medicine and also as a remedy for sore-throat. It is also used as a substitute of citric acid in beverages.

TARTARIC ACID, DIHYDROXYUCCINIC ACID

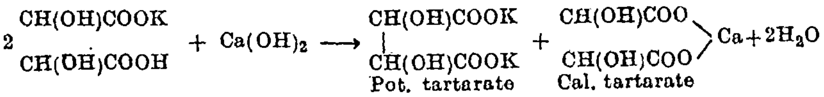
It is the classical example of a compound having two asymmetric carbon atoms :

$$\begin{array}{c}{}^*\text{CH(OH)COOH}\\ {}^*\text{CH(OH)COOH}\end{array}$$

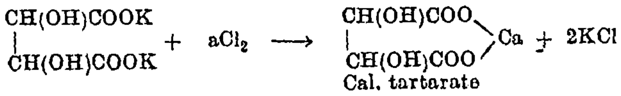
Thus it exhibits the phenomenon of optical isomerism and exists in four forms : dextro, laevo, meso and racemic. Ordinary natural acid is the dextro variety.

Tartaric acid occurs in grapes, tamarind and other fruits either free or as potassium acid salt. During the later stages of fermentation of grape juice to wine, the potassium tartarate is thrown out as a brown crust, known as *argol* or *tartar*. In 1769 Scheele first isolated tartaric acid from argol and even today it continues to be the chief source of industrial acid.

Preparation. Argol which is crude potassium acid tartarate, is dissolved in boiling water and the solution is nearly neutralised with milk of lime. The potassium acid tartarate reacts with lime to form normal potassium tartarate and insoluble calcium tartarate. The calcium tartarate is separated by filtration, and calcium chloride is then added to the filtrate when the normal potassium salt is also precipitated as calcium tartarate.



$$2\begin{array}{l}\text{CH(OH)COOK}\\ \text{CH(OH)COOH}\end{array} + \text{Ca(OH)}_2 \longrightarrow \begin{array}{l}\text{CH(OH)COOK}\\ |\\ \text{CH(OH)COOK}\\ \text{Pot. tartarate}\end{array} + \begin{array}{l}\text{CH(OH)COO}\diagdown\\ \qquad\qquad\qquad\;\;\text{Ca}\\ \text{CH(OH)COO}\diagup\\ \text{Cal. tartarate}\end{array} + 2H_2O$$



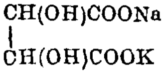
$$\begin{array}{l}\text{CH(OH)COOK}\\ |\\ \text{CH(OH)COOK}\end{array} + \text{aCl}_2 \longrightarrow \begin{array}{l}\text{CH(OH)COO}\diagdown\\ \qquad\qquad\qquad\;\;\text{Ca}\\ \text{CH(OH)COO}\diagup\\ \text{Cal. tartarate}\end{array} + 2\text{KCl}$$

The calcium tartarate obtained in the two steps is washed with water and treated with calculated quantity of dilute sulphuric acid which precipitates calcium sulphate and liberates tartaric acid in solution. The calcium sulphate is removed by filtration and the solution of tartaric acid is concentrated and crystallised.

Properties (*Physical*). Dextro tartaric acid crystallises in large monoclinic prisms without any water of crystallisation. It melts at 167—170°. It is readily soluble in alcohol but insoluble in ether. The solution in water is extremely sour and is dextrorotatory. However, upon heating, the solution is rendered optically inactive owing to racemisation.

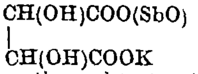
(*Chemical*). Tartaric acid is at once a dicarboxylic acid and also a disecondary alcohol.

(1) As a dibasic acid it forms acid and normal salts and esters. Two of its important salts are :



$$\begin{array}{l}\text{CH(OH)COONa}\\ |\\ \text{CH(OH)COOK}\end{array}$$

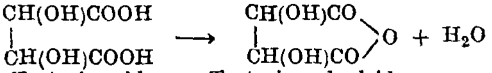
Sod. pot. tartarate
(Rochelle salt)



$$\begin{array}{l}\text{CH(OH)COO(SbO)}\\ |\\ \text{CH(OH)COOK}\end{array}$$

Pot. antimonyl tartarate
(Tartar emetic)

(2) *Action of heat.* When heated above its melting point, tartaric acid splits out a molecule of water and forms anhydride.

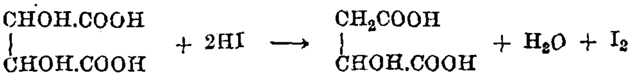


$$\begin{array}{l}\text{CH(OH)COOH}\\ |\\ \text{CH(OH)COOH}\end{array} \longrightarrow \begin{array}{l}\text{CH(OH)CO}\\ |\\ \text{CH(OH)CO}\end{array}\!\!>\text{O} + \text{H}_2\text{O}$$

Tartaric acid — Tartaric anhydride

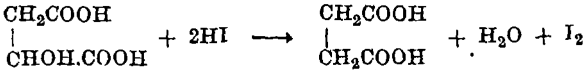
On strong heating, the acid is decomposed into free carbon and a variety of other compounds. When heated with concentrated sulphuric acid, it deposits carbon rapidly and a mixture of CO, CO_2 and SO_2 is evolved.

(3) *Reduction with HI.* As an alcohol, tartaric acid is reduced by warming with concentrated hydriodic acid, first forming malic acid then succinic acid.



$$\begin{array}{l}\text{CHOH.COOH}\\ |\\ \text{CHOH.COOH}\end{array} + 2\text{HI} \longrightarrow \begin{array}{l}\text{CH}_2\text{COOH}\\ |\\ \text{CHOH.COOH}\end{array} + \text{H}_2\text{O} + \text{I}_2$$

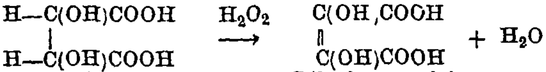
Tartaric acid — Malic acid



$$\begin{array}{l}\text{CH}_2\text{COOH}\\ |\\ \text{CHOH.COOH}\end{array} + 2\text{HI} \longrightarrow \begin{array}{l}\text{CH}_2\text{COOH}\\ |\\ \text{CH}_2\text{COOH}\end{array} + \text{H}_2\text{O} + \text{I}_2$$

Hydroxysuccinic acid — Succinic acid

(4) *Oridation.* Tartaric acid is very sensitive to oxidising gents and gives a silver mirror when warmed with ammoniacal ilver nitrate. On oxidation with hydrogen peroxide it forms ihydroxy maleic acid.

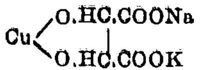


$$\begin{array}{l}\text{H—C(OH)COOH}\\ \quad|\\ \text{H—C(OH)COOH}\end{array} \xrightarrow{\text{H}_2\text{O}_2} \begin{array}{l}\text{C(OH,COOH}\\ \|\\ \text{C(OH)COOH}\end{array} + \text{H}_2\text{O}$$

Tartaric acid — Dihydroxymaleic acid

With strong oxidising agents, tartaric acid is converted to oxalic acid.

(5) *Formation of complexes.* Like other polyhydroxy compounds, tartaric acid prevents the precipitation of hydroxides of heavy metals owing to the formation of soluble complex salts. The *Fehling's solution* containing copper sulphate, Rochelle salt and sodium hydroxide remains clear, as the insoluble copper hydroxide first formed goes into solution owing to the formation of the complex.



Fehling reagent complex

Uses. Tartaric acid and its salts are used in medicine and industry.

(1) Tartaric acid is used as acidulant in making sweet drinks (*Sharbats*).

(2) *Seidlitz powder* used as a laxative, contains tartaric acid in a white wrapper and a mixture of Rochelle salt and sodium bicarbonate in the blue wrapper. When the powders are dissolved in water separately and mixed, carbon dioxide gas is evolved

(3) *Baking powders* contain potassium acid tartarate and sodium bicarbonate. When mixed with dough, they form carbon dioxide during the baking process. This leads to an open texture in breads and cakes.

(4) Sodium potassium tartarate is also used in the communications industry (microphone crystals) and in making of mirrors.

(5) Fehling's solution containing sodium potassium tartarate is used for detecting reducing agents *e.g.*, aldehydes.

(6) *Tartar emetic, potassium antimonyl tartarate*, when administered orally causes nausea and vomiting. It has, therefore, been used as an eliminant for poisons taken into the stomach. It is also used as a mordant in dyeing and calico printing.

Tests. (1) Tartaric acid chars rapidly when heated in a test-tube and emits an odour of burnt sugar.

(2) Upon heating with concentrated sulphuric acid, it chars with the evolution of CO, CO_2, SO_2.

(3) A neutral aqueous solution of tartaric acid when warmed with ammoniacal solution of silver nitrate, forms a shining mirror.

(4) When calcium chloride is added to a neutral solution of tartaric acid, a white precipitate of calcium tartarate is obtained which dissolves in sodium hydroxide. On boiling the solution the precipitate reappears. (*Distinction from Oxalic acid*).

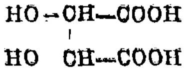
(5) If tartaric acid is mixed with a little ferrous sulphate solution, and a few drops of hydrogen peroxide are added, and the excess of sodium hydroxide, a deep violet colour is produced.

Structure. (1) As shown by elementary analysis and the determination of molecular weight by the silver salt method, the molecular formula of tartaric acid is $C_4H_6O_6$.

(2) It forms two series of salts and esters (acid and normal) and thus the molecule contains two COOH groups. Further, since tartaric acid does not split out a molecule of carbon dioxide on heating, the two carboxyl groups are linked to different carbon atoms.

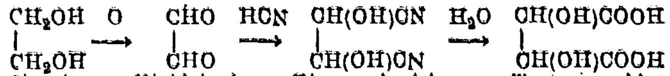
(3) Its ethyl ester reacts with acetic anhydride to form diacetyl derivative which shows the presence of two OH groups in the molecule. Obviously these are linked to different carbon atoms as tartaric acid is quite a stable compound.

(4) Taking into consideration the above facts the formula of tartaric acid could be written as



$$\begin{array}{l}\text{HO}-\text{CH}-\text{COOH}\\ \qquad\;\;|\\ \text{HO}\quad\text{CH}-\text{COOH}\end{array}$$

(5) The structure of tartaric acid is borne out by the fact that it forms succinic acid upon reduction with hydriodic acid. It has been further confirmed by the following synthesis from glycol.



$$\begin{array}{l}CH_2OH\\ |\\ CH_2OH\end{array}\xrightarrow{O}\begin{array}{l}CHO\\ |\\ CHO\end{array}\xrightarrow{HCN}\begin{array}{l}CH(OH)CN\\ |\\ CH(OH)CN\end{array}\xrightarrow{H_2O}\begin{array}{l}CH(OH)COOH\\ |\\ CH(OH)COOH\end{array}$$

Glycol Dialdehyde Di-cyanohydrin Tartaric acid

CITRIC ACID, 2, HYDROXYPROPANE-1, 2, 3-TRICARBOXLIC ACID

Citric acid occurs in many fruits, especially unripe fruits of the citrus family *e.g.*, lemons, *galgals* and oranges. Lemon juice contains 7—10 per cent of citric acid.

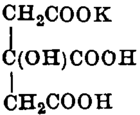
Preparation. (1) In Italy citric acid is prepared in large quantities from culled fruits (lemons) by extracting the juice, boiling to coagulate the protein substances and neutralising with calcium carbonate. The precipitated calcium citrate is collected by filtration and decomposed with the calculated quantity of dilute sulphuric acid. The calcium sulphate thus precipitated is removed by filtration and the solution of citric acid evaporated to crystallisation.

(2) In 1923, U.S.A. introduced a new method of producing citric acid by the mould fermentation of carbohydrates. A dilute solution of molasses is fermented by using certain moulds (*citromycetes*). The mechanism of this peculiar reaction is not yet clear. In U.S.A., England and Japan all the citric acid is now manufactured by this method. This method is also particularly suitable for India on account of huge quantities of molasses available from sugar mills.

Properties. (*Physical*). Citric acid forms large prismatic crystals containing one molecule of water of crystallisation. The hydrated acid loses its water of crystallisation when heated at 130° and then melts at 153°. Citric acid is not optically active as it contains no asymmetric carbon atom. It is readily soluble in water and alcohol but is sparingly soluble in ether.

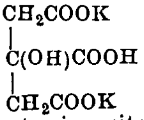
(*Chemical*). Citric acid is a hydroxy tribasic acid. The position of the OH group is α with respect to one COOH and β with respect to the others. Thus it behaves both as an α-hydroxy acid and a β-hydroxy acid.

(1) It forms three series of salts and esters. Thus :



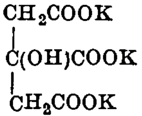
$$\begin{array}{l} CH_2COOK \\ | \\ C(OH)COOH \\ | \\ CH_2COOH \end{array}$$

Mono-potassium citrate



$$\begin{array}{l} CH_2COOK \\ | \\ C(OH)COOH \\ | \\ CH_2COOK \end{array}$$

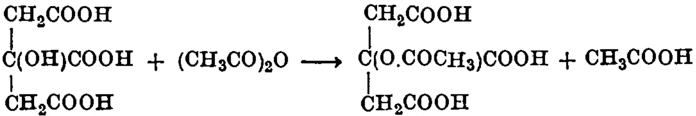
Di-potassium citrate



$$\begin{array}{l} CH_2COOK \\ | \\ C(OH)COOK \\ | \\ CH_2COOK \end{array}$$

Tri-potassium citrate

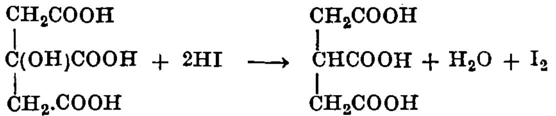
(2) It reacts with acetic anhydride to form monoacetyl derivative.



$$\begin{array}{l} CH_2COOH \\ | \\ C(OH)COOH \\ | \\ CH_2COOH \end{array} + (CH_3CO)_2O \longrightarrow \begin{array}{l} CH_2COOH \\ | \\ C(O.COCH_3)COOH \\ | \\ CH_2COOH \end{array} + CH_3COOH$$

Citric acid Monoacetyl-citric acid

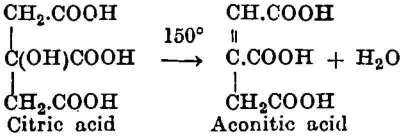
(3) The alcoholic OH group is reduced by the action of hydriodic acid giving **Tricarballylic acid.**



$$\begin{array}{l} CH_2COOH \\ | \\ C(OH)COOH \\ | \\ CH_2.COOH \end{array} + 2HI \longrightarrow \begin{array}{l} CH_2COOH \\ | \\ CHCOOH \\ | \\ CH_2COOH \end{array} + H_2O + I_2$$

Citric acid Tricarballylic acid

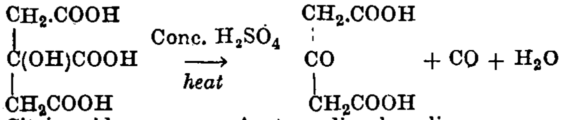
(4) When heated to 150°, nitric acid splits out a molecule of water to form *aconitic acid* (*Cf.* β-hydroxy acid).



$$\begin{array}{l} CH_2.COOH \\ | \\ C(OH)COOH \\ | \\ CH_2.COOH \end{array} \xrightarrow{150^\circ} \begin{array}{l} CH.COOH \\ \| \\ C.COOH \\ | \\ CH_2COOH \end{array} + H_2O$$

Citric acid Aconitic acid

(5) When heated with concentrated sulphuric acid, it yields acetone dicarboxylic acid (*Cf.* α-hydroxy acids).



$$\begin{array}{l} CH_2.COOH \\ | \\ C(OH)COOH \\ | \\ CH_2COOH \end{array} \xrightarrow[heat]{Conc.\ H_2SO_4} \begin{array}{l} CH_2.COOH \\ | \\ CO \\ | \\ CH_2COOH \end{array} + CO + H_2O$$

Citric acid Acetone dicarboxylic acid

Uses. (1) Citric acid is used for making lemonades and as a mordant in dyeing.

(2) Sodium citrate is added to milk given to babies as it prevents the curdling of milk in stomach and makes it more digestible.

(3) Magnesium citrate is used in medicine as an antacid and laxative.

(4) Ferric ammonium citrate on exposure to sunlight changes to ferrous salt and is, therefore, used in making blue-print paper.

(5) Citric acid esters (tributyl citrate) are good plasticizers for lacquers and varnishes.

Tests. (1) Upon heating in a test tube, citric acid melts without charring. However, on prolonged heating, charring occurs and irritating fumes are evolved. *(Distinction from tartaric acid).*

(2) When heated with concentrated sulphuric acid, citric acid is decomposed evolving carbon monoxide which burns with a blue flame at the mouth of the test tube. After some time thè decomposition proceeds with evolution of carbon dioxide and the blue flame goes out.

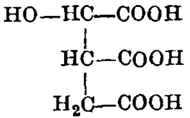
(3) When calcium chloride is added to a neutral solution of citric acid, no precipitate is produced. However, on boiling the liquid, a white precipitat of calcium citrate insoluble in potassium hydroxide is obtained. *(Distinction from tartaric acid).*

Structure and Synthesis. (1) The molecular formula of citric acid is $C_6H_8O_7$.

(2) It forms three series of salts and esters ; hence it is a tribasic acid and contains three COOH groups in the molecules. Further since it does not split out a molecule of carbon dioxide on heating, no two COOH groups are linked to the same carbon in the molecule.

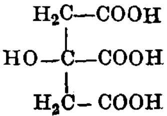
(3) Citric acid forms a mono-acetyl derivative with acetic anhydride and, therefore, contains one OH group.

(4) From the above considerations it is clear that citric acid can have one of the following formula :



$$\begin{array}{l}HO{-}HC{-}COOH\\ \quad HC{-}COOH\\ \quad H_2C{-}COOH\end{array}$$

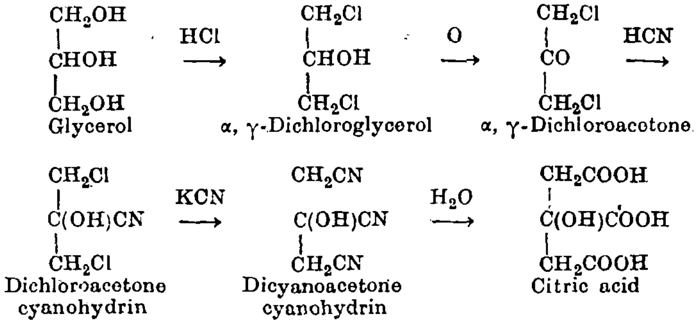
I



$$\begin{array}{l}\quad H_2C{-}COOH\\ HO{-}C{-}COOH\\ \quad H_2C{-}COOH\end{array}$$

II

(5) Citric acid can be synthesised from glycerol by the following scheme ;



Since the product of synthesis is identical with natural citric acid the structure II for the acid is confirmed.

3. AMINO ACIDS

They are fatty acids in which a hydrogen of the hydrocarbon radical is replaced by $-NH_2$ group. They are designated as, α, β, γ or δ-amino acids according to the position of the NH_2 group in the molecule. Thus :

$CH_2NH_2.COOH$	Aminoacetic acid
$CH_3.CHNH_2.COOH$	α-Aminopropionic acid
$CH_2NH_2.CH_2COOH$	β-Aminopropionic acid, etc.

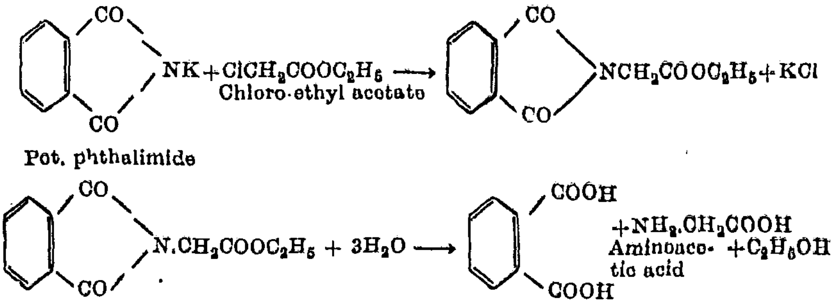
The amino acids are of considerable importance in Biochemistry as many of them are produced by the hydrolysis of proteins.

Preparation. *α-Amino acids can be prepared* :

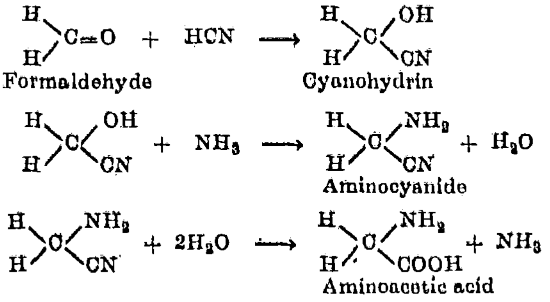
(1) By the action of ammonia on halogen substituted acids.

$$\underset{\text{Chloroacetic acid}}{CH_2Cl.COOH} + NH_3 \longrightarrow \underset{\text{Aminoacetic acid}}{CH_2NH_2.COOH} + HCl$$

(2) By the treatment of halogen-substituted acids with potassium phthalimide and subsequent hydrolysis of the product. (*Gabriel synthesis*).



(3) By reaction between an aldehyde and hydrogen cyanide in the presence of ammonia and hydrolysis of the amino-nitrile has formed. (*Streker's synthesis*).



$$\underset{\text{Formaldehyde}}{H_2C{=}O} + HCN \longrightarrow \underset{\text{Cyanohydrin}}{H_2C(OH)CN}$$

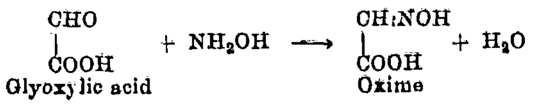
$$H_2C(OH)CN + NH_3 \longrightarrow \underset{\text{Aminocyanide}}{H_2C(NH_2)CN} + H_2O$$

$$H_2C(NH_2)CN + 2H_2O \longrightarrow \underset{\text{Aminoacetic acid}}{H_2C(NH_2)COOH} + NH_3$$

In actual practice the synthesis is carried in one operation by treating the aldehyde with a mixture of ammonium chloride and potassium cyanide in aqueous solution. Thus HCN and NH_3 for the reaction and alkali for hydrolysis are produced in the reaction mixture.

$$KCN + H_2O \longrightarrow HCN + KOH$$
$$KOH + NH_4Cl \longrightarrow KCl + NH_3 + H_2O$$

(4) By the formation of oximes of aldehydic or ketonic acids and their reduction.



$$\underset{\text{Glyoxylic acid}}{CHO.COOH} + NH_2OH \longrightarrow \underset{\text{Oxime}}{CH{:}NOH.COOH} + H_2O$$

$$\begin{matrix} CH{:}NOH \\ | \\ COOH \end{matrix} + 4H \longrightarrow \underset{\text{Aminoacetic acid}}{\begin{matrix} CH_2.NH_2 \\ | \\ COOH \end{matrix}} + H_2O$$

General Properties. (*Physical*). The amino acids are colourless, crystalline substances having high melting points. Most of the amino acids are sweet in taste. They are soluble in water and insoluble in alcohol and ether. Their aqueous solutions are neutral to litmus. All these properties are indicative of their salt-like nature. This is explained by the fact that the acid and the basic group being present in the same molecule, amino acids form an 'internal salt' formula or '**Zwitter ion**'. Thus :

$$\underset{\text{Glycine}}{H_2NCH_2.COOH} \rightleftharpoons H_2NCH_2.CO\overset{-}{O} + \overset{+}{H} \rightleftharpoons \underset{\text{Zwitter ion}}{H_3\overset{+}{N}CH_2.CO\overset{-}{O}}$$

Except glycine, they are all optically active.

(*Chemical*). The chemical behaviour of amino acids is a blend of that of the primary amines and of the fatty acids. However, the reactivity of each functional group is suppressed by the presence of the other.

(1) At the COOH group they form salts, esters, acid chlorides and amides. Thus glycine yields the following derivatives :

$$\underset{\text{Salt}}{NH_2.CH_2.COONa} \qquad \underset{\text{Ester}}{NH_2.CH_2.COOC_2H_5}$$

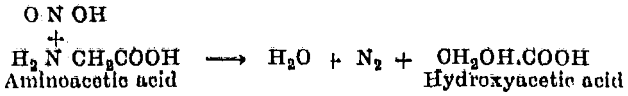
$$\underset{\text{Acid chloride}}{NH_2.CH_2.COCl} \qquad \underset{\text{Amide}}{NH_2.CH_2.CONH_2}$$

(2) At the amino group, the amino acids behave like primary amines. Thus they react with strong acid to form salts ; can be alkylated and acylated.

$$\underset{\text{Glycine}}{HOOC.CH_2NH_2} + HCl \longrightarrow \underset{\text{Glycine hydrochloride}}{HOOC.CH_2NH_2HCl}$$

$$\underset{\text{Glycine}}{HOOC.CH_2NH_2} + \underset{\text{Benzoyl chloride}}{C_6H_5COCl} \longrightarrow \underset{\text{Benzoyl glycine}}{HOOC.CH_2NHCOC_6H_5} + HCl$$

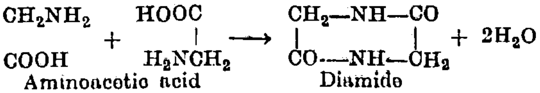
They react with nitrous acid to form hydroxy acids.



$$\underset{\text{Aminoacetic acid}}{\overset{\overset{O\,N\,OH}{+}}{H_2N}CH_2COOH} \longrightarrow H_2O + N_2 + \underset{\text{Hydroxyacetic acid}}{CH_2OH.COOH}$$

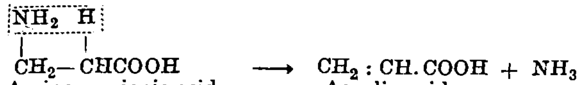
(3) ACTION OF HEAT. The behaviour of amino acids on heating is analogous to that of the hydroxy acids.

(*i*) α-amino acids lose two molecules of water between two molecules of the acid and form cyclic diamides.



$$\underset{\text{Aminoacetic acid (2 molecules)}}{\begin{matrix} CH_2NH_2 \\ \\ COOH \end{matrix} + \begin{matrix} HOOC \\ | \\ H_2NCH_2 \end{matrix}} \longrightarrow \underset{\text{Diamide}}{\begin{matrix} CH_2-NH-CO \\ | \qquad\qquad | \\ CO-NH-CH_2 \end{matrix}} + 2H_2O$$

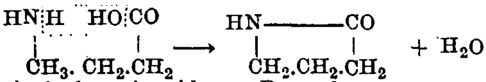
(*ii*) β-amino acids split out a molecule of ammonia and yield unsaturated acids.



$$\overset{NH_2\ \ H}{CH_2-CHCOOH} \longrightarrow CH_2:CH.COOH + NH_3$$

β-Aminopropionic acid — Acrylic acid

(*iii*) γ- and δ-amino acids lose a molecule of water forming internal anhydrides called **lactams**.



$$\overset{HN\,H\ \ HO\,CO}{CH_3.CH_2.CH_2} \longrightarrow \overset{HN\text{———}CO}{CH_2.CH_2.CH_2} + H_2O$$

γ-Aminobutyric acid — γ-Butyrolactam

GLYCINE, AMINOACETIC ACID, $CH_2.NH_2.COOH$

It is the simplest amino acid known Since it has a sweet taste and was first isolated by the hydrolysis of glue, it is commonly named as *glycine* or *glycocoll* (Greek, *glycys*=sweet ; *colla*=glue). It occurs in urine of horse as hippuric acid (*hippos*=horse) or benzoylglycine from which it can be obtained by hydrolysis with hydrochloric acid.

$$\underset{\text{Benzoylglycine}}{C_6H_5CO.NHCH_2COOH} + H_2O \longrightarrow \underset{\text{Benzoic acid}}{C_6H_5COOH} + \underset{\text{Glycine}}{NH_2CH_2COOH}$$

Preparation. Glycine can be synthesised by various methods used for the preparation of amino acids. In the laboratory it is generally obtained by dissolving chloroacetic acid in liquor ammonia at room temperature.

$$\underset{\text{Chloroacetic acid}}{CH_2Cl.COOH} + 2NH_3 \longrightarrow \underset{\text{Aminoacetic acid}}{CH_2NH_2.COOH} + NH_4Cl$$

The resulting solution is treated with cupric hydroxide when a deep blue solution of copper-glycine is produced.

$$\underset{\text{Glycine}}{2CH_2NH_2.COOH} + Cu(OH)_2 \longrightarrow \underset{\text{Copper glycine}}{(CH_2NH_2.COO)_2Cu} + 2H_2O$$

The solution is filtered and crystallised to give deep blue needles of copper-glycine. These are dissolved in water and hydrogen sulphide is passed through the solution.

$$\underset{\text{Copper glycine}}{(CH_2NH_2.COO)_2Cu} + H_2S \longrightarrow \underset{\text{Glycine}}{2CH_2NH_2COOH} + CuS$$

The precipitate of cupric sulphide is filtered off and the solution crystallised to yield glycine.

Properties. Glycine forms white crystals, m.p. 235°. It is very soluble in water but insoluble in alcohol and ether. Its aqueous solutions are neutral to litmus.

Chemically it behaves both as an acid and as a primary amine.

(1) AMPHOTERIC CHARACTER. Glycine forms salts with alkalis and hydrochlorides with hydrochloric acid.

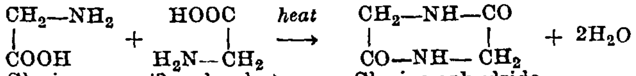
$$\underset{\text{Glycine}}{CH_2NH_2.COOH} + NaOH \longrightarrow \underset{\text{Sodium amino acetate}}{CH_2NH_2.COONa} + H_2O$$

$$\underset{\text{Glycine}}{CH_2NH_2.COOH} + HCl \longrightarrow \underset{\text{Glycine hydrochloride}}{HCl.NH_2CH_2COOH}$$

Both the acid and the basic group being present in the same molecule, it also forms an internal salt or *Zwitter ion.*

$$\underset{\text{Glycine}}{NH_2CH_2COOH} \rightleftharpoons \underset{\text{Zwitter ion}}{\overset{+}{N}H_3CH_2CO\overset{-}{O}}$$

(2) ACTION OF HEAT. Two molecules of glycine condense to form an anhydride.



$$\begin{array}{lcl}CH_2\text{—}NH_2 & & HOOC \\ | & + & | \\ COOH & & H_2N\text{—}CH_2\end{array} \xrightarrow{heat} \begin{array}{l}CH_2\text{—}NH\text{—}CO \\ |\qquad\qquad\quad | \\ CO\text{—}NH\text{—}CH_2\end{array} + 2H_2O$$

Glycine (2 molecules) Glycine anhydride

(3) DECARBOXYLATION. When heated with sodalime, it splits out a molecule of carbon dioxide yielding methylamine.

$$\underset{\text{Glycine}}{NH_2CH_2COOH} + CaO \longrightarrow \underset{\text{Methylamine}}{CH_3NH_2} + CaCO_3$$

(4) ACTION WITH NITROUS ACID. Nitrous acid decomposes glycine to form glycollic acid with the evolution of nitrogen gas.

$$\underset{\text{Aminoacetic acid}}{NH_2CH_2.COOH} + HO.NO \longrightarrow \underset{\text{Glycollic acid}}{HO.CH_2COOH} + N_2 + H_2O$$

(5) ACTION WITH FORMALDEHYDE. When an aqueous solution of glycine is treated with an excess of formaldehyde solution, it yields methylene glycine.

$$\underset{\text{Formaldehyde}}{CH_2\vdots O} \; \boxed{+\;H_2}\vdots \underset{\text{Glycine}}{NCH_2COOH} \longrightarrow \underset{\text{Methylene glycine}}{CH_2{:}NCH_2COOH} + H_2O$$

Benzaldehyde reacts similarly with glycine.

Uses. (1) Glycine is utilized in the body for detoxification of substances ; thus it combines with benzoic acid to form benzoylglycine which is eliminated in urine.

(2) It is used in medicine for the treatment of certain muscular disorders.

(3) It is also employed for the manufacture of resins and varnishes.

QUESTIONS

1. What are substituted acids ? How are they named ?

2. Describe the methods of preparation of halogenated acids. What is the action of alkalis on these acids ?

3. Describe the general methods of synthesis of hydroxy acids. Survey their physical and chemical characters.

4. Describe the characteristic behaviour of α, β, γ-hydroxy acids and amino acids.

5. How is lactic acid obtained in the laboratory ? Give an account of the action of heat on α, β, γ-hydroxy acids.

6. How can you prepare lactic acid ? What reactions show that it is both an alcohol and an acid ? Explain the isomerism of lactic acid.

7. How is citric acid obtained from lemon juice ? Write suitable reactions to show that it contains ; (*a*) one hydroxyl group, (*b*) three carboxyl groups. How are citrates distinguished from oxalates ?
(*Kurukshetra B.Sc. II, 1967*)

8. How is tartaric acid obtained from nature ? How can you prepare from tartaric acid : (*a*) malic acid ; (*b*) meso-tartaric acid, and (*c*) succinic acid.
(*Kalyani B.Sc. Hons., 1967*)

9. What happens when the following are heated :

(*i*) α-hydroxy isobutyric acid,
(*ii*) β-methyl, γ-hydroxy valeric acid,
(*iii*) 3-hydroxy-hexanoic acid ?
(*Panjab B.Sc. II, 1967*)

10 What happens when α (alpha), β (beta) and γ (gamma) amino and hydroxy acids are heated separately.
(*Udaipur B.Sc. II, 1967*)

11. How many isomers are possible for the following compounds ? Give the structures of the respective geometrical and optical isomers.

(*i*) Lactic acid (*ii*) Crotonic acid
(*iii*) Tartaric acid (*iv*) 2-Butene.
(*Jadavpur B.Sc., 1968*)

12. Give an account of methods available for the synthesis of α-amino acids. Taking glycine as an example, discuss in brief the chemical characteristics. Explain the action of heat on α-, β- and γ- amino acids separately.
(*Ujjain B.Sc., 1968*)

13. What are amino acids ? How are these synthesised. Show their relation to polypeptides.
(*Banaras B.Sc., 1968*)

14. Discuss the analytical and synthetic evidences that led to the structure of citric acid.
(*Utkal B.Sc., 1968*)

15. Describe the methods available for the preparation of the hydroxy acids. Give an account of the more important properties of these compounds.
(*Viswa Bharti B.Sc., 1969*)

16. What are hydroxy acids and how are they prepared. Taking lactic acid as an example describe the important chemical properties. How will you destinguish α, β and γ hydroxy acids ?
(*Udaipur B.Sc., 1969*)

17. Give an account of the preparation of α, β, and γ hydroxy acids. How are these distinguished from one another ?
(*Bombay B.Sc., 1969*)

18. How is citric acid prepared ? What are its uses ? Discuss its constitution.
(*Meerut B.Sc., 1969*)

19. What are amino acids ? Discuss their importance. How are the following amino acids synthesised ? (*a*) Glycine (*b*) Alanine (*c*) Tyrosine.
(*Behrampur B.Sc., 1969*)

20. How is tartaric acid prepared synthetically and what are its important reactions ? Discuss the stereoisomerism of tartaric acid.
(*Tribhuvan B.Sc., 1969*)

23

Acid Derivatives

ROBERT W.E. VON BUNSEN
(1811–1899)

German. Prolific work in the field of analytical chemistry. His work with cacodyl and its compounds was outstanding. He developed many pieces of apparatus used in the organic laboratory.

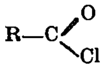
The group of compounds derived from acids by replacement of the —H, —OH, or =O of the carboxyl group by other atoms or groups are called *acid derivatives.* They are acid halides, acid anhydrides, acid esters, acid amides and nitriles. These classes of compounds differ widely in properties but show one reaction in common, *i.e., on simple hydrolysis all acid derivatives yield free carboxylic acids.*

1. ACID HALIDES

Acid halides are the derivatives of acids in which the –OH of the –COOH group has been replaced by the halogen atom.

$$\underset{\text{Acid}}{R-\overset{\overset{\displaystyle O}{\|}}{C}-OH} \xrightarrow[+X]{-OH} \underset{\text{Acid halide}}{R-\overset{\overset{\displaystyle O}{\|}}{C}-X}$$

The acid chlorides are by far the most important of the acid halides and will be discussed in detail. They have the type formula



$$R{-}C\overset{O}{\underset{Cl}{<}} \quad \text{or} \quad RCOCl$$

and contain the grouping $-COCl$.

The acid halides are named after the parent acids. The ending *-ic acid* is replaced by *-yl halide.* Thus :

PARENT ACID	ACID HALIDE
Formic acid, $HCOOH$	Formyl chloride, $HCOCl$
Acetic acid, CH_3COOH	Acetyl chloride, CH_3COCl

Similarly acetyl chloride could be named as *ethanoyl chloride* (IUPAC) after ethanoic acid.

METHODS OF PREPARATION

(1) ACTION OF PCl_3 AND PCl_5 ON ACIDS. Acid chlorides may be obtained by the action of phosphorus trichloride or phosphorus pentachloride on acids or their salts which are cheaper.

$$\underset{\text{Acetic acid}}{3CH_3COOH} + PCl_3 \longrightarrow \underset{\text{Acetyl chloride}}{3CH_3COCl} + H_3PO_3$$

$$CH_3COOH + PCl_5 \longrightarrow CH_3COCl + POCl_3 + HCl$$

(2) ACTION OF $SOCl_2$ ON ACIDS. Sometimes acid halides are prepared by the action of thionyl chloride on acids.

$$\underset{\text{Propionic acid}}{CH_3CH_2COOH} + SOCl_2 \longrightarrow \underset{\text{Propionyl chloride}}{CH_3CH_2COCl} + SO_2 + HCl$$

This method is superior to the first one in asmuch as the by-products being gases escape leaving the acid chloride in the pure state.

GENERAL PROPERTIES

(*Physical*). The lower acyl chlorides are colourless, pungent smelling liquids ; the higher members are colourless solids. They fume when exposed to moist air. They are insoluble in water but slowly dissolve in it by reason of hydrolysis.

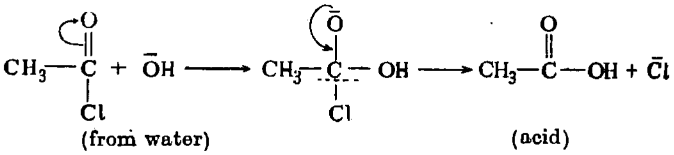
(*Chemical*). The chlorine atom linked to the acyl group is much more loosely held than in alkyl chlorides and can be readily replaced by other atoms or groups. Therefore, acid chlorides are excellent reagents to introduce RCO- or acyl group in other molecules (*acylation*).

(1) The acid chlorides are readily hydrolysed with water to form the parent acid and hydrogen chloride.

$$\underset{\text{Acetyl chloride}}{CH_3CO\boxed{Cl + H}OH} \longrightarrow \underset{\text{Acetic acid}}{CH_3COOH} + HCl$$

The lower members react vigorously.

Mechanism :



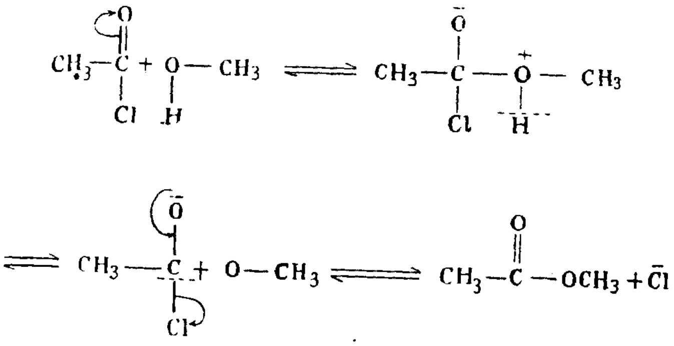
$$CH_3{-}\overset{O}{\overset{\|}{\underset{Cl}{\underset{|}{C}}}} + \bar{O}H \longrightarrow CH_3{-}\overset{\bar{O}}{\overset{|}{\underset{Cl}{\underset{|}{C}}}}{-}OH \longrightarrow CH_3{-}\overset{O}{\overset{\|}{C}}{-}OH + \bar{Cl}$$

(2) They react with alcohols to form esters.

$$CH_3CO\,Cl + H\,OC_2H_5 \longrightarrow CH_3COOC_2H_5 + HCl$$

Acetaldehyde Ethyl alcohol Ethyl acetate

Mechanism :



(3) They react with ammonia to form amides and with primary and secondary amines giving *N*-substituted amides.

$$CH_3CO\,Cl + H\,NH_2 \longrightarrow CH_3CONH_2 + HCl$$

Acetyl chloride Acetamide

$$CH_3COCl + H_2NR \longrightarrow CH_3CO.NHR + HCl$$

P-amine N-alkylacetamide

(4) They react with sodium salts of the fatty acids to form acid anhydrides.

$$CH_3CO\,Cl + Na\,OOC.CH_3 \longrightarrow (CH_3CO)_2O + NaCl$$

Acetyl chloride Sod. acetate Acetic anhydride

(5) When reduced with hydrogen in the presence of finely divided palladium as catalyst, acyl chlorides are reduced to aldehydes.

$$CH_3COCl + H_2 \longrightarrow CH_3CHO + HCl$$

Acetyl chloride Acetaldehyde

(6) They react with Grignard reagents to produce ketones.

$$CH_3CO\,Cl + IMg\,C_2H_5 \longrightarrow CH_3COCC_2H_5 + MgI.Cl$$

Acetyl chloride Ethylmagnesium iodide Ethyl methyl ketone

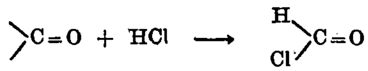
(7) They react with aromatic hydrocarbons in the presence of anhydrous aluminium chloride to form aromatic ketones (*Friedel-Crafts reaction*).

$$C_6H_6 + ClCOCH_3 \longrightarrow C_6H_5COCH_3 + HCl$$

Benzene Acetyl chloride Acetophenone

FORMYL CHLORIDE, METHANOYL CHLORIDE, HCOCl

Formyl chloride is the first member of the class. It is not known to exist at ordinary temperature. There is evidence of its existence at low temperatures (—80°). A mixture of carbon monoxide and hydrogen chloride, however, behaves as formyl chloride in certain reactions.



$$>C{=}O + HCl \longrightarrow \begin{matrix}H\diagdown\\ \\ Cl\diagup\end{matrix}\!C{=}O$$

Carbon monoxide Formyl chloride

ACETYL CHLORIDE, ETHANOYL CHLORIDE, CH_3COCl

Acetyl chloride is the most important acyl halide. According to the accepted abbreviation of *acetyl group* as 'Ac', the formula of acetyl chloride may be written as AcCl.

Preparation. Acetyl chloride is prepared by the action of phosphorus trichloride on glacial acetic acid.

$$3CH_3COOH + PCl_3 \longrightarrow 3CH_3COCl + H_3PO_3$$

A distillation flask (250 ml.) is fitted with a tap funnel and connected to water-condenser leading to a receiver guarded by a calcium chloride tube to exclude moisture. (Fig. 23·1). 50 gm. of glacial acetic acid are placed in the distillation flask which is cooled by immersion in cold water. Then 40 gm (25 ml.) of phosphorus trichloride are added dropwise from the tap-funnel. When all has been added, the flask is warmed on a water bath to 40—50°. As the evolution of hydrogen chloride slackens, the temperature is raised to boiling. The acetyl chloride that distils over is collected in the receiver cooled by ice water. It is again purified by distilling from the receiver flask in the usual way. The fraction distilling between 50° and 54° is collected.

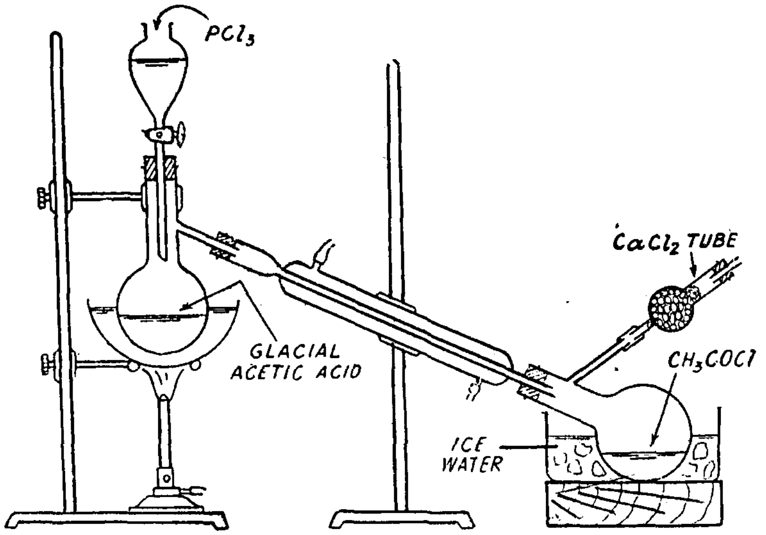


Fig. 23·1. Preparation of acetyl chloride.

Note. The preparation should be carried in fume-cupboard as large volume of hydrogen chloride gas is evolved during the reaction.

Properties. Acetyl chloride is a colourless pungent-smelling liquid, b.p. 52°. It is soluble in ether and chloroform. It fumes in moist air due to the formation of hydrogen chloride through hydrolysis.

The chemical reactions of acetyl chloride have been mentioned under the general treatment of acyl halides. Thus it reacts with alcohols, ammonia, amines etc., in the usual way replacing hydrogen atoms by acetyl groups (*Acetylation*).

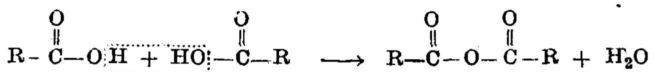
$$\underset{\text{Alcohol}}{ROH} + \underset{\text{Acetyl chloride}}{CH_3COCl} \longrightarrow \underset{\text{Ester}}{CH_3COOR} + HCl$$

$$\underset{\text{Amine}}{RNH_2} + \underset{\text{Acetyl chloride}}{CH_3COCl} \longrightarrow \underset{\text{Acetylamine}}{RNH.COCH_3} + HCl$$

Uses. Acetyl chloride is largely used as an acetylating agent, *i.e.*, for introducing acetyl group in organic compounds. It is also used to detect the presence of OH groups in organic molecules and to estimate their number.

2. ACID ANHYDRIDES

When two molecules of an organic acid lose a molecule of water between the two OH groups, the derivative formed is called the *acid anhydride*.



$$\underset{\text{(2 molecules of acid)}}{R-\overset{O}{\overset{\|}{C}}-O\text{H} + \text{HO}-\overset{O}{\overset{\|}{C}}-R} \longrightarrow \underset{\text{Acid anhydride}}{R-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-R} + H_2O$$

Thus in acid anhydrides we have two acyl groups (RCO—) connected through an oxygen bridge. They have the formula

$$RCO-O-OCR \quad \text{or} \quad (RCO)_2O$$

Acid anhydrides are named after the acids from which they are derived by substituting '*anhydride*' for '*acid*'. Thus the anhydride of acetic acid is called acetic anhydride or *ethanoic anhydride* (IUPAC).

$$\underset{\text{Acetic Acid}}{2CH_3COOH} \longrightarrow \underset{\text{Acetic anhydride}}{(CH_3CO)_2O} + H_2O$$

Similarly the anhydride derived from propionic acid is called propionic anhydride or propanoic anhydride, $(CH_3CH_2CO)_2O$.

The acid anhydrides could also be regarded as *acyl oxides* just as ethers are thought of as alkyl oxides. Thus acetic anhydride may be called acetyl oxide since it contains two acetyl groups linked to the oxide oxygen.

The anhydrides are termed '*simple*' or '*mixed*' according as the two acyl groups attached to the oxide oxygen are same or different. However, only the simple anhydrides are of interest and will be discussed here.

METHODS OF PREPARATION

(1) The acid anhydrides are generally prepared by reaction between an acid chloride and the salt of a fatty acid.

$$\underset{\text{Acetyl chloride}}{CH_3CO{:}Cl} + \underset{\text{Sod. acetate}}{Na{:}OOCCH_3} \longrightarrow \underset{\text{Acetic anhydride}}{(CH_3CO)_2O} + NaCl$$

By taking the salt and acid chloride of different acids, this method could be used to prepare mixed anhydrides.

$$\underset{\text{Acid chloride}}{RCOCl} + \underset{\text{Sod. salt}}{R\,COONa} \longrightarrow \underset{\substack{\text{Anhydride}\\ \text{(Mixed)}}}{RCO.O.COR'} + NaCl$$

(2) The higher anhydrides can also be obtained by distilling fatty acids with acetic anhydride.

$$\underset{\text{Acid}}{2RCOOH} + \underset{\text{Acetic anhydride}}{(CH_3CO)_2O} \rightleftharpoons \underset{\text{Anhydride}}{(RCO)_2O} + 2CH_3COOH$$

The removal of the more volatile acetic acid by distillation, forces the equilibrium to the right and thus the fatty acid is completely converted into the anhydride.

GENERAL PROPERTIES

(*Physical*). Excepting formic anhydride, which is unstable, the lower members of the series are colourless mobile liquids with a sharp pungent odour. The higher members are odourless and crystalline solids. They are only slightly soluble in water but dissolve in organic solvents like alcohol and ether. The anhydrides are somewhat more volatile than the acids from which they are derived.

(*Chemical*). The acid anhydrides give reactions analogous to those of acyl chlorides which are also in reality the mixed anhydrides of carboxylic acids and hydrogen chloride. Thus they react with the same reagents as the acid chlorides but with less vigour.

(1) Acid anhydrides are hydrolysed with water to form the original acids.

$$\underset{\text{Acetic anhydride}}{CH_3CO{:}O.COCH_3} + H{.}OH \longrightarrow \underset{\text{Acetic acid}}{2CH_3CO.OH}$$

(2) They react with alcohols to form esters.

$$\underset{\text{Acetic anhydride}}{CH_3CO{:}O.COCH_3} + \underset{\text{Ethyl alcohol}}{H{:}OC_2H_5} \longrightarrow \underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + CH_3COOH$$

(3) They react with ammonia to form amides.

$$\underset{\text{Acetic anhydride}}{CH_3CO.O.COCH_3} + H{:}NH_2 \longrightarrow \underset{\text{Acetamide}}{CH_3CONH_2} + CH_3COOH$$

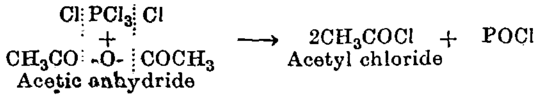
(4) They react with amines to form N-substituted amides.

$$\underset{\text{Acetic anhydride}}{CH_3CO{:}O.COCH_3} + \underset{\text{Amine}}{H{:}HNR} \longrightarrow \underset{\text{N-alkylacetamide}}{CH_3CONHR} + CH_3COOH$$

(5) They react with dry hydrogen chloride to form acyl chlorides.

$$\underset{\text{Acetic anhydride}}{CH_3CO\,O.COCH_3 + H\,Cl} \longrightarrow \underset{\text{Acetyl chloride}}{CH_3COCl} + CH_3COOH$$

(6) They also react with phosphorus pentachloride to form acyl chlorides.



$$\underset{\text{Acetic anhydride}}{\overset{Cl\,PCl_3\,Cl\\ +}{CH_3CO\,\text{-O-}\,COCH_3}} \longrightarrow \underset{\text{Acetyl chloride}}{2CH_3COCl} + POCl_3$$

Like the acid chlorides, the acid anhydrides are also used as acylating reagents. However, only half the molecule of acid anhydride is used in acylation, the other half being converted to the acid.

ACETIC ANHYDRIDE, ETHANOIC ANHYDRIDE, $(CH_3CO)_2O$

It is the most important acid anhydride.

Preparation. Acetic anhydride is prepared :

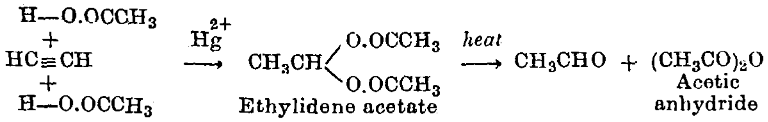
(1) By distilling a mixture of anhydrous sodium acetate and acetyl chloride.

$$\underset{\text{Sod acetate}}{CH_3COO\,Na} + \underset{\text{Acetyl chloride}}{CH_3CO\,Cl} \longrightarrow \underset{\text{Acetic anhydride}}{(CH_3CO)_2O} + NaCl$$

(2) By passing chlorine into a mixture of sodium acetate and sulphur dichloride and distilling. (*Commercial*).

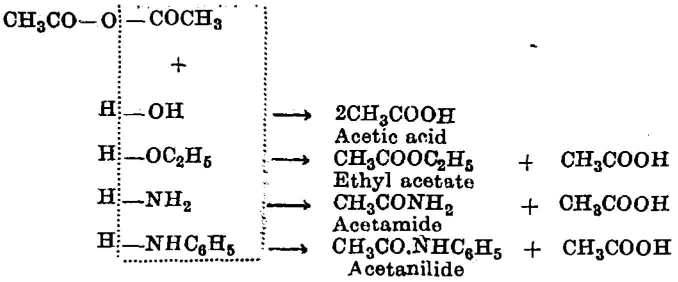
$$\underset{\text{Sod. acetate}}{8CH_3COONa} + SCl_2 + 2Cl_2 \longrightarrow \underset{\text{Acetic anhydride}}{4(CH_3CO)_2O} + 6NaCl + Na_2SO_4$$

(3) By passing acetylene into glacial acetic acid in the presence of mercuric sulphate as catalyst and distilling the resulting ethylidene acetate. (*Commercial*).



Laboratory Preparation. 55 gm. of powdered sodium acetate are placed in a 250 ml. distilling flask cooled in ice-water. 40 gm. of acetyl chloride are placed in a tap-funnel which is fitted into the neck of the distilling flask. The acetyl chloride is slowly run on to the sodium acetate, and the flask is shaken after each addition. The distilling flask is then connected to an air-condenser, and heated with a Bunsen flame. The distillate of crude acetic anhydride is redistilled using an air-condenser when the pure anhydride is obtained.

Properties. Acetic anhydride is a colourless, neutral liquid, b.p. 139°, with a sharp pungent odour. It is sparingly soluble in cold water but readily soluble in ether and benzene. It undergoes reactions similar to those of acetyl chloride, although less vigorously in most cases. Thus it reacts with water to form acetic acid ; with alcohol to form ethyl acetate ; with ammonia to form acetamide ; and with aniline to form acetanilide.



$$CH_3CO{-}O{-}COCH_3 + H{-}OH \longrightarrow 2CH_3COOH$$ (Acetic acid)

$$CH_3CO{-}O{-}COCH_3 + H{-}OC_2H_5 \longrightarrow CH_3COOC_2H_5 + CH_3COOH$$ (Ethyl acetate)

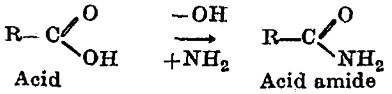
$$CH_3CO{-}O{-}COCH_3 + H{-}NH_2 \longrightarrow CH_3CONH_2 + CH_3COOH$$ (Acetamide)

$$CH_3CO{-}O{-}COCH_3 + H{-}NHC_6H_5 \longrightarrow CH_3CO.NHC_6H_5 + CH_3COOH$$ (Acetanilide)

Uses. Acetic anhydride is used : (1) as an acetylating agent; (2) in the preparation of some medicines (*aspirin*) ; (3) for the manufacture of *acetate rayon* from cotton.

3. Acid Amides

Acid amides are the derivatives of acids in which the OH of the carboxyl group is replaced by the amino group, $-NH_2$.



Amides have the type formula $RCONH_2$ and characterised by the presence of the *amido group*, $-CONH_2$.

Amides may be regarded as derivatives of ammonia in which one H-atom of ammonia molecule is replaced by acyl group, RCO—

$$\underset{\text{Ammonia}}{NH_3} \xrightarrow[+RCO]{-H} \underset{\text{Acid amide}}{RCONH_2}$$

Amides are commonly named after the parent acid by putting the suffix *-amide* instead of *-ic acid.* Thus :

$HCONH_2$	Formamide
CH_3CONH_2	Acetamide

The IUPAC name of an amide is derived from the name of the parent acid by substituting the suffix *-amide* for *-oic acid.* Thus formamide (derived from methanoic acid) is named as methanamide and acetamide (derived from ethanoic acid) is named as ethanamide.

METHODS OF PREPARATION

(1) *By heating ammonium salts.* Ammonium salts of fatty acids upon strong heating lose a molecule of water to form amides.

$$\underset{\text{Amm. salt}}{R.CO.ONH_4} \longrightarrow \underset{\text{Amide}}{R.CO.NH_2} + H_2O$$

(2) *By ammonolysis of acid derivatives.* Acid chlorides, anhydrides and esters react with concentrated ammonia solution at ordinary temperature to form amides.

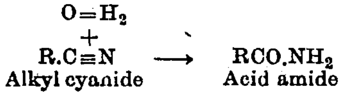
$$\underset{\text{Acid chloride}}{RCOCl} + NH_3 \longrightarrow \underset{\text{Amide}}{RCONH_2} + HCl$$

$$\underset{\text{Acid anhydride}}{(RCO)_2O} + NH_3 \longrightarrow RCONH_2 + RCOOH$$

$$\underset{\text{Ester}}{RCOOR'} + NH_3 \longrightarrow RCONH_2 + R'OH$$

The free acids produced in the above reactions, however, combine with excess of ammonia to give ammonium salts.

(3) *By partial hydrolysis of alkyl cyanides.* Alkyl cyanides when shaken with cold concentrated hydrochloric acid, add a molecule of water and yield amides.



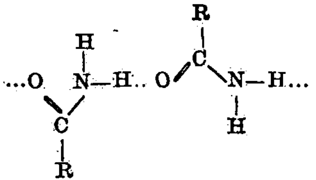
$$\underset{\text{Alkyl cyanide}}{\overset{\overset{O=H_2}{+}}{R.C\equiv N}} \longrightarrow \underset{\text{Acid amide}}{RCO.NH_2}$$

The complete hydrolysis of alkyl cyanides will, however, yield ammonium salt of the corresponding fatty acid.

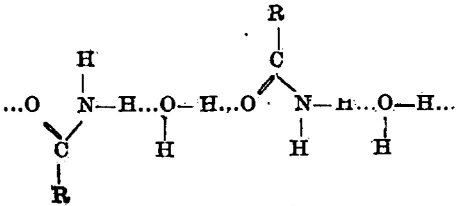
GENERAL PROPERTIES

(*Physical*). With the exception of formamide, all the amides are colourless crystalline solids. Their boiling points are considerably higher than those of the parent acids. Lower amides dissolve in water giving neutral solutions.

Acid amides possess quite high boiling points because they are capable of forming strong intermolecular hydrogen bonds. Owing to this linkage between the H atom and a highly electronegative N-atom the hydrogen bond forming' nature is much pronounced here. They also form 'co-associated'molecules with water, accounting for their solubility in water.



Intermolecular hydrogen bonding



Hydrogen bonding with water.

(*Chemical*). (1) Although amides are neutral to litmus, they behave as weak acids or weak bases. Thus they form salts with acids and yield metallic derivatives with mercuric oxide.

$$\underset{\text{Acetamide}}{CH_3CONH_2} + HCl \longrightarrow \underset{\text{Salt}}{CH_3CONH_2HCl}$$

$$2CH_3CONH_2 + HgO \longrightarrow \underset{\text{Mercury acetamide}}{(CH_3CONH)_2Hg} + H_2O$$

However, the salts produced are unstable and are at once decomposed by water to give back the amides.

(2) On boiling with water, amides are hydrolysed to form the parent acid and ammonia.

$$\underset{\text{Acetamide}}{CH_3CO\boxed{NH_2 + H}OH} \longrightarrow \underset{\text{Acetic acid}}{CH_3COOH} + NH_3$$

The hydrolysis takes place rapidly in the presence of acids and far more rapidly in the presence of alkalis.

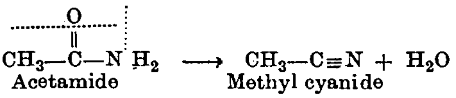
(3) Amides react with nitrous acid to form acids, nitrogen and water.

$$\begin{array}{l} HO\vdots N\vdots O \\ RCO\vdots N\vdots H_2 \\ \text{Amide} \end{array} \longrightarrow \underset{\text{Acid}}{RCOOH} + N_2 + H_2O$$

(4) Amides are reduced with sodium and alcohol yielding primary amides.

$$\underset{\text{Acetamide}}{CH_3CONH_3} + 2H_2 \longrightarrow \underset{\text{Ethylamine}}{CH_3CH_2NH_2} + H_2O$$

(5) When heated with phosphorus pentoxide, amides split out a molecule of water to form alkyl cyanides.

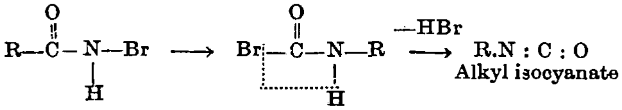


$$CH_3-\overset{\overset{\Large O}{\|}}{C}-NH_2 \longrightarrow CH_3-C\equiv N + H_2O$$

Acetamide Methyl cyanide

(6) When a mixture of amide, bromine and sodium hydroxide, is heated, a primary amine is formed (**Hofmann's reaction**).

$$\underset{\text{Amide}}{RCONH_2} + Br_2 \longrightarrow \underset{\text{Monobromo-amide}}{RCONHBr} + HBr$$



$$R-\overset{\overset{O}{\|}}{C}-\underset{\underset{H}{|}}{N}-Br \longrightarrow Br-\overset{\overset{O}{\|}}{C}-\underset{\underset{H}{|}}{N}-R \xrightarrow{-HBr} \underset{\text{Alkyl isocyanate}}{R.N:C:O}$$

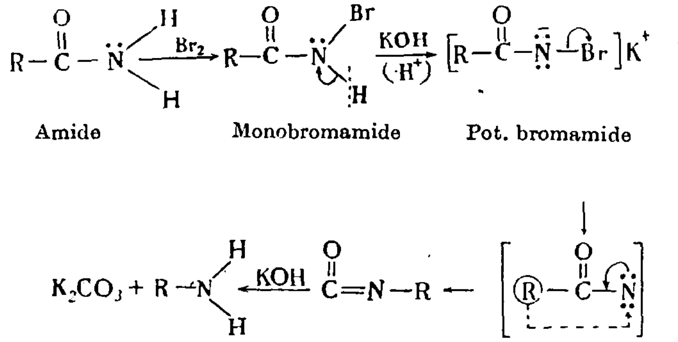
$$RN\boxed{CO + H}\boxed{O}H \longrightarrow \underset{\text{Amine}}{RNH_2} + CO_2$$

The resulting amine has one carbon atom less than the original amide. Hence this reaction is often employed for shortening a carbon chain in organic molecules.

Since amides are high-melting crystalline solids, they are often prepared from acids and amines as characteristic derivatives for their identification.

Mechanism :

The reaction proceeds *via* a number of intermediates as *bromamide* R.CO.NH.Br, *pot. bromamide* $[R.CO.NBr]^-K^+$ and *isocyanate* R.N=C=O, which have been isolated. The sequence of their formation may be represented as



Amide Monobromamide Pot. bromamide

Amine Isocyanate

Structure of Amides. The amphoteric character of amides is explained satisfactorily by the fact that they exist in tautomeric forms

$$R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}NH_2 \rightleftharpoons R{-}\overset{\overset{\displaystyle OH}{|}}{C}{=}NH$$

Keto form Enol form

The keto form behaves as a weak base, while the enol form is capable of forming metallic derivatives.

ACETAMIDE, ETHANAMIDE, CH_3CONH_2

It is the most important amide.

Preparation Acetamide is prepared by heating ammonium acetate.

$$\underset{\text{Amm. acetate}}{CH_3COONH_4} \longrightarrow \underset{\text{Acetamide}}{CH_3CONH_2} + H_2O$$

In actual practice it is convenient to start with ammonium carbonate and glacial acetic acid. The excess of acetic acid used retards the side-reaction in which ammonium acetate is decomposed to form acetic acid and ammonia.

18 gm. of powdered ammonium carbonate is gradually added to 60 ml. of glacial acetic acid in a 250 ml. round-bottomed flask. When effervescence has ceased, a long air-condenser is fitted to the flask and the contents boiled for about 4 hours. The resulting mixture is then quickly transferred to a distilling flask fitted with a thermometer and an air-condenser for distillation. When the temperature reaches 215°, the receiver is changed. The distillate obtained upon cooling solidifies to a colourless, crystalline mass which is practically pure acetamide. This is further purified by crystallising from acetone

Properties. Acetamide forms long colourless needles, m.p. 82°, b.p. 223°. It has often a smell of mice owing to impurities but when purified by crystallising from acetone it is colourless. It is soluble in water and alcohol.

Acetamide upon hydrolysis with sodium hydroxide gives sodium acetate and ammonia. (*Test*)

$$\underset{\text{Acetamide}}{CH_3CONH_2} + NaOH \longrightarrow \underset{\text{Sod. acetate}}{CH_3COONa} + NH_3$$

It undergoes Hofmann reaction to form methylamine.

$$\underset{\text{Acetamide}}{CH_3CONH_2} \xrightarrow{Br_2,\ NaOH} \underset{\text{Methylamine}}{CH_3NH_2}$$

Other reactions of acetamide have been mentioned above.

QUESTIONS

1. What are acid halides and anhydrides, and acid amides ? Write the type formula of each class.

2. Describe the general methods of preparation, properties and uses of acid chlorides. *Point out the difference in the reactivity of the halogen atom of acid halides and that of alkyl halides.*

3. Describe with essential practical details the preparation of acetyl chloride in the laboratory ? *What are its main properties and uses ?*

4. Starting from acetic acid, outline the preparation of acetyl chloride and acetic anhydride. How do these substances react with (*a*) ethyl alcohol, (*b*) ammonia, and (*c*) water ?

5. What are amides ? Compare and contrast their chemical behaviour with that of primary amines.

6. How is acetamide prepared ? How would you hydrolyse it and test for the products formed ?

7. Describe two methods for the preparation of acetamide. What is the action on acetamide of (*a*) nitrous acid, (*b*) bromine and sodium hydroxide, and (*c*) phosphorus pentoxide ?

8. What classes of substances are obtained when the hydroxyl group in (*a*) a primary monohydric alcohol, (*b*) a monobasic organic acid is replaced by the group NH_2 ? Name and give a brief account of the preparation of the NH_2 compounds from any such alcohol and acid you may choose.

9. Describe a convenient method of making acetic anhydride in the laboratory. In what important particulars does it differ from ethyl acetate ? How would you obtain a specimen of pure ethyl acetate from anhydride.

10. What is the difference in reactivity of the chlorine atom present in acetyl chloride and chloroacetic acid ?

11. A substance of the formula $C_4H_{10}O_4$ yields on acetylation with acetic anhydride a derivative of the formula $C_{12}H_{18}O_8$. How many hydroxyl groups are present in the substances ? What is its probable structure ?

12. Write out equations to describe the action, if any, of acetyl chloride on any *five* of the following compounds separately :—

(*a*) Dimethylamine.

(*b*) Methylamine.

(*c*) Benzoic acid.

(*d*) Tertiary butyl alcohol.

(*e*) Benzophenone.

(*f*) Phenol.

(*g*) Methyl alcohol. (*Rajasthan B.Sc., 1956*)

13. How would you prepare acetyl chloride in the laboratory ? What happens when acetyl chloride reacts with (*a*) reducing agent, (*b*) methyl ethylamine, (*c*) sodium propionate, and (*d*) isopropyl alcohol ?

Mention its importance as a reagent. (*Bihar B.Sc., 1956 Supp.*)

14. Describe the laboratory preparation of acetic anhydride. How does acetic anhydride react with (*a*) methyl alcohol ; (*b*) aniline ; (*c*) succinic acid ; and (*d*) glucose ? Give equations. (*Gauhati B.Sc., 1961*)

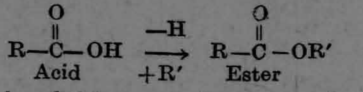
15. What methods are available for the preparation of acetamide ? What is the action of (*a*) caustic soda, (*b*) phosphorus pentoxide, (*c*) bromine and caustic soda, (*d*) nitrous acid on acetamide ? (*Rangoon B.Sc., 1962*)

24

Esters

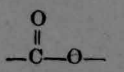
MICHEL E. CHEVREUL
(1786—1889)
French. His work with fats and oils is outstanding. He brought out the importane of the value of melting point and boiling point for the characterisation of organic substances.

Esters are the derivatives of acids in which the H atom of the COOH group is replaced by an alkyl group.



$$\underset{\text{Acid}}{R-\overset{\overset{\displaystyle O}{\|}}{C}-OH} \xrightarrow[+R']{-H} \underset{\text{Ester}}{R-\overset{\overset{\displaystyle O}{\|}}{C}-OR'}$$

The type formula of this class of compounds is RCOOR or RCOOR' The grouping



$$-\overset{\overset{\displaystyle O}{\|}}{C}-O- \quad \text{or} \quad -COO-$$

is called the *ester group*.

Esters are by far the most important class of acid derivatives. A large number of them occur in flowers and fruits which owe their fragrance to these compounds.

Analogy to Salts. Esters are analogous to salts which are similar metallic derivatives of acids. Thus both esters and salts can be formed from an acid and a hydroxy compound by the elimination of a water molecule.

(*i*) *Ester formation* :

$$\underset{\text{Acid}}{RCOOH} + \underset{\text{Ethyl alcohol}}{HOC_2H_5} \longrightarrow \underset{\text{Ester}}{RCOOC_2H_5} + H_2O$$

(*ii*) *Salt formation* :

$$\underset{\text{Acid}}{RCOOH} + \underset{\text{Sod. hydroxide}}{HONa} \longrightarrow \underset{\text{Salt}}{RCOONa} + H_2O$$

However, the similarity between esters and salts is only superficial and the two classes of compounds differ radically in properties. The chief points of difference are listed below :

ESTERS	SALTS
(1) Esters are non-ionised compounds.	(1) They are ionised compounds.
(2) They are neutral in character.	(2) They may be neutral, and also acidic or basic owing to hydrolysis.
(3) They are, in general, volatile, pleasant smelling liquids.	(3) They are generally odourless and non-volatile solids.
(4) Insoluble in water but soluble in organic solvents.	(4) Generally soluble in water but insoluble in organic solvents.
(5) Their reactions being molecular are slow.	(5) Their reactions being ionic are instantaneous.
(6) They are easily hydrolysed back to the parent acid and alcohol.	(6) They are generally speaking stable. The salts of weak acids and alkalis (*e.g.*, NaCN), however, undergo hydrolysis.

NOMENCLATURE

The names of esters are derived from the name of the alkyl group linked to the acid radical followed by the *trivial* name of the acid with the ending *-ic* changed to *-ate*. Thus :

FORMULA	COMMON NAME	IUPAC NAME
$HCOOC_2H_5$	Ethyl formate	Ethyl methanoate
$CH_3COOC_2H_5$	Ethyl acetate	Ethyl ethanoate
$CH_3CH_2COOCH_3$	Methyl propionate	Methyl propanoate

ISOMERISM

(1) Esters exhibit chain isomerism at the alkyl groups.

(2) They show a new type of metamerism when the two alkyl radicals linked to the ester grouping exchange positions. Thus :

$CH_3COOC_2H_5$	Ethyl acetate	*are isomeric*
$C_2H_5COOCH_3$	Methyl propionate	

(3) Esters are also isomeric with fatty acids. Thus

$HCOOCH_3$	Methyl formate	*are isomeric*
CH_3COOH	Acetic acid	

METHODS OF PREPARATION

(1) *Esterification.* Esters are usually prepared by heating a mixture of the acid and alcohol in the presence of concentrated sulphuric acid or hydrogen chloride gas.

$$\underset{\text{Acid}}{RCOOH} + HOR' \rightleftharpoons \underset{\text{Ester}}{RCOOR'} + H_2O$$

The mineral acid accelerates the rate of ester formation by removing the water formed (*Law of Mass Action*) and by furnishing H^+ ions which act as catalyst.

Esterification can also be carried by passing a mixture of vapours of acid and alcohol over an oxide catalyst (*Thoria*, ThO_2) at 300°.

(2) *Alcoholysis of Acid chlorides.* Esters are obtained conveniently and rapidly by the action of acid chlorides with alcohols.

$$\underset{\text{Acid chloride}}{RCO\boxed{Cl +} \!\!\!\!\!\!\!\!\!\!\!\! } \underset{\text{Alcohol}}{\boxed{H}OR'} \longrightarrow \underset{\text{Ester}}{RCOOR'} + HCl$$

(3) *Silver salt method.* Silver salts of acids react with alkyl halides to form esters.

$$\underset{\text{Silver salt}}{RCOO\boxed{Ag + I}} \underset{\text{Alkyl iodide}}{R'} \longrightarrow \underset{\text{Ester}}{RCOOR'} + AgI$$

The method is employed where direct esterification is low or inefficent.

(4) *Condensation of aldehydes.* Esters can be prepared by the condensation of aldehydes in the presence of aluminium ethylate $Al(C_2H_5)_3$. **(Tishchenko reaction).**

$$\begin{matrix} RCO-H \\ + \\ O{=}HCR \\ \text{(2-molecules} \\ \text{of aldehyde)} \end{matrix} \longrightarrow \underset{\text{Ester}}{RCOOCH_2R}$$

(5) *With diazomethane.* Methyl esters are prepared very conveniently by the treatment of an acid with ethereal solution of diazomethane.

$$\underset{\text{Acid}}{RCOOH} + \underset{\text{Diazomethane}}{CH_2N_2} \longrightarrow \underset{\text{Methyl ester}}{RCOOCH_3} + N_2$$

PHYSICAL CHARACTERISTICS

(1) The lower esters of carboxylic acids are neutral colourless liquids having specific pleasant odours. Higher members are odourless crystalline solids.

(2) The boiling points of methyl and ethyl esters are lower than those of corresponding acids.

(3) They are in general lighter than and insoluble in water. All esters are soluble in organic solvents.

(4) Many esters are excellent solvents for other organic substances.

CHEMICAL CHARACTERISTICS

Structurally esters stand midway between ethers and anhydrides.

$$\underset{\text{Ether}}{R{-}O{-}R} \qquad \underset{\text{Ester}}{RCO{-}O{-}R} \qquad \underset{\text{Anhydride}}{RCO{-}O{-}OCR}$$

In ethers the central oxygen atom is joined to two alkyl groups, in anhydrides to two acyl groups, while in esters to one alkyl group and one acyl group. Thus esters are more reactive than esters but less so than anhydrides and show reactions of both classes.

(1) *Hydrolysis.* Esters are slowly decomposed by water to form the parent acid and alcohol.

$$\underset{\text{Ester}}{RCO\vdots OR' + H\vdots OH} \rightleftharpoons \underset{\text{Acid}}{RCOOH} + R'OH$$

The rate of hydrolysis is much accelerated by the presence of acids or alkalis. When hydrolysis is carried with an alkali, it takes place far more rapidly than acid hydrolysis. While the alkali acts as a catalyst, it also fixes the acid produced forming salts and thus retards the backward reaction. Since the alkali salts of the higher acids are soaps, alkaline hydrolysis of esters in general is known as *Saponification.*

(2) *Reduction.* Esters are reduced by sodium and alcohol or by hydrogen in the presence of copper chromite as catalyst to form alcohols.

$$\underset{\text{Acid}}{RCOOR'} + 4H \longrightarrow \underset{\text{Alcohols}}{RCH_2OH} + R'OH$$

(3) *Ammonolysis.* Esters react with ammonia to form amides and alcohols.

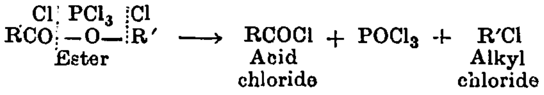
$$\underset{\text{Ester}}{RCOOR} + NH_3 \longrightarrow \underset{\text{Acid amide}}{RCONH_2} + \underset{\text{Alcohol}}{ROH}$$

(4) *Alcoholysis.* By treatment with alcohols a higher alcohol residue can be replaced by a lower alcohol residue.

$$\underset{\text{Ethyl ester}}{RCOOC_2H_5} + \underset{\text{Methyl alcohol}}{CH_3OH} \rightleftharpoons \underset{\text{Methyl ester}}{RCOOCH_3} + \underset{\text{Alcohol}}{C_2H_5OH}$$

This change takes place quickly by heat and in the presence of a catalyst.

(5) *Action of PCl_5.* Esters are decomposed by phosphorus pentachloride to form an acid chloride and an alkyl chloride.



$$\underset{\text{Ester}}{RCO\overset{Cl\ PCl_3\ Cl}{\vdots{-}O{-}\vdots}R'} \longrightarrow \underset{\text{Acid chloride}}{RCOCl} + POCl_3 + \underset{\text{Alkyl chloride}}{R'Cl}$$

USES OE ESTERS

(1) Esters are used for making artificial flavours and essences *e.g.*, methyl butyrate — *pineapple* ; isoamyl acetate — *banana oil* ; isoamyl valerate — *apples* ; octyl acetate — *oranges* etc.

(2) They are very widely used as solvents for making paints, lacquers and as plasticisers.

(3) Amyl acetate is used as an odour bait in grass hoppers poison.

ETHYL ACETATE, ETHYL ETHANOATE, $CH_3COOC_2H_5$

It is the ethyl ester of acetic acid and is a typical member of the class.

Preparation. Ethyl acetate is made on a large scale and also in the laboratory by heating acetic acid and ethyl alcohol in the presence of sulphuric acid.

$$CH_3COOH + HOC_2H_5 \longrightarrow CH_3COOC_2H_5 + H_2O$$

50 ml. of ethyl alcohol are placed in a distilling flask and equal volume of concentrated sulphuric acid is run into it with constant shaking. The distilling flask is fitted with a tap-funnel and connected to a water condenser (*see* Fig. 24·1). A few pieces of unglazed procelain are introduced into the flask which is then heated in an oil bath until the temperature reaches 140°. A mixture of equal volumes of acetic acid and alcohol (100 ml. each) is now gradually added from the tap-funnel at about the same rate as the liquid distils over into the receiver. The distillation is continued for 5 minutes after the addition of the acetic acid and alcohol mixture has been completed. The distillate is placed in a separating funnel and shaken with sodium carbonate solution to remove acids, and then with a saturated solution of calcium chloride to remove alcohol. The lower aqueous layer is rejected in two operations and finally the ethyl acetate layer is transferred to a small flask containing fused calcium chloride. It is allowed to stand with occasional shaking for about 30 minutes. The liquid is then filtered and distilled and the fraction coming over between 74° and 79° is collected.

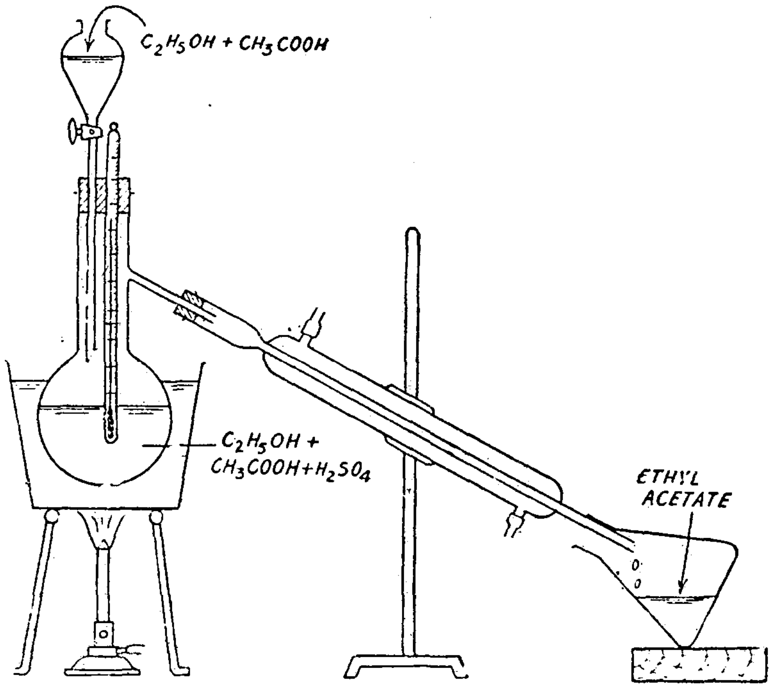


Fig. 24·1. Preparation of ethyl acetate.

Properties. (*Physical*). Ethyl acetate is a colourless liquid, b.p. 71°, having a characteristic odour of bad apples. It is sparingly soluble in water, and is miscible with organic solvents in all proportions.

(*Chemical*). Ethyl acetate gives all general reactions of esters :

(1) On heating with water in the presence of strong acids or alkalis, it is hydrolysed to form acetic acid and ethyl alcohol.

$$\underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + HOH \longrightarrow \underset{\text{Acetic acid}}{CH_3COOH} + \underset{\text{Ethyl alcohol}}{C_2H_5OH}$$

(2) It reacts with ammonia forming acetamide and ethyl alcohol

$$\underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + NH_3 \longrightarrow \underset{\text{Acetamide}}{CH_3CONH_2} + \underset{\text{Ethyl alcohol}}{C_2H_5OH}$$

(3) It is decomposed by phosphorus pentachloride to form acetyl chloride and ethyl chloride.

$$\underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + PCl_5 \longrightarrow \underset{\text{Acetyl chloride}}{CH_3COCl} + C_2H_5Cl + POCl_3$$

(4) On reduction with sodium and boiling alcohol, it is converted to ethyl alcohol.

$$\underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + 4H \longrightarrow \underset{\text{Ethyl alcohol}}{2C_2H_5OH}$$

(5) On warming with sodium metal it undergoes condensation between two molecules giving ethyl acetoacetate.

$$\underset{\text{Ethyl acetate (2 molecules)}}{CH_3CO\boxed{OC_2H_5 + H}CH_2COOC_2H_5} \longrightarrow \underset{\text{Ethyl acetoacetate}}{CH_3COCH_2COOC_2H_5} + C_2H_5OH$$

Uses. Ethyl acetate is used in the preparation of artificial fruit essences and as a solvent in making smokeless powders. It is also employed as a solvent in the ebullioscopic method for determining molecular weights.

What are waxes ?

Waxes are the esters of higher fatty acids and long-chain monohydric alcohols. They are widely distributed in plants and animals where they often serve as protective agents.

Bees-wax, *myricyl palmitate*, $C_{15}H_{31}COOC_{16}H_{33}$. It is the ester of palmitic acid and cetyl alcohol, $C_{30}H_{61}OH$. It is obtained from the honeycomb of the bee.

Supermaceti, *cetyl palmitate*, $C_{15}H_{31}COOC_{30}H_{61}$. It is the ester of palmitic acid and cetyl alcohol. It is a crystalline wax obtained from sperm oil, which comes from the head of the sperm whale.

Carnauba wax, *myricyl cerotate*, $C_{25}H_{51}COOC_{30}H_{61}$. It is the ester of myricyl alcohol and cerotic acid, $C_{25}H_{51}COOH$. It is obtained from the leaves of Brazilian palm.

Waxes are of considerable practical value and are used for making boot polishes, electrical insulators, water-proofings, cosmetics, candles, matches, gramophone records, carbon papers, etc.

ESTERS OF INORGANIC ACIDS

The inorganic acids also form esters by replacement of one or more H atoms by alkyl groups. Thus :

$$\underset{\text{Nitric acid}}{HNO_3} \xrightarrow[+C_2H_5]{-H} \underset{\text{Ethyl nitrate}}{C_2H_5NO_3}$$

A dibasic acid like sulphuric acid gives rise to two series of esters according as one or both the H-atoms in its molecule are replaced by alkyl groups. Thus :

$$\underset{\substack{\text{Ethyl hydrogen sulphate}\\ \textit{(Acid ester)}}}{C_2H_5HSO_4} \qquad \underset{\substack{\text{Diethyl sulphate}\\ \textit{(Normal ester)}}}{(C_2H_5)_2SO_4}$$

Esters of halogen acids are known as alkyl halides but are exceptional in that they do not contain oxygen.

The esters of inorganic acids are named like salts, the name of the alkyl group being substituted for that of the metallic atom. They can be prepared by methods analogous to those used for esters of organic acids. Upon hydrolysis they yield the parent acid and alcohol.

ETHYL HYDROGEN SULPHATE, $C_2H_5HSO_4$

It is the acid ester of sulphuric acid and is also named as *ethyl sulphuric acid.*

Preparation. (1) It is prepared by heating ethyl alcohol with an excess of concentrated sulphuric acid at 100°.

$$\underset{\text{Ethyl alcohol}}{C_2H_5OH} + H|HSO_4 \longrightarrow \underset{\substack{\text{Ethyl hydrogen}\\ \text{sulphate}}}{C_2H_5HSO_4} + H_2O$$

(2) It is also obtained by the action of ethylene with sulphuric acid.

$$\underset{\text{Ethylene}}{CH_2{=}CH_2} + H.HSO_4 \longrightarrow C_2H_5HSO_4$$

Properties. Ethyl hydrogen sulphate is an oily liquid with a strong acid reaction. It is readily soluble in water. It cannot be distilled with decomposition.

Chemically, ethyl hydrogen sulphate behaves both as an acid and as an ester. Thus it decomposes carbonates liberating carbon dioxide, and when hydrolysed by boiling water it yields ethyl alcohol and sulphuric acid.

$$C_2H_5|HSO_4 + H|OH \longrightarrow \underset{\text{Ethyl alcohol}}{C_2H_5OH} + H_2SO_4$$

It also shows the following peculiar reactions :

(1) When heated alone, it gives diethyl sulphate.

$$2C_2H_5HSO_4 \longrightarrow \underset{\text{Diethyl sulphate}}{(C_2H_5)_2SO_4} + H_2SO_4$$

(2) When heated with excess of sulphuric acid at 160°, it yields ethylene.

$$C_2H_5HSO_4 \longrightarrow \underset{\text{Ethylene}}{C_2H_4} + H_2SO_4$$

(3) When heated with ethyl alcohol at 140°, it forms diethyl ether.

$$C_2H_5HSO_4 + HOC_2H_5 \longrightarrow \underset{\text{Diethyl ether}}{C_2H_5OC_2H_5} + H_2SO_4$$

Ethyl hydrogen sulphate is frequently used for the preparation of ethyl derivatives as like alkyl halides it readily enters into double decomposition reactions with many reagents.

DIMETHYL SULPHATE, $(CH_3)_2SO_4$

It is the most important ester of sulphuric acid since it is a valuable methylating agent.

Preparation. (1) Dimethyl sulphate is prepared by heating methyl alcohol with concentrated sulphuric acid and then distilling the product (Methyl hydrogen sulphate) under reduced pressure.

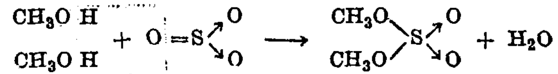
$$\underset{\substack{\text{Methyl}\\\text{alcohol}}}{CH_3OH} + H_2SO_4 \longrightarrow \underset{\substack{\text{Methyl hydrogen}\\\text{sulphate}}}{CH_3HSO_4} + H_2O$$

$$2CH_3HSO_4 \longrightarrow \underset{\text{Dimethyl sulphate}}{(CH_3)_2SO_4} + H_2SO_4$$

(2) It may be prepared by heating methyl iodide with silver sulphate.

$$\underset{\substack{\text{Methyl}\\\text{iodide}}}{2CH_3I} + Ag_2SO_4 \longrightarrow \underset{\substack{\text{Dimethyl}\\\text{sulphate}}}{(CH_3)_2SO_4} + 2AgI$$

(3) It is also produced technically by passing sulphur trioxide into cooled methyl alcohol.



Methyl alcohol Dimethyl sulphate

Properties. Dimethyl sulphate is a heavy, colourless liquid, b.p. 188°, without any odour. It is immiscible with water. It causes inflammation of the skin and is extremely poisonous. Its vapours if inhaled, destroy lungs, cause paralysis and often prove fatal.

Dimethyl sulphate is a typical ester and on boiling with alkalis forms methyl alcohol and sodium sulphate.

$$\underset{\text{Dimethyl sulphate}}{(CH_3)_2SO_4} + 2NaOH \longrightarrow \underset{\text{Methyl alcohol}}{2CH_3OH} + Na_2SO_4$$

It reacts with hydroxy and amino compounds to form the corresponding methyl derivatives. Thus :

$$\underset{\text{Alcohol}}{ROH} + \underset{\text{Dimethyl sulphate}}{CH_3SO_4CH_3} \longrightarrow \underset{\text{Alkyl methyl ether}}{ROCH_3} + CH_3HSO_4$$

$$\underset{\text{Amine}}{RNH_2} + CH_3SO_4CH_3 \longrightarrow \underset{\text{Alkylmethyl amine}}{RNHCH_3} + CH_3HSO_4$$

Hence, it is commonly used for the methylation (introduction of methyl group) of alcohols, phenols and amines.

DIETHYL SULPHATE, $(C_2H_5)_2SO_4$

Diethyl sulphate may be prepared by the same methods as dimethyl sulphate. It is obtained industrially by passing ethylene into cold concentrated sulphuric acid.

$$2C_2H_4 + H_2SO_4 \longrightarrow (C_2H_5)_2SO_4$$

Diethyl sulphate is a heavy colourless liquid, b.p. 208°. It is also poisonous. It is used for introducing ethyl groups into compounds containing hydroxy and amino groups.

ETHYL NITRATE, $C_2H_5.O.NO_2$

It is the most important alkyl nitrate.

Preparation. (1) It is prepared by the action of concentrated nitric acid on ethyl alcohol in the presence of urea.

$$\underset{\text{Ethyl alcohol}}{C_2H_5\boxed{OH + H}O.NO_2} \longrightarrow \underset{\text{Ethyl nitrate}}{C_2H_5O.NO_2} + H_2O$$

(2) It is also obtained by heating ethyl iodide with silver nitrate.

$$\underset{\text{Ethyl iodide}}{C_2H_5\boxed{I + Ag}O.NO_2} \longrightarrow \underset{\text{Ethyl nitrate}}{C_2H_5.O.NO_2} + AgI$$

Properties. Ethyl nitrate is a colourless pleasant smelling liquid, b.p. 88°. It is heavier than water in which it is practically insoluble.

Upon boiling with water, it is hydrolysed to form ethyl alcohol and nitric acid.

$$\underset{\text{Ethyl nitrate}}{C_2H_5.O.NO_2} + HOH \longrightarrow \underset{\text{Ethyl alcohol}}{C_2H_5OH} + \underset{\text{Nitric acid}}{HO.NO_2}$$

When reduced with tin and hydrochloric acid, it forms hydroxylamine and ethyl alcohol.

$$\underset{\text{Ethyl nitrate}}{C_2H_5O.NO_2} + 6H \longrightarrow C_2H_5OH + \underset{\text{Hydroxylamine}}{NH_2OH} + H_2O$$

The above reaction shows clearly that in ethyl nitrate molecule, the ethyl group is linked to nitrogen through an oxygen atom.

ETHYL NITRITE, $C_2H_5O.N:O$

Of the esters of nitrous acid, ethyl nitrite is by far the most important. It is isomeric with nitroethane.

Preparation. Ethyl nitrite is prepared by the distillation of a mixture of ethyl alcohol, sodium nitrite, and concentrated sulphuric acid.

$$\underset{\text{Ethyl alcohol}}{C_2H_5\boxed{OH + H}ONO} \longrightarrow \underset{\text{Ethyl nitrite}}{C_2H_5.O.N:O} + H_2O$$

It is also obtained by the action of nitrogen trioxide (nitrous anhydride) on ethyl alcohol.

$$\underset{\text{Ethyl alcohol}}{2C_2H_5OH} + N_2O_3 \longrightarrow \underset{\text{Ethyl nitrite}}{2C_2H_5O.N{:}O} + H_2O$$

Properties. Ethyl nitrite is usually gaseous at ordinary temperature. Upon cooling it becomes a colourless liquid, b.p. 17°, having a characteristic smell of apples. It is soluble in water.

Ethyl nitrite is easily hydrolysed in the presence of alkali giving ethyl alcohol and nitrous acid.

$$\underset{\text{Ethyl nitrite}}{C_2H_5O.N{:}O + H{\cdot}OH} \longrightarrow \underset{\text{Ethyl alcohol}}{C_2H_5OH} + \underset{\text{Nitrous acid}}{HO.N{:}O}$$

When reduced with tin and hydrochloric acid, ethyl nitrite is decomposed forming ethyl alcohol and hydroxylamine.

$$\underset{\text{Ethyl nitrite}}{C_2H_5O{-}N{=}O} + 6H \longrightarrow \underset{\text{Ethyl alcohol}}{C_2H_5OH} + NH_3 + H_2O$$

The above reaction furnishes evidence that in ethyl nitrite molecule, the ethyl group is not directly linked to the nitrogen but through an oxygen atom.

Uses. (1) Ethyl nitrite accelerates the pulse and lowers the blood pressure and is, therefore, used as medicine for the treatment of asthma and heart diseases. (2) It breaks down easily to yield nitrous acid and hence its use as a source of nitrous acid in organic synthesis.

AMYL NITRITE, $C_5H_{11}.O.NO$

It is prepared by heating a mixture of amyl alcohol, sodium nitrite and concentrated sulphuric acid. It is a yellow volatile liquid having a pleasant odour. Like ethyl nitrite it is used as a source of nitrous acid in organic synthesis and for the treatment of asthma and heart troubles.

NITROALKANES

They are the derivatives of alkanes in which one hydrogen atom is replaced by a nitro group, NO_2. Thus :

$$\underset{\text{Methane}}{CH_4} \xrightarrow[+NO_2]{-H} \underset{\text{Nitromethane}}{CH_3NO_2}$$

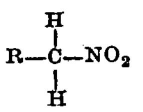
As a class these compounds are also called *aliphatic nitro-compounds* in distinction to analogous aromatic compounds.

NOMENCLATURE

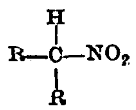
The nitroalkanes are named by prefixing 'nitro' to the name of the parent hydrocarbon :

$C_2H_5NO_2$	Nitroethane
$C_3H_7NO_2$	Nitropropane

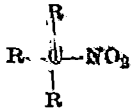
They are further distinguished as primary, secondary and tertiary nitro-compounds according as the nitro group is linked to a primary, secondary or a tertiary carbon atom.



Primary



Secondary



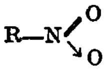
Tertiary

According to the IUPAC system, position of the nitro group is indicated by a number.

$CH_3.CH_2.CH_2NO_2$	1-Nitropropane
$CH_3.CH(NO_2)CH_3$	2-Nitropropane

ISOMERISM

Besides chain and position isomerism, nitroalkanes show functional isomerism with alkyl nitrites



Nitro-compound

$R—O—N{=}O$

Nitrite

Thus nitromethane, $CH_3.NO_2$, is isomeric with methyl nitrite $CH_3.O.NO$.

METHODS OF PREPARATION

(1) By the direct action of fuming nitric acid on higher alkanes.

$$\underset{\text{n-Hexane}}{C_6H_{14}} + HO.NO_2 \longrightarrow \underset{\text{Nitrohexane}}{C_6H_{13}.NO_2} + H_2O$$

Until fairly recently this method was more or less of academic interest only. Now it has become possible to carry the nitration of even the lowest alkanes in the vapour phase at high temperature. Since the lower hydrocarbons are available in large amounts from petroleum distillation, this method is being used in the U.S.A. for the technical production of nitromethane, nitroethane and nitropropanes.

(2) By the action of silver nitrite on alkyl iodides.

$$\underset{\text{Ethyl iodide}}{C_2H_5I} + AgNO_2 \longrightarrow \underset{\text{Nitroethane}}{C_2H_5NO_2} + AgI$$

In this method some isomeric alkyl nitrite is also obtained but it can be removed easily by fractional distillation.

(3) By heating an aqueous solution of sodium nitrite with an α-halogenated carboxylic acid.

$$\underset{\text{Chloroacetic acid}}{CH_2Cl.COOH} + NaNO_2 \longrightarrow \underset{\text{Nitroacetic acid}}{CH_2NO_2COOH} + NaCl$$

$$CH_2NO_2COOH \longrightarrow \underset{\text{Nitromethane}}{CH_3NO_2} + CO_2$$

GENERAL CHARACTERISTICS

(Physical). Nitroalkanes are colourless pleasant-smelling liquids. Their boiling points are much higher than the isomeric nitrites.

$CH_3.NO_2$	b.p. 101°	$C_2H_5.NO_2$	b.p. 113°
$CH_3.O.NO$	b.p. —12°	$C_2H_5.O.NO$	b.p. 17°

They are sparingly soluble in water giving neutral solutions.

(*Chemical*). As a rule the NO_2 group activates the H atoms which are attached to the same carbon atom and hence nitroalkanes show many interesting reactions.

(1) REDUCTION. When reduced with tin and hydrochloric acid, they form primary amines.

$$\underset{\text{Nitroethane}}{C_2H_5NO_2} + 6H \longrightarrow \underset{\text{Ethylamine}}{C_2H_5.NH_2} + 2H_2O$$

However, on reduction in a neutral medium (zinc dust and NH_4Cl solution), they yield the hydroxylamine.

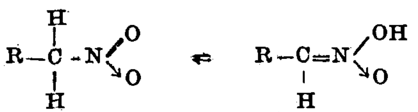
$$\underset{\text{Nitroethane}}{C_2H_5NO_2} + 4H \longrightarrow \underset{\text{Ethylhydroxylamine}}{C_2H_5.NHOH} + H_2O$$

(2) HYDROLYSIS. When boiled with hydrochloric acid, alkanes are hydrolysed to form a carboxylic acid and hydroxylamine.

$$\underset{\text{Nitroethane}}{CH_3CH_2NO_2} + H_2O \longrightarrow \underset{\text{Acetic acid}}{CH_3COOH} + \underset{\text{Hydroxylamine}}{NH_2OH}$$

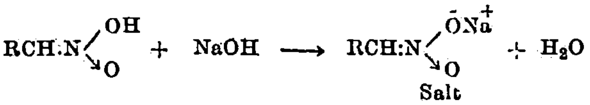
(3) ACTION WITH ALKALIS. Primary and secondary nitro-compounds form salts and are, therefore, acidic in character. This is due to tautomerism.

I II



Pseudo acid Aci-form

The form I is called the *pseudo-acid* while form II is known as the *aci-form*. The aci-form dissolves in alkalis to form salts.



Salt

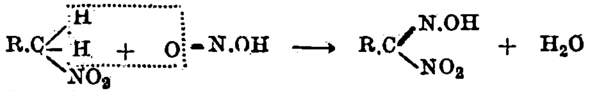
The tertiary nitro-compounds having no hydrogen atom linked to α-carbon are incapable of forming salts.

(4) ACTION WITH HALOGENS. Primary and secondary nitro-compounds are readily halogenated in the presence of alkali only in the α-position. Thus :

$$\underset{\text{Nitromethane}}{CH_3.NO_2} + 3Cl_2 \longrightarrow \underset{\text{Chloropicrin}}{CCl_3.NO_2} + 3HCl$$

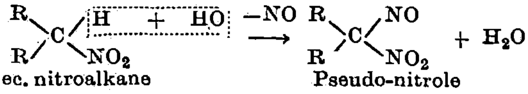
Chloropicrin is now manufactured by this method.

(5) ACTION WITH NITROUS ACID. (*i*) Primary nitro-compounds react with nitrous acid to form nitrolic acids which dissolve in sodium hydroxide solution producing red solutions.



Nitroalkane Nitrolic acid

(*ii*) Secondary nitro-compounds react with nitrous acid to form *pseudo-nitroles* which dissolves in sodium hydroxide to give blue solutions.



(*iii*) Tertiary nitro-compounds fail to react with nitrous acid since they have no α-hydrogen atom.

The above reactions of nitroalkanes with nitrous acid form the basis of Victor Meyer's test for the distinction between primary, secondary and tertiary alcohols.

(6) CONDENSATION WITH ALDEHYDES. Owing to the presence of the active α-hydrogen, nitroalkanes undergo condensation with aldehydes. Thus :

$$\underset{\text{Aldehyde}}{R.CHO} + \underset{\text{Nitromethane}}{CH_3.NO_2} \longrightarrow \underset{\text{Hydroxy-nitroalkane}}{R.CH(OH)CH_2.NO_2}$$

This condensation is similar to aldol condensation.

USES OF NITROALKANES

(1) Since they are less inflammable and less toxic, nitro-alkanes are now finding wide application as industrial solvents *e.g*, for oils, fats, shellac, rubber and cellulose derivatives.

(2) Their reaction with nitrous acid forms the basis of the Victor Meyer's test for the distinction of primary, secondary and tertiary alcohols.

How to distinguish between Nitroalkanes and Alkyl Nitrites. The nitroalkanes may be distinguished from the alkyl nitrites by the following reactions :

(1) On reduction nitroalkanes are converted into primary amines, while alkyl nitrites yield an alcohol and ammonia.

$$\underset{\text{Nitromethane}}{CH_3.NO_2} + 6H \longrightarrow \underset{\text{Methyl amine}}{CH_3.NH_2} + 2H_2O$$

$$\underset{\text{Methyl nitrite}}{CH_3.O.NO} + 6H \longrightarrow \underset{\text{Methyl alcohol}}{CH_3.OH} + NH_3 + H_2O$$

(2) Nitroalkanes are not decomposed by the action of alkalis, while alkyl nitrites like other esters are hydrolysed to form an alcohol and an alkali nitrite.

$$\underset{\text{Nitromethane}}{CH_3NO_2} \longrightarrow \text{No action, simply dissolves}$$

$$\underset{\text{Methyl nitrite}}{CH_3.O.NO} + NaOH \longrightarrow \underset{\text{Methyl alcohol}}{CH_3OH} + NaNO_2$$

QUESTIONS

1. What are esters ? How do they differ from salts ?

2. What is an ester ? Mention the general principles to be observed in the preparation of these compounds, and the nature and properties of esters as a class.

3. Describe two methods for preparing esters. How do esters react with (*a*) water, (*b*) aqueous caustic soda, (*c*) concentrated ammonia ?

4. Describe the preparation of ethyl acetate in the laboratory. Discuss the conditions for the optimum yield of the product.

5. Give the preparation, properties and uses of Methyl sulphate, Ethyl nitrite, and Ethyl nitrate.

6. What are aliphatic nitro-compounds ? How will you distinguish between ethyl nitrate and nitroethane ?

7. Give an account of the methods of preparation, properties and reactions of aliphatic nitro-compounds ? How would you distinguish between a primary, a secondary and a tertiary nitro-compound.

8. Discuss the isomerism of nitro-compounds with alkyl nitrites. Give reactions which point to the difference in the structure of two types of derivatives.

9. What are the important properties of ethyl acetate ? Write a note on its constitution. (*Madras B.Sc., 1955*)

10. Describe the preparation and uses of dimethyl sulphate. (*Madras B.Sc., 1955*)

11. Describe the preparation and chief properties of nitro-paraffins. What other alkyl derivatives of nitrous acid are known and in what respects do they differ from nitro paraffins ? (*Andhra B.Sc., 1955*)

12. Describe how you would distinguish between :

(*a*) Nitroethane and ethyl nitrite.

(*b*) Ethyl cyanide and ethyl isocyanide.

(*c*) Ethyl alcohol and dimethyl ether

How do you account for the differences in their behaviour ? (*Bihar B.Sc., 1955*)

13. Describe the modern method of preparing nitro-paraffins. With the help of suitable examples explain their important chemical properties. (*Venkateswara B.Sc. II, 1964*)

25

Acetoacetic Ester and Malonic Ester

JOHANNES A. WISLICENUS
(1835—1902)

German Research Chemist, best known for the acetoacetic ester and malonic ester synthesis, and for the synthetic production of lactic acid

ACETOACETIC ESTER, $CH_3CO.CH_2.COOC_2H_5$

It is the ethyl ester of acetoacetic acid, $CH_3CO.CH_2COOH$. Hence it is named as *ethyl acetoacetate*. It is popularly known as simply *acetoacetic ester* since it could be regarded as the acetyl derivative of acetic ester *i.e.*, ethyl acetate. On account of its great reactivity, acetoacetic ester is one of the most valuable reagents in synthetic chemistry. Also, it is the classical and the most thoroughly investigated example of keto-enol tautomerism.

Preparation. Acetoacetic ester is prepared by refluxing anhydrous ethyl acetate containing a little alcohol with sodium. The sodium reacts with alcohol to form sodium ethoxide, C_2H_5ONa, which causes the condensation of two molecules of ethyl acetate yielding acetoacetic ester.

$$\underset{\text{Ethyl acetate (2 molecules)}}{CH_3CO\boxed{OC_2H_5 + H}CH_2COOC_2H_5} \longrightarrow \underset{\text{Acetoacetic ester}}{CH_3CO.CH_2COOC_2H_5} + C_2H_5OH$$

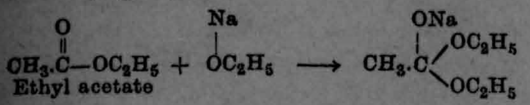
After refluxing, the solution is acidified and the insoluble oily layer of acetoacetic ester is separated and dried.

The above condensation between two molecules of ethyl acetate (**Claisen condensation**) is a rather complex reaction and according to Claisen takes place as follows :

(1) Sodium reacts with ethyl alcohol forming sodium ethoxide.

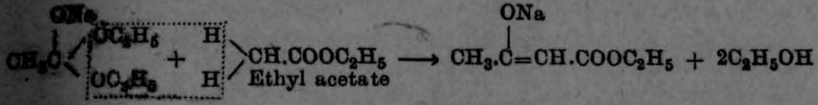
$$C_2H_5OH + Na \longrightarrow \underset{\text{Sod. ethoxide}}{C_2H_5ONa} + H$$

(2) The sodium ethoxide adds to a molecule of ethyl acetate at the carbonyl group.



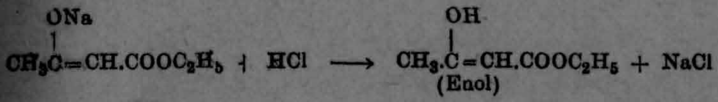
$$\underset{\text{Ethyl acetate}}{CH_3.\overset{\overset{O}{\|}}{C}-OC_2H_5} + \overset{\overset{Na}{|}}{O}C_2H_5 \longrightarrow CH_3.\overset{\overset{ONa}{|}}{C}\begin{smallmatrix}OC_2H_5\\ OC_2H_5\end{smallmatrix}$$

(3) The addition product obtained in step (2) reacts with a second molecule of ethyl acetate.

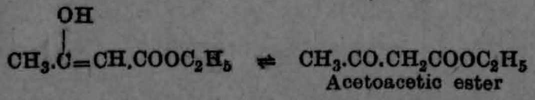


$$CH_3.\overset{\overset{ONa}{|}}{C}\begin{smallmatrix}OC_2H_5\\ OC_2H_5\end{smallmatrix} + \underset{\text{Ethyl acetate}}{\begin{smallmatrix}H\\ H\end{smallmatrix}CH.COOC_2H_5} \longrightarrow CH_3.\overset{\overset{ONa}{|}}{C}=CH.COOC_2H_5 + 2C_2H_5OH$$

(4) On acidification, the product of step (3) yields the enol form of acetoacetic ester which at once tautomerises to yield acetoacetic ester.



$$CH_3\overset{\overset{ONa}{|}}{C}=CH.COOC_2H_5 + HCl \longrightarrow \underset{\text{(Enol)}}{CH_3.\overset{\overset{OH}{|}}{C}=CH.COOC_2H_5} + NaCl$$



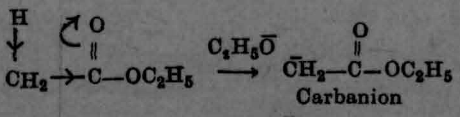
$$CH_3.\overset{\overset{OH}{|}}{C}=CH.COOC_2H_5 \rightleftharpoons \underset{\text{Acetoacetic ester}}{CH_3.CO.CH_2COOC_2H_5}$$

It is clear from the above mechanism that only a small quantity of alcohol is needed since it is liberated in step (2) and hence can function repeatedly.

Mechanism

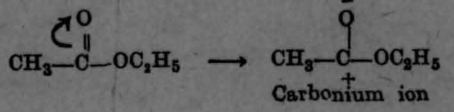
(*i*) $C_2H_5ONa \longrightarrow \underset{\text{Ethoxide ion}}{C_2H_5\bar{O}} + \overset{+}{Na}$

(*ii*)



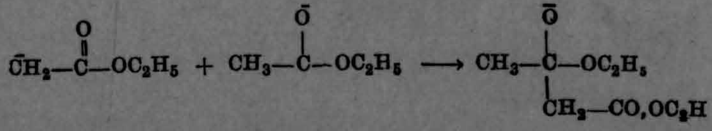
$$\overset{H}{\downarrow}CH_2 \to \overset{\overset{O}{\|}}{C}-OC_2H_5 \xrightarrow{C_2H_5\bar{O}} \underset{\text{Carbanion}}{\bar{C}H_2-\overset{\overset{O}{\|}}{C}-OC_2H_5}$$

(*iii*)

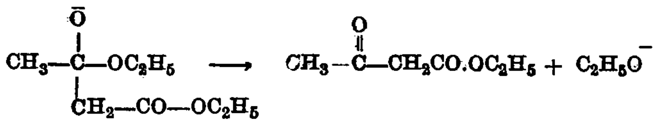


$$CH_3-\overset{\overset{O}{\|}}{C}-OC_2H_5 \longrightarrow \underset{\text{Carbonium ion}}{CH_3-\overset{\overset{\bar{O}}{|}}{\underset{+}{C}}-OC_2H_5}$$

(*iv*)



$$\bar{C}H_2-\overset{\overset{O}{\|}}{C}-OC_2H_5 + CH_3-\overset{\overset{\bar{O}}{|}}{C}-OC_2H_5 \longrightarrow CH_3-\overset{\overset{\bar{O}}{|}}{\underset{\underset{CH_2-CO,OC_2H}{|}}{C}}-OC_2H_5$$

(v) 

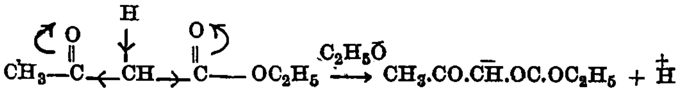
$$CH_3-\overset{\bar{O}}{\underset{CH_2-CO-OC_2H_5}{\overset{|}{\underset{|}{C}}}}-OC_2H_5 \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-CH_2CO.OC_2H_5 + C_2H_5\bar{O}$$

(vi) $C_2H_5\bar{O} + \overset{+}{H} \longrightarrow C_2H_5OH$

Properties. (*Physical*). Acetoacetic ester is a colourless, pleasant smelling liquid, b.p. 181°. It is sparingly soluble in water but dissolves readily in alcohol and ether. It is neutral to litmus.

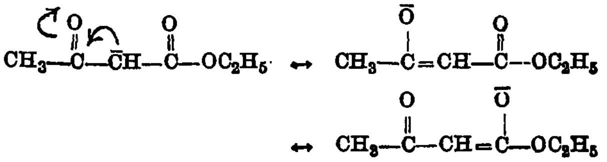
(*Chemical*). Acetoacetic ester contains a keto group and an ester group and gives reactions of both.

Acetoacetic ester molecule contains a very reactive methylene group ($-CH_2-$). The two hydrogen atoms of the methylene group can be readily replaced by sodium. The unexpected reactivity of these hydrogens may be attributed to the fact that central methylene group is flanked by two highly activating carbonyl groups which make the C—H linkage very weak thus facilitating the proton release in presence of a polar reagent.



$$CH_3-\overset{O}{\overset{\|}{C}}-\overset{H}{CH}-\overset{O}{\overset{\|}{C}}-OC_2H_5 \xrightarrow{C_2H_5\bar{O}} CH_3.CO.\bar{C}H.OC.OC_2H_5 + \overset{+}{H}$$

The anion produced above, is considerably stabilized by resonance



$$CH_3-\overset{O}{\overset{\|}{C}}-\bar{C}H-\overset{O}{\overset{\|}{C}}-OC_2H_5 \longleftrightarrow CH_3-\overset{\bar{O}}{\overset{|}{C}}=CH-\overset{O}{\overset{\|}{C}}-OC_2H_5 \longleftrightarrow CH_3-\overset{O}{\overset{\|}{C}}-CH=\overset{\bar{O}}{\overset{|}{C}}-OC_2H_5$$

The anion produced above, at once forms a sodio-derivative with Na^+.

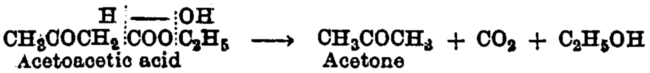
Its important reactions are :

(1) REDUCTION. When reduced with sodium amalgam, it forms β-hydroxybutyric ester.

$$CH_3CO.CH_2COOC_2H_5 + 2H \longrightarrow CH_3.CHOH.CH_2COOC_2H_5$$

Acetoacetic ester β-Hydroxybutyric ester

(2) KETONIC HYDROLYSIS. When boiled with dilute acids (sulphuric acid), the ester group is hydrolysed and at the same time split out from the molecule resulting in the formation of acetone.



$$\overset{H\,\vdots\text{———}\vdots OH}{CH_3COCH_2\vdots COO\vdots C_2H_5} \longrightarrow CH_3COCH_3 + CO_2 + C_2H_5OH$$

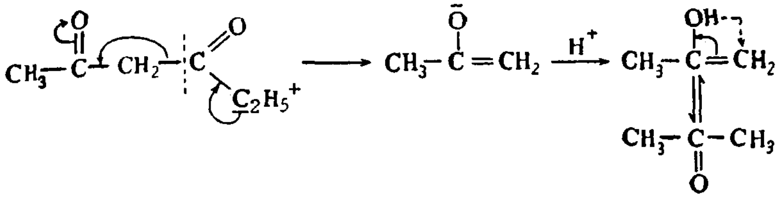
Acetoacetic acid Acetone

The reaction is so called because a ketone is the chief product.

The ketone formed is always found to contain the CH_3CO— group. Phosphoric acid is a very good catalyst for ketonic hydrolysis and the yield of ketone is raised up to 95 per cent.

Mechanism :

The mechanism of this reaction is still uncertain but in all probability the carbonyl group $>C=O$, facilitates the removal of CO_2 as

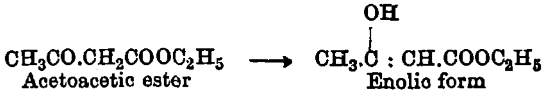


(3) ACID HYDROLYSIS. When treated with concentrated alkali (alcoholic potash), it is hydrolysed at the ester group and at the same time the acetyl group at the other end is detached from the molecule resulting in the formation of two molecules of acetic acid.

$$\underset{\text{Acetoacetic ester}}{CH_3.\overset{HO\,H}{CO{:}CH_2}\overset{H{:}OH}{COO{:}C_2H_5}} \longrightarrow \underset{\text{Acetic acid}}{CH_3COOH + CH_3COOH} + \underset{\text{Ethyl alcohol}}{C_2H_5OH}$$

This reaction is so called because an acid is the chief product.

(4) *FORMATION OF SODIO DERIVATIVE. When treated with* sodium ethoxide, it forms sodioacetoacetic ester.



$$\underset{\text{Acetoacetic ester}}{CH_3CO.CH_2COOC_2H_5} \longrightarrow \underset{\text{Enolic form}}{CH_3.\overset{OH}{\overset{|}{C}} : CH.COOC_2H_5}$$

$$CH_3.C(OH).CH.COOC_2H_5 + C_2H_5ONa$$

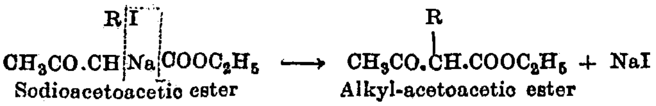
$$\longrightarrow \underset{\text{Sodioacetoacetic ester}}{CH_3.C(ONa){:}\,CHCOOC_2H_5} + C_2H_5OH$$

Sodioacetoacetic ester is further utilised to synthesise a variety of ketones and acids. It is best expressed by the enolic formula but for the sake of simplicity we will henceforth write it as

$$CH_3CO.CHNa.COOC_2H_5$$

Synthetic Applications. Being a very reactive substance acetoacetic ester enters into reaction with many reagents to form a variety of organic compounds. The term **acetoacetic ester synthesis** is applied to such reactions.

(1) ALKYLACETOACETIC ESTERS. The sodioacetoacetic ester when reacted with alkyl halides yields an alkylacetoacetic ester. Thus :

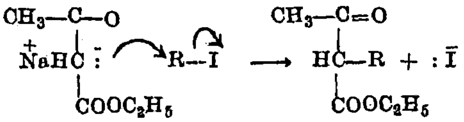


$$\underset{\text{Sodioacetoacetic ester}}{CH_3CO.CH\overset{R|I}{|Na|}COOC_2H_5} \longrightarrow \underset{\text{Alkyl-acetoacetic ester}}{CH_3CO.\overset{R}{C}H.COOC_2H_5} + NaI$$

The monosubstituted derivative obtained above still contains a replaceable H atom which can be substituted by Na by treatment with sodium ethoxide. The sodioderivative thus obtained upon reaction with a suitable alkyl halide (R'I) would give a dialkyl. acetoacetic ester $CH_3CO.CRR'.COOC_2H_5$.

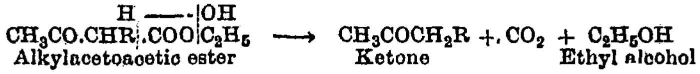
Mechanism :

The sodioderivative forms a carbanion where Rl attacks by $S_N{}^2$ mechanism.



$$\overset{+}{Na}H\overset{CH_3-C-O}{\underset{COOC_2H_5}{\bar{C}:}} \; R-I \longrightarrow H\overset{CH_3-C=O}{\underset{COOC_2H_5}{C}}-R + :\bar{I}$$

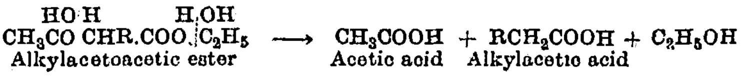
(2) KETONES. Like acetoacetic ester, its alkyl derivatives obtained in reaction (1.) when boiled with dilute sulphuric acid undergo ketonic hydrolysis yielding ketones. Thus :



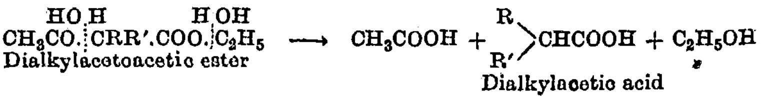
$$\underset{\text{Alkylacetoacetic ester}}{CH_3CO.CH\overset{H}{R}.COO\overset{OH}{C_2H_5}} \longrightarrow \underset{\text{Ketone}}{CH_3COCH_2R} + CO_2 + \underset{\text{Ethyl alcohol}}{C_2H_5OH}$$

$$\underset{\text{Dialkylacetoacetic ester}}{CH_3CO.CRR'\overset{H\;\;\;OH}{COO}C_2H_5} \longrightarrow \underset{\text{Ketone}}{CH_3COHC\begin{matrix}R\\R'\end{matrix}} + CO_2 + \underset{\text{Ethyl alcohol}}{C_2H_5OH}$$

(3) FATTY ACIDS. Like acetoacetic ester, its alkyl derivatives when treated with a concentrated alkali, undergo acid hydrolysis and yield fatty acids.

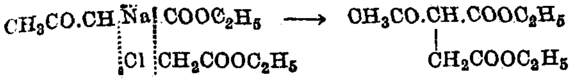


$$\underset{\text{Alkylacetoacetic ester}}{\overset{HO\,H}{CH_3CO}\,CHR.\overset{H\,OH}{COO.C_2H_5}} \longrightarrow \underset{\text{Acetic acid}}{CH_3COOH} + \underset{\text{Alkylacetic acid}}{RCH_2COOH} + C_2H_5OH$$

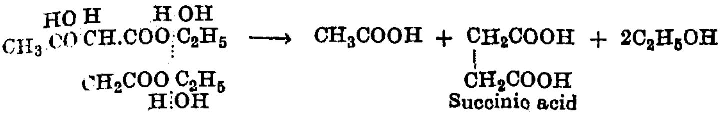


$$\underset{\text{Dialkylacetoacetic ester}}{\overset{HO.H}{CH_3CO.}CRR'.\overset{H\,OH}{COO.C_2H_5}} \longrightarrow CH_3COOH + \underset{\text{Dialkylacetic acid}}{\begin{matrix}R\\R'\end{matrix}\!>CHCOOH} + C_2H_5OH$$

(4) DICARBOXYLIC ACIDS. They may be prepared by the interaction of sodioacetoacetic ester and a halogen-substituted ester, followed by acid hydrolysis. Thus, reaction with ethyl chloroacetate would yield succinic acid.

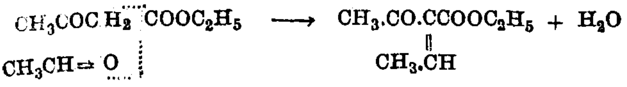


$$\mathrm{CH_3CO.CH\,Na\,COOC_2H_5 + Cl\,CH_2COOC_2H_5 \longrightarrow CH_3CO.\underset{\displaystyle CH_2COOC_2H_5}{CH}.COOC_2H_5}$$

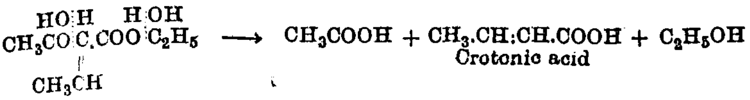


$$\mathrm{\overset{HO\,H}{CH_3.CO}\,CH.\overset{H\,OH}{COO}\,C_2H_5 \atop \quad CH_2COO\,\underset{H\,OH}{C_2H_5}} \longrightarrow \mathrm{CH_3COOH + \underset{\displaystyle \underset{\text{Succinic acid}}{CH_2COOH}}{CH_2COOH} + 2C_2H_5OH}$$

(5) UNSATURATED ACIDS. Acetoacetic ester undergoes condensation with aldehydes and ketones to form products which upon acid hydrolysis yield unsaturated acids. Thus :



$$\mathrm{CH_3COCH_2COOC_2H_5 + CH_3CH{=}O \longrightarrow CH_3.CO.\underset{\displaystyle \underset{\displaystyle CH_3.CH}{\|}}{C}COOC_2H_5 + H_2O}$$



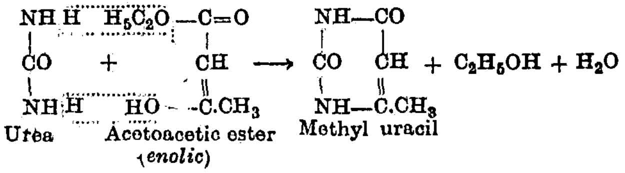
$$\mathrm{\overset{HO\,H}{CH_3CO}\,\underset{\displaystyle \underset{\displaystyle CH_3CH}{\|}}{C}.\overset{H\,OH}{COO}\,C_2H_5 \longrightarrow CH_3COOH + \underset{\text{Crotonic acid}}{CH_3.CH{:}CH.COOH} + C_2H_5OH}$$

(6) HIGHER ALKANES. Acetoacetic ester and its alkyl derivatives on electrolytic reduction yield higher alkanes. Thus :

$$\underset{\text{Acetoacetic ester}}{\mathrm{CH_3.CO.CH_2.COOC_2H_5}} + 10\mathrm{H} \longrightarrow \underset{\text{n-Butane}}{\mathrm{CH_3.CH_2.CH_2.CH_3}} + 2\mathrm{H_2O} + \mathrm{C_2H_5OH}$$

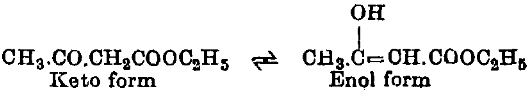
$$\underset{\text{Alkylacetoacetic ester}}{\mathrm{CH_3.CO.CHR.COOC_2H_5}} + 10\mathrm{H} \longrightarrow \underset{\text{2-Alkylbutane}}{\mathrm{CH_3CH_2.CHR,CH_3}} + 2\mathrm{H_2O} + \mathrm{C_2H_5OH}$$

(7) RING COMPOUNDS. Acetoacetic ester has a continuous chain of four carbon atoms with two functional groups and hence enters into reaction with many reagents to form stable ring compounds. For example, with urea it forms *methyl uracil* which is an intermediate in the synthesis of uric acid



$$\underset{\text{Urea}}{\mathrm{CO(NH_2)_2}} + \underset{\text{Acetoacetic ester (enolic)}}{\mathrm{H_5C_2O{-}C{=}O,\;CH,\;HO{-}C.CH_3}} \longrightarrow \underset{\text{Methyl uracil}}{\mathrm{NH{-}CO,\;CO,\;CH,\;NH{-}C.CH_3}} + \mathrm{C_2H_5OH + H_2O}$$

STRUCTURE OF ACETOACETIC ESTER. The chemical properties of acetoacetic ester for long presented a difficulty since they could not be explained in terms of one structural formula. After thorough investigation it was suggested that ordinary acetoacetic ester was an equilibrium mixture of two forms :



$$\underset{\text{Keto form}}{\mathrm{CH_3.CO.CH_2COOC_2H_5}} \rightleftharpoons \underset{\text{Enol form}}{\mathrm{CH_3.\overset{\displaystyle OH}{\overset{|}{C}}{=}CH.COOC_2H_5}}$$

and each of these forms could at once be converted to the other. This particular type of tautomerism between a keto form and enol form was termed as **keto enol tautomerism.** A chemical reagent that reacts with one form will upset the equilibrium in the direction of that form, so that the substance appeared to react as 100 per cent keto form or 100 per cent enol form.

The existence of the above equilibrium in acetoacetic ester is supported by its reactions.

REACTIONS SUPPORTING THE KETO FORM. (1) Acetoacetic ester forms addition compounds with hydrocyanic acid and forms oxime with hydroxylamine.

(2) On reduction the ketonic CO is converted to CHOH and it gives β-hydroxybutyric acid.

(3) On ketonic hydrolysis it yields acetone which proves the presence of a ketonic CO in the original molecule.

REACTIONS SUPPORTING THE ENOL FORM. (1) Acetoacetic ester when treated with acetyl chloride forms an acetyl derivative which proves the presence of an OH group in the molecule.

(2) It gives deep red coloration with ferric chloride and hence contains the structure C=C—OH which is characteristic of phenols.

(3) It adds a molecule of bromine to form a dibromide which shows the presence of an alkene linkage in the molecule.

SEPARATION OF THE KETO AND ENOL FORMS. Guided by the above considerations regarding the structure of acetoacetic ester, Knorr (1911) succeeded in separating the keto and enol forms. The pure keto form of the ester was obtained by cooling ordinary acetoacetic ester to —78° and then extracting with organic solvents. The enol form was prepared by treating sodioacetoacetic ester with dry hydrogen chloride gas at —78°. Knorr found that the two forms so obtained had characteristic properties.

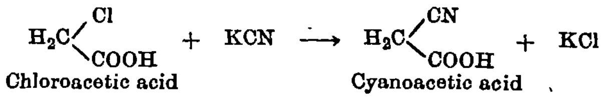
KETO FORM	ENOL FORM
(*i*) Long colourless needles, m.p. —39°.	(*i*) Colourless oil, liquid boils at —78°.
(*ii*) Refractive index, 1·4225	(*ii*) Refractive index, 1·4430.
(*iii*) Gives no coloration with ferric chloride and does not react with bromine.	(*iii*) Gives deep red coloration with ferric chloride and combines with bromine.

The separation of the keto and enol forms of acetoacetic ester proved beyond doubt that it was an equilibrium mixture of these forms. From a measurement of the refractive index of the two forms and that of ordinary acetoacetic ester, Knorr was able to show that the latter consisted of 92 per cent of the keto form and 8 per cent of the enol form.

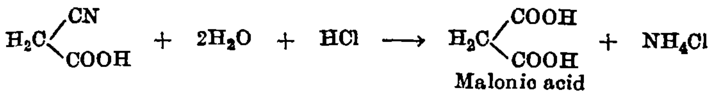
MALONIC ESTER, $CH_2(COOC_2H_5)_2$

It is the diethyl ester of malonic acid, $CH_2(COOC_2H_5)_2$. Its full name is *diethyl malonate* although it is commonly referred to as *malonic ester*. It is a most valuable reagent for the synthesis of a variety of organic acids.

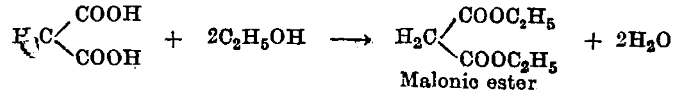
Preparation. Malonic ester is prepared from chloroacetic acid by first converting it to cyanoacetic acid and then passing hydrogen chloride gas into a solution of cyanoacetic acid and ethyl alcohol.



$$\underset{\text{Chloroacetic acid}}{H_2C\begin{smallmatrix}\diagup Cl\\ \diagdown COOH\end{smallmatrix}} + KCN \longrightarrow \underset{\text{Cyanoacetic acid}}{H_2C\begin{smallmatrix}\diagup CN\\ \diagdown COOH\end{smallmatrix}} + KCl$$



$$H_2C\begin{smallmatrix}\diagup CN\\ \diagdown COOH\end{smallmatrix} + 2H_2O + HCl \longrightarrow \underset{\text{Malonic acid}}{H_2C\begin{smallmatrix}\diagup COOH\\ \diagdown COOH\end{smallmatrix}} + NH_4Cl$$

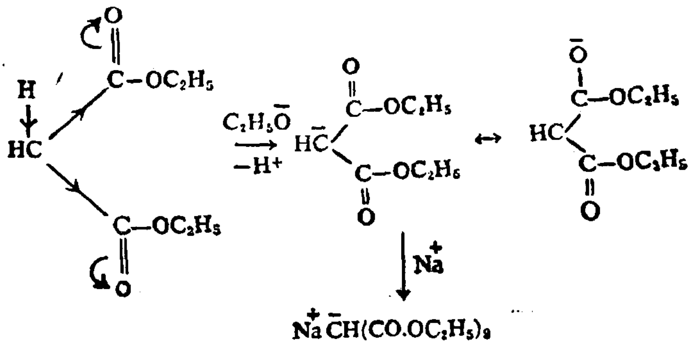


$$H_2C\begin{smallmatrix}\diagup COOH\\ \diagdown COOH\end{smallmatrix} + 2C_2H_5OH \longrightarrow \underset{\text{Malonic ester}}{H_2C\begin{smallmatrix}\diagup COOC_2H_5\\ \diagdown COOC_2H_5\end{smallmatrix}} + 2H_2O$$

Properties. (*Physical*). Malonic ester is a colourless liquid with a pleasant fruity odour. It boils at 199° and is sparingly soluble in water.

(*Chemical*). In malonic ester molecule we have a methylene group joined to an ester group on either side.

As in acetoacetic ester the H atoms of methylene group ($—CH_2—$) here also have been sandwiched between two electron-attracting carbonyl groups. It, therefore, becomes extremely reactive and readily forms sodio-derivatives with sodium ethoxide ($C_2H_5\overset{-}{O}\overset{+}{Na}$).

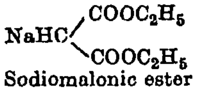


Sodio-malonic ester

According to an older view, the formation of sodiomalonic ester proceeds through the formation of an enol just as in acetoacetic ester, but for convenience we would use the above simple formula in our discussion.

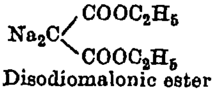
Malonic ester Synthesis. Like acetoacetic ester, malonic ester is an excellent synthetic reagent. All syntheses carried by means of malonic ester are termed *malonic ester synthesis.* This is chiefly based on two reactions.

(*a*) One or both the H atoms of the methylene group can be replaced by sodium by the action of sodium ethoxide forming :



$$NaHC\begin{matrix} COOC_2H_5 \\ COOC_2H_5 \end{matrix}$$

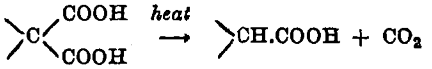
Sodiomalonic ester



$$Na_2C\begin{matrix} COOC_2H_5 \\ COOC_2H_5 \end{matrix}$$

Disodiomalonic ester

(*b*) The derivatives of malonic ester in which the two COOH groups are linked to the same carbon split out a molecule of carbon dioxide when heated just above its melting point which results in the removal of one carbonyl group.



$$>C\begin{matrix} COOH \\ COOH \end{matrix} \xrightarrow{heat} >CH.COOH + CO_2$$

The following classes of compounds can be synthesised with the help of malonic ester.

(1) Fatty acids. Sodiomalonic ester reacts with alkyl halides to form alkylmalonic esters which upon hydrolysis and heating yield fatty acids. Thus n-butyric acid can be obtained as follows :

$$C_2H_5I + NaHC(COOC_2H_5)_2 \longrightarrow C_2H_5CH(COOC_2H_5)_2 + NaI$$

$$\xrightarrow{Hydrol.} C_2H_5CH(COOH)_2 \xrightarrow{Heat} \underset{\text{n-Butyric acid}}{C_2H_5CH_2COOH} + CO_2$$

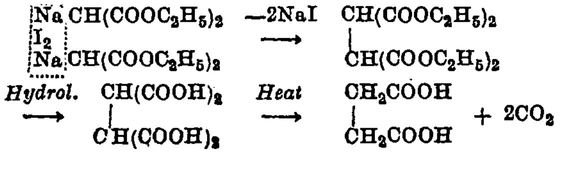
Starting with sodio-alkyl-malonic ester and by repeating the above steps we can synthesise dialkylacetic acids, $R_2CH.COOH$. Thus dimethylacetic acid can be obtained as below :

$$CH_3I + NaCH(COOC_2H_5)_2 \longrightarrow CH_3CH(COOC_2H_5)_2$$

$$CH_3CH(COOC_2H_5)_2 \xrightarrow{C_2H_5ONa} CH_3NaC(COOC_2H_5)_2$$

$$\xrightarrow{CH_3I} (CH_3)_2C(COOC_2H_5)_2 \xrightarrow[\& heat]{Hydrol.} \underset{\text{Dimethylacetic acid}}{(CH_3)_2CHCOOH}$$

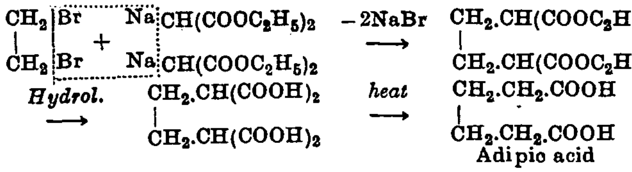
(2) Dicarboxylic acids. (*i*) Sodiomalonic ester on treatment with iodine forms a tetracarboxylic ester, which upon hydrolysis and heating yields succinic acid.



$$\begin{matrix} NaCH(COOC_2H_5)_2 \\ I_2 \\ NaCH(COOC_2H_5)_2 \end{matrix} \xrightarrow{-2NaI} \begin{matrix} CH(COOC_2H_5)_2 \\ | \\ CH(COOC_2H_5)_2 \end{matrix}$$

$$\xrightarrow{Hydrol.} \begin{matrix} CH(COOH)_2 \\ | \\ CH(COOH)_2 \end{matrix} \xrightarrow{Heat} \begin{matrix} CH_2COOH \\ | \\ CH_2COOH \end{matrix} + 2CO_2$$

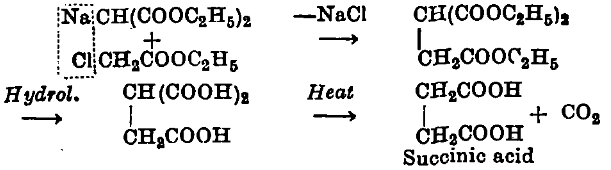
(*ii*) Higher dicarboxylic acids can be obtained by reacting sodiomalonic ester with alkylene dihalides having halogen atoms at the ends of the carbon chain. Thus :



$$\begin{array}{l}CH_2Br\\ |\\ CH_2Br\end{array} + \begin{array}{l}NaCH(COOC_2H_5)_2\\ \\ NaCH(COOC_2H_5)_2\end{array} \xrightarrow{-2NaBr} \begin{array}{l}CH_2.CH(COOC_2H_5)_2\\ |\\ CH_2.CH(COOC_2H_5)_2\end{array} \xrightarrow{Hydrol.} \begin{array}{l}CH_2.CH(COOH)_2\\ |\\ CH_2.CH(COOH)_2\end{array} \xrightarrow{heat} \begin{array}{l}CH_2.CH_2.COOH\\ |\\ CH_2.CH_2.COOH\end{array}$$

Adipic acid

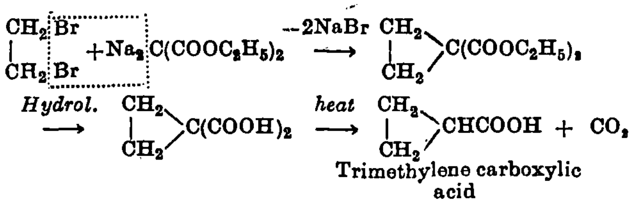
(*iii*) Dicarboxylic acids can also be prepared by reacting sodiomalonic ester with halogen substituted esters such as chloroethyl acetate.



$$\begin{array}{l}NaCH(COOC_2H_5)_2\\ \quad +\\ ClCH_2COOC_2H_5\end{array} \xrightarrow{-NaCl} \begin{array}{l}CH(COOC_2H_5)_2\\ |\\ CH_2COOC_2H_5\end{array} \xrightarrow{Hydrol.} \begin{array}{l}CH(COOH)_2\\ |\\ CH_2COOH\end{array} \xrightarrow{Heat} \begin{array}{l}CH_2COOH\\ |\\ CH_2COOH\end{array} + CO_2$$

Succinic acid

(3) CYCLIC CARBOXYLIC ACIDS. Disodiomalonic ester reacts with straight chain dihalides to form cyclic acid. Thus :



Trimethylene carboxylic acid

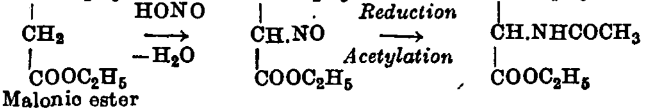
(4) UNSATURATED ACIDS. Malonic ester condenses with aldehydes and ketones in the presence of organic bases (pyridine) to form unsaturated acids. Thus :

$$CH_3CH{:}O + H_2{:}C(COOC_2H_5)_2 \xrightarrow{-H_2O} CH_3CH{:}C(COOC_2H_5)_2$$

$$\xrightarrow{Hydrol.} CH_3CH{:}C(COOH)_2 \xrightarrow{Heat} CH_3CH{:}CHCOOH + CO_2$$

Crotonic acid

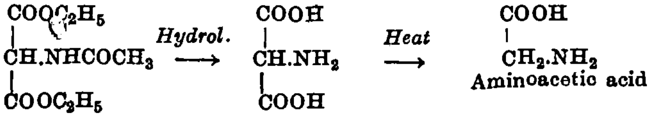
(5) AMINO ACIDS. Malonic ester is first converted to acylaminomalonic ester by first treating with nitrous acid and then zinc, acetic acid and acetic anhydride.



$$\begin{array}{l}COOC_2H_5\\ |\\ CH_2\\ |\\ COOC_2H_5\end{array} \xrightarrow[-H_2O]{HONO} \begin{array}{l}COOC_2H_5\\ |\\ CH.NO\\ |\\ COOC_2H_5\end{array} \xrightarrow[Acetylation]{Reduction} \begin{array}{l}COOC_2H_5\\ |\\ CH.NHCOCH_3\\ |\\ COOC_2H_5\end{array}$$

Malonic ester

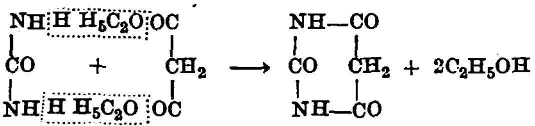
The product is hydrolysed and heated to yield the amino acid



$$\begin{array}{l}COOC_2H_5\\ |\\ CH.NHCOCH_3\\ |\\ COOC_2H_5\end{array} \xrightarrow{Hydrol.} \begin{array}{l}COOH\\ |\\ CH.NH_2\\ |\\ COOH\end{array} \xrightarrow{Heat} \begin{array}{l}COOH\\ |\\ CH_2.NH_2\end{array}$$

Aminoacetic acid

(6) **Malonyl Urea.** Like acetoacetic ester, malonic ester is also capable of forming heterocyclic compounds. Thus it reacts with urea to form malonyl urea or *Barbituric acid.*



Urea Malonic ester Barbituric acid

(7) **Keto Acids.** Sodiomalonic ester when treated with an acid chloride yields a keto acid.

$$\underset{\text{Acetyl chloride}}{CH_3COCl} + NaCH.(COOC_2H_5)_2 \longrightarrow CH_3.CO.CH(COOC_2H_5)_2$$

$$CH_3CO.CH(COOC_2H_5)_2 \xrightarrow[+2H_2O]{Hydrol.} CH_3CO.CH(COOH)_2 + 2C_2H_5OH$$

$$CH_3CO.CH(COOH)_2 \xrightarrow{heat} \underset{\text{Acetoacetic acid}}{CH_3CO.CH_2COOH} + CO_2$$

QUESTIONS

A. Acetoacetic Ester

1. How is ethyl acetoacetate prepared ? What is the mechanism of its formation ? Outline its principal synthetic applications.

2. Discuss fully the constitution of acetoacetic ester. How would you use it to synthesise (*a*) methyl ethyl ketone, (*b*) propionic acid, (*c*) valeric acid ?

3. Discuss the mechanism of the formation of acetoacetic ester. Starting with acetoacetic ester indicate the steps involved in the preparation of :

(*a*) methyl n-butyl ketone, $CH_3CO(CH_2)_3CH_3$

(*b*) n-butyric acid, $CH_3CH_2CH_2COOH$

(*c*) n-propylethylacetic acid, $CH_3CH_2CH_2CH(C_2H_5)COOH$.

4. (*a*) How is ethyl acetoacetate prepared ? Discuss the mechanism of its formation.

(*b*) What products are formed when—

(*i*) Sodium ethyl acetoacetate is treated with iodine and the product hydrolysed,

(*ii*) How can you synthesise methyl isopropyl ketone from ethyl acetoacetate ?

5. Discuss the constitution of Acetoacetic ester. and explain Tautomerism with reference to this compound.

6. How will you prepare (*i*) methyl ethyl ketone, (*ii*) methylacetic acid, from ethyl acetoacetate ? (*Allahabad B.Sc. II, 1967*)

7. How is ethyl acetoacetate prepared ? Discuss its constitution. How will you obtain the following compounds by the use of acetoacetic ester :

(*a*) methyl propyl ketone,

(*b*) crotonic acid,

(*c*) methyl uracil,

(*d*) succinic acid ? (*Udaipur B.Sc. II, 1967*)

8. Describe the synthetic uses of acetoacetic ester. What is the evidence that it exists in two isomeric forms ? (*Udaipur B.Sc., 1969*)

9. Explain the difference between tautomerism and resonance. Give some synthetic applications of acetoacetic ester. (*Panjab B.Sc., 1969*)

10. Establish the structure of acetoacetic ester. How can it be used for the preparation of methyl ethyl ketone and alpha-methyl butyric acid ? *(Delhi B.Sc., 1969)*

B. MALONIC ESTER

1. How is ethyl malonate prepared ? Outline its applications in organic synthesis.

2. How is malonic ester prepared ? Show how the following compounds may be prepared by means of the malonic ester synthesis : (*i*) butyric acid, (*ii*) dimethyl acetic acid, (*iii*) succinic acid.

3. How can you account for the great synthetic value of compounds containing active methylene group ? How can you prepare :—

(*a*) dimethylacetic acid from diethyl malonate ;

(*b*) methyl ethyl ketone from ethyl acetoacetate ;

(*c*) succinic acid from diethyl malonate :

(*d*) propionic acid from ethyl acetoacetate ?

4. Describe the preparation, properties and uses of Malonic ester. *(Kurukshetra B.Sc. II, 1967)*

5. What is a reactive methylene group ? Describe the synthetic applications of any one of the compounds containing this group. *(Gorakhpur B.Sc., 1968)*

6. Illustrate with suitable examples the use of diethyl malonate in organic ester. *(Osmania B.Sc., 1968)*

7. Describe the preparation, properties and synthetic applications of malonic ester. *(Marathwada B.Sc., 1967)*

8. How is malonic ester prepared ? Starting from this compound how would you prepare the following :—

(1) Propionic acid (3) Cinnamic acid
(4) Succinic acid (4) Barbituric acid.
(Ujjain B.Sc., 1968)

9. How is malonic ester prepared ? Give its synthetic uses. *(Poona B.Sc., 1968)*

10. Describe the preparation of malonic ester. How will you convert it into :—

(*a*) Phenyl acetic acid (*b*) Cinnamic acid
(*c*) Succinic acid (*d*) Barbituric acid. *(Bombay B.Sc., 1968)*

11. Outline the important synthetic applications of (*a*) Ethyl malonate (*b*) Ethyl acetoacetate. *(Viswa Bharati B.Sc., 1969)*

26

Fats, Oils and Soaps

PAUL SABATIER
(1854—1941)
French Chemist. He won the Nobel Prize in 1912 for his work on catalytic hydrogenation of hydrocarbons and other organic compounds.

WHAT ARE FATS AND OILS ?

Fats and oils are the triesters of glycerol with long chain organic acids, chiefly palmitic acid ($C_{15}H_{31}COOH$), stearic acid ($C_{17}H_{35}COOH$), and oleic acid ($C_{17}H_{33}COOH$). The triesters of glycerol are commonly named as **glycerides.** Glycerides are said to be 'simple' or 'mixed' according as all the three acid radicals in combination with the glycerol molecule are the same or different.

$$\begin{array}{ll} CH_2O.OC.R & CH_2O.OC.R \\ | & | \\ CH.O.OC.R & CH.O.OC.R' \\ | & | \\ CH_2.O.OC.R & CH_2.O.OC.R'' \\ \text{Simple glyceride} & \text{Mixed glyceride} \end{array}$$

Originally it was believed that fats and oils are the mixtures of simple glycerides :

$$\begin{array}{lll} CH_2.O.OC.C_{15}.H_{31} & CH_2.O.OC.C_{17}H_{35} & CH_2.O\ OC.C_{17}H_{33} \\ | & | & | \\ CH.O.OC.C_{15}H_{31} & CH.O.OC.C_{17}H_{35} & CH.O.OC.C_{17}H_{33} \\ | & | & | \\ CH_2.O.OC.C_{15}H_{31} & CH_2O.OC.C_{17}H_{35} & CH_2.O.OC.C_{17}H_{33} \\ \text{Tripalmitin} & \text{Tristearin} & \text{Triolein} \end{array}$$

Recent researches have, however, shown that all natural fats and oils invariably consist of mixtures of 'mixed glycerides'. For example, *lard* is a mixture of the oleo-palmito-stearin, palmito-distearin, stearo-dipalmitin and palmito-diolein.

The terms 'fat' and 'oil'. The natural stuff consisting of glycerol esters which is a solid at room temperature is commonly called a *fat* and the one that is liquid is called an *oil*. The two terms are purely conventional since the same substance may be a fat in one climate and an oil in another. Thus ghee is a 'fat' in winter and 'oil' in summer. Chemically the so-called fats contain relatively large proportions of combined stearic acid (m.p. 60°) and palmitic acid (m.p. 64°) and, therefore, melt at a higher temperature than 'oils' which contain a large proportion of oleic acid (m.p. 14°).

OCCURRENCE AND IMPORTANCE

Oils and fats occur widely spread in the animal and vegetable kingdom. In plants, they are present chiefly in seeds and form reserves for germination of *embryo*. In animals, fats are found in deposits under the skin and in muscles, and act as food reserves in time of hunger.

Fats are not only essential in human diet but also play important roles in many industrial processes. They are used as such in foodstuffs, paints, varnishes, polishes, cosmetics, lubricants, etc. They are also used for the manufacture of soaps, candles, explosives, plastics and a host of other useful products.

EXTRACTION AND REFINING

The fats and oils are extracted from the neutral products by three operations :

(1) *Rendering*. This consists in chopping off the tissues containing fat and heating them dry or with water until the fat is melted and can be removed.

(2) *Pressing*. Oils are obtained from seeds by crushing between rollers and then pressing in a hydraulic press. The pressed cake is used as fodder for milking cattle.

(3) *Solvent Extraction*. It is often applied to the residue of a pressing process and ensures complete removal of fat or oil. Solvents used include carbon disulphide, petroleum ether and benzene.

After separation by the above methods, the crude oil is treated with a little alkali to remove the free acids together with colloidal impurities. The oil is then bleached by agitation with Plaster of Paris and animal charcoal at 70—80°. It is finally deodorised with steam.

PROPERTIES OF FATS

(*Physical*). (1) Oils and fats are liquids or solids having no odour or taste in the pure state.

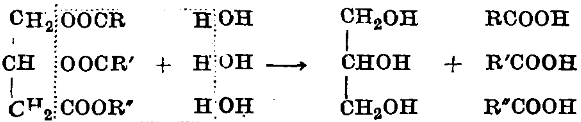
(2) They are lighter than and insoluble in water and, therefore, form the upper layer when mixed with it.

(3) They are freely soluble in organic solvents like ether, acetone, chloroform and benzene.

(4) They readily form emulsions when agitated with water in the presence of soap, gelatin or other emulsifiers.

(*Chemical*). Oils and fats show the usual hydrolytic reactions of esters. Since the oleic acid radical present in them contains ethylenic linkage, they also give addition and oxidation reactions.

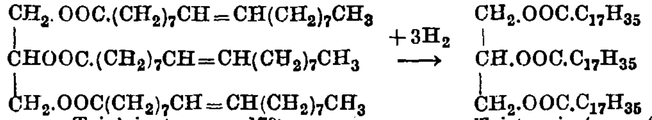
(1) **Hydrolysis.** Fats are hydrolysed by heating with water alone, or in the presence of acids to form glycerol and the free organic acids.



$$\begin{array}{lcccccc} CH_2\vdots OOCR & & H\vdots OH & & CH_2OH & & RCOOH \\ | & & & & | & & \\ CH\ \vdots OOCR' & + & H\vdots OH & \longrightarrow & CHOH & + & R'COOH \\ | & & & & | & & \\ CH_2\vdots COOR'' & & H\vdots OH & & CH_2OH & & R''COOH \\ \text{Fat} & & \text{Water} & & \text{Glycerol} & & \text{Acids} \end{array}$$

In the presence of alkalis, however, the free organic acids first produced are neutralised forming salts (*soap*).

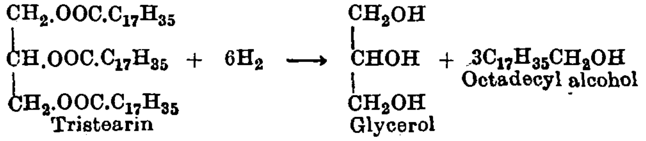
(2) **Hydrogenation.** It is carried by passing hydrogen gas under pressure into the liquid fat or oil having a fine suspension of nickel which acts as a catalyst. The oleic acid radical adds a molecule of hydrogen at the double bond and is thus converted to the stearic acid radical. This raises the melting point of the oil which hardens or solidifies. Thus :



$$\begin{array}{lcl} CH_2.OOC.(CH_2)_7CH{=}CH(CH_2)_7CH_3 & & CH_2.OOC.C_{17}H_{35} \\ | & +3H_2 & | \\ CHOOC.(CH_2)_7CH{=}CH(CH_2)_7CH_3 & \longrightarrow & CH.OOC.C_{17}H_{35} \\ | & & | \\ CH_2.OOC(CH_2)_7CH{=}CH(CH_2)_7CH_3 & & CH_2.OOC.C_{17}H_{35} \\ \text{Triolein (m.p. } -17^\circ) & & \text{Tristearin (m.p. } 60^\circ) \end{array}$$

The hydrogenation or '*hardening of oils*' is used for the manufacture of *Vegetable ghee* or '*margarine*'. Hardened oils are also extensively used for making soaps and candles.

(3) **Hydrogenolysis.** If excess of hydrogen be passed through an oil or fat, it is split into glycerol and higher aliphatic alcohols. Thus triolein forms octadecyl alcohol and glycerol.



$$\begin{array}{lcccccl} CH_2.OOC.C_{17}H_{35} & & & & CH_2OH & & \\ | & & & & | & & \\ CH.OOC.C_{17}H_{35} & + & 6H_2 & \longrightarrow & CHOH & + & 3C_{17}H_{35}CH_2OH \\ | & & & & | & & \text{Octadecyl alcohol} \\ CH_2.OOC.C_{17}H_{35} & & & & CH_2OH & & \\ \text{Tristearin} & & & & \text{Glycerol} & & \end{array}$$

This reaction which involves the splitting of the fat by hydrogen is termed *hydrogenolysis*.

(4) **Drying.** Certain fatty oils (*Linseed oil*) when exposed to air in thin layers are slowly converted to hard and elastic coatings. This process is called *drying* and is the basis of the paint and varnish industry.* The chemistry of drying which essentially involves

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***Paints.** They are made by suspending a suitable pigment in linseed oil and adding turpentine oil to thin it and thus permit an even and easy coating. In drying, turpentine evaporates immediately and linseed oil dries in a couple of days leaving a hard water-insoluble coating.

Varnishes. Best type of varnishes contain both linseed oil and a resin dissolved in a suitable solvent. The drying of the oil gives a tough film to which the resin adds gloss. "*Spirit Varnishes*" contain only resin *e.g.*, shellac, dissolved in alcohol. They dry quickly but the film lacks toughness and tends to crack. Varnishes coloured by dye or pigment are known as *lacquers*.

oxidation and polymerisation at the double bonds, is extremely complicated and obscure.

(5) **Rancidification.** Fats tend to spoil on storage and often develop unpleasant smell and taste in contact with air and moisture. The chemical changes accompanying this process of *rancidification* involve oxidation and hydrolysis. The hydrolysis of the fat produces lower fatty acids and the oxidation at the double bonds yields aldehydes. The acids and aldehydes thus produced are largely responsible for bad odour. Pure fats can be stored for long periods by exclusion of air and moisture.

MANUFACTURE OF 'VEGETABLE GHEE'

Fatty oils are usually unpalatable and cannot be used as such in food products. When they are hydrogenated in the presence of nickel, the unsaturated oleic acid radical in their molecule is converted to stearic acid radical. This change is accompanied by hardening of the oil which turns into solid fat.

$$\underset{\text{Olein (liquid oil)}}{C_3H_5(OOCC_{17}H_{33})_3} + 3H_2 \xrightarrow{\text{Ni-Cat}} \underset{\text{Stearin (solid fat)}}{C_3H_5(OOCC_{17}H_{35})_3}$$

The process of hydrogenation of the oil improves its colour, odour and taste and is, therefore, used for the preparation of 'vegetable ghee' or '*margarine*.

The simplest type of hydrogenator consists of an iron tank provided with a steam coil for heating purposes. The oil is admitted in the tank and the nickel catalyst is suspended in it. It is then heated by passing steam through the coil and hydrogen is introduced at the bottom. The unreacted hydrogen is collected and used again. The oil is kept in circulation by means of a pump. When the desired constituency has reached, the molten fat is sent to the filter press where the catalyst is removed. The product is white odourless solid which resembles '*ghee*' in appearance. It is commonly called 'artificial' or 'vegetable' ghee. In India *vegetable ghee* is being prepared in large quantities from cotton seed oil (*Kotogem*), and coconut oil and ground-nut oil (*Dalda*).

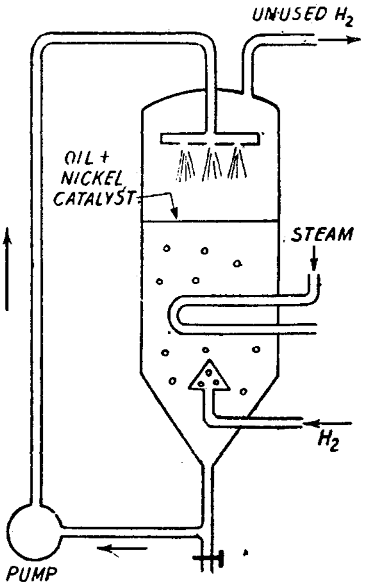


Fig. 26·1. Manufacture of vegetable ghee from oils.

ANALYSIS OF OILS AND FATS

The industrial value of a particular fat depends on its composition and purity. It may contain free acids and adulterated non-fatty impurities. A number of physical and chemical tests have been devised to evaluate a given fat. The usual physical constants that are determined are melting point, specific gravity and refractive index. The fat is then subjected to the following quantitative chemical tests.

(1) **Acid Value.** *It is the number of milligrams of potassium hydroxide required to neutralise 1 gram of the oil or fat.* The acid value of a fat is determined by dissolving a weighed quantity of it in alcohol and titrating the solution against standard alkali using phenolphthalein as indicator. It tells the amount of free fatty acid present in a fat.

(2) **Saponification Value.** *It is the number of milligrams of potassium hydroxide required to completely saponify 1 gram of the oil or fat.* The saponification value can be determined by refluxing a weighed quantity of the fat with excess of standard alcoholic potash solution, and then titrating the unused alkali against a standard acid.

The saponification value of a fat is of great importance as it gives an estimate of the non-fatty impurities. It also tells the amount of alkali that would be actually required by the fat for its conversion to soap.

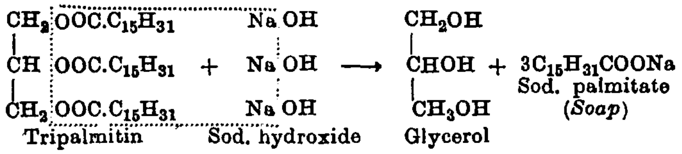
(3) **Iodine Value.** *It is the number of grams of iodine that combine with 100 grams of oil or fat.* It is determined by *Hubl's method* by treating a carbon tetrachloride solution of a weighed amount of the fat, with a solution of iodine and mercuric chloride in alcohol. The unused iodine is titrated against standard thiosulphate solution.

The iodine value of an oil or fat indicates the proportion of unsaturated acid radical present in it. It is of great importance in characterising individual fats and also for finding their suitability as soap materials.

(4) **Reichert-Meissl Value.** *It is the number of mls. of 0·1 N potassium hydroxide solution required to neutralise the volatile acids obtained by the distillation of 5 grams of fat.* The Reichert-Meissl Value gives an estimate of the lower steam-volatile fatty acids present in a fat.

WHAT ARE SOAPS ?

Soaps are the alkali salts of higher fatty acids. They are maintained by the hydrolysis of fats and oils with sodium hydroxide or potassium hydroxide. Thus :



$$\begin{array}{llllll}
CH_2\,OOC.C_{15}H_{31} & & Na\,OH & & CH_2OH & \\
| & & & & | & \\
CH\,OOC.C_{15}H_{31} & + & Na\,OH & \longrightarrow & CHOH & +\ 3C_{15}H_{31}COONa \\
| & & & & | & \text{Sod. palmitate} \\
CH_2\,OOC.C_{15}H_{31} & & Na\,OH & & CH_2OH & (\textit{Soap}) \\
\text{Tripalmitin} & & \text{Sod. hydroxide} & & \text{Glycerol} &
\end{array}$$

The common *toilet soaps* are the sodium soaps prepared from fatty oils. The soaps prepared from solid fats are relatively hard and are used as ***household soaps.***

The sodium soaps in general possess a hard consistency and are termed **hard soaps**. The potassium soaps which are softer and more soluble are called **soft soaps**. These are used for special purposes *e.g.*, shaving sticks, shaving cream and shampoo.

MANUFACTURE OF SOAP

In India the main source of toilet soaps is coconut oil which is available in large amounts in South India. Palm oil, cotton seed oil, ground-nut oil and olive oil are also used. In actual practice, mixture of *hardened* oils or solid fats and fatty oils are employed in soap-making, the blend being chosen to meet the expected requirements.

Soap may be prepared either by boiling the fat with sodium hydroxide solution (*Hot Process*) or by mixing them thoroughly in cold when the reaction proceeds slowly (*Cold Process*). The hot process is mostly employed for making toilet soaps, while the cold process is generally used for 'household' or *washing soaps.*

Hot Process. The manufacture of soap by the *hot process* is carried by the following steps :—

(1) BOILING. The operation of boiling the fat with sodium hydroxide solution (*soda lye*) is carried in an iron tank (soap kettle) having at the bottom closed steam-coils for indirect heating and perforated or open steam-coils for direct heating.

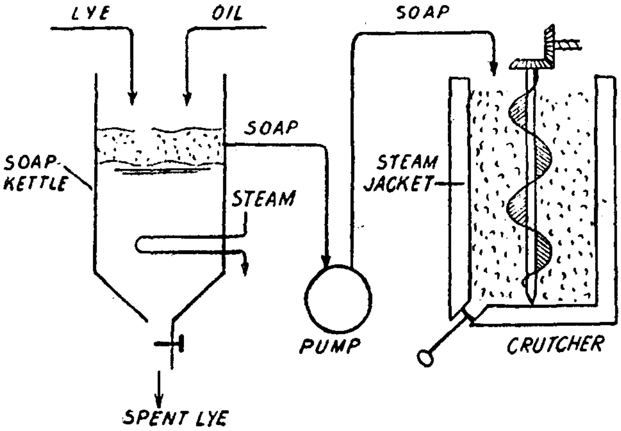


Fig. 26·2. Manufacture of Soap (*Hot Process*).

The molten fat or oil is run into the soap kettle and appropriate quantity of *soda lye* is added. The contents of the kettle are boiled by passing steam through the open-coil and thus kept in a good state of agitation all the time. Alkali is maintained in slight excess, more of it being added if necessary. The fat is thus saponified to the extent of about 80 per cent.

$$\text{Fat} + \text{Soda lye} \longrightarrow \text{Glycerol} + \text{Soap}$$

(2) SALTING OUT. The mixture of soap, glycerol and lye resulting from step (1) is heated by closed steam coils and salt is

added to it. The soap being insoluble in salt solution (*common ion effect*) is thrown out and floats to the surface as a curdy mass. The aqueous layer containing glycerol ("sweet waters") is run off and sent to the glycerol recovery plant. The soap left in the kettle is again boiled with fresh soda lye for completing the saponification and the *spent lye* run off. Finally, the soap is boiled with water to wash away any alkali and allowed to settle.

(3) FINISHING. The upper layer of soap obtained from step (2) is drawn off from the kettle. It is then pumped to a steam jacketed tank fitted with a mechanical stirrer (*crutcher*). Here soap is thoroughly mixed with glycerol till it becomes homogeneous. It is finally drawn out into frames and solidified. The solid soap is dried by means of hot air and milled with perfumes and colour to thin shavings, which are stamped into cakes.

Cold Process. The molten fat or oil is mixed with the required amount of *soda lye* in the crutcher (*see* Fig. 26·3). The saponification is allowed to take place in cold with mechanical stirring. The process is continued till the soap begins to set. At this stage, it is drawn out and allowed to solidify in frames. This solid soap is cut into bars which are finally dried and sold as *washing soap.*

Of the two processes of soap-making described above, the *hot process* is decidedly superior. It is more economical and yields the purest stuff, all impurities and excess of alkali being completely removed. The glycerol, which is an important by-product can also be recovered in this method.

Modern Continuous Process. In a recently developed process (*Ittner Process*), the hydrolysis of fat is carried with water under pressure and at elevated temperatures in the presence of lime or zinc oxide (catalyst). Hot water is fed into the *hydrolyser* near the top and fat near the bottom. The hydrolysis is rapid and complete. The fatty acids thus produced rise to the surface and are drawn out at the top, while the glycerol is removed in water leaving at the bottom. The fatty acids are then pumped to another

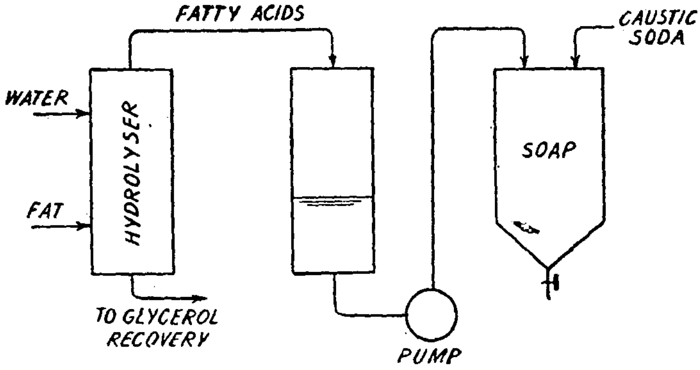


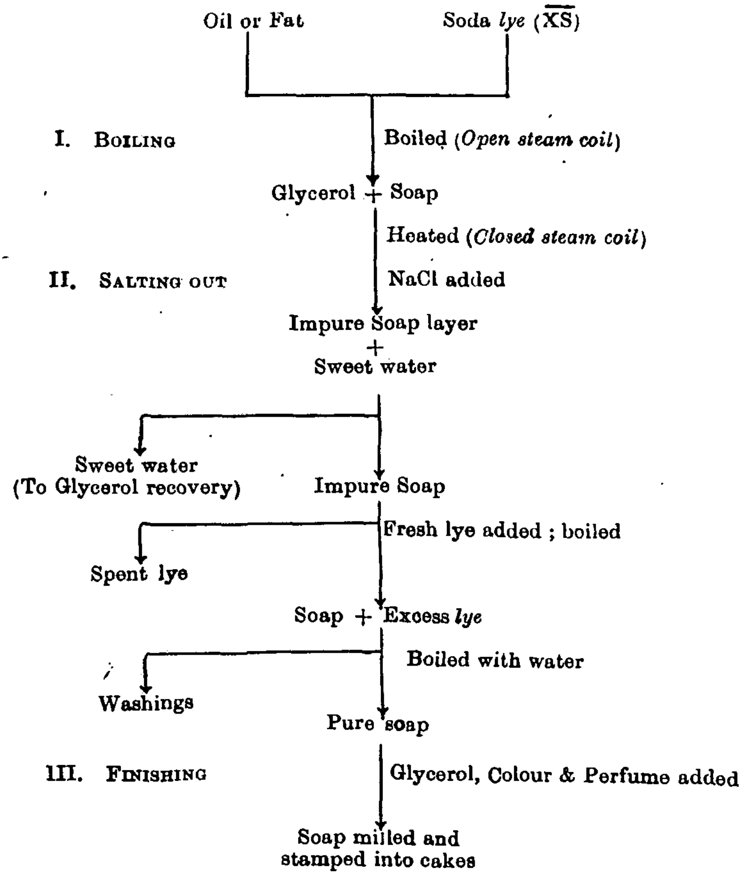
Fig. 26·3. Flowsheet for continuous soap-making process.

vessel (*neutraliser*) where they are neutralised with caustic soda, or the cheaper *soda ash* to form soap.

In another process (Twitchell process), the hydrolysis is effected by means of a catalyst consisting of dilute sulphuric acid and aromatic sulphonic acids.

The *hot process* of making soap is being gradually replaced by the newer processes described above which are continuous and hence more economical and easily controlled.

Cleansing Action of Soap. The dirt on the skin or clothes is sticking with the help of greasy matter. When rubbed with soap and water, it is easily washed away. The action of soap is twofold : (*i*) It emulsifies the grease and thus loosens the dirt particles : (*ii*) Soap forms a colliodal solution in water and thus removes dirt by adsorption on its particles.



FLOWSHEET OF SOAP MANUFACTURE (HOT PROCESS)

QUESTIONS

1. What are fats or oils ? What products are formed when they are saponified ?

2. Give an account of the general properties of fats and oils with special reference to hydrolysis, rancidity hardening and drying.

3. In what respects do fats differ from oils ? Indicate the industrial importance of natural products.

4. Write a short essay on fats and oils.

5. Write explanatory notes on : Saponification and iodine values of oils.

6. What do you know about the chemical nature of oils, fats and waxes? Write a short essay on the hydrogenation of vegetable oils.

7. What are iodine value and Saponification value ? Discuss the principles underlying the manufacture of soap. *(Jammu & Kashmir B. Sc., 1960)*

8. What is the chemical nature of oils and fats ? Explain the significance of :—

   (*a*) Acid value ;
   (*b*) Saponification value ; and
   (*c*) Iodine value. *(Venkateswara B.Sc., 1962)*

9. Write an essay on the chemistry and industrial uses of fats and oils. *(Gorakhpur B. Sc., 1962)*

10. What are oils and fats ? Discuss their important industrial applications ? *(Marathwada B. Sc. III, 1963)*

11. Write a short note on hydrogenation of oils. *(Aligarh B.Sc. II, 1964)*

12. What are soaps ? Describe the manufacture of toilet soap. *(Venkateswara B.Sc. II, 1964)*

13. Write an essay on the chemistry of fats ond oils. *(Ceylon B.Sc., 1968)*

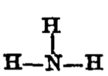
27

Amines

AUGUST W. VON HOFMANN
(1818—1892)

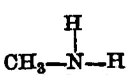
German. He worked chiefly with the amines, triphenylmethane dyes, isonitriles and mustard oils. Students are familiar with his method of preparation of amines.

Amines are the derivatives of ammonia in which one or more H-atoms have been replaced by alkyl groups. They are designated as primary, secondary and tertiary amines according as one, two or three hydrogen atoms in ammonia molecule have been replaced by alkyl groups.



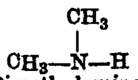
$H-\overset{H}{\overset{|}{N}}-H$

Ammonia



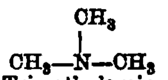
$CH_3-\overset{H}{\overset{|}{N}}-H$

Methylamine
(Primary)



$CH_3-\overset{CH_3}{\overset{|}{N}}-H$

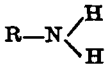
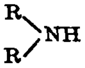
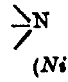
Dimethylamine
(Secondary)



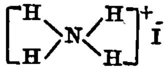
$CH_3-\overset{CH_3}{\overset{|}{N}}-CH_3$

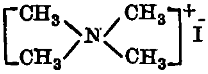
Trimethylamine
(Tertiary)

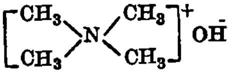
The type formulae of the three classes of amines and their characteristic groups are given below :

CLASS	TYPE FORMULA	CHARACTERISTIC GROUP
Primary amine	 or RNH_2	$-NH_2$ *(Amine group)*
Secondary amine	 or R_2NH	$>NH$ *(Imino group)*
Tertiary amine	 or R_3N	 *(Nitrile group)*

In addition to amines there are known such derivatives in which all the four hydrogen atoms of the ammonium radical have been replaced by alkyl groups. These are called **Tetra-alkylammonium salts** or **Quaternary ammonium salts**. Thus :


Ammonium iodide


Tetramethylammonium iodide


Tetramethylammonium hydroxide

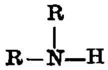
Like ammonia, aliphatic amines give alkaline reactions. They are, in fact, the inorganic bases, while alcohols although containing OH groups like the inorganic bases, are neutral substances.

NOMENCLATURE

Amines are named either by the Common System or the IUPAC System.

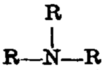
(1) The COMMON SYSTEM of naming this class of compounds is to call them alkyl-substituted ammonias, though the word 'ammonia' is contracted to 'amine'. Thus the three types of amines are named as

$R-NH_2$
Alkylamine
(Primary)



$R-\overset{\overset{\textstyle R}{|}}{N}-H$

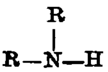
Dialkylamine
(Secondary amine)



$R-\overset{\overset{\textstyle R}{|}}{N}-R$

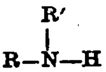
Trialkylamine
(Tertiary amine)

The secondary and tertiary amines are designated as *'symmetrical'* (simple) or *'unsymmetrical'* (mixed) according as the alkyl radicals bonded to N atom are identical or different.



$R-\overset{\overset{\textstyle R}{|}}{N}-H$

Symmetrical or
secondary amine

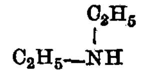


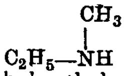
$R-\overset{\overset{\textstyle R'}{|}}{N}-H$

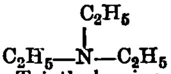
Unsymmetrical or
mixed secondary amine

The common name of an individual amine is a one word-name which is obtained by naming the alkyl radicals attached to N atom in alphabetic order and adding the suffix amine. In secondary and tertiary amines if the same alkyl radical is bonded to N atom twice or thrice, the prefix *di-* or *tri-* is placed before the name of the alkyl radical. Thus :

$C_2H_5NH_2$
Ethylamine

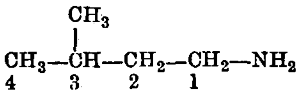

$C_2H_5-\overset{C_2H_5}{\overset{|}{N}}H$
Diethylamine


$C_2H_5-\overset{CH_3}{\overset{|}{N}}H$
Ethylmethylamine


$C_2H_5-\overset{C_2H_5}{\overset{|}{N}}-C_2H_5$
Triethylamine

(2) According to the IUPAC SYSTEM, the common names are permissible for lower members. The primary amines are named as alkylamines ($R-NH_2$) and the functional group $-NH_2$ is symbolised by the ending 'amine'. If necessary, the carbon chain bearing the amine group ($-NH_2$) is numbered starting from the end nearer this group.

$\underset{4}{CH_3}\underset{3}{CH_2}\underset{2}{CH_2}\underset{1}{CH_2}NH_2$
1-Butylamine

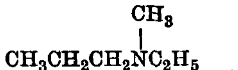

$\underset{4}{CH_3}-\underset{3}{\overset{CH_3}{\overset{|}{C}}H}-\underset{2}{CH_2}-\underset{1}{CH_2}-NH_2$
3-Methyl-1-butylamine

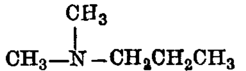
The mixed secondary and tertiary amines are assigned IUPAC names by regarding them as N-alkyl substituted derivatives of the basic primary amine with the largest (or most complex) alkyl radical bonded to nitrogen atom. The remaining alkyl radicals with N-prefixes are named in alphabetical order and joined to the name of the basic amine as suffix. The letter *N* prefixed to the name of an alkyl radical indicates that it is directly attached to nitrogen. Thus :

$CH_3-CH_2-NH_2$
Ethylamine
(Primary)

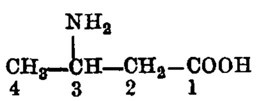

$CH_3-CH_2-\overset{CH_3}{\overset{|}{N}}H$
N-Methylethylamine
(Secondary)

Here the secondary amine is derived from ethylamine by substituting methyl radical for H of NH_2. The two alkyl radicals attached to N are ethyl (C_2H_5-) and methyl (CH_3-) of which obviously the former is larger; hence the basic amine is ethylamine. By joining the name of the smaller methyl radical with prefix *N*, to the name of the basic amine we get full name *N*-methylethylamine. Similarly,

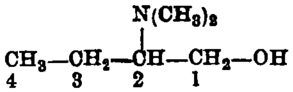

$CH_3CH_2CH_2\overset{CH_3}{\overset{|}{N}}C_2H_5$
N-Ethyl-N-Methylpropylamine


$CH_3-\overset{CH_3}{\overset{|}{N}}-CH_2CH_2CH_3$
N, N-Dimethylpropylamine

In polyfunctional compounds, the functional groups of primary, secondary and tertiary amines *viz.*, $-NH_2$ (amino), $-NHR$ (alkylamino), $-NR_2$ (dialkylamino) respectively are named as substituents. For example,


$\underset{4}{CH_3}-\underset{3}{\overset{NH_2}{\overset{|}{C}}H}-\underset{2}{CH_2}-\underset{1}{COOH}$

3-amino-1-butanoic acid



$$\underset{4}{CH_3}—\underset{3}{CH_2}—\underset{2}{\overset{N(CH_3)_2}{\overset{|}{C}H}}—\underset{1}{CH_2}—OH$$

2-dimethylamino-1-butanol

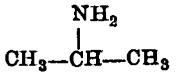
ISOMERISM

(1) Amines show chain isomerism due to different constitution of the alkyl groups :

$CH_3CH_2CH_2CH_2.NH_2$
n-Butylamine

Isobutylamine

(2) Primary amines show position isomerism due to different location of the amino group on the carbon chain.

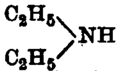


$$CH_3—\overset{NH_2}{\overset{|}{C}H}—CH_3$$

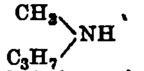
2-Aminopropane

$CH_3.CH_2.CH_2.NH_2$
1-Aminopropane

(3) Primary and secondary amines exhibit metamerism which arises from different alkyl groups attached to the central N-atom. Thus :



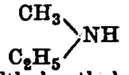
Diethylamine



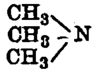
Methylpropylamine

(4) Amines also show another interesting type of isomerism when the same molecular formula may stand for a primary, a secondary and a tertiary amine. Thus C_3H_9N represents

$CH_3CH_2CH_2NH_2$
Propylamine



Ethylmethylamine



Trimethylamine

METHODS OF FORMATION

The general methods of formation of amines may be classified as follows :

(*i*) *Methods yielding mixtures of amines,*

(*ii*) *Methods for Primary amines,*

(*iii*) *Methods for Secondary amines, and*

(*iv*) *Methods for Tertiary amines.*

Methods yielding mixtures of Amines

(1) **Ammonolysis of Alkyl halides** (*Hofmann Synthesis*). When an alkyl halide is heated with an alcoholic solution of ammonia in a sealed tube, a mixture of primary, secondary and tertiary amines along with the quaternary salt is obtained. Thus :

$$\underset{\text{Methyl iodide}}{CH_3\boxed{I + H}NH_2} \quad \underset{\text{Ammonia}}{} \longrightarrow \underset{\text{Methylamine}}{CH_3NH_2} + HI$$

$$CH_3NH_2 + CH_3I \longrightarrow \underset{\text{Dimethylamine}}{(CH_3)_2NH} + HI$$

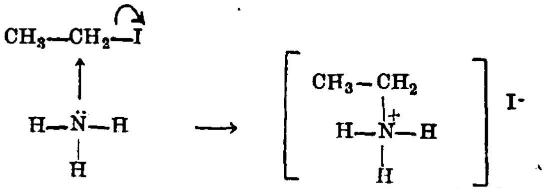
$$(CH_3)_2NH + CH_3I \longrightarrow \underset{\text{Trimethylamine}}{(CH_3)_3N} + HI$$

$$(CH_3)_3N + CH_3I \longrightarrow \underset{\text{Tetramethylammonium iodide}}{(CH_3)_4NI}$$

The amines, however, at once react with the halogen halide produced in the process to form addition salts : $CH_3NH_2.HI$; $(CH_3)_2NH.HI$; $(CH_3)_3N.HI$. Thus in actual practice the resulting mixture consists of different amine salts and the quaternary salt. This is then treated with caustic soda and distilled in steam. The primary, secondary and tertiary amines pass over, while the quaternary salt which is stable to caustic alkali is left behind.

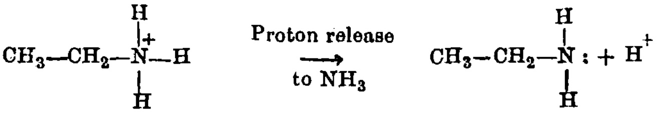
Mechanism :

The reaction proceeds in the following manner which involves a neutral nucleophilic nitrogen (having a lone pair of electrons). Here, ethyl-ammonium iodide salt is produced first.



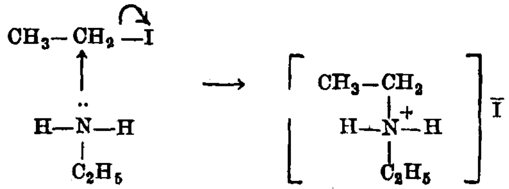
Ethyl-ammonium iodide

Nitrogen atom of ammonia molecule donates the lone pair of electrons to the carbon atom attached with the halogen and a covalent bond is established between nitrogen and carbon. Since the lone pair is now equally shared by N and C, nitrogen losing half of the control acquires a positive charge. Further, in presence of excess of ammonia, there takes place a proton release as :

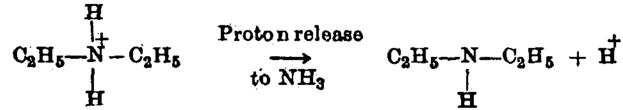


Ethyl-ammonium ion　　Ethylamine (Primary)

When ethyl iodide is in excess, a subsequent reaction occurs by the same mechanism and the primary amine produced above supplies the necessary lone pair of electrons.



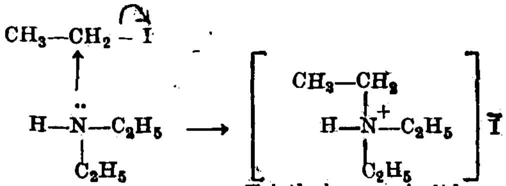
Diethyl-ammonium iodide



$$C_2H_5-\overset{H}{\underset{H}{\overset{|+}{N}}}-C_2H_5 \xrightarrow[\text{to } NH_3]{\text{Proton release}} C_2H_5-\underset{H}{\underset{|}{N}}-C_2H_5 + \overset{+}{H}$$

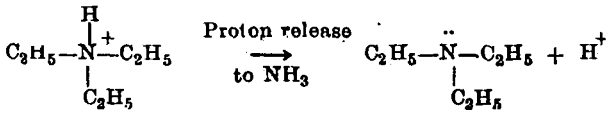
Diethyl-ammonium ion   Diethylamine (*Secondary*)

Secondary amine having a long pair at the N atom, reacts with another molecule of ethyl iodide.



$$CH_3-CH_2-I + H-\underset{C_2H_5}{\overset{\cdot\cdot}{N}}-C_2H_5 \longrightarrow \left[H-\overset{CH_3-CH_2}{\underset{C_2H_5}{\overset{|+}{N}}}-C_2H_5 \right]\overline{I}$$

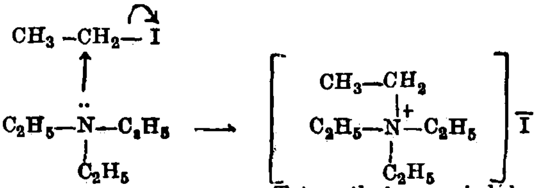
Triethyl amm. iodide



$$C_2H_5-\overset{H}{\underset{C_2H_5}{\overset{|+}{N}}}-C_2H_5 \xrightarrow[\text{to } NH_3]{\text{Proton release}} C_2H_5-\underset{C_2H_5}{\overset{\cdot\cdot}{N}}-C_2H_5 + \overset{+}{H}$$

Triethylamine (*Tertiary*)

The tertiary amine is also nucleophilic and can further react with ethyl iodide to form tetraethyl-ammonium iodide.



$$CH_3-CH_2-I + C_2H_5-\underset{C_2H_5}{\overset{\cdot\cdot}{N}}-C_2H_5 \longrightarrow \left[C_2H_5-\overset{CH_3-CH_2}{\underset{C_2H_5}{\overset{|+}{N}}}-C_2H_5 \right]\overline{I}$$

Totra-ethyl amm. iodide

Since it does not contain an N—H bond, it cannot lose a proton to ammonia and hence is the final product.

(2) **Ammonolysis of Alcohols.** An alcohol and ammonia are heated together at 300—400° under pressure in the presence of a catalyst together (Al_2O_3, ThO_2) when directly a mixture of primary, secondary and tertiary amines is obtained. Thus :

$$\underset{\text{Methyl alcohol}}{CH_3\boxed{OH + H}} \underset{\text{Ammonia}}{NH_2} \longrightarrow \underset{\text{Methylamine}}{CH_3NH_2} + H_2O$$

$$CH_3NH_2 + CH_3OH \longrightarrow \underset{\text{Dimethylamine}}{(CH_3)_2NH} + H_2O$$

$$(CH_3)_2NH + CH_3OH \longrightarrow \underset{\text{Trimethylamine}}{(CH_3)_3N} + H_2O$$

The primary amines may be obtained as the main product by using a large excess of ammonia.

Methods of formation of Primary Amines

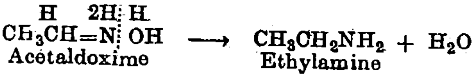
(1) **Reduction of Nitroalkanes.** Primary amines are obtained by reducing nitroalkanes with tin and hydrochloric acid, or with hydrogen and nickel catalyst. Thus :

$$\underset{\text{Nitroethane}}{C_2H_5NO_2} + 3H_2 \longrightarrow \underset{\text{Ethylamine}}{C_2H_5NH_2} + 2H_2O$$

This method is becoming increasingly important as more nitroalkanes are being made available by the vapour phase nitration of alkanes.

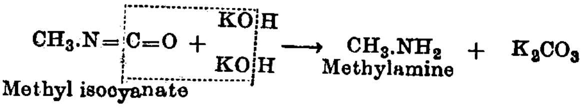
(2) **Reduction of Cyanides and Oximes.** Alkyl cyanides and oximes of aldehydes and ketones on reduction with sodium and alcohol give primary amines.

$$\underset{\text{Methyl cyanide}}{CH_3C{\equiv}N} + 4[H] \longrightarrow \underset{\text{Ethylamine}}{CH_3.CH_2.NH_2}$$



$$\underset{\text{Acetaldoxime}}{CH_3\overset{H}{C}H{=}N\overset{2H\,H}{\vdots}OH} \longrightarrow \underset{\text{Ethylamine}}{CH_3CH_2NH_2} + H_2O$$

(3) **Hydrolysis of Isocyanates.** Primary amines can also be prepared by the hydrolysis of alkyl isocyanates with caustic potash.



$$\underset{\text{Methyl isocyanate}}{CH_3.N{=}C{=}O} + \begin{matrix} KO\vdots H \\ KO\vdots H \end{matrix} \longrightarrow \underset{\text{Methylamine}}{CH_3.NH_2} + K_2CO_3$$

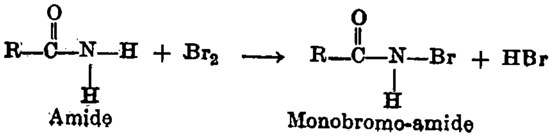
This method is not very useful on account of the inaccessibility of the alkyl isocyanates.

(4) **Hofmann's Hypobromite Method** (*Hofmann*, 1881). Primary amines are most conveniently prepared by treating the acid amides with bromine and alkali (hypobromite). The overall reaction involves the splitting out of the carbonyl group of the acid amide as carbon dioxide and thus converting it into amine.

$$\underset{\text{Amide}}{R.CO.NH_2} + \underset{\text{Sod. hypobromite}}{NaBrO} \longrightarrow \underset{\text{Amine}}{RNH_2} + CO_2 + NaBr$$

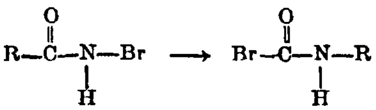
The above reaction, in fact, takes place by the following steps :

(*i*) Bromine reacts with the acid amide to form monobromoamide.



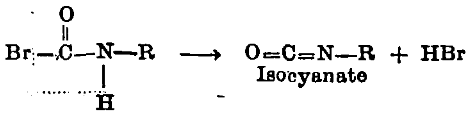
$$\underset{\text{Amide}}{R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}\underset{\underset{\displaystyle H}{|}}{N}{-}H} + Br_2 \longrightarrow \underset{\text{Monobromo-amide}}{R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}\underset{\underset{\displaystyle H}{|}}{N}{-}Br} + HBr$$

(*ii*) The alkyl group and bromine atom then exchange positions due to an isomeric change.



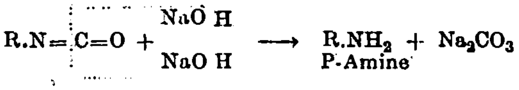
$$\mathrm{R-\overset{\overset{\displaystyle O}{\|}}{C}-\underset{\underset{\displaystyle H}{|}}{N}-Br \longrightarrow Br-\overset{\overset{\displaystyle O}{\|}}{C}-\underset{\underset{\displaystyle H}{|}}{N}-R}$$

(*iii*) The product of step (*ii*) splits out a molecule of hydrogen bromide in the presence of alkali.



$$\mathrm{Br-\overset{\overset{\displaystyle O}{\|}}{C}-\underset{\underset{\displaystyle H}{|}}{N}-R \longrightarrow \underset{\text{Isocyanate}}{O=C=N-R} + HBr}$$

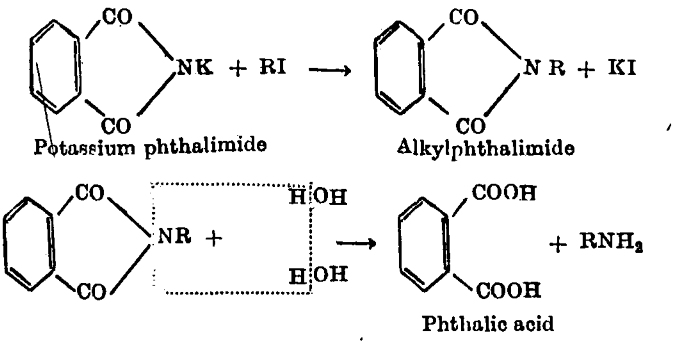
(*iv*) The isocyanate is finally hydrolysed to form the amine.



$$\mathrm{R.N{=}C{=}O + \begin{matrix}NaO\ H\\ NaO\ H\end{matrix} \longrightarrow \underset{\text{P-Amine}}{R.NH_2} + Na_2CO_3}$$

Hofmann's method is very useful for preparing lower primary amines only, since amides with more than seven carbon atoms in the chain give mainly the alkyl cyanides. The method is particularly important as it offers a means of converting the easily available fatty acids into amines. It also affords a method of descending a homologous series.

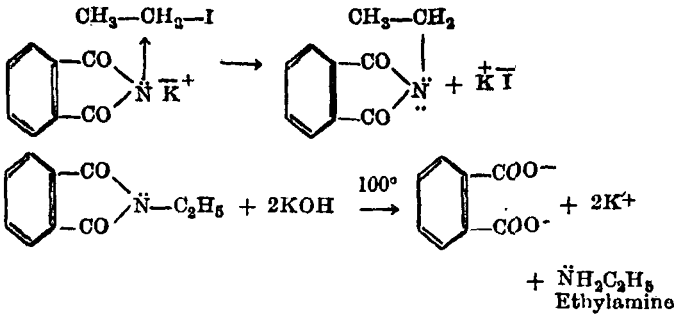
(5) **Gabriel's Phthalimide Method** (*Gabriel*, 1887). This method consists in the treatment of potassium phthalimide with alkyl halide to form alkylphthalimide which on hydrolysis with hydrochloric acid gives a primary amine.



This is one of the best methods for the preparation of primary amines.

Mechanism :

The reaction involves the same type of nucleophilic attack by potassium phthalimide on alkyl halide as was discussed in the case of reaction between NH_3 and ethyl iodide.



(6) **Decarboxylation of amino acids.** This is carried by heating the amino acid with barium oxide, or by contact with putrefying bacteria.

$$\underset{\text{Glycine}}{CH_2NH_2COOH} \longrightarrow \underset{\text{Methylamine}}{CH_3NH_2} + CO_2$$

(7) **From Grignard reagents.** Primary amines can also be prepared by reaction between a Grignard reagent and chloroamine, $Cl.NH_2$.

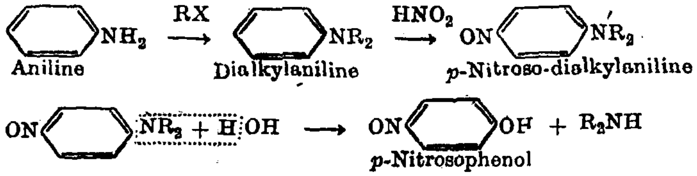
$$R\vdots MgX + \underset{\text{Chloramine}}{Cl\vdots —NH_2} \longrightarrow \underset{\text{P-Amine}}{RNH_2} + MgX.Cl$$

Methods of Preparation of Secondary Amines

(1) By heating a primary amine with the calculated amount of alkyl halide.

$$\underset{\text{P-Amine}}{RNH_2} + \underset{\text{Alkyl halide}}{RX} \longrightarrow \underset{\text{S-Amine}}{R_2NH} + HX$$

(2) **Hydrolysis of *p*-Nitroso-dialkylanilines.** Aniline is heated with the appropriate alkyl halide and the product is then treated with nitrous acid. The *p*-nitroso-dialkylaniline thus obtained on boiling with sodium hydroxide yields a secondary amine.



This is an excellent method for the preparation of secondary amines.

(3) **Hydrolysis of dialkylcyanamides.** A pure secondary amine can be obtained by the hydrolysis of a dialkylcyanamide which has been previously derived by the action of alkyl halide on sodium cyanamide.

$$\underset{\text{Sod. cyanamide}}{Na_2N.CN} + 2RX \longrightarrow \underset{\text{Dialkylcyanamide}}{R_2N.CN} + 2NaX$$

$$R_2N.CN + 2H_2O \longrightarrow \underset{\text{S-Amine}}{R_2NH} + CO_2 + NH_3$$

(4) By reduction of alkyl isocyanide with nascent hydrogen.

$$\underset{\text{Isocyanide}}{R.N \overset{\rightarrow}{=} C} + 4[H] \longrightarrow \underset{\text{Methylalkylamine}}{R.NH.CH_3}$$

This method is of academic interest only and yields methylalkyl amine.

Methods of Preparation of Tertiary Amines

(1) By heating an alcoholic solution of ammonia with the calculated amount of the alkyl halide.

$$\underset{\text{Alkyl iodide}}{3RI} + NH_3 \longrightarrow \underset{\text{T-Amine}}{R_3N} + 3HI$$

(2) They are best prepared by heating the corresponding quaternary ammonium hydroxide which is conveniently obtained by the action of moist silver oxide on the quaternary iodide.

$$\underset{\substack{\text{Tetramethylammonium}\\ \text{iodide}}}{(CH_3)_4N.I} + AgOH \longrightarrow \underset{\substack{\text{Tetramethylammonium}\\ \text{hydroxide}}}{(CH_3)_4N.OH} + AgI$$

$$(CH_3)_4N.OH \xrightarrow{heat} \underset{\text{Trimethylamine}}{(CH_3)_3N} + CH_3OH$$

SEPARATION OF MIXTURES OF AMINES

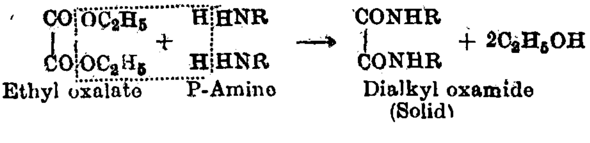
When the mixture contains the three amine salts and the quaternary salt, it is first distilled with potassium hydroxide solution. The three amines set free from their salts distil over. The quaternary salt however, remains unchanged by alkali and being non-volatile is left behind. The distillate which consist of a mixture of the primary, secondary and tertiary amines may now be separated by the following methods.

(1) **Fractional distillation.** The amines can be separated by fractional distillation since their boiling points are fairly different. However, the success of this method is mainly due to the high efficiency of the modern industrial fractionating apparatus which permits almost complete separation of the amines.

In the laboratory, the chemical methods of separation are generally employed.

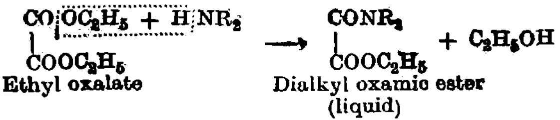
(2) **Hofmann's Method.** (*Action of Ethyl oxalate*). The mixture of amines is heated with ethyl oxalate, when

(*i*) the primary amine forms a dialkyl oxamide which is a crystalline solid.



$$\underset{\text{Ethyl oxalate}}{\begin{matrix} CO\,OC_2H_5 \\ | \\ CO\,OC_2H_5 \end{matrix}} + \underset{\text{P-Amine}}{\begin{matrix} H\,HNR \\ \\ H\,HNR \end{matrix}} \longrightarrow \underset{\substack{\text{Dialkyl oxamide}\\ \text{(Solid)}}}{\begin{matrix} CONHR \\ | \\ CONHR \end{matrix}} + 2C_2H_5OH$$

(*ii*) the secondary amine forms a dialkyloxamic ester, which is an oily liquid.



$$\begin{array}{l}CO\,|\,OC_2H_5 + H\,|\,NR_2\\ |\\ COOC_2H_5\end{array} \longrightarrow \begin{array}{l}CONR_2\\ |\\ COOC_2H_5\end{array} + C_2H_5OH$$

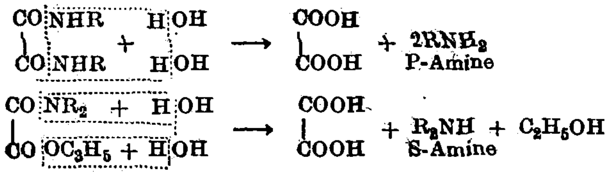
Ethyl oxalate — Dialkyl oxamic ester (liquid)

The second ester group does not react, possibly due to '*steric hindrance*'.

(*iii*) *the tertiary amine does not react at all.*

The reaction mixture is now fractionally distilled. The tertiary amine distils over and forms the first fraction. This is followed by dialkyl oxamic ester which forms the second fraction. The dialkyl oxamide remains behind in the flask.

The dialkyloxamide and the dialkyl oxamic ester separated as above are hydrolysed with alkali to regenerate the amine which is distilled off.



$$\begin{array}{l}CO\,|\,NHR \quad H\,|\,OH\\ | \qquad\quad + \\ CO\,|\,NHR \quad H\,|\,OH\end{array} \longrightarrow \begin{array}{l}COOH\\ |\\ COOH\end{array} + \underset{\text{P-Amine}}{2RNH_2}$$

$$\begin{array}{l}CO\,|\,NR_2 + H\,|\,OH\\ |\\ CO\,|\,OC_3H_5 + H\,|\,OH\end{array} \longrightarrow \begin{array}{l}COOH\\ |\\ COOH\end{array} + \underset{\text{S-Amine}}{R_2NH} + C_2H_5OH$$

(3) **Hinsberg s Method.** (*Action of aromatic sulphonyl chloride*). The mixture of amines is treated with benzene sulphonyl chloride, $C_6H_5SO_2Cl$, and made alkaline with potassium hydroxide.

(*i*) the primary amine forms alkyl sulphonamide.

$$C_6H_5SO_2\,|Cl + H|\,\underset{\text{P-Amine}}{HNR} \longrightarrow \underset{\text{Alkyl sulphonamide}}{C_6H_5SO_2.NHR} + HCl$$

This dissolves in potassium hydroxide, due to the formation of the potassium salt of the enolic sulphonamide.

(*ii*) the secondary amine forms dialkyl sulphonamide.

$$C_6H_5SO_2\,|Cl + H|\,\underset{\text{S-Amine}}{NR_2} \longrightarrow \underset{\text{Dialkylsulphonamide}}{C_6H_5SO_2.NR_2} + HCl$$

This is insoluble in potassium hydroxide, since it has no replaceable hydrogen atom attached to the nitrogen atom and is incapable of forming the enol form.

(*iii*) the tertiary amine does not react with benzenesulphonyl chloride.

The resulting alkaline solution is distilled when the tertiary amine passes over and the remaining mixture is filtered ; the filtrate on acidification gives the sulphonamide of the primary amine, while the solid residue is the sulphonamide of the secondary amine. The two sulphonamides thus isolated are hydrolysed with hydrochloric acid to regenerate the individual amines which are distilled

$$C_6H_5SO_2\boxed{NHR + H}OH \longrightarrow \underset{\text{Benzenesulphonic acid}}{C_6H_5SO_2OH} + \underset{\text{P- Amine}}{RNH_2}$$

$$C_6H_5SO_2\boxed{NR_2 + H}OH \longrightarrow C_6H_5SO_3H + \underset{\text{S- Amine}}{R_2NH}$$

In modern practice benzenesulphonyl chloride has been replaced by *p*-toluenesulphonyl chloride, $CH_3.C_6H_4.SO_2Cl$.

PHYSICAL CHARACTERISTICS

(1) The lower amines are colourless gases or volatile liquids having a powerful fishy and ammoniacal odour. The highest members are colourless solids.

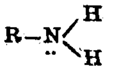
(2) They are all lighter than water.

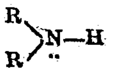
(3) The lower members are very soluble in water but the solubility falls with the increase of molecular weight.

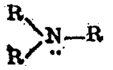
(4) The boiling points of amines show a gradual rise with the increase of molecular weight.

CHEMICAL CHARACTERISTICS

The molecules of primary, secondary and tertiary amines are made of 1, 2 or 3 alkyl groups linked to a trivalent nitrogen atom carrying 2, 1 or no H atoms respectively.


(Primary)


(Secondary)


(Tertiary)

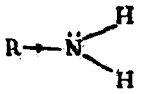
(*i*) The alkyl groups are comparatively stable and do not give substitution reactions.

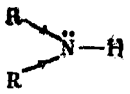
(*ii*) Just like the N-atom of ammonia molecule, the central N-atom of amines has a lone pair of electrons and can extend its valency to five (4 covalent and one electrovalent). Then amines form compounds with water and acids that are analogous to ammonium salts.

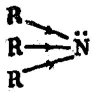
The amines thus act as bases (having a lone pair and proton acceptor) and their basic character follows the order :

tertiary > secondary > primary.

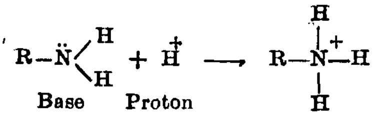
The increase in strength of amines is due to increased number of electron-repelling alkyl radicals in the molecule.







The repulsive action of alkyl radicals enhances the availability of the electron pair for bonding with a proton.



$$\underset{\text{Base}}{R-\ddot{N}\begin{smallmatrix}H\\H\end{smallmatrix}} + \underset{\text{Proton}}{\overset{+}{H}} \longrightarrow R-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{\overset{+}{N}}}-H$$

(*iii*) The hydrogen atoms directly attached to the N-atom are very reactive and can easily be replaced by other atoms or groups.

Owing to the difference in their structural formulae, the three types of amines show many characteristic reactions.

REACTIONS GIVEN BY ALL CLASSES OF AMINES

(1) **Action with Water ; formation of ammonium bases.** All the three classes of amines dissolve in water giving distinctly alkaline solutions. Just as ammonia reacts with a molecule of water to form ammonium hydroxide, amines react with water to form **alkylammonium hydroxides.** Thus :

$$\underset{\text{Methylamine}}{CH_3NH_2} + H_2O \longrightarrow \underset{\text{Methylammonium hydroxide}}{CH_3NH_3OH}$$

$$(CH_3)_2NH + H_2O \longrightarrow \underset{\text{Dimethylammonium hydroxide}}{(CH_3)_2NH_2OH}$$

$$\underset{\text{Trimethylamine}}{(CH_3)_2N} + H_2O \longrightarrow \underset{\text{Trimethylammonium hydroxide}}{(CH_3)_3NHOH}$$

The alkylammonium hydroxides ionise in water and furnish $\overset{-}{OH}$ ions.

$$CH_3NH_3OH \rightleftharpoons CH_3NH_3^+ + \overset{-}{OH}$$

In general, amines are stronger bases than ammonia, their strength being in the order : *Tertiary* > *Secondary* > *Primary.*

(2) **Action with Acids ; formation of salts.** Amines combine with acids to form salts. Thus methylamine reacts with hydrochloric acid to form methylammonium chloride.

$$\underset{\text{Methylamine}}{CH_3NH_2} + HCl \longrightarrow \underset{\text{Methylammonium chloride}}{[CH_3NH_3]^+\overset{-}{Cl}}$$

These salts are often written as amine hydrochlorides, amine sulphates, etc.

$CH_3NH_2.HCl$	Methylamine hydrochloride
$[(CH_3)_2NH]_2.H_2SO_4$	Dimethylamine sulphate

The amine salts are suitable in water and regenerate the amine on treatment with a strong base such as NaOH. The salt with chloropropionic acid is used for the determination of molecular weights of amines.

(3) **Action with Alkyl halides.** A primary amine reacts with an alkyl halide to form a secondary amine, and a secondary amine reacts with it to form a tertiary amine.

$$CH_3NH_2 + CH_3I \longrightarrow \underset{\text{Dimethylamine}}{(CH_3)_2NH} + HI$$

$$(CH_3)_2NH + CH_3I \longrightarrow \underset{\text{Trimethylamine}}{(CH_3)_3N} + HI$$

A tertiary amine combines with a molecule of alkyl halide to form a quaternary ammonium halide.

$$\underset{\text{Trimethylamine}}{(CH_3)_3N} + CH_3I \longrightarrow \underset{\text{Q. amm. iodide}}{(CH_3)_4NI}$$

Thus for its conversion to the quaternary salt, a primary amine will need *three* molecules of the alkyl halide; a secondary amine *two* molecules; and a tertiary amine only one molecule. By experimentally determining the amount of the alkyl halide actually used for the conversion of a given amine to the quaternary salt, we can know its 'class'.

REACTIONS GIVEN BY PRIMARY AND SECONDARY AMINES

(4) **Action with Acid chlorides; acylation.** Primary and secondary amines react with an acid chloride (or acid anhydride) to give acyl derivatives in which a hydrogen atom of the amino-group is replaced by an acyl radical (*acylation*). Thus:

$$\underset{\text{Methylamine}}{CH_3NH_2} + \underset{\text{Acetyl chloride}}{ClOCCH_3} \longrightarrow \underset{\text{Acetylmethylamine}}{CH_3NH.OCCH_3} + HCl$$

$$\underset{\text{Dimethylamine}}{(CH_3)_2NH} + ClOCCH_3 \longrightarrow \underset{\text{Acetyldimethylamine}}{(CH_3)_2N.OCCH_3} + HCl$$

Primary amines (having two available hydrogens) can yield a diacyl derivative but under forcing conditions. Tertiary amines having no available H atom do not react with acyl chlorides and are thus at once distinguished from primary and secondary amines.

The monoacetyl derivatives of primary and secondary amines are well-defined crystalline substances and are often used to characterise the amines.

(5) **Action with Nitrous acid.** Primary and secondary amines both react with nitrous acid but in a different fashion.

(*i*) Primary amines having two available H atoms, react with nitrous acid to form primary alcohols with the evolution of nitrogen (*Test*).

$$\mathrm{CH_3N\boxed{H_2 + O}{=}N{-}OH \longrightarrow CH_3.N{=}N.OH + H_2O}$$

Diazo hydroxide
(Unstable)

$$\mathrm{CH_3.N{=}N.OH \longrightarrow CH_3OH + N_2}$$

The overall reaction may be written as :

$$\mathrm{\underset{Methylamine}{CH_3NH_2} + HONO \longrightarrow \underset{Methyl\ alcohol}{CH_3OH} + N_2 + H_2O}$$

(*ii*) Secondary amines having only one available H atom react with nitrous acid to form *nitrosoamines.*

$$\mathrm{\underset{Dimethylamine}{(CH_3)_2N\boxed{H + HO}NO} \longrightarrow \underset{Dimethylnitrosoamine}{(CH_3)_2N.NO} + H_2O}$$

Nitrosoamines are yellow oils. When warmed with a little phenol and a few drops of concentrated sulphuric acid, they produce a green solution which on making alkaline with sodium hydroxide solution, turns deep blue or violet The reaction (**Liebermann's reaction**) is used as a test for the secondary amines.

(*iii*) Tertiary amines with no available H atoms fail to give a replacement reaction with nitrous acid ; they simply form an *addition salt*, $\mathrm{R_3N.HNO_2}$.

The different behaviour of nitrous acid with the three classes of amines is used for distinguishing between them.

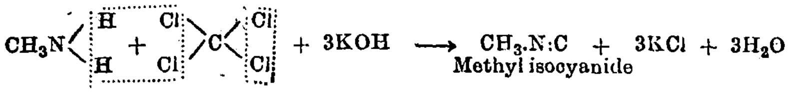
(6) **Action with Grignard reagents.** Primary and secondary amines react with Grignard reagents to form hydrocarbons.

$$\mathrm{RNH\boxed{H + CH_3}\underset{\substack{Methylmagnesium\\ iodide}}{MgI} \longrightarrow CH_4 + RNH.MgI}$$

$$\mathrm{R_2N\boxed{H + CH_3}MgI \longrightarrow CH_4 + R_2N.MgI}$$

REACTIONS GIVEN BY PRIMARY AMINES ONLY

(7) **Carbylamine reaction.** Primary amines form carbylamines or isocyanides when warmed with chloroform and alcoholic potash.



$$\mathrm{CH_3N}\begin{smallmatrix}\mathrm{H}\\ \mathrm{H}\end{smallmatrix} + \begin{smallmatrix}\mathrm{Cl}\\ \mathrm{Cl}\end{smallmatrix}\mathrm{C}\begin{smallmatrix}\mathrm{Cl}\\ \mathrm{Cl}\end{smallmatrix} + \mathrm{3KOH} \longrightarrow \underset{\mathrm{Methyl\ isocyanide}}{\mathrm{CH_3.N{:}C}} + \mathrm{3KCl} + \mathrm{3H_2O}$$

The isocyanide thus produced has extremely unpleasant odour and hence this reaction is an excellent test for primary amines. Secondary and tertiary amines do not give this reaction.

(8) **Mustard oil reaction.** Primary amines form isothiocyanates or 'mustard oils' when warmed with carbon disulphide and mercuric chloride.

$$\underset{\text{P-Amine}}{R.N\boxed{H_2 \;+\; S}=C=S} \xrightarrow{HgCl_2} \underset{\text{Mustard oil}}{R.N:C:S} + H_2S$$

The isothiocyanate thus produced has a pungent 'mustard-like' odour which can be easily recognised. Hence this reaction is also used as a test for primary amines.

REACTIONS GIVEN BY TERTIARY AMINES ONLY

(9) **Oxidation.** A tertiary amine on mild oxidation with hydrogen peroxide forms the *amine oxide*. Thus :

$$\underset{\text{Trimethylamine}}{(CH_3)_3N:} + \ddot{O}: \longrightarrow \underset{\text{Trimethylamine oxide}}{(CH_3)_3N\rightarrow O}$$

Here the trivalent N atom co-ordinates with an oxygen atom and extends its valency to four.

METHYLAMINE, CH_3NH_2

It is the simplest amine known. It is formed during the dry distillation of wood and bones.

Preparation. (1) Methylamine is best prepared in the laboratory by the action of caustic potash on acetamide (*Hofmann's hypobromite reaction*).

$$\underset{\text{Acetamide}}{CH_3CONH_2} + Br_2 + 4KOH \longrightarrow \underset{\text{Methylamine}}{CH_3NH_2} + 2KBr + K_2CO_3 + 2H_2O$$

(2) By heating ammonium chloride with two equivalents of formaldehyde (*formalin*) (INDUSTRIAL). The ammonia produced by dissociation of ammonium chloride reacts with two molecules of formaldehyde as follows :

$$\underset{\text{Ammonia}}{NH_3} + \underset{\substack{\text{Formaldehyde}\\ \text{(2 moles)}}}{CH_2\boxed{O + HCHO}} \longrightarrow \underset{\text{Methylamine}}{CH_3NH_2} + HCOOH$$

(3) By passing a mixture of the vapours of methyl alcohol and ammonia over heated alumina. The dimethylamine and trimethylamine produced along with methylamine are removed by fractional distillation (*Industrial*).

$$\underset{\text{Methyl alcohol}}{CH_3\,\vdots\,OH} + \underset{\text{Ammonia}}{H\,\vdots\,NH_2} \longrightarrow \underset{\text{Methylamine}}{CH_3NH_2} + H_2O$$

Laboratory Preparation. Set up the apparatus as shown in Fig. 27·1. Place 20 grams acetamide and 18 mls. bromine in the flask and then add 200 mls. of 10 per cent caustic potash solution gradually with cooling and shaking till the reaction mixture becomes deep yellow. A strong solution of caustic potash (50 gms. in 100 mls.) is warmed and introduced through the tap-funnel and the reaction mixture carefully heated to 70°. When the yellow colour is completely discharged, the contents of the flask are distilled and the condensed methylamine passing over collects in dilute hydrochloric acid. The ditillation is discontinued when the liquid coming over is no more basic to litmus. The liquid in the receiver is evaporated on a water-bath to get solid methylamine hydrochloride. If required the free amine can be recovered from it by distillation with the alkali.

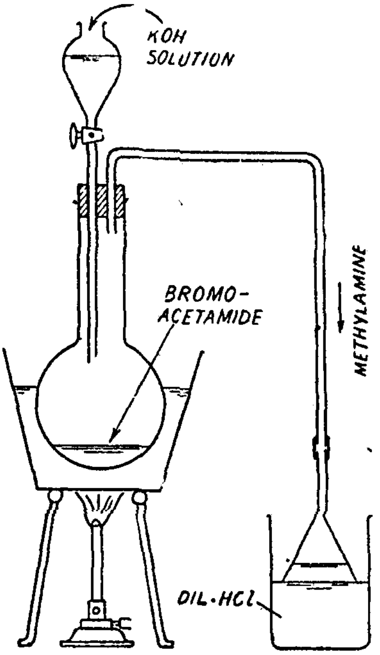


Fig. 27·1. Preparation of methylamine.

Properties. (*Physical*). Methylamine is a colourless gas with *ammonia-like but fishy odour.* Upon cooling it condenses to a liquid which boils at 6·5°. It is exceedingly soluble in water giving alkaline solution.

(*Chemical*). Chemically, it behaves as a typical primary amine and gives all the general reactions described before. It burns in air with a yellow flame. It combines with hydrochloric acid to form methylammonium chloride which is hygroscopic in nature.

Methylamine is used as a refrigerant.

Ethylamine, $C_2H_5NH_2$. Ethylamine is the second member of the homologous series of primary amines. It is produced by the putrefaction of yeast and flour.

Preparation. (1) Ethylamine is commonly prepared by the action of ethyl chloride with excess of alcoholic ammonia.

$$C_2H_5Cl + NH_3 \longrightarrow C_2H_5NH_2 + HCl$$

(2) By passing a mixture of ethylene and ammonia over heated catalyst.

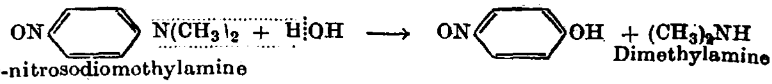
$$\begin{array}{c} H—NH_2 \\ + \\ CH_2{=}CH_2 \end{array} \longrightarrow CH_3CH_2NH_2$$

Properties. Ethylamine is a colourless liquid, b.p. 19°. It has ammonia-like odour and a bitter taste. It is highly soluble in water and burns with a yellow flame. It gives all the chemical reactions of a primary amine. It reacts with bleaching powder to form N-dichloroethylamine, $C_2H_5NCl_2$.

DIMETHYLAMINE, $(CH_3)_2NH$

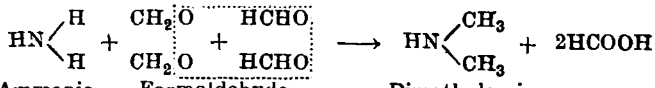
It occurs in small quantities in *Peruvian guano* and pyroligneous acid.

Preparation. (1) It can be prepared in a pure state by the hydrolysis of *p*-nitrosodiomethylaniline with caustic soda solution.



p-nitrosodiomethylamine Dimethylamine

(2) By heating ammonium chloride with four equivalents of formaldehyde (*formalin*). The ammonia dissociated from NH_4Cl reacts with four molecules of formaldehyde as follows :



$$HN{<}^{H}_{H} + \begin{matrix}CH_2O\\CH_2O\end{matrix} + \begin{matrix}HCHO\\HCHO\end{matrix} \longrightarrow HN{<}^{CH_3}_{CH_3} + 2HCOOH$$

Ammonia Formaldehyde (4 molecules) Dimethylamine

Properties. Dimethylamine is a colourless gas having ammoniacal odour. On cooling it condenses to a liquid boiling at 7°.

Chemically, it behaves as a typical secondary amine. Thus on treatment with nitrous acid it gives the oily nitrosodimethylamine.

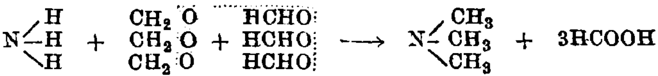
$$(CH_3)_2N\boxed{H + HO}NO \longrightarrow \underset{\text{Nitrosodiomethylamine}}{(CH_3)_2N.NO} + H_2O$$

Dimethylamine is used for dehairing hides.

TRIMETHYLAMINE, $(CH_3)_3N$

It is the simplest tertiary amine. If occurs in beet-sugar molasses and excreta of fish.

Preparation. (1) Trimethylamine is prepared by heating a mixture of ammonium chloride and paraformaldehyde.



$$N\begin{matrix}-H\\-H\\-H\end{matrix} + \begin{matrix}CH_2O\\CH_2O\\CH_2O\end{matrix} + \begin{matrix}HCHO\\HCHO\\HCHO\end{matrix} \longrightarrow N\begin{matrix}-CH_3\\-CH_3\\-CH_3\end{matrix} + 3HCOOH$$

Ammonia Formaldehyde (5 molecules) Trimethylamine

(2) It is obtained on a large scale by the destructive distillation of beet sugar molasses.

Properties. Trimethylamine is a colourless gas (b.p. 3·5°) having ammoniacal-fishy odour. Upon heating under pressure, it decomposes to form methyl chloride.

$$\underset{\text{Trimethylamine}}{(CH_3)_3N} + 4HCl \longrightarrow \underset{\text{Methyl chloride}}{3CH_3Cl} + NH_4Cl$$

Trimethylamine is used as a source of industrial methyl chloride.

QUATERNARY AMMONIUM COMPOUNDS

Tetraalkylammonium halides. They are prepared either by treating ammonia with excess of an alkyl halide, or by direct action between a tertiary amine and the alkyl halide.

$$(CH_3)_3N + CH_3I \longrightarrow [(CH_3)_4N]I$$

Trimethylamine — Tetramethylammonium iodide

They are white crystalline compounds. They are soluble in water in which they are completely dissociated.

$$[(CH_3)_4N]I \longrightarrow [(CH_3)_4N]^+ + I$$

On heating they decompose to form a tertiary amine and an alkyl halide.

$$[(CH_3)_4N]I \longrightarrow (CH_3)_3N + CH_3I$$

Trimethylamine

Tetraalkylammonium hydroxides. They are obtained by the action of moist silver oxide (AgOH) on a tetraalkylammonium halide. Thus :

$$[(CH_3)_4N]I + AgOH \longrightarrow [(CH_3)_4N]OH + AgI$$

Tetramethylammonium hydroxide

Tetraalkylammonium hydroxides are white deliquescent crystalline solids. They absorb carbon dioxide from the atmosphere, forming carbonates. They are decomposed by heat ; only tetramethylammonium hydroxide splits out a molecule of methyl alcohol and forms a tertiary amine.

$$(CH_3)_4N.OH \longrightarrow (CH_3)_3N + CH_3OH$$

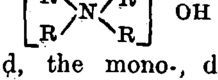
Trimethylamine

Other tetraalkylammonium hydroxides give an alkene and water.

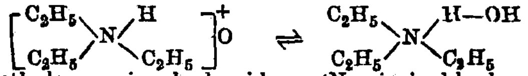
$$(C_2H_5)_4N.OH \longrightarrow (C_2H_5)_3N + C_2H_4 + H_2O$$

Triethylamine

They are very soluble in water and are as strong bases as sodium hydroxide or potassium hydroxide. Their aqueous solutions precipitate the hydroxide of the heavy metals from solutions of their salts. They are completely ionised in solutions and have the structure



On the other hand, the mono-, di- and tri-alkylammonium hydroxides formed by the combination of primary, secondary and tertiary amine respectively, are weak bases. It is due to this fact that these compounds are not wholly ionised, and mostly exist as non-ionised hydroxides. Thus :



Triethylammonium hydroxide (Non-ionised hydroxide)

DISTINCTION BETWEEN THREE CLASSES OF AMINES

The primary, secondary and tertiary amines can be distinguished from each other by noting the differences in their properties and reactions.

PRIMARY	SECONDARY	TERTIARY
(1) Basic character :— Their aqueous solutions are basic to litmus.	They are more basic than primary amines.	They are more basic than secondary amines.
(2) Action of alkyl halides :— They combine with 3 molecules of halide to from quaternary salt.	Combine with 2 molecules of halide to form quaternary salt.	Combine with one molecule of halide to form quaternary salt.
(3) Action of acyl halides :— They form mono- and also diacetyl derivatives.	Form monoacetyl derivatives only.	No action.
(4) Action of nitrous acid :— They form primary alcohols *with evolution of nitrogen.*	Form yellow oily nitrosoamines which when warmed with phenol and sulphuric acid, and then alkalified, give a deep blue colour. *No nitrogen is evolved.*	Form addition salts only.
(5) Carbylamine reaction :— When warmed with chloroform and alcoholic potash, they give the obnoxious smell of carbylamine.	No action.	No action.
(6) Mustard oil reaction :— When warmed with carbon disulphide and mercuric chloride, mustard-like smell is given.	No action.	No action.

Note : The reactions 4, 5 and 6 given above are commonly used as tests for the three classes of amines.

GOING UP AND DOWN A HOMOLOGOUS SERIES

The reactions of amines furnish methods of converting an aliphatic compound into its higher or lower homologue.

Stepping up a Series. Adding of one carbon atom—"*stepping up*" in a homologous series can be accomplished by the scheme given below :—

$$\underset{\text{Methanol}}{CH_3OH} \xrightarrow{PI_3} CH_3I \xrightarrow{KCN} CH_3CN \xrightarrow{Red.} CH_3CH_2NH_2 \xrightarrow{HNO_2} \underset{\text{Ethanol}}{CH_3CH_2OH}$$

Alternative scheme :—

$$\underset{\text{Methanol}}{CH_3OH} \xrightarrow{PI_3} CH_3I \xrightarrow{KCN} CH_3CN \xrightarrow{\textit{Hydrol.}} CH_3CO_2H \longrightarrow CH_3CHO \xrightarrow{\textit{Red.}} \underset{\text{Ethanol}}{CH_3CH_2OH}$$

Stepping down a Series. Removal of one carbon atom—"*stepping down*"—in a homologous series can be accomplished by the following scheme.

$$\underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow{\textit{Oxid.}} CH_3CO_2H \xrightarrow[NH_4\text{ salt}]{\textit{heat}} CH_3CONH_2 \xrightarrow{Br/KOH} CH_3NH_2 \xrightarrow{HNO_2} \underset{\text{Methanol}}{CH_3OH}$$

Alternative scheme :—

$$\underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow{\textit{Oxid.}} CH_3CO_2H \xrightarrow[\textit{heat}]{NaOH/CaO} CH_4 \xrightarrow{Cl_2} CH_3Cl \xrightarrow{\textit{Aq.}\,KOH} \underset{\text{Methanol}}{CH_3OH}$$

The schemes shown above run from 'alcohol to alcohol' but they also indicate the methods of ascending and descending from 'alkyl halide to alkyl halide', and from 'amine to amine'.

QUESTIONS

1. What are amines ? How would you classify them ? What are the various methods of their preparation ? Indicate their characteristic reactions.

2. What are primary, secondary and tertiary amines ? Describe the preparation and chemical properties of aromatic amines and show in what respects they differ from aliphatic amines.

3. How would you distinguish between a primary, a secondary and a tertiary amine ?

Describe the preparation and properties of tetramethylammonium hydroxide. What happens when it is heated ? Write equations.

4. Write notes on : Carbylamine reaction, Mustard Oil reaction, and Schotten-Baumann reaction.

5. How are amines prepared ? Give their chemical properties. How do you distinguish the various kinds of amines ?

6. Give an account of the properties of the primary, secondary and tertiary amines. Discuss how you would distinguish between the three classes of amines.

7. Write down the structural formulae and give the names of four amines having the molecular formula C_5H_9N. and describe how any one of them may be prepared. By what reactions could they be distinguished ?

8. How will you convert :

(*i*) a primary into a secondary amine,

(*ii*) a secondary into a tertiary amine,

(*iii*) a lower into a higher amine, and

(*iv*) a higher into a lower amine.

9. What are amines ? Give formulae for two primary, two secondary and one tertiary aliphatic amine, and name them.

Describe the method employed in separating these amines occurring together in a mixture. (*Vikram B.Sc. II, 1963*)

10. What are amines ? How would you distinguish among primary, secondary and tertiary amines ? (*Marathwada B.Sc. II, 1963*)

11. What are amines ? How would you classify and separate them ? Give the methods of their preparation and characteristic reactions. (*Poona B.Sc. III, 1963*)

12. What are amines ? How are they classified ? How can the different classes be distinguished and separated from one another? (*Aligarh B.Sc. II, 1964*)

13. Give the different methods available for the preparation of aliphatic amines. How is the separation of primary, secondary and tertiary amines effected ? (*Poona B.Sc. II, 1964*)

14. How would you separate a mixture of *n*-propylamine, diethylamine and triethylamine ? (*Panjab B.Sc. II, 1964*)

15. How do you distinguish between primary, secondary and tertiary amines ? Describe a method of separation of primary, secondary and tertiary amines from a mixture containing all of them. (*Sambalpur B.Sc., 1968*)

16. Give examples of primary, secondary and tertiary amines and discuss the action of (*a*) nitrous acid ; and (*b*) methyl iodide on them. (*Viswa Bharati B.Sc., 1969*)

17. Describe methods of synthesis of primary alkyl amines and discuss their chemical reactions. (*Marathwada B.Sc., 1969*)

18. What do you understand by the term primary, secondary and tertiary amines ? Describe at least one method by which the primary amine can be distinguished from a secondary amine. How will you convert ethyl amine into methylamine ? (*Jammu & Kashmir B.Sc., 1969*)

19. (*a*) How can primary, secondary and tertiary amines be distinguished using nitrous acid ?

(*b*) How will you proceed to separate a mixture containing ethyl alcohol, ethylamine and acetaldehyde ? (*Tribhuvan B.Sc., 1969*)

28

Cyanogen Compounds

ARTHUR HANTZSCH
(1857—1935)

German. Known for his theory regarding the stereochemistry of nitrogen and for outstanding synthetic work. He also gave his theory of chromo-isomerism-change of colour of dyes as related to structural change.

The monovalent group —CN is termed the cyanogen group and the compounds containing this group are called **cyanogen compounds**. Many of them are important synthetic reagents.

CYANOGEN, N⋮C.C⋮N

Cyanogen occurs in traces in blast furnace gases and coal gas. It was discovered by Gay Lussac in 1815.

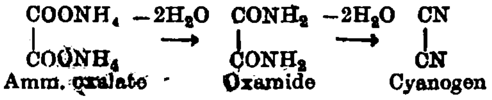
Preparation. Cyanogen may be prepared : (1) By heating mercuric cyanide in presence of mercuric chloride.

$$Hg(CN)_2 + HgCl_2 \longrightarrow \underset{\text{Cyanogen}}{C_2N_2} + Hg_2Cl_2$$

(2) By heating a solution containing copper sulphate and sodium cyanide.

$$CuSO_4 + 2NaCN \longrightarrow Cu(CN)_2 + Na_2SO_4$$
$$2Cu(CN)_2 \longrightarrow Cu_2(CN)_2 + \underset{\text{Cyanogen}}{C_2N_2}$$

(3) By heating ammonium oxalate or oxamide, with phosphorus pentoxide

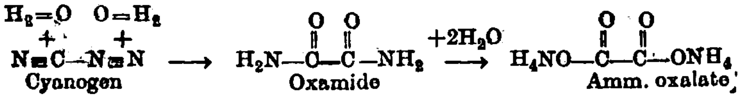


$$\underset{\text{Amm. oxalate}}{\begin{matrix}COONH_4\\|\\COONH_4\end{matrix}} \xrightarrow{-2H_2O} \underset{\text{Oxamide}}{\begin{matrix}CONH_2\\|\\CONH_2\end{matrix}} \xrightarrow{-2H_2O} \underset{\text{Cyanogen}}{\begin{matrix}CN\\|\\CN\end{matrix}}$$

This method of formation proves the constitution of cyanogen.

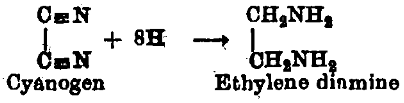
Properties. (*Physical*). Cyanogen is a colourless gas with pungent smell recalling that of bitter almonds. Liquid cyanogen boils at —21·4°. It is soluble in water and is extremely pisonous.

(*Chemical*). Cyanogen burns with a bluish-red flame. When hydrolysed with concentrated hydrochloric acid, it is converted first to oxamide and then to ammonium oxalate.



$$\underset{\text{Cyanogen}}{\begin{matrix}H_2{=}O \quad O{=}H_2\\ + \qquad\quad +\\ N{\equiv}C{-}C{\equiv}N\end{matrix}} \longrightarrow \underset{\text{Oxamide}}{H_2N{-}\overset{\overset{O}{\|}}{C}{-}\overset{\overset{O}{\|}}{C}{-}NH_2} \xrightarrow{+2H_2O} \underset{\text{Amm. oxalate}}{H_4NO{-}\overset{\overset{O}{\|}}{C}{-}\overset{\overset{O}{\|}}{C}{-}ONH_4}$$

On reduction with tin and hydrochloric acid it yields ethylene diamine.



$$\underset{\text{Cyanogen}}{\begin{matrix}C{\equiv}N\\|\\C{\equiv}N\end{matrix}} + 8H \longrightarrow \underset{\text{Ethylene diamine}}{\begin{matrix}CH_2NH_2\\|\\CH_2NH_2\end{matrix}}$$

When heated, it polymerises to a brown amorphous powder called '*paracyanogen*'.

HYDROGEN CYANIDE, HYDROCYANIC ACID, HCN

Hydrogen cyanide was first discovered by Scheele (1782) who obtained it by the hydrolysis of the gulcoside *amygdalin* present in bitter almonds.

$$\underset{\text{Amygdalin}}{C_{20}H_{27}O_{11}N} + 2H_2O \xrightarrow{acid} HCN + \underset{\text{Benzaldehyde}}{C_6H_5CHO} + \underset{\text{Glucose}}{2C_6H_{12}O_6}$$

It also occurs in the leaves of certain tropical plants and in the kernel of some fruits (peach, plum, cherry). It is a weak acid and hence its name is 'hydrocyanic acid' or *prussic acid.*

Preparation. (1) Hydrogen cyanide is prepared most conveniently in the laboratory by adding concentrated sulphuric acid to a solution of sodium cyanide.

$$NaCN + H_2SO_4 \longrightarrow HCN + NaHSO_4$$

(2) It is prepared technically by passing trimethylamine (derived from beet-sugar molasses) through fire-clay tubes heated to 1000°.

$$\underset{\text{Trimethylamine}}{(CH_3)_3N} \longrightarrow HCN + 2CH_4$$

(3) Two recently developed industrial methods are :

$$CO + NH_3 \xrightarrow[Al_2O_3]{500\text{-}700^\circ} HCN + H_2O$$

$$2NH_3 + 3O_2 + \underset{\text{Methane}}{2CH_4} \xrightarrow[Pt.]{1000^\circ} 2HCN + 6H_2O$$

(4) It may also be obtained by heating ammonium formate, or formamide, with phosphorus pentoxide.

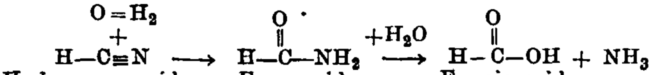
$$\underset{\text{Amm. formate}}{HCOONH_4} \xrightarrow{-H_2O} \underset{\text{Formamide}}{HCONH_2} \xrightarrow{-H_2O} \underset{\text{Hydrogen cyanide}}{HCN}$$

This mode of formation shows that hydrogen cyanide is the nitrile of formic acid (*formonitrile*).

Properties. (*Physical*). Hydrogen cyanide is a colourless volatile liquid, b.p. 26°. It has a peculiar smell like that of bitter almonds. It is miscible in all proportions with water, alcohol and ether. It is a deadly and quick-acting poison, 0 05 gram being fatal dose. Its action is said to be due to its adsorption on red blood corpuscles which at once fail to function as 'oxygen-carrier' during respiration.

(*Chemical*). Hydrogen cyanide vapours burn in air with a violet flame. Its important reactions are :

(1) HYDROLYSIS. When hydrolysed by inorganic acids, it first forms formamide and then formic acid.



$$\underset{\text{Hydrogen cyanide}}{\overset{O=H_2 \atop +}{H-C\equiv N}} \longrightarrow \underset{\text{Formamide}}{H-\overset{\overset{O}{\|}}{C}-NH_2} \xrightarrow{+H_2O} \underset{\text{Formic acid}}{H-\overset{\overset{O}{\|}}{C}-OH} + NH_3$$

Hydrogen cyanide Formamide Formic acid

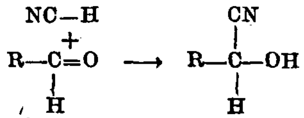
In this reaction —CN group is converted to —COOH group and hence it is often employed for the introduction of carboxyl group in organic compounds.

(2) REACTION. On reduction with nascent hydrogen it forms methylamine.

$$\underset{\text{Hydrogen cyanide}}{H-C\equiv N} + 4[H] \xrightarrow{C_2H_5OH/Na} \underset{\text{Methylamine}}{CH_3NH_2}$$

Methylamine is obtained industrially by passing a mixture of the vapours of HCN and H_2 over a metallic catalyst at 200—300°.

(3) FORMATION OF CYANOHYDRINS. It reacts with aldehydes and ketones to form cyanohydrins which are important synthetic intermediates.



$$\underset{\text{Aldehyde}}{\overset{NC-H \atop +}{R-\underset{H}{\overset{}{C}}=O}} \longrightarrow \underset{\text{Cyanohydrin}}{R-\underset{H}{\overset{CN}{C}}-OH}$$

Aldehyde Cyanohydrin

(4) FORMATION OF SALTS. Hydrogen cyanide is a very weak acid, much weaker than carbonic acid, and forms salts known as cyanides.

$$HCN + NaOH \longrightarrow \underset{\text{Sod. cyanide}}{NaCN} + H_2O$$

Sodium cyanide (or potassium cyanide) reacts with alkyl halides to form alkyl cyanides or nitriles.

$$\underset{\text{Alkyl iodide}}{RI} + KCN \longrightarrow \underset{\text{Alkyl cyanide}}{RCN} + KI$$

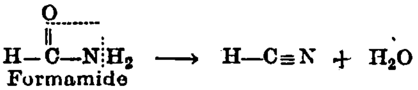
(5) CYANOGEN CHLORIDE. The hydrogen of HCN can be replaced by the action of chlorine on sodium cyanide, to form cyanogen chloride.

$$NaCN + Cl_2 \longrightarrow NaCl + \underset{\text{Cyanogen chloride}}{Cl-CN}$$

Cyanogen chloride is valuable in synthesis.

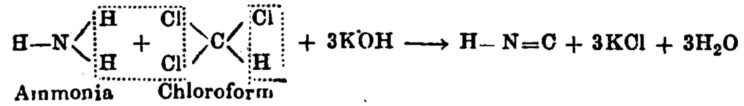
Uses. Hydrogen cyanide is used as a fumigant for destroying rats and insects ; in the metallurgy of gold and silver ; in electroplating baths ; and as a reagent in organic synthesis where formation of cyanohydrin is an intermediate step.

Structure of Hydrogen cyanide. The formation of hydrogen cyanide by dehydration of formamide shows that it has the structure $H-C\equiv N$.



$$\underset{\text{Formamide}}{H-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2} \longrightarrow H-C\equiv N + H_2O$$

(2) On the other hand, its formation by heating a mixture of ammonia, chloroform and potassium hydroxide indicates that its structure is $H-N=C$.



$$H-N{<}^{H}_{H} + {}^{Cl}_{Cl}{>}C{<}^{Cl}_{H} + 3KOH \longrightarrow H-N=C + 3KCl + 3H_2O$$

Ammonia Chloroform

But according to the electronic theory of valency, $H-N=C$ is an unstable structure and it should be written as $H-N\overset{\rightarrow}{=}C$.

(3) Therefore, it has been suggested that hydrogen cyanide is a tautomeric substance and consists of two forms in equilibrium.

$$H-C\equiv N \rightleftharpoons \underset{\text{Hydrogen isocyanide}}{H-N\overset{\rightarrow}{=}C}$$

It exists entirely as HCN form, while HNC form is present only in traces.

The existence of the two forms in hydrogen cyanide has been proved by examination of its Raman spectrum which consists of two bonds, one corresponding to that of alkyl cyanide ($R-C\equiv N$) and the other corresponding to that shown by isocyanides ($R-N\overset{\rightarrow}{=}C$). However the second bond is extremely feeble indicating that only 0·55 per cent of the isocyanide form is present.

ALKYL CYANIDES OR NITRILES, $R-C\equiv N$

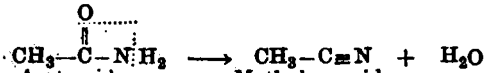
Being the alkyl derivatives of hydrogen cyanide, they are named as *alkyl cyanides*. They are also referred to as *acid nitriles*, since like other acid derivatives they form acids on hydrolysis. Thus methyl cyanide, CH_3CN, is also named as *acetonitrile* as it gives acetic acid when hydrolysed.

Methods of Preparation. (1) Alkyl cyanides are more conveniently prepared by heating potassium cyanide with alkyl halides in dilute alcoholic solutions.

$$CH_3\boxed{I + K}CN \longrightarrow CH_3CN + KI$$

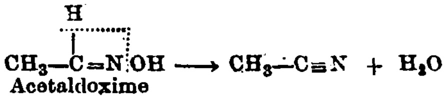
Methyl iodide Methyl cyanide

(2) By treating amides and aldoximes with strong dehydrating agents (P_2O_5 or SO_2Cl_2).



$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2 \longrightarrow CH_3-C\equiv N + H_2O$$

Acetamide Methyl cyanide

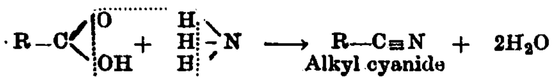


$$CH_3-\overset{\overset{\displaystyle H}{|}}{C}=N\,OH \longrightarrow CH_3-C\equiv N + H_2O$$

Acetaldoxime

This mode of formation proves the structure of alkyl cyanides.

(3) A newer industrial method consists in passing a mixture of the vapours of a carboxylic acid and ammonia over heated alumina at 500°



$$R-C\begin{cases} O \\ OH \end{cases} + \begin{matrix} H \\ H \\ H \end{matrix}\!\!>N \longrightarrow R-C\equiv N + 2H_2O$$

Acid Ammonia Alkyl cyanide

(4) By the action of Grignard reagents with cyanogen chloride.

$$R\boxed{MgCl + Cl}-CN \longrightarrow RCN + MgCl_2$$

Cyanogen chloride

General Properties. (*Physical*). The lower alkyl cyanides (up to C_{14}) are colourless liquids having a peculiar but not unpleasant odour. The higher members are crystalline solids. They are moderately soluble in water but their solubility falls with the increase of molecular weight. They are readily soluble in organic solvents. They are much less poisonous than hydrogen cyanide.

(*Chemical*). Like the acetylenic linkage, the CN triple bond in alkyl cyanides is capable of numerous addition reactions. The important reactions of alkyl cyanides are given below :

(1) HYDROLYSIS. Alkyl cyanides when hydrolysed by acids or alkalis are converted to the corresponding carboxylic acids through the intermediate formation of an amide.

$$CH_3-C\equiv N \overset{O=H_2}{+} \longrightarrow CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2$$

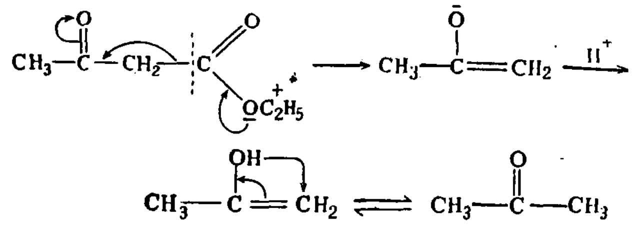
Methyl cyanide Acetamide

$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-\boxed{NH_2 + H}OH \longrightarrow CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-OH + NH_3$$

Acetamide Acetic acid

If carried out with alkaline hydrogen peroxide, the hydrolysis may be halted at the amide stage.

Mechanism :



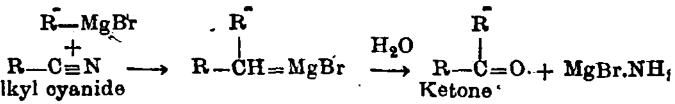
(2) REDUCTION. On reduction with sodium and alcohol, they give primary amines. (*Mendius reaction*).

$$\underset{\text{Methyl cyanide}}{CH_3-C\equiv N} + 4[H] \longrightarrow \underset{\text{Ethylamine}}{CH_3CH_2NH_2}$$

(3) STEPHEN'S REACTION. Alkyl cyanides undergo Stephen's reaction to form aldehydes.

$$\underset{\text{Alkyl cyanide}}{R-C\equiv N} \xrightarrow[SnCl_2/HCl]{2[H]} \underset{\text{Aldimine}}{R-CH{=}NH} \xrightarrow{H_2O} \underset{\text{Aldehyde}}{RCHO} + NH_3$$

(4) Action with G.R. They react with Grignard reagents to form ketones.

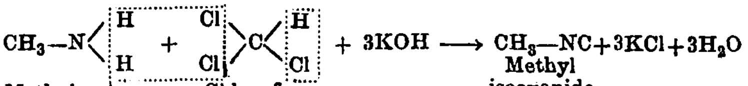


$$\underset{\text{Alkyl cyanide}}{\overset{\overset{\text{R—MgBr}}{+}}{R-C\equiv N}} \longrightarrow R-\overset{\overset{R}{|}}{C}H{=}MgBr \xrightarrow{H_2O} \underset{\text{Ketone}}{R-\overset{\overset{R}{|}}{C}{=}O} + MgBr.NH$$

ALKYL ISOCYANIDES OR CARBYLAMINES, $R-N\equiv C$

They are isomeric with alkyl cyanides and are derived from *hydrogen isocyanide*, $H-N\equiv C$. They are also called **isonitriles** or **carbylamines** since they could be thought of as derivatives of primary amines in which the H atoms of NH_2 group are replaced by a carbon.

Methods of Preparation. (1) By heating a mixture of primary amine and chloroform with alcoholic potash (*Carbylamine reaction*).



$$\underset{\text{Methylamine}}{CH_3-N\begin{matrix}H\\H\end{matrix}} + \underset{\text{Chloroform}}{\begin{matrix}Cl\\Cl\end{matrix}>C<\begin{matrix}H\\Cl\end{matrix}} + 3KOH \longrightarrow \underset{\text{Methyl isocyanide}}{CH_3-NC} + 3KCl + 3H_2O$$

This mode of formation shows that the alkyl radical in isocyanides is directly liked to N atom.

(2) By the action of an alkyl halide on silver cyanide.

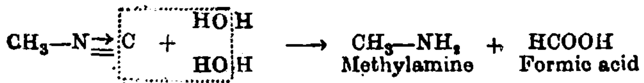
$$\underset{\text{Ethyl iodide}}{C_2H_5I} + AgCN \longrightarrow \underset{\text{Ethyl isonitrile}}{C_2H_5NC} + AgI$$

A small amount of the isomeric cyanide is also formed.

General Properties. (*Physical*). Alkyl isocyanides are colourless volatile liquid with extremely unpleasant odour. Their boiling points are lower than the isomeric cyanides. They are only slightly soluble in water and are more poisonous than the cyanides.

(*Chemical*). Isocyanides are very reactive substances and give the following reactions :—

(1) HYDROLYSIS. They are hydrolysed by dilute acids to form a primary amine and formic acid. *They are not hydrolysed by alkalis.*



$$\underset{\text{Methyl isocyanide}}{CH_3{-}N\overset{\rightarrow}{=}C} + \begin{matrix} HO\,H \\ HO\,H \end{matrix} \longrightarrow \underset{\text{Methylamine}}{CH_3{-}NH_2} + \underset{\text{Formic acid}}{HCOOH}$$

$$(Cf.\ CH_3CN + 2H_2O \longrightarrow CH_3COOH + NH_3)$$

(2) REDUCTION. When reduced with nascent hydrogen, or with hydrogen in the presence of nickel, isocyanides give secondary amines in which one of the alkyl groups is always methyl group.

$$\underset{\text{Methyl isocyanide}}{CH_3{-}N\overset{\rightarrow}{=}C} + 4H \longrightarrow \underset{\text{Dimethylamine}}{CH_3{-}NH{-}CH_3}$$

$$(Cf.\ CH_3CN + 4H \longrightarrow CH_3CH_2NH_2)$$

(3) On heating for some time at 250°, they are converted to the *isomeric cyanides.*

$$\underset{\text{Alkyl isocyanide}}{R.NC} \longrightarrow \underset{\text{Alkyl cyanide}}{R.CN}$$

It shows that alkyl cyanides are more stable than isocyanides.

(4) They readily combine with a number of substances.

$$RNC + O \longrightarrow \underset{\text{Isocyanates}}{RNCO}$$

$$RNC + S \longrightarrow \underset{\text{Isothiocyanates}}{RNCS}$$

$$RNC + Cl_2 \longrightarrow RNCCl_2$$

These reactions favour the formula $R{-}N{=}C<$ for isocyanides. The isocyanides can be distinguished from the isomeric cyanides by their repulsive odour and reactions (1) and (2) given above.

CYANIC ACID, $HN{=}C{=}O$

Cyanic acid is a tautomeric substance and exists in two forms:

$$\underset{\text{Cyanic acid}}{HO{-}C{\equiv}N} \rightleftharpoons \underset{\text{Isocyanic acid}}{HN{=}C{=}O}$$

Ordinary liquid cyanic acid is entirely the iso-form, which fact is supported by its Raman spectrum. Moreover, the alkyl derivatives of the iso-form only are known.

Preparation. Urea on distillation gives *cyanuric acid,* $(HNCO)_3$, which when heated decomposes to cyanic acid.

$$\underset{\text{Urea}}{3CO(NH_2)_2} \longrightarrow \underset{\text{Cyanuric acid}}{(HNCO)_3} + 3NH_3$$

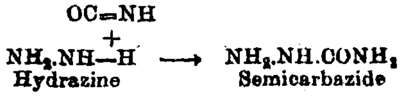
$$(HNCO)_3 \longrightarrow \underset{\text{Cyanic acid}}{3HNCO}$$

Properties. Cyanic acid is a colourless, very volatile liquid which is stable only below 0°. It has a smell like that of acetic acid. It is a very strong acid and causes blisters on the skin.

Above 0°, cyanic acid at once forms the tripolymers *cyanuric acid* and *cyamelide.* Aqueous solutions of the acid are rapidly hydrolysed to give carbon dioxide and ammonia.

$$HN{=}C{=}O + OH_2 \longrightarrow NH_3 + CO_2$$

With hydrazine, it gives semicarbazide.



$$\underset{\text{Hydrazine}}{\overset{\overset{OC{=}NH}{+}}{NH_2.NH{-}H}} \longrightarrow \underset{\text{Semicarbazide}}{NH_2.NH.CONH_2}$$

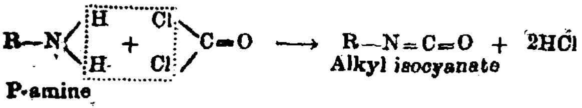
ALKYL ISOCYANATES, R.N:C:O

The alkyl derivatives of iso-form of cyanic acid are known as *alkyl isocyanates.*

Methods of Preparation. (1) By heating alkyl halides with silver cyanate.

$$\underset{\substack{\text{Methyl}\\\text{iodide}}}{CH_3I} + AgCNO \longrightarrow \underset{\substack{\text{Methyl}\\\text{isocyanate}}}{CH_3NCO} + AgI$$

(2) By the action of carbonyl chloride on primary amines.

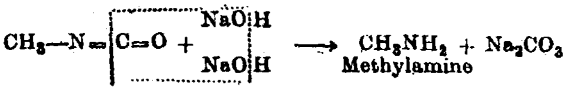


$$\underset{\text{P-amine}}{R{-}N\!\begin{cases}H\\H\end{cases}} + \begin{matrix}Cl\\Cl\end{matrix}\!\!>C{=}O \longrightarrow \underset{\text{Alkyl isocyanate}}{R{-}N{=}C{=}O} + 2HCl$$

This mode of formation proves the structure of isocyanates.

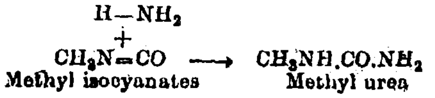
General Properties. Alkyl isocyanates are volatile liquids with exceedingly pungent odours. When impure, they tend to polymerise to trimers.

On hydrolysis with alkalis, they are decomposed to form a primary amine. Thus :

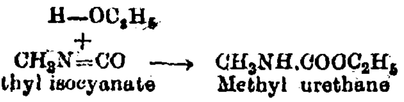


$$CH_3{-}N{=}C{=}O + \begin{matrix}NaO|H\\NaO|H\end{matrix} \longrightarrow \underset{\text{Methylamine}}{CH_3NH_2} + Na_2CO_3$$

They combine with ammonia and alcohols to give derivatives of urea and urethane, $NH_2COOC_2H_5$, respectively.



$$\underset{\text{Methyl isocyanates}}{\overset{\overset{H{-}NH_2}{+}}{CH_3N{=}CO}} \longrightarrow \underset{\text{Methyl urea}}{CH_3NH.CO.NH_2}$$



$$\underset{\text{Methyl isocyanate}}{\overset{\overset{H{-}OC_2H_5}{+}}{CH_3N{=}CO}} \longrightarrow \underset{\text{Methyl urethane}}{CH_3NH.COOC_2H_5}$$

QUESTIONS

1. Give the preparation and properties of cyanogen. Mention two of its important reactions.

2. Describe the important methods of preparing hydrogen cyanide. What happens when it is hydrolysed by acids, and reduced with nascent hydrogen ? Write its structural formula.

3. Give the general methods of preparation and reactions of alkyl cyanides.

4. What are alkyl isocyanides ? How do they differ from alkyl cyanides ?

5. Make a comparison between the following pairs of compounds as regards their mode of preparation and their reactions :—Methyl cyanide and Methyl isocyanide.

6. Describe the characteristic reactions of the following groups :

$$-CN, -CH_2OH, -NH_2, -OH, \text{ and } -CHO$$

7. How is hydrocyanic acid prepared ? What are its important properties ? Describe the action of hydrolyzing and reducing agents upon HCN.

8. What are cyanides and isocyanides ? How are they obtained ? What are the products formed when

(*a*) boiling alkaline solution ;

(*b*) hot dil. mineral acid ;

(*c*) hydrogen in presence of nickel, react with them ?

9. How is acetonitrile prepared ? What are its important properties ? (*Madras B.Sc., 1955*)

10. How are alkyl cyanides and isocyanides prepared ? How can these two be distinguished from one another ? Give equations. (*Allahabad B.Sc., 1957*)

11. Describe the methods for the preparation of alkyl cyanides and isocyanides. Describe their properties and discuss their structure. (*Punjab B.Sc., 1960*)

12. Discuss critically the structural formulae of alkyl cyanides and alkyl isocyanides. How can these classes of compounds be prepared and distinguished ? (*Patna B.Sc., 1962*)

13. Describe the general methods for the preparation of alkyl isocyanides. Discuss their constitution and properties. (*Pakistan B.Sc., 1963*)

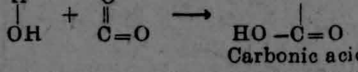
29

Derivatives of Carbonic Acid

WILLIAM A. NOYES
(1857—1941)

American. Was for years the editor of the Journal of the American Chemical Society and Head of the Chemistry department of the University of Illinois. His work includes investigation of camphor, atomic weight determination and electron theory of valency. Author of text-books in organic and general chemistry.

Carbonic acid is a unique organic acid. It is dibasic and yet contains one carbon only It is produced when carbon dioxide is passed into water



$$H-OH + O=C=O \longrightarrow HO-\overset{HO}{\overset{|}{C}}=O$$

Carbonic acid

The acid is unstable and has not been isolated in the free state. However, it forms a number of useful stable derivatives.

The anhydride of carbonic acid (CO_2) and its salts are discussed in detail in text-books of inorganic chemistry. Here we will consider only those derivatives which are analogous to the acid chlorides, acid esters and acid amides of carboxylic acids.

Carbonic acid could also be regarded as hydroxylic acid, HO.COOH. Thus some of its derivatives are named likewise :

$Cl.COOC_2H_5$	Ethyl chloroformate
$Cl.CONH_2$	Chloroformamide

CARBONYL CHLORIDE, $COCl_2$

Carbonyl chloride is the diacid chloride of carbonic acid. It is popularly known as **phosgene** (Gk. *phos* = light ; L. *genere* = born), since Davy discovered it in 1812 by exposing a mixture of carbon monoxide and chlorine to light.

Preparation. (1) Carbonyl chloride is prepared on a large scale by the action of carbon monoxide on chlorine in the presence of activated charcoal (catalyst) at 200°.

$$CO + Cl_2 \xrightarrow{C,\ 200^\circ} \underset{\text{Carbonyl chloride}}{COCl_2}$$

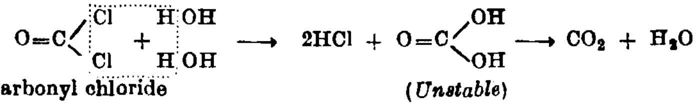
(2) It is also formed by the oxidation of chloroform in air and light.

$$\underset{\text{Chloroform}}{CHCl_3} + O \longrightarrow COCl_2 + HCl$$

Properties. Carbonyl chloride is a colourless gas (b.p. 80°) having an odour resembling that of new-mown hay. It is highly poisonous. It readily dissolves in benzene and toluene.

Carbonyl chloride gives all the reactions typical of acid chlorides. Thus :

(1) *Hydrolysis.* It is slowly decomposed by water to form carbon dioxide and hydrogen chloride.

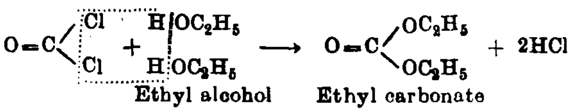


$$\underset{\text{Carbonyl chloride}}{O{=}C\begin{smallmatrix}Cl\\Cl\end{smallmatrix}} + \begin{smallmatrix}H\,OH\\H\,OH\end{smallmatrix} \longrightarrow 2HCl + \underset{(\textit{Unstable})}{O{=}C\begin{smallmatrix}OH\\OH\end{smallmatrix}} \longrightarrow CO_2 + H_2O$$

(2) *Alcoholysis.* It reacts with alcohols to form esters known as chloroformates. Thus :

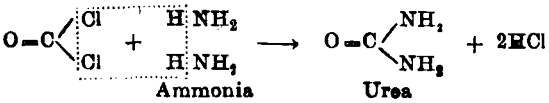
$$\underset{(\textit{excess})}{Cl.CO\,Cl} + \underset{\text{Ethyl alcohol}}{H\,OC_2H_5} \longrightarrow \underset{\text{Ethyl chloroformate}}{Cl.COOC_2H_5} + HCl$$

However, with excess of alcohol and in the presence of pyridine it yields a diester.



$$O{=}C\begin{smallmatrix}Cl\\Cl\end{smallmatrix} + \underset{\text{Ethyl alcohol}}{\begin{smallmatrix}H\,OC_2H_5\\H\,OC_2H_5\end{smallmatrix}} \longrightarrow \underset{\text{Ethyl carbonate}}{O{=}C\begin{smallmatrix}OC_2H_5\\OC_2H_5\end{smallmatrix}} + 2HCl$$

(3) *Ammonolysis.* It reacts with ammonia to form urea.



$$O{=}C\begin{smallmatrix}Cl\\Cl\end{smallmatrix} + \underset{\text{Ammonia}}{\begin{smallmatrix}H\,NH_2\\H\,NH_2\end{smallmatrix}} \longrightarrow \underset{\text{Urea}}{O{=}C\begin{smallmatrix}NH_2\\NH_2\end{smallmatrix}} + 2HCl$$

With primary or secondary amines, carbonyl chloride gives substituted ureas.

Uses. Carbonyl chloride has been used as a *war gas*. It is employed for the preparation of Michler's ketone which is an important dye intermediate. In general carbonyl chloride is used in organic synthesis for the introduction of the carbonate radical in other substances.

Chloroformic acid, *Chlorocarbonic acid*, Cl.CO.OH. It is the mono-acid chloride of carbonic acid. It is unstable but its esters are known. They are prepared by the action of excess of carbonyl chloride with alcohols as described above. Ethyl chloroformate is a colourless liquid, b.p. 94°. It behaves chemically both as an acid chloride and as an ester. It reacts with ammonia to form urethane. It is used for the synthesis of ethyl esters by action with Grignard reagents.

ETHYL CARBONATE, $(C_2H_5O)_2CO$

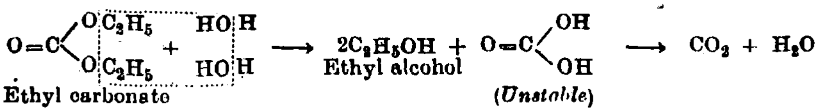
It is a typical carbonate ester. It is prepared by heating carbonyl chloride with excess of ethyl alcohol in the presence of pyridine.

$$COCl_2 + 2C_2H_5OH \longrightarrow \underset{\text{Ethyl carbonate}}{CO(OC_2H_5)_2} + 2HCl$$

It can also be obtained by boiling silver carbonate with ethyl iodide.

$$Ag_2CO_3 + 2C_2H_5I \longrightarrow \underset{\text{Ethyl carbonate}}{(C_2H_5)_2CO_3} + 2AgI$$

Ethyl carbonate is a colourless, sweet-smelling liquid, b.p. 126°. It is insoluble in water but gradually reacts with it to form alcohol and carbon dioxide.



It is used for the introduction of $-CO_2R$ group in organic compounds.

Carbamic acid, *Aminoformic acid*, NH_2COOH. It is the mono-amide of carbonic acid. It does not exist in stable condition but its salts and esters are known.

Ammonium carbamate, $NH_2CO.ONH_4$. It is prepared by the direct combination of dry ammonia and carbon dioxide.

$$2NH_3 + CO_2 \longrightarrow NH_2.CO.ONH_4$$

It is a white crystalline solid, very soluble in water. When warmed with water, it yields ammonium carbonate.

$$NH_2COONH_4 + H_2O \longrightarrow (NH_4O)_2CO$$

Urethanes. The esters of carbamic acid are known as urethanes. The ethyl ester of the acid or 'urethane' is prepared by the action of ammonia on ethyl chloroformate.

$$\underset{\text{Ammonia}}{H_2N\boxed{H + Cl}}COOC_2H_5 \longrightarrow \underset{\text{Urethane}}{NH_2.COOC_2H_5} + HCl$$

Urethane is a crystalline solid, m.p. 50°. It is soluble in water, alcohol and ether. It is a valuable hypnotic.

UREA, CARBAMIDE, $NH_2.CO.NH_2$

It is the diamide of carbonic acid or *carbamide.* In 1773 Roulle for the first time isolated urea from urine and hence its name. Urea is the chief vehicle of nitrogen excretion in man and mammals, being formed by decomposition of proteins and excreted in urine. It was the first organic compound to be synthesised, from an inorganic source (Wohler, 1828) and was of historical importance in overthrowing the 'Vital force theory'.

Preparation. (1) *From Urine.* Concentrated urine is mixed with a hot solution of oxalic acid. The sparingly soluble urea oxalate, $2CO(NH_2)_2.H_2C_2O_4$, separates as crystals which are filtered off. These are then boiled with an aqueous suspension of calcium carbonate, which liberates urea and throws down insoluble calcium oxalate. The calcium oxalate is removed by filtration and the solution of urea is evaporated to dryness on a water-bath. The residue is finally recrystallised from alcohol to give pure crystalline urea.

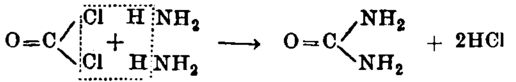
(2) *Wohler's synthesis.* Wohler synthesised urea first by heating a solution of potassium cyanate and ammonium sulphate. The reaction takes place in two steps :

$$2KCNO + (NH_4)_2SO_4 \longrightarrow K_2SO_4 + \underset{\text{Amm. cyanate}}{2NH_4CNO}$$

$$NH_4.CNO \longrightarrow \underset{\text{Urea}}{NH_2.CO.NH_2}$$

This method is of historical interest only.

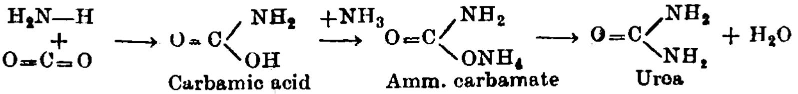
(3) In the laboratory urea can be prepared readily by the action of ammonia on carbonyl chloride.



$$O{=}C\begin{matrix}Cl\;\;H\,NH_2\\ + \\ Cl\;\;H\,NH_2\end{matrix} \longrightarrow O{=}C\begin{matrix}NH_2\\ NH_2\end{matrix} + 2HCl$$

Carbonyl chloride Urea

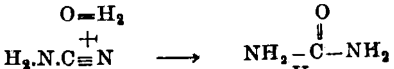
(4) A recent method of the manufacture of urea consists in allowing liquid ammonia and liquid carbon dioxide to react to form ammonium carbonate which on heating to 150° under pressure yields urea.



$$\begin{matrix}H_2N{-}H\\ +\\ O{=}C{=}O\end{matrix} \longrightarrow O{=}C\begin{matrix}NH_2\\ OH\end{matrix} \xrightarrow{+NH_3} O{=}C\begin{matrix}NH_2\\ ONH_4\end{matrix} \longrightarrow O{=}C\begin{matrix}NH_2\\ NH_2\end{matrix} + H_2O$$

Carbamic acid Amm. carbamate Urea

(5) Urea is also prepared industrially by the partial hydrolysis of cyanamide in feebly acid solution.



$$\begin{matrix}O{=}H_2\\ +\\ H_2.N.C{\equiv}N\end{matrix} \longrightarrow NH_2{-}\overset{\overset{O}{\|}}{C}{-}NH_2$$

Cyanamide Urea

The old method of making urea by hydrolysis of calcium cyanamide is now obsolete.

Properties. (*Physical*). Urea forms long colourless needles, m.p. 133°. It is very soluble in water and alcohol, but insoluble in ether. Its aqueous solutions are neutral to litmus. It has a cooling taste.

(*Chemical*). Urea gives the usual reactions of a diamide, since its molecule consists of two amide groups, the CO group being held in common. But the single carboxyl group is not able to suppress completely the basic character of both the amino groups. Therefore, in certain respects, NH_2CONH_2, also behaves like amines.

(1) ACTION OF HEAT. When urea is heated gently, two molecules of it split out a molecule of ammonia to form *Biuret*.

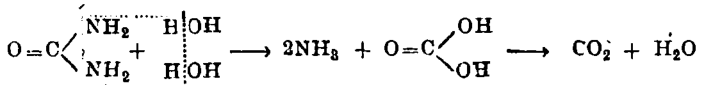
$$\underset{\text{Urea (2 molecules)}}{NH_2CO.NH\vdots H + NH_2\vdots CO.NH_2} \longrightarrow \underset{\text{Biuret}}{NH_2.CO.NH.CO.NH_2} + NH_3$$

When dissolved in dilute sodium hydroxide solution and treated with a drop of copper sulphate solution, a violet coloration is produced (*Biuret reaction*). This reaction is given by urea and all other compounds containing the grouping $—CO.NH_2$.

(2) FORMATION OF SALTS. Urea behaves as a monoacid base and forms well-defined crystalline salts with acids such as nitric acid and oxalic acid.

$$\underset{\text{Urea nitrate}}{NH_2.CO.NH_2.HNO_3} \qquad \underset{\text{Urea oxalate}}{2CO(NH_2)_2.H_2C_2O_4}$$

(3) HYDROLYSIS. Like other amides urea is hydrolysed by boiling with acids or alkalis.

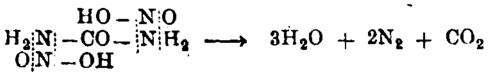


Urea Unstable

or $CO(NH_2)_2 + 2H_2O \longrightarrow 2NH_3 + CO_2 + H_2O$

The enzyme *urease* (obtainable from soyabeans) also causes the above change quantitatively. The ammonia evolved can be easily estimated volumetrically and hence this reaction is used for the accurate determination of urea in solutions.

(4) ACTION OF NITROUS ACID. Urea is decomposed by nitrous acid with liberation of nitrogen.

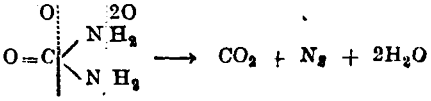


$$\begin{array}{l} \quad HO-N\vdots O \\ H_2\vdots N\vdots -CO-\vdots N\vdots H_2 \\ \; O\vdots N-OH \end{array} \longrightarrow 3H_2O + 2N_2 + CO_2$$

This reaction is employed to destroy nitrous acid in analytical works.

(5) ACTION OF ALKALINE HYPOBROMITE. When treated with alkaline solution of potassium or sodium hypobromite, urea is oxidised to form carbon dioxide, nitrogen and water.

$$\underset{\text{Sod. hypobromite}}{3NaBrO} \longrightarrow 3NaBr + 3O$$



The excess of alkali dissolves carbon dioxide, leaving the only gaseous product nitrogen which can be collected and measured. Thus, this reaction is also used for the estimation of urea.

(6) ACTION OF ACID CHLORIDES. Acid chlorides and acid anhydrides react with urea to form acid derivatives known as ureides. Thus :

$$CH_3CO\vdots Cl + H\vdots NHCONH_2 \longrightarrow CH_3CO.NHCONH_2 + HCl$$

Acetyl chloride Urea Acetylurea

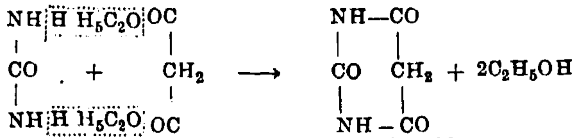
Here urea acts as an amine.

(7) ACTION WITH HYDRAZINE. Urea reacts with hydrazine to form semicarbazide which is used as a reagent for the identification of aldehydes and ketones.

$$NH_2CO\vdots NH_2 + H\vdots NH.NH_2 \longrightarrow NH_2CONH.NH_2 + NH_2$$

Urea Hydrazine Semicarbazide

(8) FORMATION OF RING COMPOUNDS. Urea reacts with many other compounds to form cyclic *ureides*. Thus with malonic ester it gives malonyl urea or *barbituric acid.*



Urea Malonic ester Barbituric acid

Uses. Urea is used : (1) as a fertilizer ; (2) for making formaldehyde-urea plastics which are light and unbreakable (in medicine as diuretic and for making barbiturates which are excellent hypnotics ; (4) as a stabiliser for explosive (nitrocellulose) ; and (5) for making hydrazine by action with sodium hypochlorite (Hofmann's reaction).

Tests. (1) Upon heating with sodium hydroxide solution, urea produces ammonia.

(2) On adding sodium nitrite to a solution of urea in dilute hydrochloric acid, nitrogen is given out.

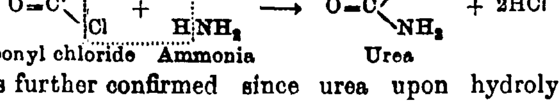
(3) On dry heating urea in a test-tube, ammonia is evolved.

The residue is dissolved and the solution alkalified with a few drops of sodium hydroxide, then dilute copper sulphate solution is added to it. A violet colour shows the presence of urea. (**Biuret test**).

(4) On addition of nitric acid to a concentrated solution of urea, white crystalline urea nitrate separates.

Structure. (1) The molecular formula of urea has been determined to be CON_2H_4.

(2) Its synthesis from carbonyl chloride and ammonia indicates that urea has the symmetrical diamide formula.



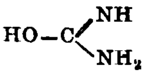
Carbonyl chloride Ammonia Urea

This is further confirmed since urea upon hydrolysis forms ammonia.

(3) Urea combines with one molecule of nitric acid or hydrochloric acid to form salts, which shows that it is a monoacid base.

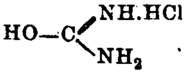
This behaviour is incompatible with the amide formula since amides do not form salts with acids. Furthermore, a peculiar feature of urea salts is that only one molecule of monobasic acid is present e.g., $CO(NH_2)_2.HCl$.

(4) To explain away point (3) Chattaway proposed another structure for urea :



$$HO-C\begin{matrix}\nearrow NH \\ \searrow NH_2\end{matrix}$$

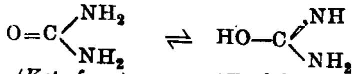
Since the imido group, $=NH$, is strongly basic, the above formula can yield salts with one molecule of monobasic acid :



$$HO-C\begin{matrix}\nearrow NH.HCl \\ \searrow NH_2\end{matrix}$$

(5) The Raman spectrum of urea shows the presence of $-C=N$ group in urea molecule, while X-ray examination of its crystals points to the symmetrical amide formula.

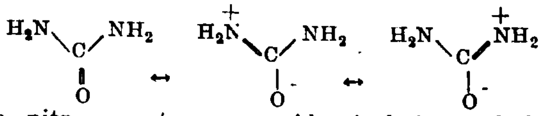
(6) In view of the conflicting evidence it appears that urea is a tautomeric substance and consists of two forms in equilibrium.



$$O=C\begin{matrix}\nearrow NH_2 \\ \searrow NH_2\end{matrix} \rightleftharpoons HO-C\begin{matrix}\nearrow NH \\ \searrow NH_2\end{matrix}$$

(*Keto form*) (*Enol form*)

Now it is believed that urea is a resonance hybrid :



Both the nitrogen atoms are identical in the hybrid molecule. Further, the negatively charged oxygen atom is capable of co-ordinating with one proton (H^+) and thus forming 'monoacid salts'. The resonance of urea explains satisfactorily its dual behaviour.

Estimation of Urea. The estimation of urea in urine or in other physiological specimens can be done by two methods.

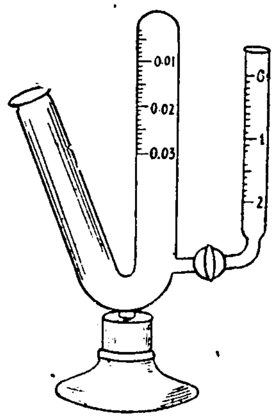


Fig. 29·1. Doemus Hinds Ureometer.

(1) HYPOBROMITE METHOD. In this method urea is decomposed by means of alkaline sodium hypobromite solution (*see* reaction 5 of urea) and the volume of nitrogen evolved measured.

The estimation is carried in an apparatus known as Ureometer (Fig. 29·1). The large central tube is filled with freshly prepared hypobromite solution (10g NaOH/25 mls. H_2O+25 mls. Br_2), while the sample of urine under examination is put in the narrow side-tube. Now 1 ml. of urine is introduced into the large tube by opening the tap. Nitrogen begins to be evolved. When the decomposition is complete, the volume of gas collected is read off. The wide tube is so graduated as to give directly the weight of urea per ml. of the sample of urine.

The hypobromite method is not strictly accurate.

(2) UREASE METHOD. This is the modern method of estimation of urea. Here urea is hydrolysed by the enzyme *urease* (*see* reaction 3 of urea) and the ammonia evolved determined volumetrically.

The apparatus for the purpose consists of three washing test-tubes as shown in Fig. 29 2. The test-tube A contains water which removes any ammonia from the air drawn through the apparatus 25 mls of urine. 5 grams of powdered soyabean and a little liquid paraffin (*to prevent frothing*) is placed in the test-tube *B* which is warmed by immersion in hot water. After allowing the mixture to stand for 15 minutes, a current of air is aspirated from A to C. The ammonia evolved in test-tube B is thus swept into the test-tube C where it is absorbed in the standard acid. This is continued for an hour. Then 5 grams of potassium carbonate are added to the test-tube B in order to decompose any ammonium carbonate formed in it. The ammonia produced is again conveyed to test-tube C by a current of air and absorbed in the acid. Finally the apparatus is disconnected and the acid back-titrated against standard alkali in order to know the amount of ammonia evolved during the reaction. Knowing the amount of ammonia, we can at once calculate the amount of urea present in 25 mls. of urine with the help of the equation,

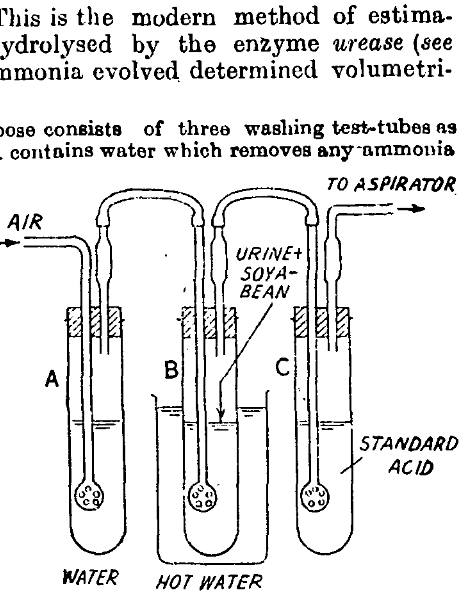


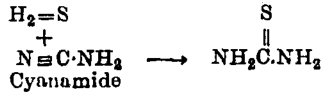
Fig. 29·2. Estimation of urea by the Urease method.

$$\underset{\text{Urea}}{CO(NH_2)_2} + H_2O \longrightarrow CO_2 + \underset{\text{Ammonia}}{2NH_3}$$

The Urease method of estimation of urea is convenient and accurate as compared to the hypobromite method.

Thiourea, *Thiocabamide,* $(NH_2)_2C{:}S$. It is prepared by a method similar to Wohler's synthesis of urea, by heating ammonium thiocyanate at 170°.

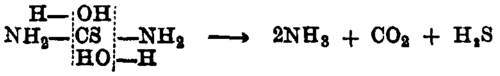
$$NH_4CNS \longrightarrow \underset{\text{Thiourea}}{NH_2.CS.NH_2}$$



$$\begin{matrix} H_2{=}S \\ + \\ N{\equiv}C{\cdot}NH_2 \end{matrix} \longrightarrow \overset{\overset{S}{\|}}{NH_2C.NH_2}$$

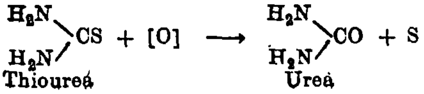
Cyanamide

Properties. Thiourea is a white crystalline solid, m.p. 180°. It is moderately soluble in water. When heated with dilute acids or alkalis, it is hydrolysed



$$\begin{matrix} & H\text{—}\vdots OH\vdots & \\ NH_2\text{—}\vdots & CS & \vdots\text{—}NH_2 \\ & \vdots HO\vdots\text{—}H & \end{matrix} \longrightarrow 2NH_3 + CO_2 + H_2S$$

On oxidation with alkaline permanganate, thiourea reverts to urea.



$$\begin{matrix} H_2N \\ H_2N \end{matrix}\!\!>\!CS + [O] \longrightarrow \begin{matrix} H_2N \\ H_2N \end{matrix}\!\!>\!CO + S$$

Thiourea Urea

Uses. Thiourea is used to protect wool and furs from pests. It is also used in making plastics and as a reagent for the estimation of lead and cadmium.

QUESTIONS

1. Describe the preparation and properties of carbonyl chloride. Mention the chief uses of the compound.

2. Why urea is called carbamide ? Describe the products obtained by the action of following reagents on urea :

(*a*) Nitrous acid ; (*b*) Caustic soda ; and (*c*) Bromine in caustic soda.

3. Give an account of the constitution and distinguishing properties of urea. How would you prepare a specimen of this substance (*a*) synthetically, (*b*) from a natural source ?

4. Describe Wohler's synthesis of urea. Write equations. Explain the changes which are induced in urea by (*a*) heat, (*b*) nitrous acid, (*c*) aqueous alkalis, (*d*) nitric acid. (*Gauhati B.Sc., 1955*)

5. How is urea manufactured ? Discuss the constitution assigned to the compound. What is the action of (*i*) nitrous acid, (*ii*) alkaline hypobromite, and (*iii*) malonic ester on urea. (*Nagpur B.Sc., 1957*)

6. How is urea prepared commercially ? How will you direct its presence ? Discuss also the constitution of urea. (*Rajasthan B.Sc., 1959*)

7. How is urea manufactured ? Describe the action of (*a*) heat, (*b*) nitrous acid, (*c*) malonic ester on urea.

0·4 gm. of a sample of impure urea on treatment with alkaline sodium hypobromite gave 112·0 c.c. of nitrogen at N.T.P. Calculate the purity of the urea. [*Answer* 75%] (*Delhi B.Sc., 1960*)

8. Discuss the constitution of Uric acid. Give its synthesis from urea and ethyl cyanoacetate. Show the inter-relationship that exists amongst the members of the purine group. (*Sardar Vallabhbhai B.Sc., 1961*)

9. Discuss fully the constitution of Uric acid. (*Patna B.Sc., 1961*)

10. How is urea obtained on a large scale ? State its important uses. How does it react with (*a*) Sodium hydroxide, (*b*) Nitric acid, (*c*) Nitrous acid and (*d*) alkaline hypochlorite ? (*Kalyani B.Sc. II, 1967*)

30

Aliphatic Diazo Compounds

HOMER ADKINS
(1892—1949)
American. His main interest was in the fields of the catalysis and organic synthesis. Co-author of both text and laboratory manual of organic chemistry. Professor of Chemistry in the University of Wisconsin.

The aliphatic diazo compounds are characterised by the presence of the group $>CN_2$. The type formula for these compounds is R_2CN_2.

DIAZOMETHANE, CH_2N_2

It is the simplest and the best known representative of the class.

Preparation. Diazomethane is obtained in excellent yield by distilling N-nitrosomethylurea with aqueous potassium hydroxide. The N-nitrosomethylurea needed for the reaction is produced by adding sodium nitrite to an aqueous solution of methylamine hydrochloride containing urea (*Arndt and Amende, 1930*).

$$\underset{\text{Urea}}{NH_2.CO.NH|H} + \underset{\substack{\text{Methylammonium-}\\ \text{chloride}}}{ClH_3N|CH_3} \xrightarrow{\text{heat}} \underset{\text{N-Methylurea}}{NH_2.CO.NH.CH_3} + NH_4Cl$$

$$NH_2.CO.NH.CH_3 + \underset{\text{Nitrous acid}}{HONO} \longrightarrow \underset{\text{N-Nitrosomethylurea}}{NH_2.CO.N(NO).CH_3} + H_2O$$

$$NH_2.CO.N(NO).CH_3 + KOH \longrightarrow \underset{\text{Diazomethane}}{CH_2N_2} + KCNO + 2H_2O$$

Properties. Diazomethane is a yellow, highly toxic gas. Liquid substance boils at —24°. It is neutral and soluble in ether. Since it explodes even in the gaseous state at low temperatures, it is handled in ether solution for carrying various synthetic reactions.

Diazomethane is an unstable but very reactive compound. It decomposes readily as indicated below :

$$CH_2N_2 \longrightarrow CH_2 : + N_2$$

The methylene group thus produced as intermediate polymerizes to give higher alkanes, $-(CH_2)_x-$. Diazomethane gives two types of synthetic reactions :

(*i*) in which nitrogen is lost ; and

(*ii*) in which nitrogen is retained.

Reactions in which N_2 is lost

Diazomethane reacts with a substance containing an active H atom to form its methyl derivative which is accompanied by evolution of nitrogen gas. Thus :

$$HCl + \underset{\text{Diazomethane}}{CH_2N_2} \longrightarrow \underset{\text{Methyl chloride}}{CH_3Cl} + N_2$$

$$\underset{\text{Alcohol}}{ROH} + CH_2N_2 \longrightarrow \underset{\text{Methyl ether}}{R.O.CH_3} + N_2$$

$$\underset{\text{Amine}}{RNH_2} + CH_2N_2 \longrightarrow \underset{\text{Methyl amine}}{R.NH.CH_3} + N_2$$

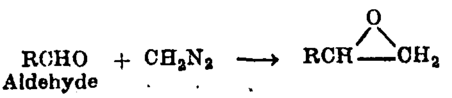
$$\underset{\text{Aldehyde}}{RCHO} + CH_2N_2 \longrightarrow \underset{\text{Methyl ketone}}{R.CO.CH_3} + N_2$$

$$\underset{\text{Acid}}{RCOOH} + CH_2N_2 \longrightarrow \underset{\text{Methyl ester}}{RCOOCH_3} + N_2$$

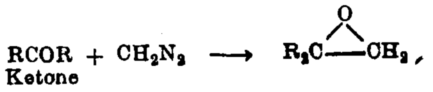
$$\underset{\text{Amide}}{RCONH_2} + CH_2N_2 \longrightarrow \underset{\text{N-Methylamide}}{RCONHCH_3} + N_2$$

Obviously diazomethane is a very useful methylating agent.

Aldehydes and ketones also react with diazomethane to form ethylene oxide derivatives. Thus :



$$\underset{\text{Aldehyde}}{RCHO} + CH_2N_2 \longrightarrow \overset{\quad O}{RCH\!-\!\!-\!CH_2}$$



$$\underset{\text{Ketone}}{RCOR} + CH_2N_2 \longrightarrow \overset{\quad O}{R_2C\!-\!\!-\!CH_2},$$

Reactions in which N_2 is retained

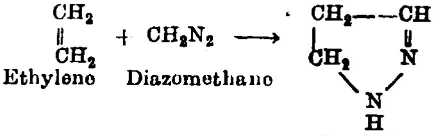
(*i*) Diazomethane reacts with acid chlorides (aliphatic or aromatic to form *diazoketones* which upon warming with water in the presence of a silver catalyst give carboxylic acids.

$$\underset{\text{Acid chloride}}{R.COCl} + \underset{\text{Diazomethane}}{2CH_2N_2} \longrightarrow \underset{\text{Diazoketone}}{R.CO.CHN_2} + CH_3Cl + N_2$$

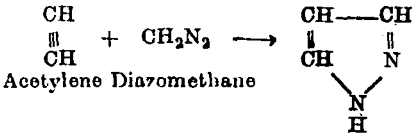
$$R.CO.CHN_2 + H_2O \xrightarrow{\text{Ag. cat.}} \underset{\text{Higher acid}}{R.CH_2.COOH} + N_2$$

Since the acid produced contains one carbon more than the original acid, it provides an excellent method to convert a given acid into the next higher homologue.

(2) *Formation of Heterocyclic compounds.* Diazomethane adds on ethylene and acetylene to form *pyrazoline* and *pyrazole* respectively.



Pyrazoline

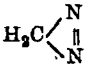


Pyrazole

(3) *Reduction.* When reduced with sodium amalgam, diazomethane gives methylhydrazine.

$$\underset{\text{Diazomethane}}{CH_2N_2} + 4H \longrightarrow \underset{\text{Methyl hydrazine}}{CH_3.NH.NH_2}$$

Structure. The two structural formulae suggested for diazomethane are :



$CH_2{=}N{\equiv}N$

(Curtius, 1889) (Angeli, 1907)

Boersh (1935) has shown by electron diffraction studies that the diazomethane molecule is linear. It is best represented as a resonance hybrid.

$$CH_2{=}\overset{+}{N}{=}\overset{-}{\ddot{N}}: \leftrightarrow \overset{-}{\ddot{C}}H_2{-}\overset{+}{N}{\equiv}N:$$

DIAZOACETIC ESTER, ETHYL DIAZOACETATE, $CHN_2.COOC_2H_5$

It can be prepared conveniently by reaction between cooled solutions of the hydrochloride of ethyl glycine and sodium nitrite.

$$\underset{\substack{\text{Ethyl glycine}\\ \text{hydrochloride}}}{ClNH_3\,CH_2COOC_2H_5} + NaNO_2 \longrightarrow \underset{\text{Diazoacetic ester}}{CHN_2.COOC_2H_5} + NaCl + 2H_2O$$

Properties. Diazoacetic ester is a yellow oil, b.p. 141°. It is insoluble in water but soluble in alcohol and ether. Its chemical reactions are exactly similar to those of diazomethane.

Diazoacetic ester is a relatively unstable substance. It undergoes decomposition slowly at ordinary temperatures but on heating the decomposition takes place explosively:

Reactions in which N_2 is lost

Diazoacetic ester reacts with substances containing an active H-atom but less vigorously than diazomethane. Thus :

$$\underset{}{HCl} + \underset{\text{Diazoacetic ester}}{N_2CHCOOC_2H_5} \xrightarrow[\text{(warm)}]{\text{(Conc. HCl)}} \underset{\text{Ethyl chloroacetate}}{CH_2Cl.COOC_2H_5} + N_2$$

$$HOH + N_2CHCOOC_2H_5 \xrightarrow[\text{(boil)}]{\text{(Dil. HCl)}} \underset{\text{Ethylglycollate}}{CH_2OH.COOC_2H_5} + N_2$$

$$\underset{\text{Alcohol}}{ROH} + N_2CHCOOC_2H_5 \longrightarrow \underset{\text{Ethyl alkoxyacetate}}{R.O.CHCOOC_2H_5} + N_2$$

$$\underset{\text{Acid}}{RCOOH} + N_2CHCOOC_2H_5 \longrightarrow \underset{\text{Ethyl acylglycollate}}{RCO.O.CH_2.COOC_2H_5} + N_2$$

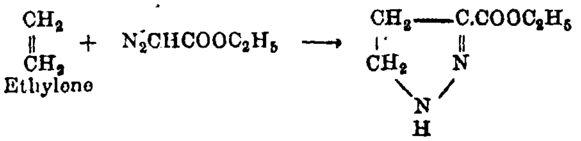
$$I_2 + N_2CHCOOC_2H_5 \longrightarrow \underset{\text{Ethyl diiodoacetate}}{CHI_2COOC_2H_5} + N_2$$

On heating a solution of diazoacetic ester in ligroin in presence of a copper powder catalyst, diethyl fumarate is produced.

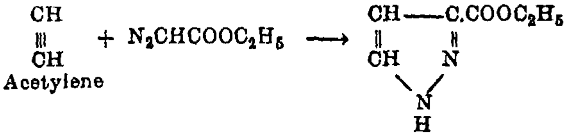
$$\underset{\text{Diazoacetic ester}}{2N_2CHCOOC_2H_5} \longrightarrow \underset{\text{Diethyl fumarate}}{C_2H_5OOCCH{=}CHCOOC_2H_5} + 2N_2$$

Reactions in which N_2 is retained

(1) FORMATION OF HETEROCYCLIC COMPOUNDS. Diazoacetic ester adds on ethylene and acetylene to form heterocyclic carboxylic esters.

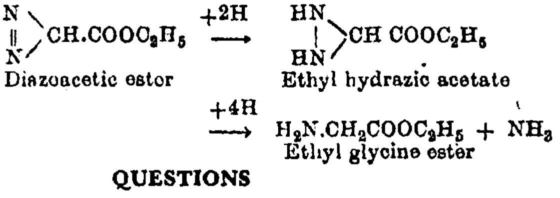


Ethyl pyrozoline-3-carboxylate



Ethyl pyrazole-3-carboxylate

(2) REDUCTION. Upon reduction with zinc and acetic acid, diazoacetic ester forms ammonia and glycine ester.



QUESTIONS

1. What are aliphatic diazo compounds ? Write the type formula of this class of compounds.

2. Describe the synthetic reactions of diazomethane with special reference to methylation.

3. Discuss briefly the uses of diazomethane as an organic reagent. *(Ceylon B.Sc., 1968)*

4. Describe the preparation and reactions of diazomethane. Discuss its structure *(Kurukshetra B.Sc., 1969)*

31

Cycloalkanes

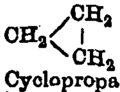
M. Gomberg
(1866 – 1947)
American. Worked with Baeyer and with Victor Meyer ; he synthesised tetraphenylmethane. Later obtained triphenylmethyl as a result of his work on synthesis of hexaphenylethane; was for many years Professor of Organic Chemistry at the Michigan University.

So far we have studied the open-chain carbon compounds only. There are a large number of compounds known which contain rings of carbon atoms and yet bear a close resemblance to the aliphatic compounds in behaviour. These are known as **alicyclic** compounds (*ali*, from aliphatic+*cyclic* = *alicyclic*).

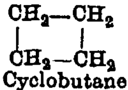
There are a variety of alicyclic compounds known but we will discuss in this chapter the saturated alicyclic hydrocarbons only.

The Cycloalkanes

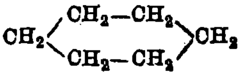
The saturated alicyclic hydrocarbons are named as *cycloalkanes* or *cycloparaffins*. Since they contain a number of methylene groups joined together to form a ring, they are also named as the **polymethylenes**, the number of carbon atoms comprising the ring being indicated by a Greek or Latin prefix. For example,



Cyclopropane,
Trimethylene



Cyclobutane,
Tetramethylene



Cyclohexane,
Hexamethylene

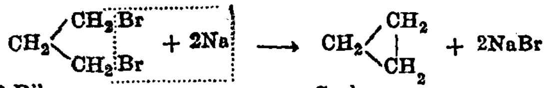
Cycloalkanes have the general formula C_nH_{2n} which is the same as for alkenes. They do not contain a double bond and yet have two hydrogen atoms less than the corresponding open-chain alkanes as a consequence of the ring structure.

Five and six-membered cycloalkanes occur in natural petroleum and are often referred to as *naphthenes.*

METHODS OF FORMATION

Cycloalkanes can be prepared by the following general methods :—

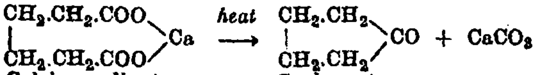
(1) **Action of sodium on dibromoalkanes** (*Freund's method*). The dibromoalkanes having the bromine atoms at the terminal carbon atoms when treated with sodium (or zinc) form cycloalkanes. Thus :



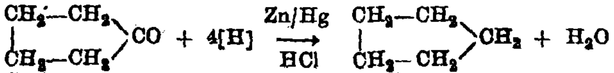
1, 3-Dibromopropane Cyclopropane

This method is really an extension of Wurtz reaction.

(2) **Heating of cyclic Ca-salts.** When the calcium salts of certain higher dicarboxylic acids of the oxalic acid series are distilled, cyclic ketones are obtained which on Clemmensen reduction yield cycloalkanes.



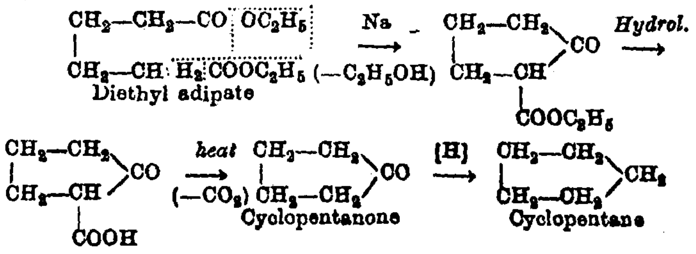
Calcium adipate Cyclopentanone



Cyclopentanone Cyclopentane

Cyclopropane cannot be prepared by this method.

(3) **Internal acetoacetic ester condensation** (*Dieckmann's method*). The esters of adipic, pimelic and suberic acids when treated with sodium undergo intramolecular acetoacetic ester condensation and form cyclic ketones which on reduction yield the corresponding cycloalkanes. Thus :

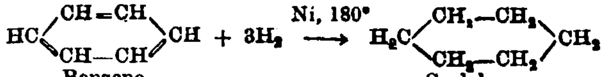


Diethyl adipate

Cyclopentanone Cyclopentane

(4) **Catalytic hydrogenation.** Cycloalkanes can be obtained by the catalytic hydrogenation of the corresponding unsaturated hydrocarbons.

Thus, benzene on reduction with hydrogen in the presence of nickel forms cyclohexane:



Benzene Cyclohexane

PHYSICAL CHARACTERISTICS

(1) Excepting the first two members which are gases at ordinary temperature, cycloalkanes are colourless liquids having pleasant odours.

(2) They boil 10—20° higher than the corresponding open-chain alkanes.

(3) They are insoluble in water but soluble in alcohol and ether.

(4) The boiling points show a gradual rise with the increase of molecular weight as shown below.

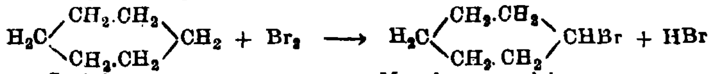
CYCLOALKANE	BOILING POINT	DENSITY
Cyclopropane, C_3H_6	—32°	—
Cyclobutane, C_4H_8	18°	0·7030
Cyclopentane, C_5H_{10}	50°	$0·654^{20}$
Cyclohexane, C_6H_{12}	81°	$0·779^{20}$
Cycloheptane, C_7H_{14}	111°	$0·810^{20}$
Cyclooctane, C_8H_{16}	151°	$0·839^{10}$

CHEMICAL CHARACTERISTICS

Cycloalkanes have saturated molecules and, therefore, give substitution reactions like the alkanes. On the other hand, the lower members form addition compounds readily, since their rings being under strain tend to open like a double bond. Thus cycloalkanes behave both like the alkanes and also like the alkenes.

The more important reactions of cycloalkanes are given below :

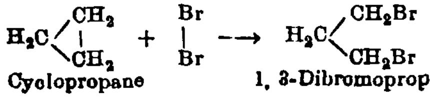
(1) **Substitution reactions.** Cycloalkanes undergo substitution by chlorine and bromine in diffused daylight to form the respective halogen compounds. Thus :



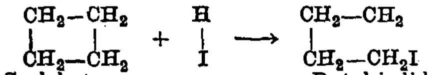
Cyclohexane Monobromocyclohexane

Cyclopropane, however, undergoes addition instead of substitution.

(2) **Addition reactions.** Cyclopropane and cyclobutane react with halogens, halogen halides, sulphuric acid, etc. to form addition compounds with ring fission. Thus :

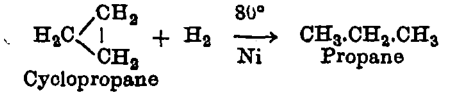


Cyclopropane 1, 3-Dibromopropane



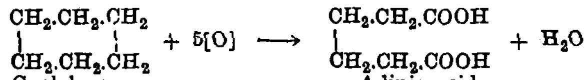
Higher members react with difficulty.

(3) **Catalytic reduction.** When mixed with hydrogen, and passed over heated nickel, cycloalkanes are converted into the corresponding open-chain saturated hydrocarbons. Thus :



Similarly, cyclobutane yields n-butane at 120°, and cyclopentane yields n-pentane at 300°. The rise in temperature of the reaction with the size of the ring shows their increasing stability. The higher cycloalkanes are not attacked by hydrogen in the presence of nickel.

(4) **Oxidation.** Unlike alkanes, cycloalkanes do not react with aqueous permanganate. However, upon oxidation with alkaline permanganate they are converted into dicarboxylic acids with ring fission.



RELATIVE STABILTY

The stability of a given cycloalkane is indicated by its tendency of ring fission. Cyclopropane readily reacts with bromine to form open-chain addition compound and is least stable. Cyclobutane does not form addition compound with bromine at ordinary temperature but reacts with hydrogen iodide with the opening of the ring, thus showing that it is more stable than cyclopropane. Cyclopentane and cyclohexane, however, react with bromine to form substitution products, the ring remaining intact. This shows that these hydrocarbons are very stable.

The relative stability of cycloalkanes is clearly indicated by the temperature of ring fission by catalytic hydrogenation :

Cyclopropane	Cyclobutane	Cyclopentane
80°	120°	300°

Cyclopropane ring is ruptured at the lowest temperature and is least stable. Cyclobutane and cyclopentane rings are progressively more stable as indicated by higher temperatures of reaction. The higher cycloalkanes are all very stable as they do not undergo catalytic hydrogenation.

As is clear from above, the stability of cycloalkanes increases with the size of the ring upto cyclopentane and from cyclohexane on all hydrocarbons are quite stable. These stability relationships have been explained under Baeyer's Strain Theory.

INDIVIDUAL MEMBERS

Cyclopropane, *Trimethylene*, C_3H_6. Cyclopropane is prepared commercially by boiling 1, 3-diodopropane with zinc dust and alcohol. In actual practice a mixture of 1, 3-dichloropropane, sodium iodide, anhydrous sodium carbonate, zinc dust and alcohol is boiled to yield the hydrocarbon.

Properties, Cyclopropane is a colourless gas having a pungent, sweetish odour. In diffused daylight it undergoes substitution with chlorine to form monochloropropane. In sunlight it adds bromine giving 1, 3-dibromopropane, and it reacts with hydrogen iodide yielding propyl iodide. When passed through a red hot tube, it is converted into propane. It is not attacked by cold potassium permanganate solution.

Cyclopropane is a general anaesthetic of great merit. In very low concentrations it can produce insensibility to pain without unconsciousness. However, it suffers from the disadvantage of forming explosive mixtures with air.

Cyclobutane, *Tetramethylene,* C_4H_8. Cyclobutane is prepared by the reduction of cyclobutane with hydrogen in presence of nickel at 100°. It is a colourless gas at ordinary temperature, b.p. 13°.

Cyclobutane is much more stable than cyclopropane. Thus it reacts with chlorine or bromine by substitution. It is not attacked by hydrogen bromide but reacts with hydrogen iodide to form n-butyl iodide. On hydrogenation at 120° it yields butane. Potassium permanganate has no action on cyclobutane.

Cyclopentane, *Pentamethylene,* C_5H_{10}. Cyclopentane occurs in Caucasian and American petroleum. It is prepared by the action of 1, 6-dibromopropane with zinc, and also by the Clemmensen reduction of cyclopentanone. It is a colourless mobile liquid, b.p. 50°. In light it reacts with bromine to form bromocyclopentane. On catalytic hydrogenation at 300°, it undergoes ring fission, giving n-pentane.

Cyclohexane, *Hexamethylene,* C_6H_{12}. Cyclohexane occurs in large quantities in Caucasian and Galacian petroleum. It is prepared industrially by the catalytic reduction of benzene at 200°.

Cyclohexane is colourless liquid, b.p. 18°. In light it undergoes substitution reaction with both bromine and chlorine. On having with alkaline potassium permanganate it is decomposed into adipic acid. When heated to a high temperature with platinum, it yields benzene.

QUESTIONS

1. What are cycloalkanes ? Assign names to the first seven members of the class.

2. What are the various methods available for the synthesis of polymethylenes ?

3. Describe the general reactions of alkanes and show how they resemble with alkanes, and also with alkenes.

4. Give the general methods available for the preparation of carbocyclic compounds. Give a brief description of Baeyer's Strain Theory and its applications.

5. Describe general methods of preparation of cycloparaffins. Write a short note on their order of stability. *(Madras B.Sc., 1960)*

6. How can cyclo-alkanes be obtained ? How far does the stability of such ring systems, depend on the number of carbon atoms present in the ring ? *(Panjab B.Sc. Suppl., 1962)*

7. Describe general methods of preparation and chemical reactions of cycloparaffins. Explain the theories of strain and strainless rings. *(Karachi B.Sc. Subs., 1963)*

8. Describe the different methods of preparing polymethylenes. What is Baeyer's Strain theory ? *(Poona B.Sc. III, 1964)*

9. Describe any four methods for the synthesis of cycloalkanes. Give a brief account of their general properties. How will you account for the gradation in the properties of various cycloalkanes ? *(Vallabhbhai B.Sc. III, 1964)*

10. Give general methods for the preparation of cycloparaffins. How will you account for their relatively high stability ? *(Jammu and Kashmir B.Sc., 1967)*

11. What are cyclo-alkanes and how would you correlate their stability and molecular structure ? Give the general methods for preparation of these compounds. *(Banaras B.Sc. II, 1967)*

32

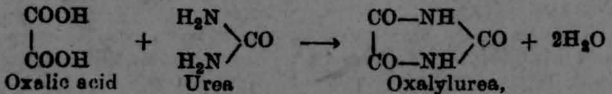
The Ureides

MORRIS S. KHRASCH
(1895— , American)
Worked with heat of combustion of organic compounds, and relationship of electronic structure to physical properties of organic compounds, Grignard reactions, alkyl mercurials. Now Professor of organic chemistry in the University of Chicago.

When a hydrogen atom of urea is replaced by an acyl group, the derivative is called a **ureide**. The ureides are prepared by the action of acids or their derivatives with urea. Thus :

$$\underset{\text{Acetyl chloride}}{CH_3COCl} + \underset{\text{Urea}}{NH_2.CO.NH_2} \longrightarrow \underset{\substack{\text{Acetylurea}\\\text{(Acetic ureide)}}}{CH_3CO.NH.CO.NH_2} + HCl$$

Similarly dicarboxylic acids react with urea to form *cyclic* ureides. Thus :



$$\begin{array}{l}COOH\\|\\COOH\end{array} + \begin{array}{l}H_2N\\H_2N\end{array}\!\!>CO \longrightarrow \begin{array}{l}CO-NH\\|\\CO-NH\end{array}\!\!>CO + 2H_2O$$

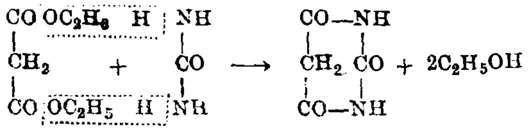
Oxalic acid Urea Oxalylurea,
Parabanic acid

The cyclic ureides may also be prepared by the condensation of a diester with urea in the presence of sodium ethoxide.

Ureides are beautifully crystalline compounds. They are hydrolysed by alkalis to form the parent acid and urea. The cyclic ureides are acidic owing to enolisation and hence they form metallic salts. Many of them are excellent drugs.

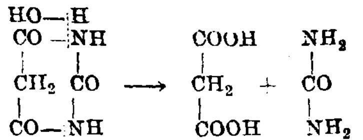
BARBITURIC ACID, MALONYLUREA

It is an important cyclic ureide and is best prepared by the condensation of malonic ester with urea in the presence of sodium ethoxide.



Malonic ester Urea Barbituric acid

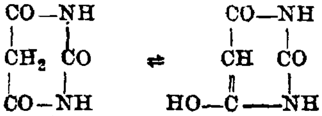
Barbituric acid is a colourless crystalline solid, m.p. 245° On warming with alkalis it is decomposed into malonic acid and urea.



Malonic acid Urea

Barbituric acid

It is strongly acidic since the $-CH_2-$ flanked by two carboxy groups readily gives the enolic form. Thus barbituric acid reacts with sodium hydroxide to form the sodium salt.

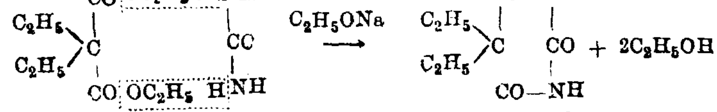


Barbituric acid Monenol

Barbituric acid and its C-alkyl derivatives are used in medicine as hypnotics and sedatives. Its formation was used by Fischer in the synthesis of uric acid.

VERONAL, BARBUTONE, C-DIETHYLBARBITURIC ACID

It is prepared by condensing diethylmalonic ester with urea.



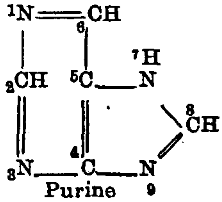
Diethylmalonic ester Urea Veronal

Veronal is a colourless, crystalline compound. m.p. 191 It is one of the most commonly used hypnotics of the present time. To some extent it is also used as sedative and in anaesthesia.

Phenobarbital or Luminal, *C-Phenylethylbarbituric acid*, is another important hypnotic of this class.

THE PURINES

Uric acid and other closely related compounds form a group of complex cyclic ureides.* They are all derived from the same parent substance 'Purine' and are, therefore, named as **purines.**



Purine

Purine is a colourless solid, m.p. 216-217°. It is highly soluble in water and has both acidic and basic properties. For the purpose of naming its derivatives, the skeleton of purine is numbered as shown above. Uric acid and caffeine are by far the most important of the purines.

URIC ACID, 2,6,8-TRIHYDROXYPURINE, $C_5H_4O_2N_4$

Uric acid is so named as it was first isolated by Scheele (1776) from human urine. It is formed in the body of man by the degradation of certain proteins. Normally only traces of it are present in the blood, and small quantities are excreted in urine. Owing to its small solubility, any temporary excess of uric acid in the blood deposits in the joints (*gout*) or in the tissues (*rheumatism*). It may sometimes accumulate in the bladder or the kidneys, forming stones.

Uric acid is the chief constituent of the excreta of birds and reptiles. '*Guano*' which is the excreta of certain sea birds, is an excellent source of uric acid.

Preparation. Uric acid may be obtained from human urine or *Guano* in which it is present mostly as ammonium salt.

(1) *From Urine.* Uric acid may be isolated from human urine by concentrating it and adding concentrated hydrochloric acid. The crystals of uric acid separate on standing.

(2) *From Guano.* Uric acid is prepared on a large scale from the excrements of birds and snakes (*guano*). The dry excrement is powdered and boiled with sodium hydroxide solution, until the

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* Purines may be thought of as cyclic *diureides* since they could be considered as built from to molecules of urea and one of a dicarboxylic acid.

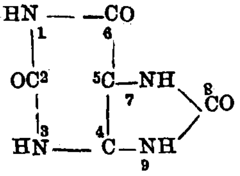
evolution of ammonia ceases. The hot solution of sodium urate thus obtained is then filtered and poured into hydrochloric acid.

$$\text{Na-urate} + HCl \longrightarrow \text{Uric acid} + NaCl$$

The uric acid separates as a fine crystalline mass on allowing the solution to stand in cold. It is filtered and dried in air.

Properties. Uric acid is a white, crystalline solid having no taste or smell. It decomposes when heated, so that it has no melting point. It is very difficultly soluble in water and is insoluble in alcohol and ether.

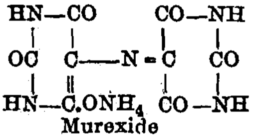
Uric acid behaves as a weak dibasic acid owing to enolisation, the H-atoms in positions 3 and 9 being replaced by metallic atoms.



Uric acid

Its salts are called urates. The sodium ammonium urates are sparingly soluble but those of litmus are freely soluble. That is why 'lithiated water' is often used as a remedy in cases of rheumatism and gout to secure the elimination of uric acid.

When uric acid is evaporated to dryness with nitric acid, it leaves a yellow residue which dissolves in ammonia to produce a purple-red colour owing to the formation of murexide (**Murexide Reaction**).



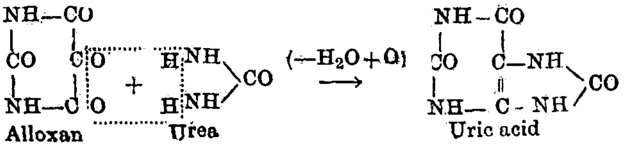
Murexide

Structure. (1) Uric acid has been shown to possess the formula $C_5H_4N_4O_3$.

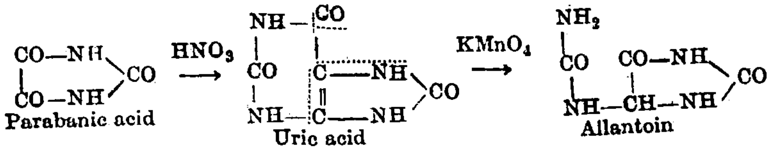
(2) Upon moderate oxidation with nitric acid, it breaks up into alloxan and urea.

$$\underset{\text{Uric acid}}{C_5H_4N_4O_3} + (H_2O + O) \longrightarrow \underset{\text{Urea}}{N_2H_4CO} + \underset{\text{Alloxan}}{C_4H_2N_2O_4}$$

(3) Tracing back the above reaction, we can theoretically derive the structural formula of uric acid by eliminating $(H_2O + O)$ from one molecule of urea and one molecule of alloxan.

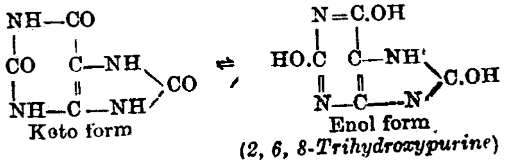


(4) The above formula of uric acid, first suggested by Medicus in 1870, is in perfect accord with its behaviour on oxidation forming allantoin and parabanic acid.



The dotted lines indicate the points of attack in the two cases.

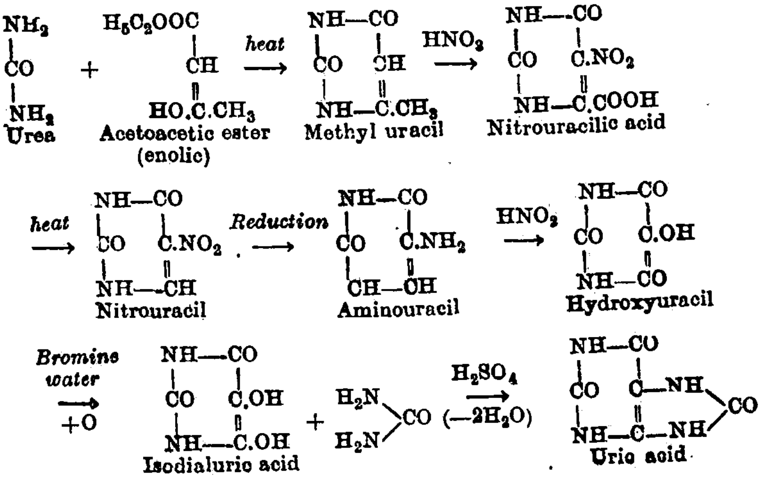
(5) Uric acid reacts with phosphorus oxychloride to form a trichloro-derivative as if it had three hydroxy groups in the molecule. Also, we know that it behaves as a weak acid although it has no carboxyl group. Therefore, we suppose that uric acid exhibits keto-enol tautomerism.



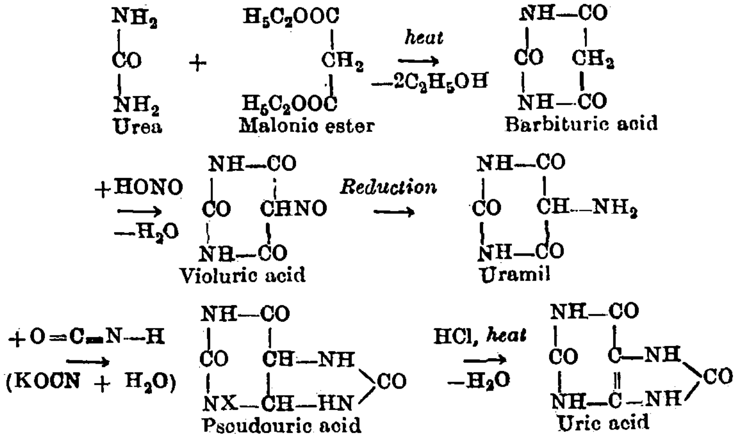
From the study of the absorption spectrum of uric acid, it has been concluded that the keto form greatly predominates in this equilibrium.

(6) **Synthesis** The structure of uric acid is finally confirmed by its synthesis which has been accomplished in many ways.

(*i*) *Beherend and Roosen Synthesis* (1887) :



The product of the synthesis was found to be identical with the natural uric acid (*ii*) *Fischer's Synthesis* (1897) :—



Tests of Uric acid. (1) Uric acid reduces Fehling's solution.

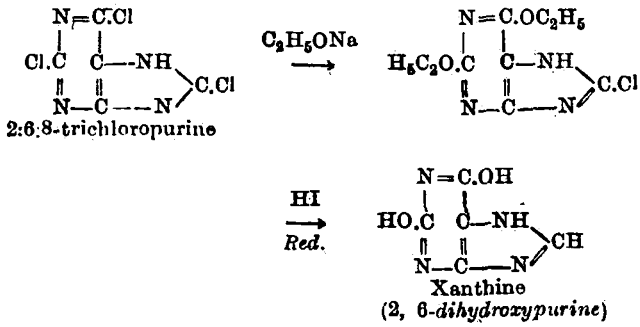
(2) It decolorises acid or alkaline solution of potassium permanganate

(3) *Murexide Test.* Add a few drops of conc. nitric acid to a little uric acid placed in a china dish, evaporate to dryness on a water-bath and add dilute ammonia. An intense purple colour indicates uric acid.

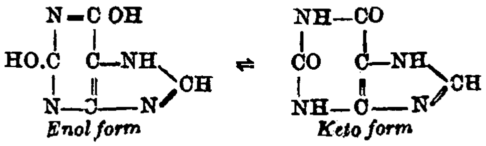
XANTHINE, 2,6-DIHYDROXYPURINE, $C_5H_4O_2N_4$

This important purine derivative is present in the blood and is excreted in urine. It also occurs in tea leaves and sprouting seedlings.

Preparation. Xanthine may be prepared from 2, 6, 8-trichloropurine obtained by the action of $POCl_3$ on uric acid.



Properties. Xanthine crystallises well. It is difficultly soluble in water. Chemically it resembles uric acid and forms salts with alkalis, and also with hydrochloric and nitric acids. Thus xanthine exists in two tautomeric forms.

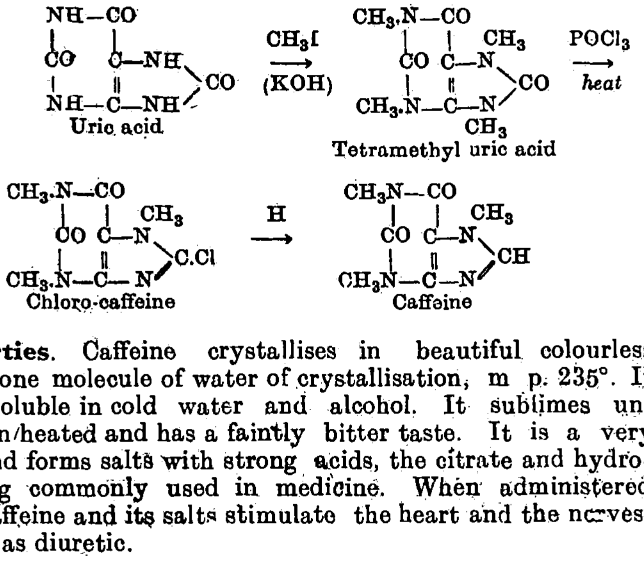


CAFFEINE, 1,3,7-TRIMETHYLXANTHINE, $C_8H_{10}O_2N_4$

Caffeine occurs in different plants all of which are sources of stimulants. It is present in dried tea leaves to the extent of 5 per cent, in coffee (1·2%) and in kola nuts (1·2%). It is also called **theine**.

Preparation. (1) *From Tea leaves.* Caffeine is prepared from damaged tea leaves by extraction with boiling water when a solution containing caffeine, proteins and tannin is obtained. The hot solution is filtered and treated with basic lead acetate in order to precipitate proteins and tannin. The precipitate is filtered off and the solution is treated with sulphuric acid to remove any excess of lead. The resulting solution is decolorised with animal charcoal and caffeine extracted from it with chloroform. The chloroform is distilled off and the residue of caffeine crystallised from water. Most of the caffeine of commerce is made by this method.

(2) *From Uric acid.* Caffeine is also manufactured from uric acid as follows. Uric acid is treated with methyl iodide in alkaline solution to form tetramethyl-uric acid. This on heating with $POCl_3$ gives chloro-caffeine which on reduction with nascent hydrogen yields caffeine.



Properties. Caffeine crystallises in beautiful colourless needles with one molecule of water of crystallisation, m p. 235°. It is sparingly soluble in cold water and alcohol. It sublimes unchanged when heated and has a faintly bitter taste. It is a very weak base and forms salts with strong acids, the citrate and hydrochloride being commonly used in medicine. When administered internally, caffeine and its salts stimulate the heart and the nerves, and also act as diuretic.

We take caffeine when we drink tea or coffee. This is why these beverages relieve fatigue and quicken the brain. However, their excessive use is harmful to digestion.

Adenine, *6-aminopurine.* It occurs in the free state in tea, sugar beets, hops, yeast, bacteria, muscles and urine. It is obtained on a fairly large scale from tea-extract and molasses.

Adenine is a colourless solid, m.p. 360°. It is highly soluble in water but dissolves in mineral acids and alkalis, forming salts.

Guanine, *2-amino-6-hydroxypurine.* It occurs along with adenine in many plants and in the organs of animals. The scales and skin of fish and reptiles consist of this purine.

Guanine is a colourless solid. It is almost insoluble in water and alcohol but dissolves in acids and alkalis, forming salts.

Theobromine, *3, 7-dimethylxanthine.* It occurs in cocoa bean to the extent of 2 per cent. It is white crystalline solid, m.p. 351°, having a slightly bitter taste. It dissolves readily in hot water. It is used in medicine as diuretic.

Hypoxanthine *6-hydroxypurine.* This purine, also named as *sarkine*, is present in muscles, spleen, liver and pancreas. Hypoxanthine is a crystalline powder which decomposes at 150° without melting. It is slightly soluble in water but dissolves in alkalis owing to salt formation.

QUESTIONS

1. What are ureides ? Give briefly their methods of preparation and properties.

2. Give the preparation and uses of veronal.

3. Describe by means of structural formulae how veronal is prepared.

4. How does uric acid occur in nature, and how would you isolate it and establish its constitution ? What relationship exists between uric acid, xanthine, and caffeine ?

5. Discuss the constitution of uric acid and describe one of its synthesis. Show its relationship to caffeine and theobromine.

6. How has the constitution of uric acid been determined ? Describe any one synthesis of uric acid. Write down the formula of Xanthine and Caffeine.

7. How will you prepare caffeine from tea leaves and uric acid ? What is the chief use of caffeine ?

8. How is uric acid obtained ? Discuss its chemistry and show its relationship to caffeine. *(Banaras B.Sc. III, 1967)*

9. Discuss the evidence both analytical and synthetical on which the structure of caffeine is based. *(Bombay B.Sc. III, 1967)*

10. How would you prepare caffeine ? What are its chief uses ? *(Panjab B.Sc. III, 1968)*

11. What are ureides and purines ? How are they related ? What is the action of nitric acid on uric acid ? Show the relationship of uric acid to caffeine. *(Saurashtra B.Sc., 1968)*

12. How is uric acid obtained ? Discuss its chemistry and show its relationship to caffeine. *(Banaras B.Sc., 1968)*

13. How is uric acid converted into :—
    (*a*) Purine,
    (*b*) Adenine,
    (*c*) Guanine.
    (Bangalore B.Sc., 1959)

14. Discuss the constitution of uric acid. How is it converted into caffeine ? *(Bombay B.Sc., 1969*

33

Carbohydrates

Emil Fischer
(1852—1919)

German chemist. He did memorable work in connection with the structure of sugars. Later he extended his research work to purines including caffeine and uric acid. He discovered phenylhydrazine.

Carbohydrates constitute an important class of organic substances which are derived from plants. They include glucose, cane sugar, cellulose, starch etc. Carbohydrates are an important food factor and form the major part of our diet. Our clothing, wooden furniture, paper, card-board, fuel are all carbohydrate stuff. We consume large amounts of carbohydrates in making synthetic fibres, photographic films, plastics, lacquers, explosives and other useful materials.

DEFINITION OF THE TERM 'CARBOHYDRATE'

Carbohydrates are the compounds of C, H and O. The last two named elements are generally present in the ratio of 2 to 1, as in water. Therefore, the compounds of this class could be represented by the general formula $C_x(H_2O)_y$. For example, we can write glucose ($C_6H_{12}O_6$) as $C_6(H_2O)_6$; cane sugar ($C_{12}H_{22}O_{11}$) as $C_{12}(H_2O)_{11}$; and so on. For this reason, French named them as carbohydrates (*hydrates of carbon*).

However, the name carbohydrate is a misnomer. While the inorganic hydrates contain loosely combined water, the compounds of this class contain no water molecules as such. They are, in fact, polyhydroxy aldehydes or ketones and it is a sheer coincidence that H and O are present in the ratio of 2 to 1. Now there are carbohydrates (rhamnose) ($C_6H_{12}O_5$) known in which the ratio of H and O is different. And then, it is also noteworthy that compounds such as formaldehyde (CH_2O) and lactic acid ($C_3H_6O_3$) which even though conforming to the formula $C_x(H_2O)_y$ are not carbohydrates.

The term carbohydrate has lost its original significance and is now used in a very wide sense as the class name for all sugars, starches, cellulose and structurally related compounds. We may, therefore, define carbohydrates as *polyhydroxy aldehydes* or *ketones*, or *substances that yield these on hydrolysis.*

OCCURRENCE

Carbolydrates are formed in nature by the reduction of carbon dioxide by living plants with the aid of green pigment chlorophyll. The overall reaction is

$$n\mathrm{CO_2} + n\mathrm{H_2O} + \textit{Energy} \longrightarrow (\mathrm{CH_2O})_n + n\mathrm{O_2}$$

The energy for the purpose is obtained from sunlight. Thus nature manufactures huge quantities of carbohydrates in the form of tissues of plants. The various processes of the fixation of CO_2 by photosynthesis and its return to the atmosphere is briefly depicted below.

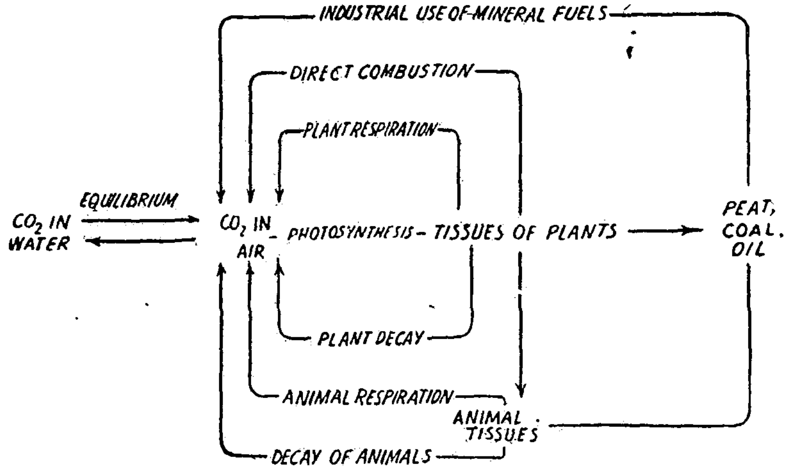


Fig. 38·1. Biochemical Carbon dioxide cycle.

The most familiar natural sugar sucrose is industrially obtained from sugar cane and sugar beets. More than 50 million tons of this sugar are obtained every year from natural sources. Glucoce and Fructose are also among many other naturally occurring sugars.

CLASSIFICATION

Carbohydrates have been divided into the following classes according to their complexity and behaviour on hydrolysis.

(1) The **Monosaccharides**, which are the simplest carbohydrates and cannot be hydrolysed *e.g.*, glucose and fructose, $C_6H_{12}O_6$.

(2) The **Oligosaccharides**, which are built of a definite number of monosaccharide molecules that are split up on hydrolysis. They include :

(*i*) The *Disaccharides*, yielding two monosaccharide molecules on hydrolysis, *e.g.*, cane sugar, $C_{12}H_{22}O_{11}$;

(*ii*) The *Trisaccharides*, yielding three Monosaccharide molecules on hydrolysis *e.g.*, raffinose, $C_{18}H_{32}O_{16}$; and so on.

(3) The **Polysaccharides**, which are built of a large but indefinite number of monosaccharide molecules that are split up on hydrolysis *e.g.*, starch, $(C_6H_{10}O_5)_n$.

The monosaccharides and oligosaccharides are soluble crystalline substances having a sweet taste and are collectively known as **sugars**. Polysaccharides, on the other hand, are insoluble amorphous substances and are, therefore, called **non-sugars**.

Carbohydrates—	*Monosaccharides*—	*Aldoses*	Sugars
		Ketoses	
	Oligosaccharides—	*Disaccharides*	
		Trisaccharides	
	Polysaccharides	... ...	...Non-sugars

MONOSACCHARIDES

Monosaccharides are all polyhydroxy aldehydes or ketones. The aldehydic sugars are called **aldoses**, while the ketonic sugars are known as **ketoses**. The aldoses and ketoses are divided into sub-classes according to the number of carbon atoms present in the molecule. Thus, we have aldobioses, aldotrioses, aldotetroses, aldopentoses, aldohexoses, ketohexoses etc.

For example,

OHC.CH$_2$OH	glycollic aldehyde is *aldobiose*
OCH.CHOH.CH$_2$OH	glyceric aldehyde is *aldotriose*
OHC.CHOH.CHOH.CHOH.CH$_2$OH	arabinose is *aldopentose*
OHC.CHOH.CHOH.CHOH.CHOH.CH$_2$OH	glucose is *aldohexose*
CH$_2$OH.CO.CHOH.CHOH.CHOH.CH$_2$OH	fructose is *ketohexose*

The monosaccharides that occur in nature are chiefly aldopentoses, aldehoxoses or ketohexoses.

GENERAL PROPERTIES

(*Physical*). Monosaccharides are colourless neutral substances having a sweet taste. They do not crystallise very well. On heating they become brown and char without melting. They are readily soluble in water, sparingly soluble in alcohol and insoluble in ether.

(*Chemical*). Aldoses and ketoses give all the reactions of aldehydes and ketones respectively, along with those of polyhydroxy alcohols. They also show certain characteristic reactions depending on the presence of the aldehydic or the ketonic group, and the OH groups in the same molecule. The more important reactions of monosaccharides are given below.

(1) **Acetylation.** Monosaccharides undergo acetylation when heated with acetic anhydride and a little anhydrous zinc chloride. Thus glucose and fructose form penta-acetyl derivatives.

$$\underset{\substack{\text{Glucose, or}\\\text{Fructose}}}{C_6H_7O(OH)_5} + \underset{\text{Acetic anhydride}}{5(CH_3CO)_2O} \longrightarrow \underset{\substack{\text{Penta-acetyl}\\\text{derivative}}}{C_6H_7O(OOCCH_3)_5} + 5CH_3COOH$$

(2) **Formation of glucosides.** Pentoses and hexoses when heated with alcohols in the presence of hydrogen chloride form ethers known as *glucosides*. Thus glucose and fructose react with methyl alcohol to give *methylglucoside* and *methylfructoside* respectively.

$$\underset{\substack{\text{Glucose or}\\\text{Fructose}}}{C_6H_{11}O_5\boxed{OH + H}OCH_3} \longrightarrow \underset{\substack{\text{Methylglucoside}\\\text{or fructoside}}}{C_6H_{11}O_5OCH_3} + H_2O$$

As we will study later on this reaction gives a clue of the existence of a ring structure in these sugars.

(3) **Formation of salts.** Monosaccharides are very feebly acidic and react with lime to form calcium salts. The glucose and fructose form *calcium glucosate* (soluble) and *calcium* fructosate (insoluble) respectively.

$$\underset{\text{Glucose}}{C_6H_{11}O_5}\boxed{OH + H}\underset{\text{Lime}}{Ca.OH} \longrightarrow \underset{\text{Calcium glucosate}}{C_6H_{11}O_5O.CaOH} + H_2O$$

The calcium glucosate is decomposed by passing carbon dioxide through the solution, thus regenerating glucose. This reaction can, therefore, be employed for the separation of glucose and fructose.

(4) **Reduction.** When monosaccharides are reduced with sodium amalgam in aqueous solution, they take up two H-atoms at the CO group and form polyhydroxy alcohols. Thus glucose yields *sorbitol*, while fructose yields two isomeric alcohols : sorbitol and mannitol.

$$\left.\begin{array}{c}\underset{\text{Glucose}}{CH_2OH.(CHOH)_3.CHOH.CHO}\\ \underset{\text{Fructose}}{CH_2OH.(CHOH)_3.CO.CH_2OH}\end{array}\right\} + 2H \longrightarrow CH_2OH.(CHOH)_4.CH_2OH$$

(5) **Oxidation.** Aldoses on oxidation form monocarboxylic acids or dicarboxylic acids containing the same number of carbon atoms, while ketoses oxidise to yield acids with a smaller number of carbon atoms. Thus glucose on mild oxidation with bromine water forms gluconic acid.

$$\underset{\text{Glucose}}{CH_2OH.(CHOH)_4.CHO} \xrightarrow{[O]} \underset{\text{Gluconic acid}}{CH_2OH.(CHOH)_4.COOH}$$

With concentrated nitric acid, however, it is oxidised at both terminal groups and forms saccharic acid.

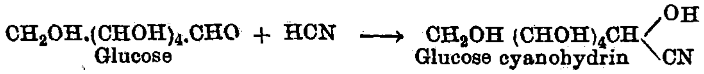
$$\underset{\text{Glucose}}{CH_2OH.(CHOH)_4.CHO} \xrightarrow{[O]} \underset{\text{Saccharic acid}}{HOOC.(CHOH)_4.COOH}$$

Fructose remains unattacked by mild oxidising agents, but when oxidised with concentrated nitric acid it yields glycollic acid and tartaric acid by cleavage at the CO group.

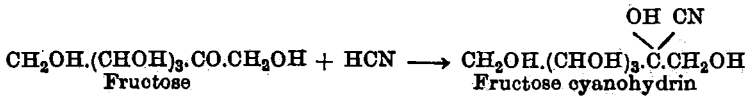
$$\underset{\text{Fructose}}{CH_2OH.(CHOH)_3.CO.CH_2OH} \xrightarrow{[O]} \underset{\text{Tartaric acid}}{HOOC(CHOH)_2COOH} + \underset{\text{Glycollic acid}}{HOOC.CH_2OH}$$

Therefore, glucose and fructose both are reducing sugars. They reduce Fehling's solution and ammoniacal silver nitrate solution.

(6) **Formation of Cyanohydrins.** Monosaccharides add a molecule of hydrogen cyanide forming cyanohydrins. Thus :



$$\underset{\text{Glucose}}{CH_2OH.(CHOH)_4.CHO} + HCN \longrightarrow \underset{\text{Glucose cyanohydrin}}{CH_2OH(CHOH)_4CH{\begin{smallmatrix}OH\\CN\end{smallmatrix}}}$$

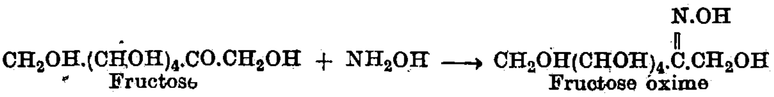


$$\underset{\text{Fructose}}{CH_2OH.(CHOH)_3.CO.CH_2OH} + HCN \longrightarrow \underset{\text{Fructose cyanohydrin}}{CH_2OH.(CHOH)_3.\overset{OH\ CN}{C}.CH_2OH}$$

(7) **Formation of Oximes.** Monosaccharides react with hydroxylamine to form the oximes by splitting out a molecule of water.

Thus :

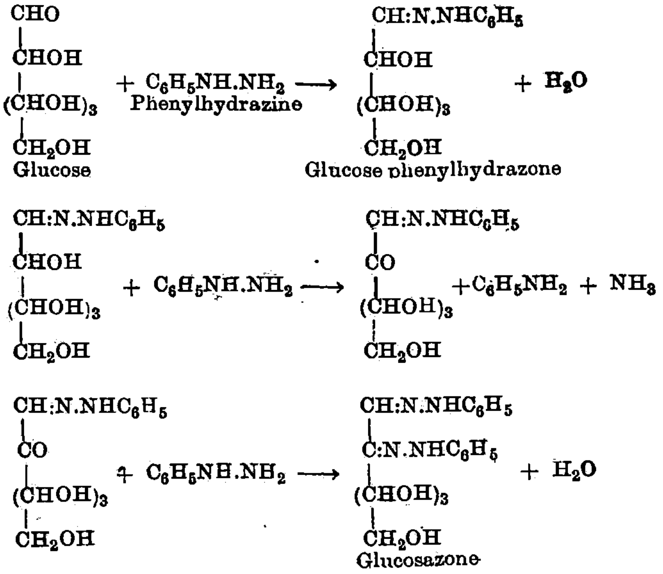
$$\underset{\text{Glucose}}{CH_2OH.(CHOH)_4.CHO} + NH_2OH \longrightarrow \underset{\text{Glucose oxime}}{CH_2OH.(CHOH)_4.CH{:}NOH} + H_2O$$



$$\underset{\text{Fructose}}{CH_2OH.(CHOH)_4.CO.CH_2OH} + NH_2OH \longrightarrow \underset{\text{Fructose oxime}}{CH_2OH(CHOH)_4.\overset{N.OH}{\overset{\|}{C}}.CH_2OH}$$

(8) **Formation of Osazones.** Monosaccharides when treated with phenylhydrazine form phenylhydrazones. However on warming with excess of phenylhydrazine they yield diphenylhydrazones which are known as *osazones*. According to the mechanism suggested by Fischer, a phenylhydrazone is first produced and then the hydroxyl group adjacent to the original aldehyde or the ketonic group, is oxidised to a carbonyl group adjacent to the original aldehyde or the ketonic group is oxidised to a carbonyl group by

a second molecule of phenylhydrazine which is reduced to aniline and ammonia. The carbonyl group thus produced now reacts with a third molecule of phenylhydrazine to yield the osazone. For example, glucose forms glucosazone as follows.

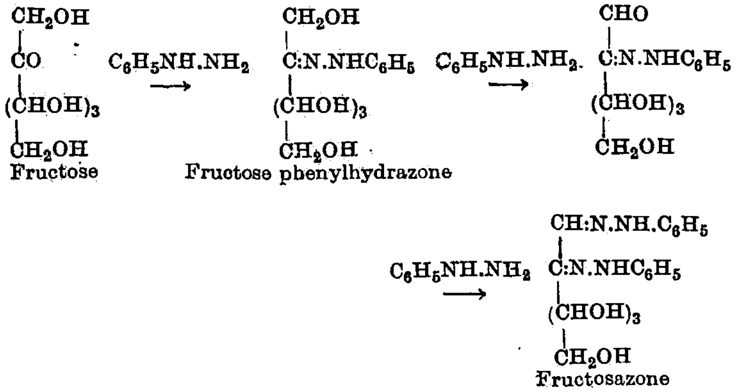


$$\begin{array}{l}\mathrm{CHO}\\|\\\mathrm{CHOH}\\|\\\mathrm{(CHOH)_3}\\|\\\mathrm{CH_2OH}\\\text{Glucose}\end{array} + \underset{\text{Phenylhydrazine}}{\mathrm{C_6H_5NH.NH_2}} \longrightarrow \begin{array}{l}\mathrm{CH{:}N.NHC_6H_5}\\|\\\mathrm{CHOH}\\|\\\mathrm{(CHOH)_3}\\|\\\mathrm{CH_2OH}\\\text{Glucose phenylhydrazone}\end{array} + \mathrm{H_2O}$$

$$\begin{array}{l}\mathrm{CH{:}N.NHC_6H_5}\\|\\\mathrm{CHOH}\\|\\\mathrm{(CHOH)_3}\\|\\\mathrm{CH_2OH}\end{array} + \mathrm{C_6H_5NH.NH_2} \longrightarrow \begin{array}{l}\mathrm{CH{:}N.NHC_6H_5}\\|\\\mathrm{CO}\\|\\\mathrm{(CHOH)_3}\\|\\\mathrm{CH_2OH}\end{array} + \mathrm{C_6H_5NH_2} + \mathrm{NH_3}$$

$$\begin{array}{l}\mathrm{CH{:}N.NHC_6H_5}\\|\\\mathrm{CO}\\|\\\mathrm{(CHOH)_3}\\|\\\mathrm{CH_2OH}\end{array} + \mathrm{C_6H_5NH.NH_2} \longrightarrow \begin{array}{l}\mathrm{CH{:}N.NHC_6H_5}\\|\\\mathrm{C{:}N.NHC_6H_5}\\|\\\mathrm{(CHOH)_3}\\|\\\mathrm{CH_2OH}\\\text{Glucosazone}\end{array} + \mathrm{H_2O}$$

Similarly fructose forms *fructosazone.*



$$\begin{array}{l}\mathrm{CH_2OH}\\|\\\mathrm{CO}\\|\\\mathrm{(CHOH)_3}\\|\\\mathrm{CH_2OH}\\\text{Fructose}\end{array} \xrightarrow{\mathrm{C_6H_5NH.NH_2}} \begin{array}{l}\mathrm{CH_2OH}\\|\\\mathrm{C{:}N.NHC_6H_5}\\|\\\mathrm{(CHOH)_3}\\|\\\mathrm{CH_2OH}\\\text{Fructose phenylhydrazone}\end{array} \xrightarrow{\mathrm{C_6H_5NH.NH_2}} \begin{array}{l}\mathrm{CHO}\\|\\\mathrm{C{:}N.NHC_6H_5}\\|\\\mathrm{(CHOH)_3}\\|\\\mathrm{CH_2OH}\end{array} \xrightarrow{\mathrm{C_6H_5NH.NH_2}} \begin{array}{l}\mathrm{CH{:}N.NH.C_6H_5}\\|\\\mathrm{C{:}N.NHC_6H_5}\\|\\\mathrm{(CHOH)_3}\\|\\\mathrm{CH_2OH}\\\text{Fructosazone}\end{array}$$

It is found that the osazones obtained from glucose and fructose are identical. Since the two sugars form the same osazone, their structure differs only in respect of two carbon atoms which take part in the formation of the osazone.

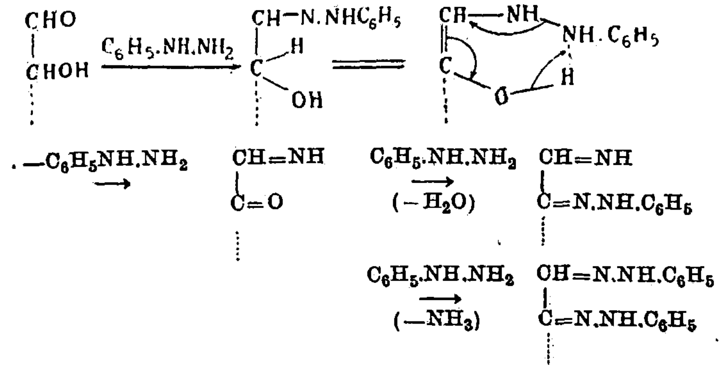
Osazones are yellow crystalline solids having sharp melting points. Their formation is used to characterise the sugars.

Mechanism:

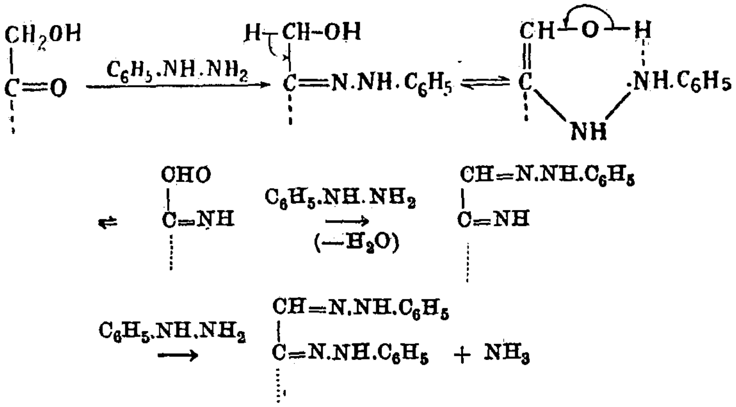
Fischer's mechanism cannot be considered to be true because phenylhydrazine is a powerful reducing agent ; this is the only reaction in which it behaves as an oxidising agent converting —CHOH— group in glucose to $\rangle C{=}O$; and $—CH_2OH$ group in fructose to $-CHO$ (second step).

Weygard (1940) suggested the following mechanism :

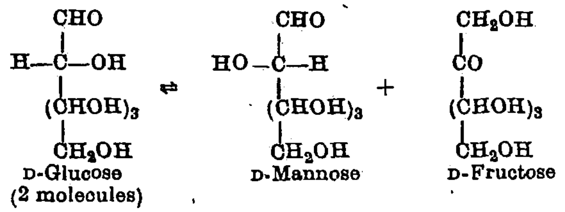
Glucose :



Fructose :

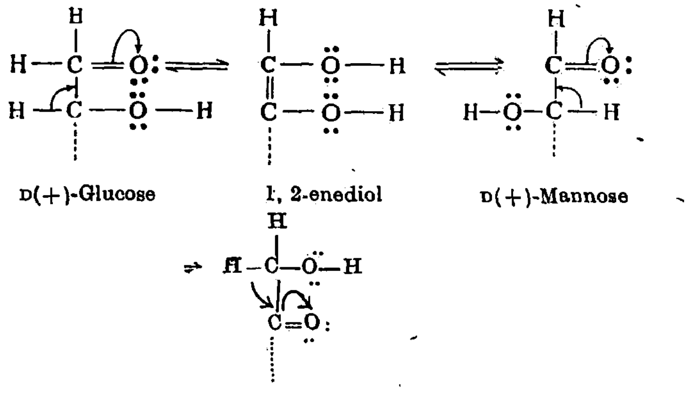


(9) **Lobry de Bruyn-van Ekenstein rearrangement** (1890). On warming with concentrated alkali, sugars first turn yellow, then brown and finally resinify. In the presence of dilute alkali or amines, sugars undergo a peculiar rearrangement yielding a mixture of isomeric sugars. Thus D-glucose when warmed with dilute sodium hydroxide, forms a mixture of D-glucose, D-mannose, and D-fructose. The same mixture is obtained if the starting material is D-fructose or D-mannose



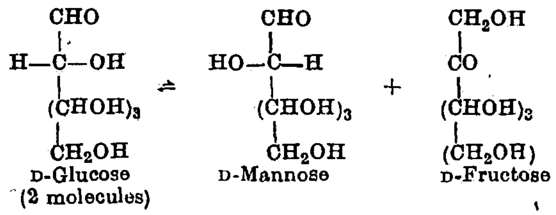
D-Glucose (2 molecules) ⇌ D-Mannose + D-Fructose

It has been suggested that the above rearrangement occurs through 1, 2-enolisation. Topper (1951) suggests that there are two geometrical isomeric enediol intermediates, both being capable of changing into fructose.



D(+)-Glucose ⇌ 1, 2-enediol ⇌ D(+)-Mannose

⇌ D (−)-Fructose



D-Glucose (2 molecules) ⇌ D-Mannose + D-Fructose

The same mixture is obtained when D-mannose or D-fructose is treated with dilute alkali. This indicates the reversible nature of the reaction.

(10) **Fermentation.** Many naturally occurring sugars *e.g.*, glucose and fructose undergo fermentation in the presence of yeast to form ethyl alcohol and carbon dioxide.

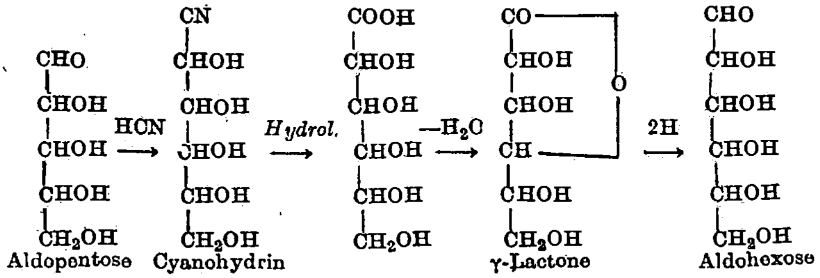
$$\underset{\text{Glucose}}{C_6H_{12}O_6} \longrightarrow \underset{\text{Ethyl alcohol}}{2C_2H_5OH} + 2CO_2$$

All monosaccharides cannot be fermented.

MUTUAL TRANSFORMATIONS

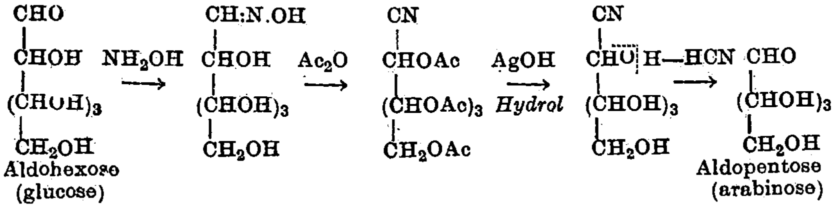
Having studied the general reactions of monosaccharides, we now proceed to discuss their mutual transformations which are of much theoretical and practical interest.

(1) **Conversion of a lower into a higher aldose.** An aldose may be converted into its next higher aldose by means of **Kiliani's synthesis.** Thus a pentose when reacted with hydrogen cyanide gives the cyanohydrin. The latter upon hydrolysis forms a polyhydroxy acid with one more C atom than the original sugar. This readily splits out a molecule of water when a γ-lactone is obtained which on reduction with sodium amalgam in slightly acidic solution is converted into aldohexose.

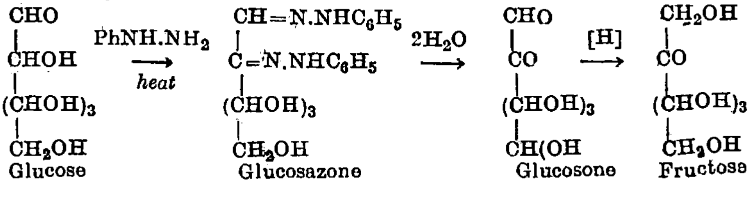


(2) **Conversion of a higher into a lower aldose.** A higher aldose can be converted to its next lower member by **Wohl's method.** The aldose is treated with hydroxylamine to give the oxime. The latter is heated with acetic anhydride, where it is dehydrated to the nitrile and also acetylated at the OH groups. The acetyl derivative thus obtained is then warmed with ammoniacal silver oxide, which removes the acetyl groups (CH_3CO = Ac) by hydrolysis and splits out a molecule of hydrogen cyanide to yield an aldose having one carbon atom less than the original sugar.

Thus :

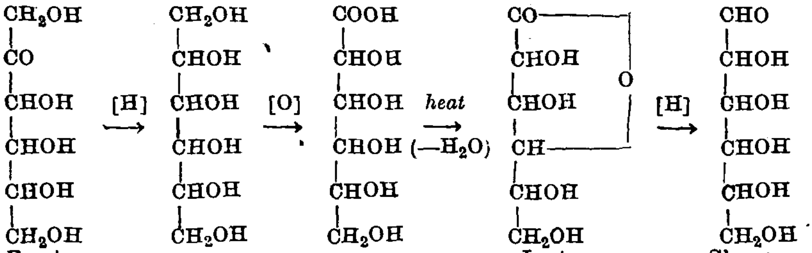


(3) **Conversion of an aldose into a ketose.** The aldose is warmed with excess of phenylhydrazine to get the osazone. This on hydrolysis with hydrochloric acid forms *osone* which on reduction with zinc and acetic acid is converted to the ketose (CHO is reduced in preference to CO) which is isomeric with the original aldose. Thus, glucose may be transformed into fructose as follows.



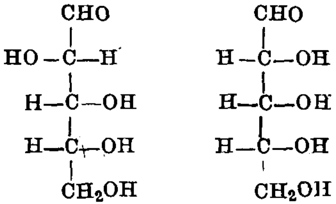
(4) **Conversion of a ketose into an aldose.** The ketose is first reduced to the corresponding polyhydric alcohol. The latter is oxidised to a monocarboxylic acid which on warming splits out a molecule of water to form the γ-lactone. This on reduction with sodium amalgam in slightly acid solution, is converted into an aldose which is isomeric with the original sugar.

Thus fructose can be transformed into glucose as follows :



Fructose γ-Lactone Glucose

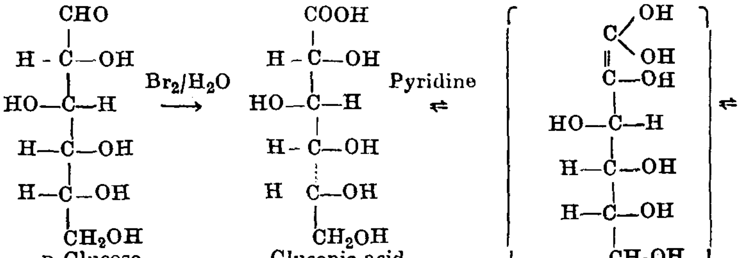
(5) **Epimerisation.** Aldoses which produce the same osazones must have identical configurations on all their asymmetric carbon atoms except α-carbon about which the H and OH groups are arranged in the reverse order. For example,



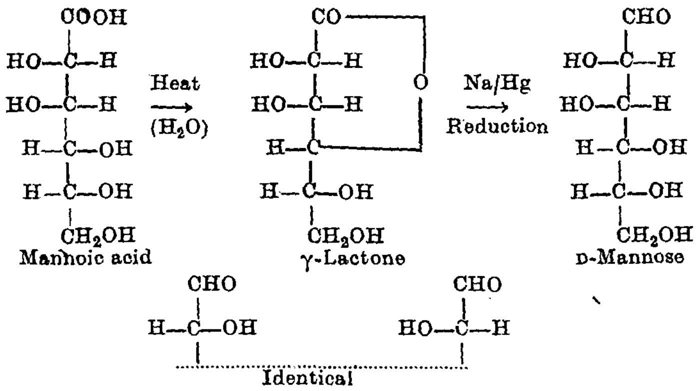
D(-)-Arabinose D(-)-Ribose

Such sugars are known as **Epimers.**

Fischer (1890) changed an aldose into its epimer via the aldonic acid. The aldonic acid was heated with pyridine (or quinoline), whereupon it was converted into an equilibrium mixture of the original acid and its epimeric acid. These were separated, and the epimeric acid lactone reduced to an aldose. The mechanism of the reaction takes place via the enol form *e.g.*, epimerisation of glucose into mannose :



D-Glucose Gluconic acid enol form



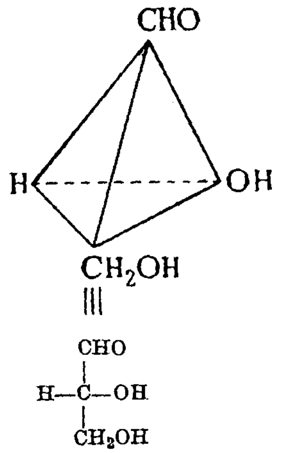
CONFIGURATION OF MONOSACCHARIDES

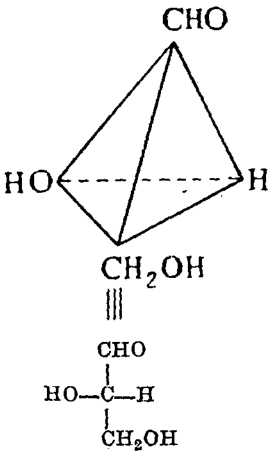
Of the monosaccharides, aldoses are *by far of greater* importance than ketoses and will be discussed in some detail. Fischer investigated the configuration of monosaccharides in the light of new ideas of stereo-chemistry proposed independently by Le Bel and van't Hoff. It was also known that a molecule containing an asymmetric carbon atom could exist as optically active isomers which differ only in the arrangement of groups in space (configuration). The number of optically active isomers is equal to 2^n, where n is the number of dissimilar asymmetric carbons.

Glycollic aldehyde, $CH_2OH.CHO$, is the simplest aldose. It has no asymmetric carbon atom in the molecule and so does not show optical isomerism. Thus there is no configurational problem and we have only one form of glycollic aldehyde.

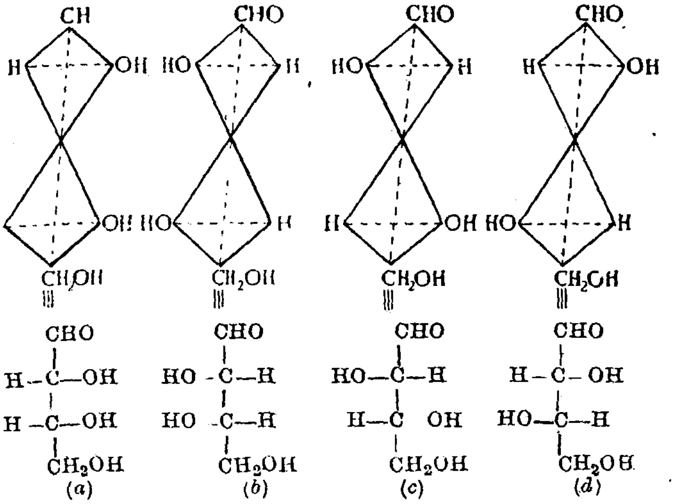
Glyceraldehyde, $CH_2OH.\overset{*}{C}HOH.CHO$, is an aldotriose. Its molecule contains one asymmetric carbon atom (*) and, therefore, exists in two optically active forms.

When the groups attached to the asymmetric carbon atom are considered to be at the vertices of a regular tetrahedron, the two possible arrangements (optically active) are :



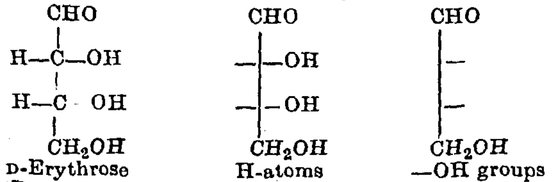


Tetroses, $CH_2OH.CHOH.CHOH.CHO$. They contain two asymmetric carbon atoms and can exist in four optically active forms. Fischer proposed planar formula for tetroses (and higher sugars also) by considering that the lower edges of the trahedra constituting the carbon chain all lay in a straight line in the plane of the paper as



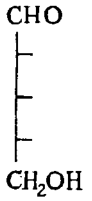
Fischer originally differentiated between the enantiomorphic pairs (mirror images) by using the symbols *d*- and *l*- for dextrorotatory and laevorotatory forms. But Rosanoff soon after replaced this system of nomenclature by proposing that a sugar having —OH group on the bottom asymmetric carbon atom towards the right of the carbon chain should be called δ-sugar and the one having —OH group to the left as λ-sugar. These symbols were changed in favour of D- and L- respectively and are almost universally accepted now. Thus (*a*) and (*b*) forms of tetroses belong respectively to D- and L-types. They are also called D-Erythrose and L-Threose ; (*c*) and (*d*) will correspondingly have D-Threose and L-Erythrose as their names. However it must be clearly understood that D- and L- have nothing to do with the direction of rotation which of course, may be mentioned by enclosing the sign of rotation within brackets as (+) or (−), wherever necessary.

The above convention of representing the projection formulae of sugar molecules is often abbreviated as follows. The H-atoms in these may be omitted or the —OH group position may alone be indicated by a short line. Thus D-Erythrose may be represented as

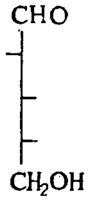


D-Erythrose (Projection) H-atoms omitted —OH groups shown

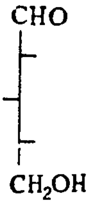
Pentoses, $CH_2OH.CHOH.CHOH.CHOH.CHO$. They contain three asymmetric carbon atoms and can exist in eight optically active forms. They correspond to the D- and L- forms of the four known pentoses : *ribose*, *arabinose*, *xylose* and *lyxose*. The configurations of the D-forms of the sugars are given below.



D-Ribose



D-Arabinose



D-Xylose

D-Lyxose

The physical and chemical properties of aldopentoses conform to the general properties of monosaccharides. However, they do not undergo fermentation.

Hexoses, $CH_2OH.CHOH.CHOH.CHOH.CHOH.CHO$. They contain four asymmetric carbon atoms and can exist in sixteen forms, which of course, correspond to the D- and L- forms of the eight known aldohexoses. These are : *glucose*, *mannose*, *galactose*, *allose*, *altrose*, *gulose*, *talose*.

Of all hexoses, D-glucose and D-fructose are the only sugars which occur in the free state. We will confine ourselves to their study.

GLUCOSE, GRAPE SUGAR, DEXTROSE, $C_6H_{12}O_6$

Glucose is by far the most important monosaccharide. It occurs in most sweet fruits and in honey. Ripe grapes contain as much as 20—30 per cent of glucose, hence its name *grape sugar*. In small amounts it is a normal constituent of human blood and urine. The urine of diabetic persons may contain glucose to the extent 8—10 per cent. In the combined form it occurs in cane sugar and other polysaccharides.

Preparation. (1) BY HYDROLYSIS OF CANE SUGAR. In the laboratory glucose may be prepared by the hydrolysis of cane sugar (*sucrose*) with dilute hydrochloric acid in alcohol solution.

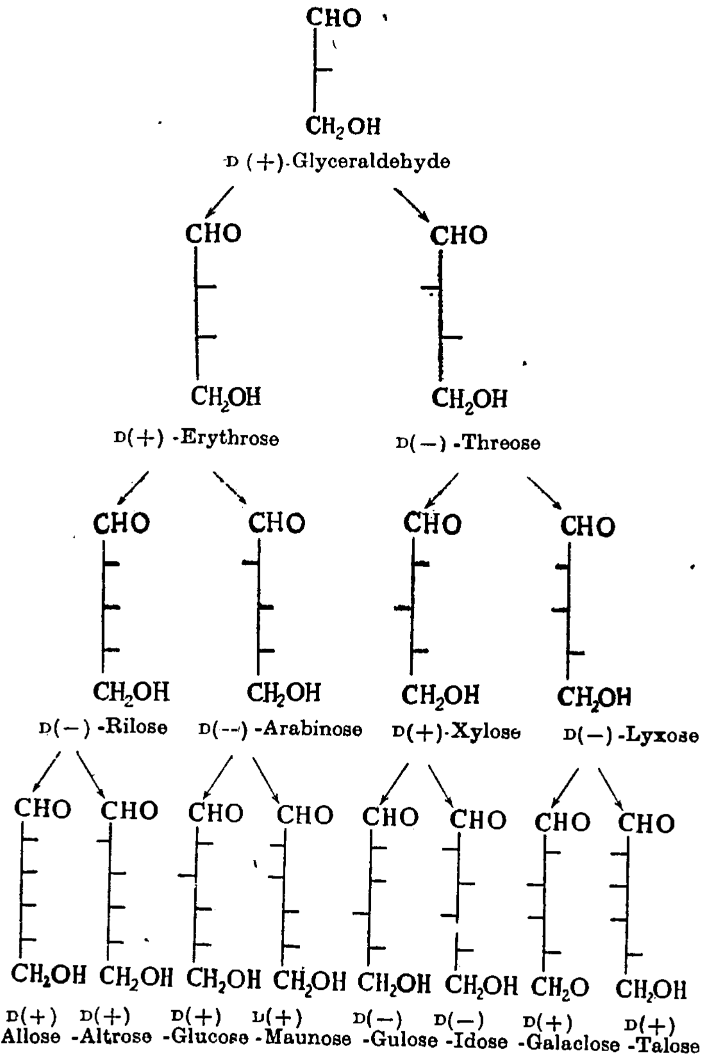
$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \longrightarrow \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

On cooling the resulting solution, glucose being almost insoluble in alcohol separates out leaving fructose in solution.

(2) BY HYDROLYSIS OF STARCH. Glucose is obtained industrially by the hydrolysis of starch (corn starch, potato starch) by heating with very dilute sulphuric acid.

$$\underset{\text{Starch}}{(C_6H_{12}O_5)_n} + nH_2O \longrightarrow \underset{\text{Glucose}}{nC_6H_{12}O_6}$$

Configuration of Aldoses



The resulting solution is neutralised with calcium carbonate, and the precipitated calcium salts are filtered off. The filtrate is decolorised with animal charcoal and then concentrated in vacuum pans until the glucose crystallises.

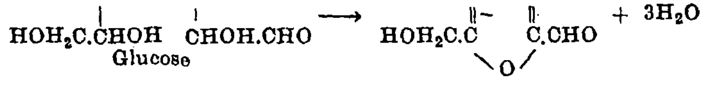
(3) BY HYDROLYSIS OF CELLULOSE. Another cheap and potent source of glucose is wood cellulose, $(C_6H_{10}O_5)_n$, which on hydrolysis with dilute mineral acid yields glucose. The details of the procedure are the same as in the manufacture of glucose from starch. This method is now being used to produce glucose for power alcohol.

Properties. (*Physical*). Glucose is a colourless crystalline solid, m.p. 146°. The monohydrate which crystallises from cold water melts at 86°. It is very soluble in water (84 g. per 100 g) but sparingly soluble in alcohol, and insoluble in ether. It is approximately three-fourths as sweet as cane sugar. Naturally occurring glucose is optically active and its solution is dextro-rotatory (hence its name *dextrose*).

(*Chemical*). Glucose behaves as a pentahydroxy aldehyde and gives all the reactions of monosaccharides.

$$\text{Glucose}\begin{cases} +(CH_3CO)_2O \longrightarrow \text{Pentaacetyl glucose} \\ +Ca(OH)_2 \longrightarrow \text{Calcium glucosate} \\ +CH_3OH \xrightarrow{HCl} \text{Methyl glucoside} \\ +H \xrightarrow{Na/Hg} \text{Sorbitol} \\ +O \xrightarrow{Br_2/H_2O} \text{Gluconic acid} \\ \quad\;\; \xrightarrow{(HNO_3)} \text{Saccharic acid} \\ +HCN \longrightarrow \text{Glucose cyanohydrin} \\ +NH_2OH \longrightarrow \text{Glucose oxime} \\ +Ph.NHNH_2 \longrightarrow \text{Glucose hydrazone} \\ \quad\;\; \xrightarrow{\text{excess}} \text{Glucosazone (m.p. 205°)} \\ +\text{Dil.}NaOH \longrightarrow \text{Glucose+Mannose+Fructose} \\ +\textit{Yeast} \longrightarrow \text{Ethyl alcohol.} \end{cases}$$

Glucose on boiling with dilute hydrochloric acid forms hydroxymethylfurfural.



Hydroxymethylfurfural

Uses. Glucose is used : (1) as a food for invalids; (2) as a sweetening agent in making candy, syrups, (jams and pharmaceutical preparations ; (3) in preserves ; (4) as a reducing agent in silvering of mirrors and to convert indigo blue to indigo white in vat dyeing ; (5) for making vinegar and wine by fermentation, as also in the form of molasses, for alcohol manufacture ; (6) as a starting material for the industrial synthesis of vitmin C.

Tests. (1) *Dry heating.* Heat a little glucose in a dry test-tube. It melts and turns brown, giving a smell of burnt sugar, and finally leaves a black residue of carbon.

(2) *Conc.* H_2SO_4. Warm a little glucose with concentrated sulphuric acid. A puffy mass of carbon is produced.

(3) *Molisch's Test.* Add two drops of a 20 per cent solution of α-naphthol in alcohol to 5 mls. of a dilute solution of glucose. Then pour carefully concentrated sulphuric acid along the side of the test-tube so as to get a lower layer of the acid. A beautiful violet colour is produced at the junction of the two liquids.

(4) *Sodium Hydroxide Solution.* Take 0·5 gm. of glucose and 5 mls. of dilute sodium hydroxide solution in a test tube. Boil the contents. It turns first yellow and then brown, and a smell of caramel is given.

(5) *Silver Mirror Test.* Warm glucose with ammoniacal silver nitrate solution. Silver mirror is produced.

(6) *Fehling's Solution.* Warm glucose with Fehling's solution. A red precipitate is obtained.

(7) *Osazone formation.* Dissolve 1 gm of glucose in 5 mls. of water and add a solution of 2 mls. of phenylhydrazine in 2 mls. of glacial acetic acid. Heat the test-tube containing the mixture in a water-bath for about 16 minutes. A yellow precipitate of glucosazone (m.p. 205°) is formed.

STRUCTURE OF D(+)-GLUCOSE

Glucose is the most widely occurring sugar in nature and is dextrorotatory in character. Its structure is established by the following steps.

(A) **Open-chain formula.** (1) The elementary analysis and molecular weight determination has given the molecular formula $C_6H_{12}O_6$ to glucose.

(2) Presence of five —OH groups is indicated by its reaction with acetic anhydride when it yields penta-acetyl derivative. These must be linked to different carbon atoms, since the compound containing two hydroxyl groups on a single carbon atom will be unstable.

(3) Glucose reduces Fehling's and ammoniacal silver nitrate solutions, forms cyanohydrin with HCN, and can be hydrogenated to sorbitol by only one molecule of hydrogen. These reactions indicate the presence of —CHO group in the molecule.

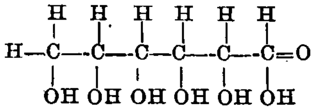
(4) On mild oxidation with bromine water, glucose is converted to gluconic acid which when reduced with excess of HI yields n-hexanoic acid.

$$\underset{\text{Glucose}}{C_6H_{11}O_5CHO} \xrightarrow{[O]} \underset{\text{Gluconic acid}}{C_6H_{11}O_5COOH} \xrightarrow{[H]} \underset{\substack{\text{n-Hexanoic}\\ \text{acid}}}{CH_3.(CH_2)_4COOH}$$

This clearly shows the presence of an aldehydic group at the *end of the chain.*

(5) That all the carbon atoms are forming an unbranched chain is proved by the fact that glucose on strong reduction with hydriodic acid (converting all —OH groups into —H) is changed into n-Hexane.

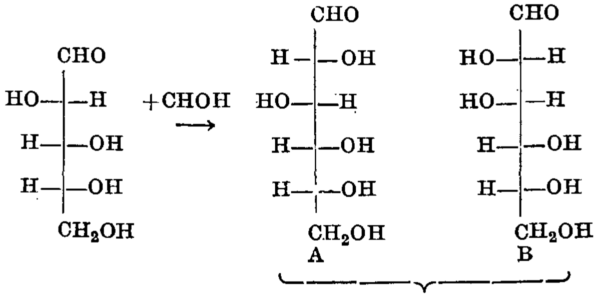
(6) From above considerations, it follows that the open-chain formula of glucose may be represented as



$$\mathrm{H{-}\overset{H}{\underset{OH}{C}}{-}\overset{H}{\underset{OH}{C}}{-}\overset{H}{\underset{OH}{C}}{-}\overset{H}{\underset{OH}{C}}{-}\overset{H}{\underset{OH}{C}}{-}\overset{H}{\underset{OH}{C}}{=}O}$$

(B) **Configuration.** Having known the open-chain structure of glucose, we proceed to dertermine the arrangement of H and OH groups about the four asymmetric carbon atoms present in the molecule.

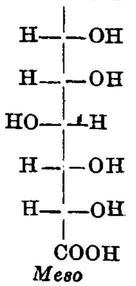
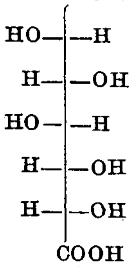
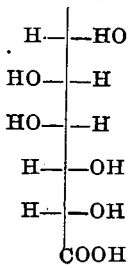
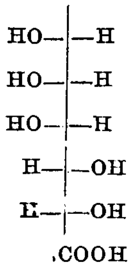
(1) D-Arabinose by Kiliani's synthesis gives D-glucose and D-mannose. Thus, theoretically, the configurations of the two hexoses can be derived by creating a new —CHOH— below the CHO group in the structure of D-arabinose. This can be done in two ways according as H is towards the left or towards the right.



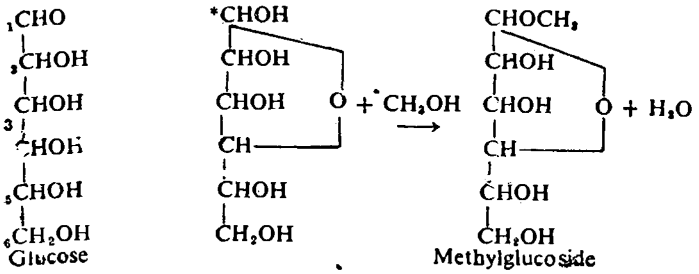
D-Glucose and D-Mannose

Therefore, D-glucose has the configuration A or B.

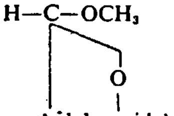
(2) By Kiliani's synthesis D-glucose yields two heptoses which on oxidation form one *meso* (inactive) and one active dibasic acid. This is possible only if D-glucose has the configuration A. The formula B would, however, give two dibasic acids both of which are active.

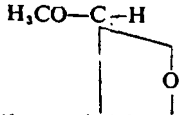
Possible dibasic acids from A		Possible dibasic acids from B	
			
Meso	*Active*	*Active*	*Active*

(C) **Ring structure.** (1) Fischer observed that D-glucose reacts with methyl alcohol to form methylglucoside which gives negative test for the CHO group. He explained this reaction by assuming the presence of a stable five-membered (γ-oxide) ring in glucose (Baeyer's theory).

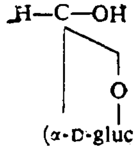


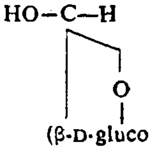
(2) It may be noted that by ring formation, the 1-carbon in glucose has become asymmetric. Hence if Fischer's assumption was correct, two isomeric methylglucosides should be possible.


(α-D-methylglucoside)

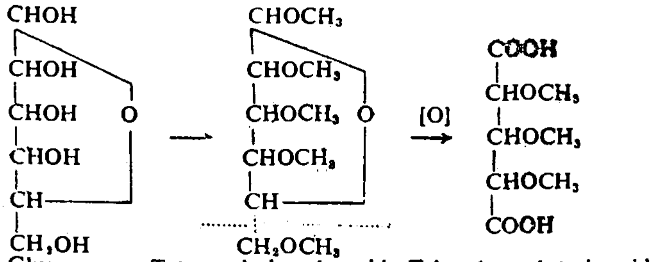

(β-D-methylglucoside)

Actually two methylglucosides, α-D-methylglucoside and β-D-methylglucoside have been isolated. Therefore there should exist the two corresponding forms of glucose.

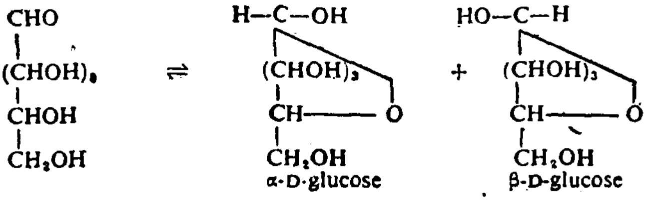

(α-D-glucose)


(β-D-glucose)

(3) Hirst found that tetramethylgucoside on oxidation with nitric acid yields trimethoxyglutaric acid which was possible only if glucose has a six-membered (δ-oxide) ring.

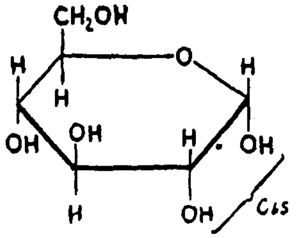


(4) Taking into consideration that D-glucose readily gives the reactions of a free—CHO group, it is argued that it exists as the equilibrium mixture :

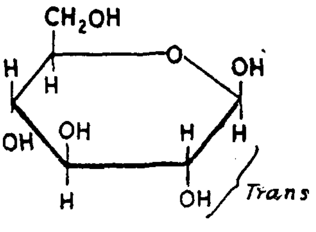


The two forms of D-glucose* have been actually isolated and the validity of the above equilibrium has been proved from a study of the phenomenon of mutarotation. The significance of the ring structure of glucose may be clearly understood by writing the formulae of α-and β-D-glucose as haxagons with complete configurations.

The six-membered oxygen-containing ring present in these formulae is called a *pyranose ring,* and the two forms of D-glucose are often spoken of α- and β-D-glucopyranose.



α-D-glucose (*Cis form*)



β-D-glucose (*Trans form*)

MUTAROTATION

A freshly prepared aqueous solution of D-glucose has a specific rotation of +113°, which gradually falls on standing to a value of +52°. This phenomenon of change in rotation first noticed by Dubruntfaut (1895), is termed mutarotation (Latin ; *muto*=to change).

Tarnet (1858) prepared two isomeric forms of glucose : (1) α-D-glucose, specific rotation +113° ; and (2) β D-glucose, specific rotation +19°. It was observed that both these forms showed

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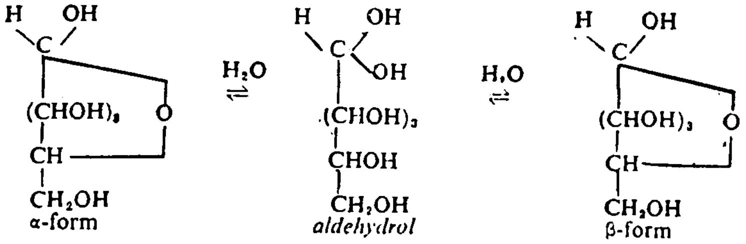
*α-D-glucose, m.p. 146°, is obtained by crystallising glucose from cold alcohol. β-D-glucose, m.p. 148-150°, is prepared by crystallising glucose from pyridine.

mutarotation, the rotation of the α-form falling and that of the β-form rising to the same constant value of +52°. Obviously, α- and β-forms are interconvertible, so that the value of +52° corresponds to the state of equilibrium between the two forms.

$$\underset{+113^\circ}{\alpha\text{-D-Glucose}} \overset{}{\underset{+52^\circ}{\rightleftharpoons}} \underset{+19^\circ}{\beta\text{-D-Glucose}}$$

Ordinary D-glucose is chiefly the α-form. This gradually changes into the β-form till an equilibrium mixture is obtained which has the specific rotation +52°. The aged solution of glucose contains approximately 38 per cent of the α-form and 62 per cent of the β-form.

According to Lowry (1925), mutarotation of the either form of glucose takes place through the formation of an open-chain *aldehydrol* as follows :



The phenomenon of mutarotation is not peculiar to glucose only, and is shown by most of the simple sugars.

FRUCTOSE, FRUIT SUGAR, LEVULOSE, $C_6H_{12}O_6$

It is present in the free state along with glucose in honey and in many fruits, hence the name *fruit sugar*. In the combined form it occurs in cane sugar, and in the polysaccharide *inulin* which is obtained from certain plants (dahlia, artichoke, etc.).

Preparation. (1) FROM CANE SUGAR. Fructose may be prepared in the laboratory by the hydrolysis of cane sugar (*sucrose*) with dilute sulphuric acid.

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \longrightarrow \underset{\text{Fructose}}{C_6H_{12}O_6} + \underset{\text{Glucose}}{C_6H_{12}O_6}$$

When the hydrolysis is complete, the excess of sulphuric acid is neutralised with barium carbonate and the filtrate concentrated. It is cooled in ice and then calcium hydroxide is added to precipitate calcium fructosate, the calcium glucosate formed remaining in solution. The calcium fructosate is removed by filtration and converted to fructose by passing carbon dioxide through its suspension in water.

$$\underset{\text{Calcium fructosate}}{C_6H_{11}O_5.O.Ca.OH} + CO_2 \longrightarrow \underset{\text{Fructose}}{C_6H_{12}O_6} + CaCO_3$$

The liberated fructose solution is freed from calcium carbonate by filtration and evaporated to a syrup. On addition of a crystal of fructose to the syrup (*seeding*) crystallisation sets in. The crop of crystals thus obtained is purified by recrystallisation from alcohol.

(2) From Inulin. Fructose is best prepared by the hydrolysis of *inulin* with dilute sulphuric acid. (*Industrial*).

$$\underset{\text{Inulin}}{(C_6H_{10}O_5)_n} + nH_2O \longrightarrow \underset{\text{Fructose}}{nC_6H_{12}O_6}$$

The resulting solution is neutralised with barium hydroxide and the precipitated barium sulphate removed by filtration. The solution thus obtained is concentrated under reduced pressure to yield the crystals of fructose.

This method is superior to the first one as it directly yields pure fructose.

Properties. (*Physical*). Fructose is a colourless crystalline solid, m.p. 105° with decomposition. It is about one and three-fourth times as sweet as cane sugar and, in fact, is the sweetest of all the sugars. It is very soluble in water but sparingly so in alcohol and insoluble in ether. Fructose is laevorotatory, hence its name *levulose*. It exhibits mutarotation and the final value of specific rotation is $-93°$.

(*Chemical*). Chemically fructose behaves as a pentahydroxy ketone. In most respects its reactions resemble with those of glucose. (*See general reactions of monosaccharides*).

$$\text{Fructose}\left\{\begin{array}{lll}
+ (CH_3CO)_2O & \longrightarrow & \text{Pentaacetyl fructose} \\
+ Ca(OH)_2 & \longrightarrow & \text{Calcium fructosate } (\textit{insoluble}) \\
+ CH_3OH & \xrightarrow{(HCl)} & \text{Methyl fructoside} \\
+ H & \xrightarrow{Na/Hg} & \text{Sorbitol + mannitol} \\
+ O & \xrightarrow{Br_2/H_2O} & \text{No action} \\
 & \xrightarrow{HNO_3} & \text{Tartaric acid + Glycollic acid} \\
+ HCN & \longrightarrow & \text{Fructose cyanohydrin} \\
+ NH_2OH & \longrightarrow & \text{Fructose oxime} \\
+ PhNH.NH_2 & \longrightarrow & \text{Fructose hydrazone} \\
 & \xrightarrow{excess} & \text{Fructosazone (m.p. 205°)} \\
+ \text{Dil. NaOH} & \xrightarrow{heat} & \text{Glucose + Mannose + Fructose} \\
+ \textit{Yeast} & \longrightarrow & \text{Ethyl alcohol}
\end{array}\right.$$

Fructose differs from ordinary ketones in that it reduces Fehling's solution and ammoniacal silver nitrate solution like glucose. This is on account of the readily oxidisable grouping $—CO\ CH_2OH$ present in the molecule.

Uses. Fructose is used as a sweetening agent in confectionary and as a substitute of cane sugar for diabetic persons.

Tests. (1) Fructose reduces Fehling's solution and ammoniacal silver nitrate solution.

(2) It gives *Molisch's test.*

(3) It forms the same osazone (m.p. 205°) as obtained from glucose.

(4) It gives a brownish red precipitate by heating with a little resorcinol in hydrochloric acid. (*Selivanoff's test*).

STRUCTURE OF FRUCTOSE

(A) **Open-chain formula.** (1) The elementary analysis and the molecular weight determination has given the formula $C_6H_{12}O_6$ to fructose.

(2) It forms a pentaacetyl derivative and hence contains five OH groups. Fructose being a stable compound, all the OH groups must be linked to different carbons.

(3) When reduced with sodium amalgam, it forms a mixture of hexahydric alcohols which on complete reduction with hydrogen iodide yield 2-iodohexane, $CH_3.CHI.CH_2.CH_2.CH_2.CH_3$. This shows the presence of a normal six-carbon chain in the molecule.

(4) Fructose forms a phenylhydrazone and, therefore, it also contains a carbonyl group —CO—.

(5) On oxidation it gives a mixture of tartaric acid (C_4) and glycollic acid (C_2). This reaction is characteristic of ketones and shows that the carbonyl group is present next to one of the end carbon atoms of the chain.

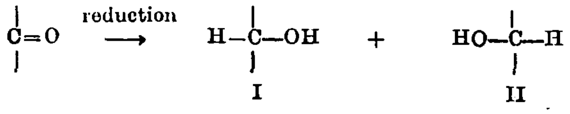
(6) From the above considerations, we can construct the molecule of fructose as follows :

$$CH_2OH.CO \vdots CHOH.CHOH.CHOH.CH_2OH$$

The dotted line indicates where the break occurs on oxidation.

(7) The ketonic formula of fructose is established by the fact that it explained very satisfactorily—

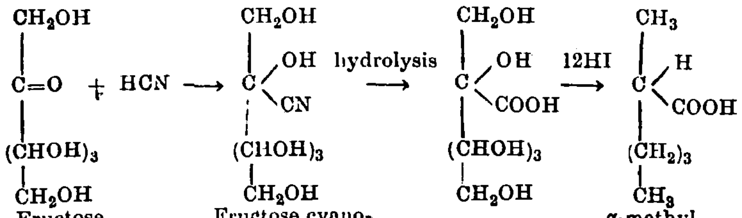
(*a*) The formation of its reduction products (sorbitol and mannitol) by action with sodium amalgam and water. These alcohols are isomeric in character differing only in configuration.



$$\text{C=O} \xrightarrow{\text{reduction}} \text{H—C—OH} + \text{HO—C—H}$$

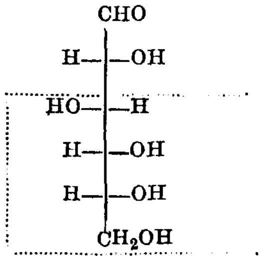
I II

(*b*) The reaction with hydrocyanic acid giving cyanohydrin which on hydrolysis gives the corresponding acid. The acid on reduction with HI gives α-methyl caproic acid.

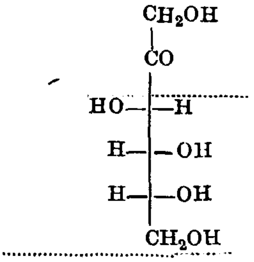


Fructose Fructose cyanohydrin α-methyl caproic acid

(B) **Configuration.** The configuration of fructose follows from the fact that it forms the same osazone as obtained from glucose. Hence, the two sugars differ only in respect of the two carbons involved in osazone formation and the rest of the molecule is identical. Thus :



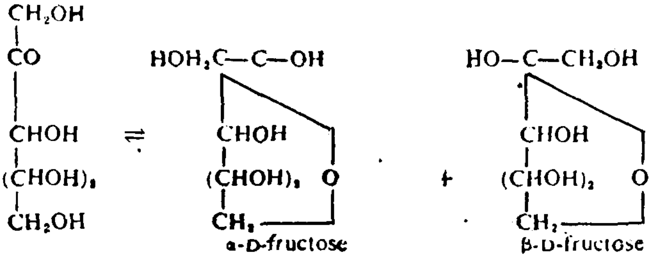
D-Glucose



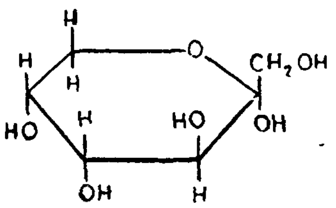
D-Fructose

(C) **Ring structure.** D-Fructose also exhibits mutarotation and, therefore, it is expected to exist in two forms. Hence it is assumed that like glucose it has δ-oxide ring in the molecule.

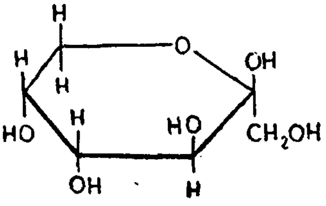
Thus :



These forms are also called α-D-fructopyranose and β-D-fructopyranose.

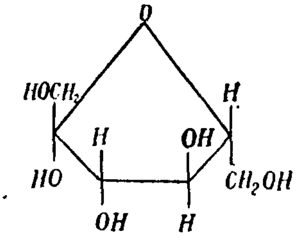


α-D-fructopyranose



β-D-fructopyranose

D-Fructose is also known to exist as γ form, which has a five-membered oxide ring and is called β-D-fructofuranose. γ-Fructose is known as a constituent of sucrose molecule.



γ-fructose

COMPARATIVE STUDY OF GLUCOSE AND FRUCTOSE

Glucose is an aldehydic hexahydric alcohol, while fructose is a ketonic hexahydric alcohol.

$CHO.CHOH \vdots CHOH.CHOH.CHOH.CH_2OH$ Glucose
$CH_2OH.CO \vdots CHOH.CHOH.CHOH.CH_2OH$ Fructose
Different⋮ Same

As indicated above two-third molecule of the compounds is same and hence they show many common reactions. The difference in their behaviour is due to the different structure in respect of the first two carbon atoms.

GLUCOSE	FRUCTOSE
Points of Resemblance :	
(1) With acetic anhydride, glucose forms a penta-acetyl derivative.	(1) Also reacts with acetic anhydride to form penta-acetyl derivative.
(2) With methanol (and HCl) gives methyl glucoside, $C_6H_{11}O_5.OCH_3$.	(2) Also forms similar product, methyl fructoside, $C_6H_{11}O_5.OCH_3$.
(3) With HCN, forms cyanohydrin.	(3) Also forms cyanohydrin.
(4) Forms oxime with NH_2OH.	(4) Also forms oxime.
(5) When heated with phenylhydrazine, forms glucosazone.	(5) Forms exactly identical osazone.
(6) On fermentation with yeast gives alcohol and CO_2.	(6) Also forms alcohol and CO_2 by fermentation.
(7) Reduces Fehling's solution and ammoniacal silver nitrate.	(7) Also reduces Fehling's solution and ammoniacal silver nitrate solution.
Points of difference :	
(1) Glucose is dextro-rotatory.	(1) Fructose is laevorotatory.
(2) Reacts with lime to form calcium glucosate, $C_6H_{12}O_6.CaO$, which is soluble in water.	(2) Forms calcium fructosate. $C_6H_{12}O_6.CaO$, but it is insoluble in water.
(3) On reduction gives sorbitol.	(3) Gives a mixture of sorbitol and mannitol.
(4) On oxidation forms gluconic acid which contains the same number of carbon atoms as glucose.	(4) Gives a mixture of glycollic acid and tartaric acid, each containing less carbon atoms thanfructose.
(5) Forms a brown resinous mass with warm NaOH solution.	(5) Does not form a resin with NaOH solution.

Tests. The tests (4) to (7) for glucose are shown by fructose as well. It can be distinguished from glucose by the following tests.

(1) **Selivanoff's Test.** To 5 mls. of a solution of resorcinol in dilute hydrochloric acid, add 1 ml. of a dilute solution of fructose and boil. A red colour or precipitate is obtained.

(2) **Furfural Test.** To 1 ml. of a dilute solution of fructose, add 1 ml. of 1% solution of α-naphthol in alcohol and 6 mls. of hydrochloric acid. Heat to boil. A violet colour is produced.

DISACCHARIDES

Just as a monosaccharide reacts with methyl alcohol to form methylglycoside it may unite with another monosaccharide (same or different) by elimination of water molecule to form a *disaccharide.*

$$C_6H_{11}O_5 \vdots OH + H \vdots O.C_6H_{11}O_5 \longrightarrow \underset{\text{Disaccharide}}{C_6H_{11}O_5.O.C_6H_{11}O_5} + H_2O$$

In all known disaccharides, glucose forms one unit, while the other unit may be a pentose or a hexose, an aldose or a ketose. The three disaccharides which occur in nature are *sucrose, lactose* and *maltose.*

SUCROSE, CANE SUGAR, $C_{12}H_{22}O_{11}$

Sucrose is by far the most important disaccharide which is widely distributed in plants, especially in sugar cane (15 to 20%), sugar beet (12 to 15%) and sugar mapple (2 to 3%). It is also present in small quantities in ripe fruits such as pineapple, apricot, banana, mango, almonds, etc. and also in honey.

Manufacture. The two important sources of commercial sugar are *sugar cane* and *sugar beet.* The 'cane' is a tropical crop, while the 'beet' grows in temperate climates. In India and Java, sugar is mostly obtained from the cane. The process consists of the following steps :

(*i*) *Extraction of the juice* ;

(*ii*) *Purification of the juice* ;

(*iii*) *Concentration and crystallisation* ; and

(*iv*) *Separation and drying of crystals.*

(1) **Extraction of the Juice.** The freshly-cut* cane is shredded and passed through a series of roller mills to squeeze out the juice. The crushed cane as it leaves the first mill is sprayed with water to ensure complete extraction. The cellulosic material left is called *bagasse.* It is used as fuel under boilers and also in the manufacture of the insulating material known as *celotex.*

The juice is extracted from beets by cutting them into slices and by soaking these in hot water. The sugar diffuses out into the water, while the colloidal constituents remain behind. This process of 'extraction' is carried in a battery of iron tanks, the extraction being done on counter current principle.

(2) **Purification of the Juice.** The raw juice contains 15 to 20 per cent of sucrose and much impurity which includes organic acids (oxalic and citric acids), mineral phosphates, proteins and colloidal colouring matter. It is purified by the operations shown in Fig. 33·2.

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*If the cut cane be allowed to stand, rapid hydrolysis sets in which results in the conversion of cane sugar into uncrystallisable glucose and fructose.

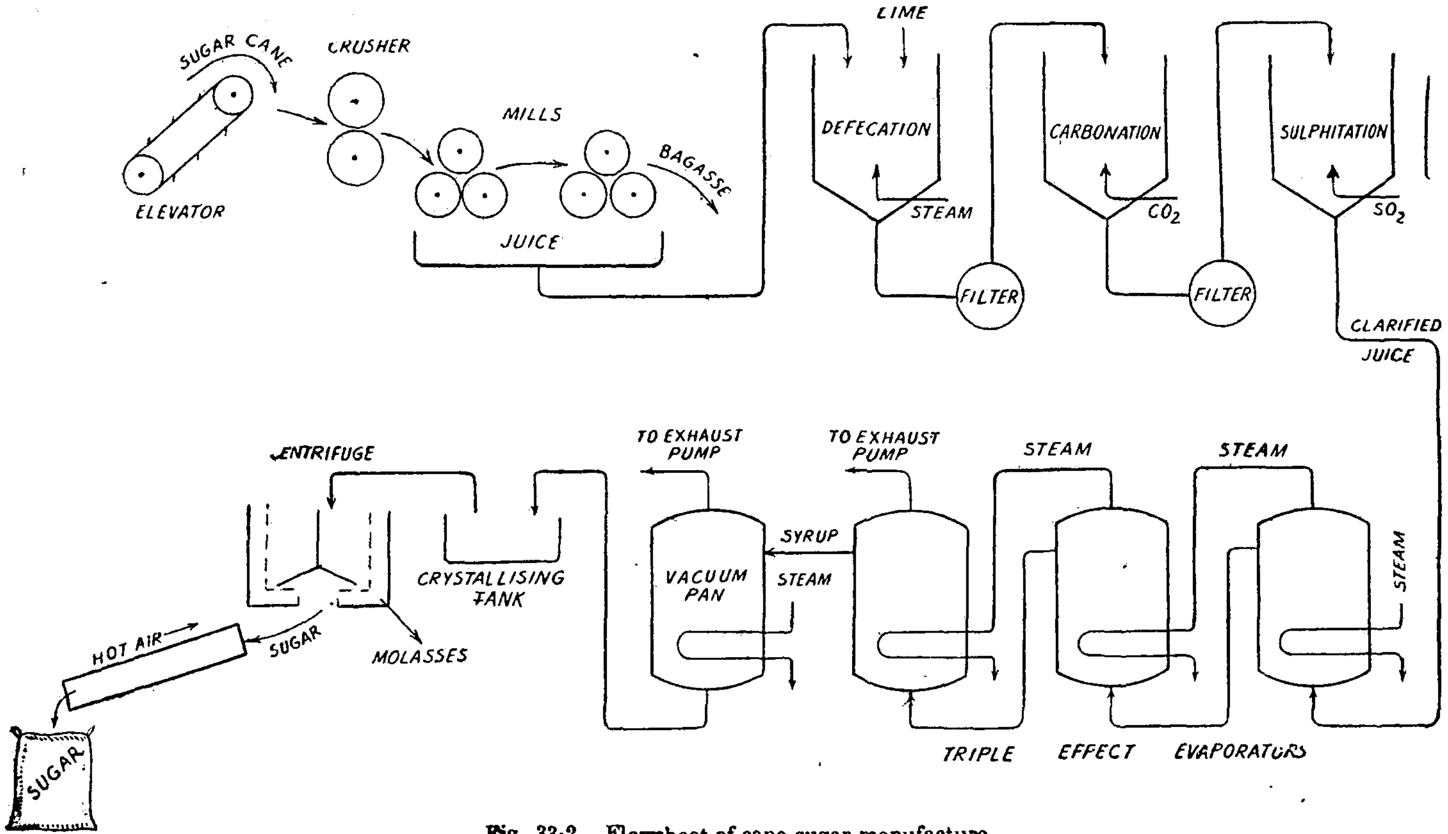


Fig. 33·2. Flowsheet of cane sugar manufacture.

(*i*) Defecation. The juice is at once run into tanks heated by steam and treated with 2-3 per cent lime. This operation called *defecation* removes free organic acids and phosphates as insoluble calcium salts. The proteins and the colloidal colouring matter is also thrown out of solution as thick scum appearing on the surface. The precipitated calcium salts and the scum are removed by filtration through canvas.

(*ii*) Carbonation. The juice after 'defecation' contains excess of lime and soluble calcium sucrate. Carbon dioxide is then passed through it. This process known as '*carbonation*' removes the excess of lime and also decomposes calcium sucrate to give back sugar.

$$\underset{\text{Calcium sucrate}}{C_{12}H_{22}O_{11}.3CaO} + 3SO_2 \longrightarrow \underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + 3CaCO_3$$

Calcium carbonate is filtered off.

(*iii*) Sulphitation. The carbonated juice is treated with sulphur dioxide. This operation, which is referred to as *sulphitation*, completes the neutralisation of lime and the decomposition of calcium sucrate. In addition the colour of the juice is bleached. The clarified juice is filtered to remove precipitated calcium sulphite.

In some countries the juice is also removed by passing it through a bed of animal charcoal or *norit* (activated coconut charcoal).

(3) **Concentration and Crystallisation.** The clarified juice is then concentrated by boiling under reduced pressure in '*multiple effect*' evaporators. In these, the steam produced in the first evaporator is used to boil the juice in the second kept at a lower pressure, the steam produced in the second being again employed to boil the juice in the third maintained at a still lower pressure, and so on.

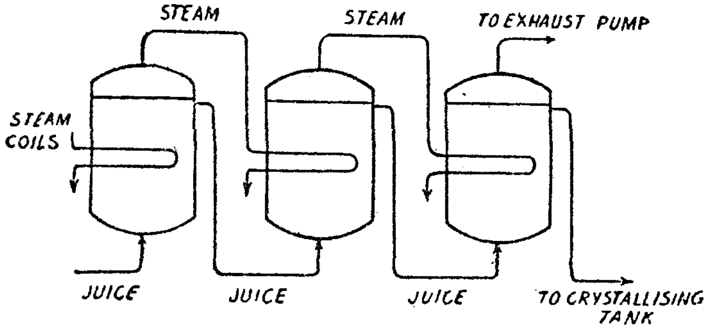


Fig. 33·3. The multiple effect evaporators.

The concentrated juice is finally passed to the 'vacuum pans' where further evaporation reduces the water content to 6—8 per cent. Here partial separation of sugar crystals takes place. The contents of the pan (*massecuite*) are discharged into the crystallising tank where crystals grow and form a thick 'crop'.

(4) **Separation and Drying of crystals.** The massecuite is then charged into centrifugal machines (Fig. 33·4) by means of which sugar crystals are separated from the mother liquor. The crystals are here sprinkled with a little water to wash away any impurities sticking to their surface. The crystals are finally dried by dropping through a chimney or a revolving cylinder where they meet a current of hot air coming up. The sugar thus obtained is about 96 per cent pure. For further purification it may be dissolved in hot water and recrystallised.

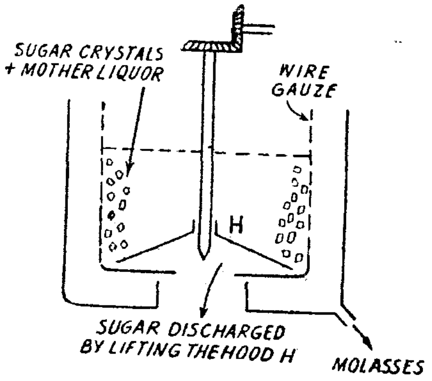


Fig. 33·4. Centrifugal machine.

The mother liquor (*molasses*) obtained after the removal of crystals contain much sucrose and may be concentrated further to get a fresh crop of crystals. In modern practice, however, it is considered more economical to ferment the molasses straightway and obtain alcohol. It contains 55—80 per cent of sugar, mostly uncrystallisable glucose and fructose, and is an excellent raw material for the manufacture of alcohol.

Sugar Industry in India. The sugar industry is one of the major industries of India. With the improvement in the quality of sugarcane and the setting up of more sugar factories in the country the Union Government has succeeded in stepping up the annual production of sugar to almost double of what it was ten years back. The biggest sugar producing State is the Uttar Pradesh and then come Bihar and Mysore in order of annual production.

STATE-WISE PRODUCTION OF SUGAR (TONNES) IN INDIA

	1953-54	*1961-62*
Uttar Pradesh	558,900	2,203,531
Bihar	146,300	358,677
Madras	71,700	116,161
Gujarat	—	33,861
Punjab	16,700	90,592
Madhya Pradesh	—	30,948
Mysore	—	137,753

Properties. (*Physical*). Sucrose forms large four-sided prismatic crystals, m.p. 186°. Leaving fructose, it is the sweetest of the sugars. At room temperature it is soluble in about one-third of its weight of water, but it is only sparingly soluble in alcohol. It is dextrorotatory, its specific rotation being $+66{\cdot}5^\circ$. It does not undergo mutarotation.

(*Chemical*). Sucrose molecule is made of one glucose unit and one fructose unit. It gives the following reactions :

(1) Action of Heat. When heated to 200°, sucrose loses water forming a brown, syrupy mass called *caramel* with a characteristic flavour, which is used for colouring rum, vinegar and many food-stuffs. At higher temperatures, sucrose chars to almost pure carbon and gives vapour of acetone, acetic acid, etc.

(2) Hydrolysis. When boiled with dilute mineral acids, or treated with enzyme invertase (*yeast*), sucrose is hydrolysed to yield an equimolecular mixture of glucose and fructose.

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \longrightarrow \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

Sucrose is dextrorotatory (+66·5°), while the resulting solution of D-glucose (+53°) and D-fructose (92·3°) is naturally laevorotatory. Since the hydrolysis of sucrose is accompanied by a reversal of rotation, it is termed the **inversion** and the product is called '***invert sugar***'. The invert sugar is a little sweeter than sucrose.

(3) Oxidation. When oxidised with concentrated nitric acid, sucrose is oxidised to oxalic acid.

$$C_{12}H_{22}O_{11} + 9O_2 \longrightarrow \underset{\text{Oxalic acid}}{6(COOH)_2} + 5H_2O$$

(4) Action with H_2SO_4. Concentrated sulphuric acid chars sucrose with the evolution of carbon dioxide and sulphur dioxide.

$$C_{12}H_{22}O_{11} + [H_2SO_4] \longrightarrow 12C + 11H_2O$$

$$C + 2H_2SO_4 \longrightarrow CO_2 + 2SO_2 + 2H_2O$$

(5) Formation of Sucrates. Sucrose is slightly acidic and reacts with the hydroxide of calcium, strontium and barium to form sucrates. Thus :

$$C_{12}H_{22}O_{11} + 3Ca(OH)_2 \longrightarrow \underset{\text{Calcium sucrate}}{C_{12}H_{22}O_{11}.3CaO} + 3H_2O$$

These compounds are decomposed when carbon dioxide is passed through their aqueous suspensions. The formation of strontium sucrate is used for the recovery of sucrose from molasses.

(6) Acetylation. When boiled with acetic anhydride and fused sodium acetate, sucrose yields the *ocfaacetate*. This shows that its molecule contains only eight free OH groups.

(7) Fermentation. Aqueous solutions of sucrose when fermented with yeast, give alcohol and carbon dioxide. The enzyme *invertase* first converts it into glucose and fructose. These sugars are then decomposed by the enzyme *zymase* to yield alcohol and carbon dioxide.

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{\textit{Invertase}} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

$$C_6H_{12}O_6 \xrightarrow{\textit{Zymase}} \underset{\text{Ethyl alcohol}}{2C_2H_5OH} + 2CO_2$$

Uses. Sucrose is used : (1) as a food and sweetening agent in candies, syrups, etc. ; (2) as a preservative for fruit products (jams, squashes) ; (3) for laboratory preparation of oxalic acid ; (4) for manufacture of sucrose octaacetate which is employed to denature alcohol to render paper transparent and oil-repellant, and to make anhydrous adhesives.

Tests. (1) On dry heating it chars giving a characteristic smell.

(2) When heated with concentrated sulphuric acid, it chars and gives out CO_2 and SO_2 gases.

(3) Responds to Molisch's test. (*See Tests of glucose*).

(4) Boil the sucrose solution with a few drops of dilute hydrochloric acid, and add Fehling's solution. A red ppt. of cuprous oxide is formed. Sucrose does not reduce Fehling's solution without first boiling it with acid. (*Distinction from glucose and fructose*).

(5) Sucrose octaacetate melts at 67°.

Sucrose also gives the Selivanoff's Test and 'Furfural Test' shown by fructose. It differs from glucose and fructose in not forming an osazone ; and it does not turn brown when heated with sodium hydroxide solution.

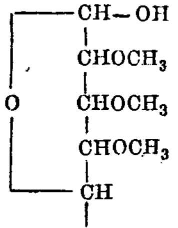
Structure. (1) Sucrose upon hydrolysis with dilute acids gives one molecule of D-glucose and one molecule of D-fructose.

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \longrightarrow \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

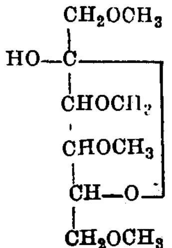
This indicates that sucrose is the anhydride of glucose and fructose.

(2) Sucrose does not reduce Fehling's solution and does not form an oxime or osazone. This shows that neither the aldehyde group of glucose nor the ketonic group of fructose is free in sucrose and that the two simple sugars are linked at these groups.

(3) On complete methylation sucrose yields an octamethyl derivative which on hydrolysis gives 2, 3, 4, 6-tetramethyl glucose and 1, 3 4, 6-tetramethylfructose.

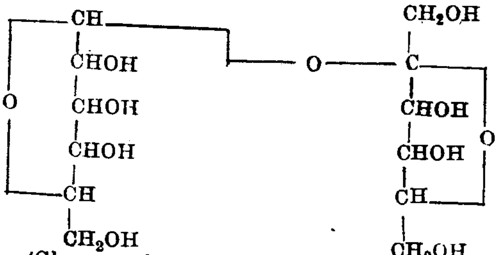


2, 3, 4, 6-tetramethylglucose



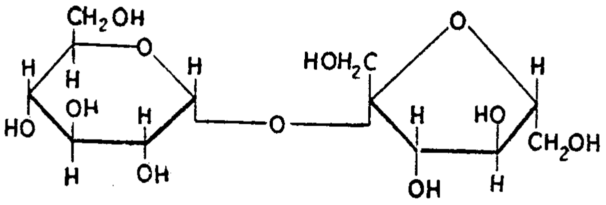
1, 3, 4, 6-tetramethylfructose

Therefore, the glucose unit has a six-membered (δ-oxide) ring, while the fructose unit has a five-membered (γ-oxide) ring. Also, the two sugars must be linked at the location of OH groups which have appeared after hydrolysis. Thus taking into consideration the configurations of D-glucose and D-fructose units, the structure of sucrose can be written as :



(Glucose unit) (Fructoseunit)

The kinetics of hydrolysis and the optical rotation of sucrose affords strong evidence that sucrose is an α-D-glucoside and β-D-fructoside. Both the structure and configuration of sucrose are shown in the following formula.



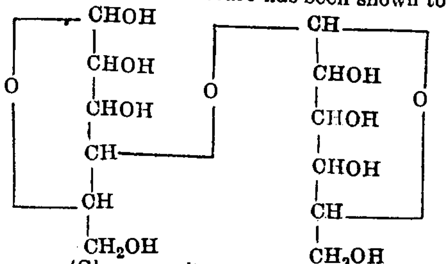
α-D-glucopyranose β-D-fructofurnanose (γ-fructose)

It may be noted that during the hydrolysis of sucrose, the β-D-fructofuranose produced first is converted to β-D-fructopyranose.

LACTOSE, MILK SUGAR, $C_{12}H_{22}O_{11}$

Lactose occurs in the milk of mammals to the extent of 2 to 5 per cent. It is prepared commercially from cow's milk by removing fat and proteins from it and then evaporating the whey to crystallisation.

Properties. Lactose is a white crystalline solid, m.p. 203° with decomposition. It is only about one-eighth as sweet as sucrose and one-tenth as soluble in water. It is dextrorotatory and undergoes mutarotation. Lactose reduces Fehling's solution ; forms an oxime and osazone. On hydrolysis with dilute acids by the enzyme *lactase*, it yields one molecule of D-glucose and one molecule of D-galactose. Its structure has been shown to be



(Glucose unit) (Fructose unit)

Uses. Lactose is used (1) as an ingredient of infant foods; and (2) as a medium for homoeopathic and biochemic medicines.

POLYSACCHARIDES

STARCH, $(C_6H_{10}O_5)_x$

The starch molecule is built of a large number of α-glucose ring units linked together by oxygen atoms. Its chemical name is *amylum.*

Starch is widely distributed in green plants, mainly in seeds and roots where it forms a reverse food supply. The chief commercial sources of starch are cereals, rice and potatoes. Starch occurs in the form of granules, which vary in shape and size depending on the source.

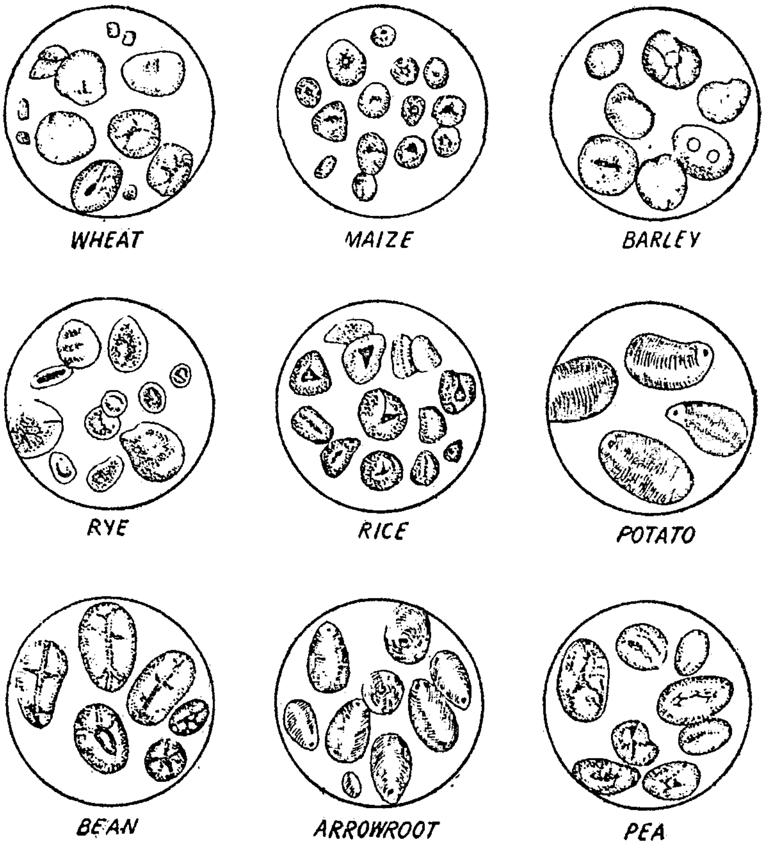


Fig. 33 5. Starch granules.

Manufacture. Starch is made commercially from wheat, maize and rice. The grains are first soaked in water to soften the crust. These are then crushed so as to break the cell walls containing starch. The pulp thus obtained is carried by a stream of water on to a fine sieve. The starch passes down in the form of a milky liquid, leaving behind the cell tissues which are used as fodder. The turbulent liquid containing starch is allowed to settle and starch separated by decantation. This is finally dried.

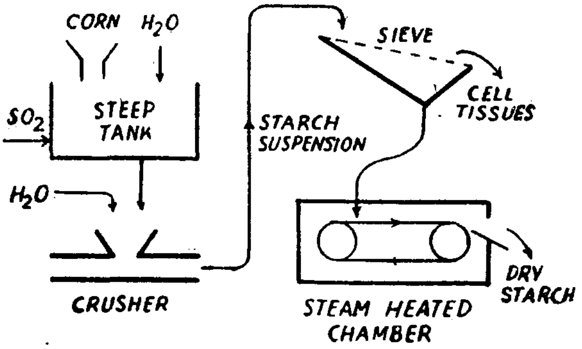


Fig. 33·6. Manufacture of starch.

Properties. Starch is a white amorphous substance having no taste or odour. It is insoluble in water but on boiling the granules burst giving a colloidal suspension, which may set to a translucent paste. The starch solutions and paste are dextro-rotatory.

(1) Starch gives a deep blue colour with iodine solution and is used as indicator for iodometric titrations.

(2) When boiled with dilute mineral acids, it is first converted into a gummy mass called **dextrin**, which on further heating gives glucose. The so-called *soluble starch* is made by digesting starch with dilute hydrochloric acid and washing the solid with water, and then with ammonia. The solid powder thus obtained gives a clear dispersion when dissolved in water.

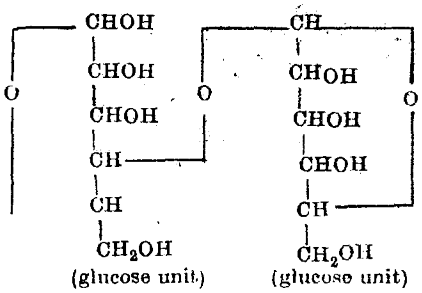
(3) In the presence of the enzyme *diastase*, starch is converted into maltose. This is an important step in the manufacture of alcohol from starch.

Uses. Starch is used as food ; as indicator ; for making adhesive pastes ; for sizing paper ; for stiffening linen in laundries ; and as a source of glucose and alcohol.

MALTOSE, MALT SUGAR, $C_{12}H_{22}O_{11}$

It is produced by the hydrolysis of starchy food-stuffs (potatoes and grains) by acids or the enzyme *diastase* present in malt.

Maltose forms white needles, m.p. 160-165°. It is very soluble in water. It is about one-third as sweet as sucrose. It is dextro-rotatory and undergoes mutarotation. Maltose reduces Fehling's solution, forms an oxime and osazone. On hydrolysis with hydrochloric acid, or the enzyme *maltase*, it forms two molecules of glucose. Its structure has been shown to be :



Maltose is used in the preparation of infant foods and malted milk.

CELLULOSE, $(C_6H_{10}O_5)_x$

The molecule of cellulose consists of a chain of about 200 β-glucose ring units.

Cellulose is the fibrous material which lends rigidity and support to the plant structure. The fibres of cotton, flax, hemp and wood are largely cellulose. Cotton and wood are the chief sources of cellulose. Cotton is almost pure cellulose, while wood also contains lignin, a substance whose chemical nature is not yet known, and other materials.

Preparation. (1) *From Cotton.* Absolutely pure or 'standard' cellulose is obtained from cotton by the extraction of fats and waxes with an organic solvent. It is then treated with alkali and sodium hypochlorite to bleach and to remove other impurities.

(2) *From Wood.* In preparation of cellulose for paper making, wood chips are cooked with sodium or calcium bisulphite, or caustic soda to remove lignin, resins, etc. It is then bleached with calcium or sodium hypochlorite. To get very pure cellulose, gums are also extracted from the product by extraction with organic solvents.

Properties. Cellulose is a colourless fibrous substance. It is insoluble in water and most organic solvents but dissolves in Schweitzer's reagent which is ammoniacal cupric hydroxide. On prolonged boiling with dilute acids, cellulose is converted into glucose. Like the sugars, it shows the reactions of an alcohol, forming esters.

Uses. Cellulose is used directly in making paper and cloth. It is also converted into several useful materials by treatment with chemical reagents.

Nitrocellulose. A mixture of nitric acid, and sulphuric acid reacts with cellulose giving 'nitrocellulose' which is, in fact, cellulose nitrate. The product containing 13 per cent or more is used as a high explosive under the name *gun-cotton*.

Celluloid. The poorly nitrated cellulose when heated with camphor under pressure gives a transparent, plastic mass which can be moulded to any form while hot. This is known as celluloid and is used for making toys, bangles and other articles of decoration.

Collodion. It is a 3 to 5 per cent solution of cellulose nitrates in three parts of ether and one part of alcohol.

Mercerized Cotton. When treated with strong alkali, cellulose swells and becomes translucent. This process of improving the appearance of cotton is called *Mercerization* after the name of its inventor, *Mercer*.

Parchment Paper. It is obtained when pure cellulose sheets are for a while treated with dilute sulphuric acid, washed and dried. The parchment paper is tough and translucent.

Rayon, Artificial Silk. It is the name used for filaments of celllulose which resemble silk in appearance. Formerly, rayon was obtained by dissolving cellulose in ammoniacal cupric hydroxide and forcing the solution through fine jets into dilute sulphuric acid. The acid removes the solvent and coagulates the cellulose.

The modern process (*Viscose Process*) consists in digesting cellulose with strong caustic solution and then adding some carbon disulphide solution. The pale yellow, jelly-like mass thus obtained is called Viscose. It is forced through fine jets into dilute sulphuric acid, when a silken thread of cellulose is developed.

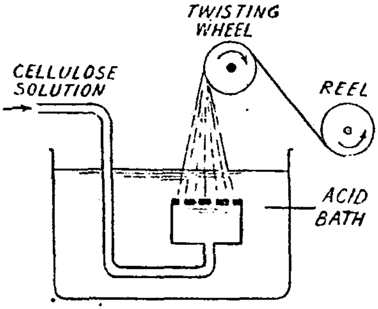


Fig. 33·7. Preparation of rayon.

Celanese. The hydroxyl groups of cellulose when treated with acetic anhydride and a little sulphuric acid, form cellulose triacetate. It is soluble in acetone and other solvents and is used for making films, lacquers and rayon. The rayon prepared from it is called *celanese*.

QUESTIONS

1. What are carbohydrates ? Why they are so called and what are their general properties ? How would you convert one into its lower or higher analogue ?

2. How have the carbohydrates been classified ? Mention the characteristic properties of each class.

3. Classify carbohydrates. How do you obtain glucose ? Discuss the action of phenylhydrazine on this compound.

4. What are monosaccharides ? Mention their important properties How is glucosazone prepared ? How would you show that glucose and fructose give identical osazones ? How can glucose be transformed into fructose ?

5. Describe the classification of carbohydrates. What is the experimental evidence to show that glucose contains an aldehyde group and fructose a ketone group ? How is glucose converted into fructose and *vice versa* ?

6. What are carbohydrates ? How are they classified ? Discuss the constitution of glucose.

7. Explain the constitution of glucose. Discuss the optical activity associated with it. (*Kurukshetra B.Sc. III, 1967*)

8. What are carbohydrates ? How are they classified ? Give evidence on which the cyclic structure of glucose is based. How can glucose be converted into fructose ? Explain, giving equations, the reactions involved. (*Allahabad B.Sc. II, 1967*)

9. Discuss the structure of glucose ? How will you convert glucose into fructose and *vice versa* ? (*Indore B.Sc. II, 1967*)

10. Establish the structure of glucose. *(Kalyani B.Sc. Hons., 1967)*

11. Discuss the constitution of glucose with special reference to the ring structure. *(Panjab B.Sc. III, 1967)*

12. Describe the manufacture of sucrose from sugar-beet. How does sucrose react with (*a*) lime water ; (*b*) acetic anhydride ; (*c*) yeast ; (*d*) conc. HNO_3 ; and (*e*) conc. and hot H_2SO_4 ? *(Panjab B.Sc. III, 1968)*

13. How may glucose be prepared from starch ? Discuss the structure of glucose, giving experimental evidence in support of it. Why was the open chain structure for glucose discarded in favour of a cyclic one ? *(Ujjain B.Sc., 1968)*

14. Discuss the constitution of D-glucose. How will you convert it into (*a*) D-fructose and (*b*) D-arabinose ? *(Bombay B.Sc., 1968)*

15. Discuss the methods of methylation of carbohydrates. Show how this helps in determining the size of the ring in D-glucose. *(Saurashtra B.Sc., 1968)*

16. Give the classification of carbohydrates. Discuss the constitution of glucose. *(Aligarh B.Sc., 1968)*

17. How do you determine the constitution of glucose ? Give evidences to support that glucose has a ring structure. *(Allahabad B.Sc., 1968)*

18. Show by reactions how it is possible to transform
    (*a*) an aldopentose into an aldohexose.
    (*b*) an aldohexose into an aldopentose.
    (*c*) an aldohexose into a ketohexose.
(Jadavpur B.Sc., 1969)

19. State how pure maltose is prepared. Describe its important reactions. *(Viswa Bharti B.Sc., 1969)*

20. What are carbohydrates ? How are these classified ? How is glucose obtained ? Discuss briefly its properties. How is glucose converted to fructose and fructose to glucose? *(Panjab B.Sc., 1969)*

21. How are carbohydrates classified ? Compare and contrast the properties of glucose and fructose. *(Vankateswara B.Sc., 1969)*

22. Discuss the structure and configuration of glucose and fructose and explain their optical properties. *(Kurukshetra B.Sc., 1969)*

23. How can you convert an aldose into a ketose and *vice versa* ? *(Udaipur B.Sc., 1969)*

24. Discuss the evidence in support of the pyranose oxide ring structure in D-glucose. *(Berhampur B.Sc., 1969)*

25. Discuss the evidence on which the structure of sucrose is based. *(Madurai B.Sc., 1969)*

26. Discuss evidence in support of the constitution of fructose. How can fructose be converted into glucose and glucose into fructose ? *(Tribhuvan B.Sc., 1969)*

34

Proteins

HENRY GILMAN
(1893— , American)
Editor of the well-known recent advanced treatise of organic chemistry. Main work on synthesis and the study of reaction mechanisms. He has researched with organometallic compounds and with furan derivatives. Now professor of organic chemistry in Iowa State College.

INTRODUCTION

The proteins are a class of complex organic compounds which are made of C, H, O and N, and which yield amino acids upon hydrolysis. They occur very widely in all plants and animals. All living matter is ultimately built of tiny units known as cells which are the basis of life, and proteins are an essential constituent of the jelly-like *protoplasm* of these cells. Thus on account of their primary importance for life, this class of compounds were named proteins (Mulder, 1838) from the Greek word '*proteois*', meaning *of the first order*.

About 19 per cent of the animal body consists of proteins. Thus skin, muscles, tissues, hair, finger nails and blood all are mostly of proteinous composition. Leather and natural fabrics such as silk and wood are built of proteins. In plants, proteins chiefly occur in seeds, the legumes, cereals and nuts being the richest sources.

Proteins, like carbohydrates and fats, are an important food factor. They are required for the growth of animal body for that means building of new cells. They are also needed for the maintenance of animal body by replacement of proteins lost by the wear and tear of organs and tissues. Therefore, animal foods like meat, eggs, milk, and cheese, and vegetable stuffs like cereals and *dals*, which contain large proportions of proteins, form an essential part of our diet.

Plants are the ultimate source of all proteins, which are synthesised by them from such simple substances as carbon dioxide (from air), nitrates (from soil), and water. When plants are eaten by an animal, the plant proteins are hydrolysed by enzymes in the process of digestion, producing amino acids. These amino acids are then absorbed by the blood and carried to the tissues where they are re-synthesised to give the required animal protein.

COMPOSITION AND MOLECULAR WEIGHTS

All proteins are made of carbon, hydrogen, oxygen and nitrogen. Most proteins also contain sulphur, while a few contain phosphorus, iron, copper and iodine as well. Although proteins differ widely in physical and chemical properties, as also in molecular size and physiological behaviour, it is remarkable that their percentage composition falls in narrow range mentioned below.

ELEMENT	PERCENTAGE
Carbon	50 to 55
Hydrogen	6·5 to 7·3
Oxygen	20 to 24
Nitrogen	15 to 18
Sulphur	0·4 to 2·5
Phosphorus	0·1 to 1·0
Metal	Traces

Proteins have such large molecules that it is not at all easy to determine their molecular weights with appreciable degree of correctness but all methods indicate very high values. For illustration, some typical approximate values are given below.

PROTEIN	APPROX. MOL. WEIGHT
Egg albumin	45,000
Haemoglobin	68,000
Casein	190,000
Urease (an enzyme)	480,000
Bushy stunt virus (a plant virus)	10,600,000

STRUCTURE OF PROTEINS

The structure of porteins was first elucidated by the German chemist Emil Fischer in 1900. He pointed out that protein molecules are made of a large number of amnio acid molecules hooked to each other in long chains. The COOH group of one molecule of amino acid, $H_2N.CHR.COOH$, reacts with the NH_2 group of another molecule, splitting out water in the process. Thus two molecules of the amino acid unite as follows.

$$\underset{\alpha\text{-Amino acid}}{H_2N.CHR.CO.\boxed{OH+H}NH.CHR.COOH} \rightarrow \underset{\text{Dipeptide}}{H_2N.CHR.CO.NH.CHR.COOH} + H_2O$$

The substance obtained is known as **dipeptide** and the group, –CONH—, produced in its molecule is termed a 'peptide bond'. It may be noted that a dipeptide also contains a free NH_2 group and a free COOH group, so that more amino acid molecules can be linked to it to yield a long chain substance containing many peptide bonds. This is called a **polypeptide** or **protein** and may be represented as

$$\underset{\text{Protein}}{H_2N.CHR.CO.(NH.CHR.CO)_n.NH.CHR.COOH}$$

Fischer synthesised a polypeptide made up of 15 glycine, CH_2NH_2COOH, and 3 leucine, $C_4H_9.CH(NH_2).COOH$ units. This polypeptide, with a formula $C_{48}H_{80}O_{19}N_{18}$, resembled with proteins in many respects.

With 24 different amino acids known, there are enormous number of theoretical ways in which we can construct large protein molecules and this accounts for the wide variety of proteins occurring in nature. Now it has been established that although the basic structure of proteins depends on amino acid residues held by peptide bonds, other type of 'cross bonds' also come into being in the formation of complex protein molecules. Therefore, it is not surprising that human ingenuity with all its vastness has not gone very far in the matter of determination of the exact structure of any natural protein.

HOW PROTEINS ARE CLASSIFIED ?

Natural proteins are divided into two main classes : (1) *Simple Proteins*, which consist of amino acid units only ; and (2) *Conjugated Proteins*, which contain other components in addition to amino acid units.

Simple proteins obtained by the chemical decomposition of natural proteins effected (by enzymes, acids or alkalis) are termed *Derived Proteins.*

Simple Proteins. Since the exact structure of individual proteins is unknown, the further classification of simple proteins into smaller groups is arbitrary and is based on their solubility and precipitation characteristics. They have been sub-divided as follows.

CLASS	CHARACTERISTICS	EXAMPLES & SOURCES
(*i*) Albumins	Soluble in water ; Coagulated by heat ; Precipitated by amm. sulphate.	***Serum albumin*** (in blood), ***Lactalbumin*** (in milk), Ovalbumin (in eggs).
(*ii*) Globulins	Insoluble in water ; Soluble in 5% NaCl.	In blood serum & tissues, seeds and nuts.
(*iii*) Glutelins	Insoluble in water ; Soluble in dilute acids & alkalis.	In cereal seeds.
(*iv*) Histones	Soluble in water ; Insoluble in alkalis.	In animal tissues.
(*v*) Prolamines	Insoluble in water ; Soluble in 79-80% alcohol.	***Zein*** (in corn).
(*vi*) Protamines	Soluble in water ; Insoluble in alcohol ; Not coagulated by heat.	In ripe fish sperm.
(*vii*) Scleroproteins (*albuminoids*)	Insoluble in water ; Soluble in conc. acids & alkalis.	***Keratins*** (in hair, nail & horn). ***Collagen*** (in skin and bones) ***Fibrein*** (silk).

Conjugated Proteins. These contain amino acid units combined with one or more additional groups of non-protein nature which are termed **prosthetic groups** (Greek ; *prosthesis* = an addition). The conjugated proteins are subdivided according to the nature of the prosthetic group present in them.

CLASS NAME	PROSTHETIC GROUP PRESENT	OCCURRENCE & EXAMPLES
(*i*) Glycoproteins, Mucins	Carbohydrate	In mucous like-fluids of animals and in egg white.
(*ii*) Nucleoproteins	Nucleic acid	In nucleus of all cells.
(*iii*) Phosphoproteins	Phosphoric acid	In case of milk and in egg yolk.
(*iv*) Chromoproteins (coloured proteins)	Contain a metal (Fe, Mg, Cu, Co, Mn) and a prosthetic group, especially a pyrrole derivative.	Haemoglobin (in blood) ; Chlorophyll (in plants) ; Hemocyanin (in blood of invertebrates) ; pigmented animal fibres as black wool and hair.

HOW ARE PROTEINS PREPARED ?

As pointed out earlier, it has not been possible to synthesise natural proteins so far. Therefore, when needed they are always obtained from natural sources. The animal tissues or plant seeds containing a protein are treated with water, dilute acid, dilute alkali, or salt solution so as to dissolve out the protein. To the extract thus obtained is added a suitable reagent (ammonium sulphate, magnesium sulphate or alcohol) which would precipitate the required protein. In case of a number of proteins present together, the individual proteins are separated by fractional precipitation carried by using different concentrations of salt solution.

GENERAL CHARACTERISTICS

(*Physical*). Proteins belonging to different classes show marked differences in their physical behaviour. However, the general physical properties of proteins may be summarised as follows :

(1) The majority of proteins are non-volatile, colourless and tasteless amorphous solids having no definite melting and boiling points. When in pure form, some of them are crystalline.

(2) As a rule, they do not form true solutions in water, alcohol and ether but dissolve in dilute salt solution, dilute acids and alkalis. A few proteins such as those in skin, hair, bones, etc., are completely insoluble.

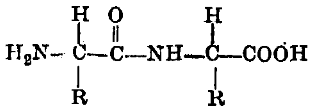
(3) Their molecules being large, proteins readily form colloidal solutions in water and do not diffuse through parchment or animal membranes. Some proteins (gelatin, egg albumin) produce thick opalescent sols with water which form gels upon cooling.

(4) Solutions of proteins are optically active, being in almost all cases laevorotatory.

(5) **Coagulation**. When heated or treated with strong mineral acids, colloidal proteins are coagulated and cannot be brought back to the colloidal form. This process which involves loss of many of the original physical properties (solubility, physiological action etc.) of the proteins is termed **denaturation**. For example, egg albumin is denatured when egg is cooked. Denaturing may also occur when a protein remains in contact with water or alcohol for a long time. Heavy metal salts (copper sulphate, mercuric chloride) and certain acids such as picric acid, tannic acid also denature proteins. Thus picric acid and tannic acid solutions are used for the treatment of burns, because they coagulate body proteins to form a protective coating. Egg white is used as an antidote for poisoning by a heavy metal as the latter is removed by adsorption in the coagulated stuff which is thrown out of the stomach by vomiting.

The proteins are also precipitated or 'salted out' from their colloidal solutions by the addition of inorganic salts such as sodium sulphate and sodium chloride, as also by water soluble organic liquids like alcohol and acetone. However, the precipitate thus produced can be obtained back in the colloidal form by the addition of excess of original solvent.

(*Chemical*). As pointed out earlier, protein molecules are built of chains of α-amino acids hooked to each other through peptide bonds. Therefore, we can visualise the chemical behaviour of proteins from the structural formula of a dipeptide which could be looked upon as a 'miniature protein'.



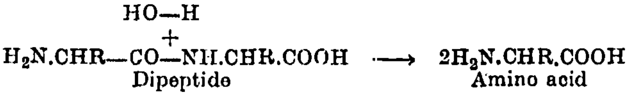
$$H_2N-\underset{R}{\overset{H}{C}}-\overset{O}{\overset{\|}{C}}-NH-\underset{R}{\overset{H}{C}}-COOH$$

(Dipeptide)

Thus proteins like amino acids contain free amino and carboxyl groups and give the reactions of both. In addition, they are easily hydrolysed to form the parent amino acids by cleavage at the peptide bonds which are weak spots in the molecule. The important reactions of amines are given below.

(1) **Formation of Salts.** Since proteins contain the basic —NH_2 group as well as the acidic —COOH group, they are amphoteric in character. Thus they combine with both acids and bases to form salts. For example, casein in milk exists as salt of calcium.

(2) **Hydrolysis.** The proteins can be hydrolysed by acids, by alkalis or by enzymes, to yield the component amino acids. This is the reverse process of the formation of proteins by union of amino acid molecules involving the elimination of water. The hydrolysis of proteins may be demonstrated by taking example of dipeptide which would take up water and split into two amino acid molecules.



$$\underset{\text{Dipeptide}}{H_2N.CHR-CO\overset{\overset{HO-H}{+}}{-}NH.CHR.COOH} \longrightarrow \underset{\text{Amino acid}}{2H_2N.CHR.COOH}$$

In actual practice, the hydrolysis of natural simple proteins takes place gradually in a number of steps, the final degradation products being amino acids.

Proteins → Proteoses → Peptones → Peptides → Amino acids

The exact number and nature of amino acids obtained from a particular amine gives clue to its structure. About 24 different amino acids have been so far isolated as products of protein hydrolysis.

(3) **Oxidation.** Proteins may be oxidised by burning or by bacteria in decay and putrefaction, yielding a variety of products—, nitrogen, amines, carbon dioxide, water—depending on conditions. The bad smell produced during putrefaction of dead animals is largely due to the formation of amines and other nitrogen products by the bacterial oxidation of body proteins.

(4) **Colour Reactions.** (*Tests for Proteins*). Proteins are detected by specific colour reactions which they give with certain reagents. These colour tests are, in fact, due to the presence of definite groups in the protein molecule and may not be shown by a particular amine if the group concerned is absent in it. Therefore, a given substance is not declared to be a protein unless it responds to majority of the colour tests. The typical of these are :

(1) YELLOW COLOUR WITH NITRIC ACID (*Xanthoproteic test*). A protein solution on warming with nitric acid turns yellow. On making it alkaline with ammonia, the colour deepens to orange. The yellow stains on fingers while working with nitric acid are caused due to this reaction.

This test is specific for proteins containing tryosine and tryptophane (amino acids having benzene ring), the yellow colour produced being due to nitration of the aromatic ring.

(2) VIOLET COLOUR WITH ALKALINE COPPER SULPHATE (*Biuret test*). When a dilute solution of copper sulphate is added to a protein solution which had been made alkaline with sodium hydroxide, reddish violet colour develops.

This test is due to the presence of at least two —NH—CO— groups in proteins as in biuret (*see under reactions of urea*).

(3) RED COLOUR WITH MERCURY DISSOLVED IN NITRIC ACID (*Millon's test*). The Millon's reagent (mercurous and mercuric nitrates dissolved in nitric acid), when added to solution of a protein produces a white precipitate which turns brick-red on boiling.

This test is due to a phenolic —OH group present in the protein molecule.

(4) VIOLET COLOUR WITH GLYOXALIC ACID (*Hopkins-Cole reaction*). When concentrated sulphuric acid is added along the side of the test-tube containing a solution of protein mixed with a little glyoxalic acid, a bluish-violet colour is obtained.

This test is specific of proteins containing the amino acid tryptophane.

USES OF PROTEINS

(1) *As food.* Many proteins are used as foods. The egg albumin, casein, cereal proteins, muscle proteins are some examples of such proteins.

(2) *As textiles.* Natural fibres such as wood and silk are proteins. Synthetic fibres made from proteins (casein, soya bean proteins) which resemble with natural silk and wool, are now available in the market.

(3) *To control physiological activity* Proteins are extremely useful as they control various physiological processes in the animal body. For example, oxygen and carbon dioxide are carried in the blood by haemoglobin. *Hormones* (secretions of ductless glands) which determine the sex of a living being and perform other such important functions in the body, are proteins.

(4) *As enzymes.* All known enzymes are proteins. The enzymes are catalysts with specific action and bring about useful changes in organic substances. Thus zymase from yeast can cause the decomposition of glucose to ethyl alcohol and carbon dioxide, while diastase converts starch to maltose and invertase changes sugar to glucose and fructose. All such reactions are of great theoretical and industrial importance.

(5) *As viruses.* Certain organic agents causing diseases are known as viruses, which are proteins. Viruses can cause smallpox, influenza, rabies, etc. But like ordinary proteins they can be denatured. If such a denatured protein is introduced in the body of an animal, it rejuvenates and multiplies and causes immunity from the disease of the original virus.

(6) *In industry.* Several proteins are used for industrial purposes, Gelatin, in photographic fims and in making animal glues ; Casein, in adhesives such as glues, in paints and as basis of certain plastics ; soya bean protein in plastics for automobile fittings. Leather and felt are proteinaceous substances of great use in industry.

QUESTIONS

1. Define the term 'Proteins'. Describe the occurrence and importance of this class of compounds.

2. Mention the average composition of proteins. What is the order of their molecular weights ?

3. Write what you know about the structure of proteins and explain clearly the terms—'peptide bond' or 'polypeptide'.

4. Give briefly the classification of natural proteins giving examples.

5. Explain what you understand by (*i*) Simple proteins, and (*ii*) Conjugated proteins. Illustrate by two examples in each case.

6. How are proteins isolated from natural sources ? Can they be synthesised in the laboratory ?

7. Give the general physical characters of the class of compounds known as proteins.

8. Write notes on : (*i*) Hydrolysis and (*ii*) Colour reactions of proteins.

9. Give an account of the classification of proteins and describe the important methods for the synthesis of α-amino acids. (*Banaras B.Sc. III, 1967*)

10. Give an account of the structure and configuration of proteins. (*Ceylon B.Sc., 1967*)

11. Describe how the constituent amino acids have been isolated from proteins. Give three methods by which amino acids are synthesised ? How are the amino acids present in the protein molecule ? (*Bombay B.Sc., 1969*)

12. Give an account of the classification of proteins. In what respects do they resemble and differ from polypeptides ? Write a note on biuret test. (*Bangalore B.Sc., 1969*)

Aromatic Compounds

35

Introductory

RUDOLPH FITTO
(1835—1910)
German Scientist. He is noted for Synthetic work in the aromatic series particularly for the reaction which bears his name. He discovered phenanthrene in coal-tar.

MEANING OF THE TERM 'AROMATIC'

Besides the aliphatic compounds, there is a group of organic compounds which are known as the '*aromatic compounds*'. The aromatic compounds differ sharply in behaviour from the aliphatic compounds. They were originally so named since most of them (oil of wintergreen, bitter almond oil, turpentine oil, oil of cloves, etc) then known possessed a pleasant odour (Greek : *aroma* = fragrant smell). Later it was realised that the chief distinction between the aliphatic and the so-called aromatic compounds is really a structural one rather than of odour. The aliphatic compounds possess an open-chain structure, while the aromatic ones have a peculiar six-carbon atom ring as is present in benzene. Thus, the term **'aromatic compounds'** *has been now adopted to cover benzene and all structurally related compounds which have a behaviour totally different from that of aliphatic compounds.*

Like the aliphatic compounds, aromatic compounds include hydrocarbons, hydroxy derivatives (alcohols, phenols), ethers, aldehydes, ketones, carboxylic acids, amines etc. We will study these classes of compounds in the following chapters.

Aromatic compounds are obtained from the animal and vegetable sources. By far the richest source of these compounds is coal-tar. In recent years petroleum has also become a potential source of aromatic hydrocarbons since by 'catalytic cyclization' normal hexane and related higher homologues are converted easily into benzene hydrocarbons.

COAL AS A SOURCE OF AROMATIC COMPOUNDS

Coal is the remains of vegetable matter which was buried under the earth about 500 million years ago. Under the influence of great pressure and heat it lost moisture and decomposed by the elimination of the gases, hydrogen and oxygen. The plant material was originally essentially cellulose, $(C_6H_{10}O_5)_n$ but with the loss of hydrogen and oxygen it became richer in carbon, and was thus converted to coal.

Coals are classified by their carbon content as follows :

(*i*) *Anthracites* are high grade coals, their carbon content being 90 to 95 per cent.

(*ii*) *Bituminous Coals* contain 70 to 90 per cent carbon and are next in quality.

(*iii*) *Lignites or Soft Brown Coals* are 60 to 75 per cent carbon. These are the lowest grade coals.

In addition to carbon, coals contain hydrogen, oxygen nitrogen, and sulphur. The fundamental structure of coal is an aromatic nucleus made of upto thirty benzene rings fused together having aliphatic side-chains. Hydrogen is present in the side-chains.

Carbonization of Coal. As already mentioned, coal is composed of complex aromatic compounds admixed with varying quantities of free carbon. On thermal decomposition or **carbonization**, it yields a variety of chemicals. But the chief purpose of carbonization of coal is the industrial production of *Coal gas*, metallurgical coke, or smokeless fuel. The chemicals are recovered as by-products.

The method employed for the carbonization of coal depends on whether *Coal gas*, or metallurgical coke is the main product required.

(1) *High-temperature Coking* : It is carried at about 1000°C when a large proportion of coal gas is produced.

(2) *Low-temperature Coking* : It is carried at about 600°C and yields a greater proportion of metallurgical fuel.

The similar range of products are formed by both the above methods but the proportions and types are different.

High-temperature carbonization—Manufacture of Coal gas. When coal is heated at 1000—1300°C in iron retorts out of contact with air (*Destructive Distillation*), the complex aromatic compounds present in it are decomposed to give the following products.

(*i*) *GAS.* The gas coming from the retorts comprises coal gas (H_2, CH_4, CO); ammonia, carbon dioxide, nitrogen which are accompanied by low molecular weight liquid aromatic hydrocarbons and volatile tarry matter. The gaseous fraction amounts to 20 per cent of the coal carbonized. It is first passed through cooled pipes when tar and ammonia liquor condenses. The gas is then washed in water and is thus freed from ammonia. Then the gas is passed through a tower where it comes in contact with 'creosote oil' which readily dissolves the benzene hydrocarbons present in the gas and on subsequent distillation yields *'benzol'*. The remaining gas is finally passed through layers of lime and ferric oxide (not shown in Fig. 35·1) to remove carbon dioxide and hydrogen sulphide, and distributed to the town through pipe-lines as **coal gas.**

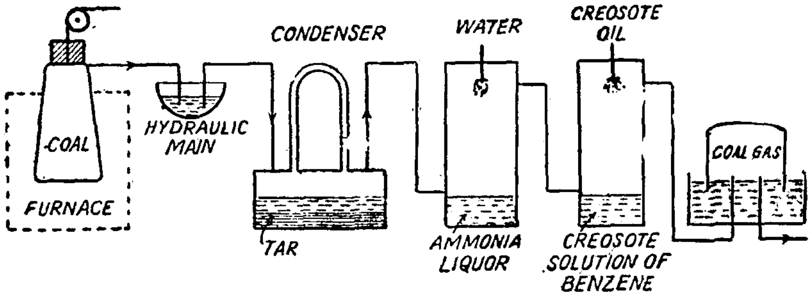


Fig. 35·1. Manufacture of Coal-gas.

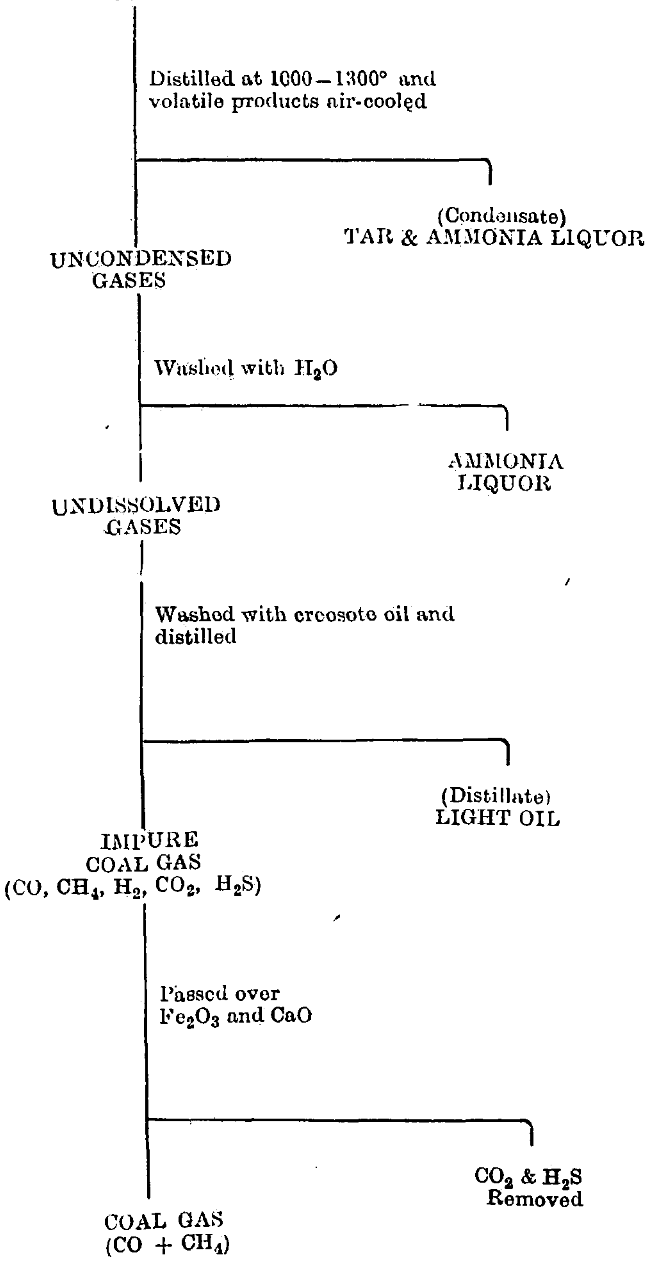
Ammonia liquor and sulphur (recovered from H_2S) are commonly used to manufacture ammonium sulphate fertilizer.

(*ii*) *BENZOL.* As described above, this is removed from the gaseous fraction by scrubbing with a high-boiling oil (creosote oil). Benzol is recovered from the oil by distillation, and the oil is re-used. The product which may amount to 5 gallons per ton of coal carbonized, is a rich source of benzene, toluene, xylenes, etc. It is refined with coal-tar fractions.

(*iii*) *COAL-TAR.* It is a black viscous liquid condensed out of the gas leaving the retort or coke oven. It is the chief product obtained from coal which is a source of many aromatic compounds —hydrocarbons, phenols and bases.

Coal-tar is about 5 per cent of the coal carbonized, or about 20 gallons per ton.

(*iv*) *COKE.* As a result of high-temperature carbonization, about 70 per cent of coal is left in the retort or coke oven as coke. It is mainly used as fuel, and in iron and steel manufacture. About



FLOWSHEET OF COAL GAS MANUFACTURE

10 per cent of coke is used for making chemicals, water gas for ammonia and methanol. It is also used for the industrial production and calcium carbide for acetylene.

Low-Temperature Carbonization. Recently low-temperature carbonization or coking has come to be important. This process is carried at 600°C for the production of smokeless domestic fuel *'Coalite'*. The products obtained are similar to those in high-temperature carbonization but the proportions and type are different

(*i*) *GAS*. The gas produced amounts to 6 per cent of the coal carbonized. Its calorific value is nearly double of the gas obtained in the high-temperature process. This is on account of higher hydrocarbon proportion (60 per cent). For the same reason, the gas is a suitable source of chemicals.

(*ii*) *CRUDE SPIRITS*. This is formed 5 gallons per ton of coal carbonized and corresponds to benzol from high temperature process. It is recovered from gas by scrubbing the high-boiling oil. It contains aliphatic hydrocarbons to the extent of 75%. It is refined with 'light oil' fraction of coal-tar, and placed in the market as 'motor spirit'

(*iii*) *LOW-TEMPERATURE TAR*. Five per cent or more of coal carbonized is converted into low-temperature tar. It may amount to 20 gallons per ton. Its main ingredients are alkanes and naphthenes. The tar on fractionation yields light oil, middle oil, and heavy oil which are further refined for motor spirit, diesel fuel, and fuel oil use.

(*iv*) *COKE*. This amounts to about 75 per cent of the coal carbonized. It is used as domestic smokeless fuel—'Coalite'.

Coal-tar Distillation. Coal-tar is now the principal source of over 200 aromatic compounds of which the more important are :

Hydrocarbons : Benzene, toluene, xylenes, naphthalene, anthracene.

Phenols : Phenol, cresols.

Basic nitrogen compounds : Pyridine (C_5H_5N), quinoline (C_9H_7N).

These components are separated from coal-tar by fractional distillation. The crude tar is first freed from water, which would cause bumping in the initial stages of distillation, by slow heating and then distilled. The actual distillation is carried in a large wrought-iron still fitted inside with a steam-pipe and heated below by fire. The still-head is connected with a long condensing *worm* immersed in water. Towards the end of the process, steam is passed into the still to prevent the caking of the residue. From the worm the condensed products are conducted into different receivers. The 'cuts' taken in the usual technical distillation of tar are listed in the table below :

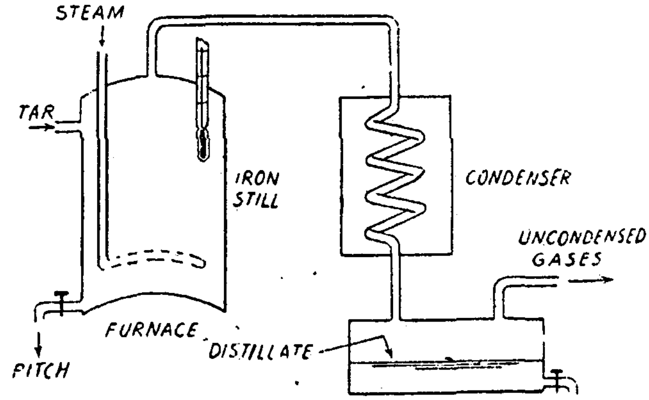


Fig. 35·2. Distillation of Coal-tar

FRACTION (*cut*)	DISTILLATION TEMPERATURE °C	SP. GR.	CHIEF CONSTITUENTS
(1) *Light oil*	Up to 170	0·9	Benzene, toluene, xylenes, naphthalene, anthracene.
(2) *Middle oil*	170—230	0·1 to 1·02	Phenol, naphthalene.
(3) *Heavy oil*	230—270	1·02 to 1·1	Cresols, phenol.
(4) *Anthracene oil*	270—360	1·1	Anthracene.

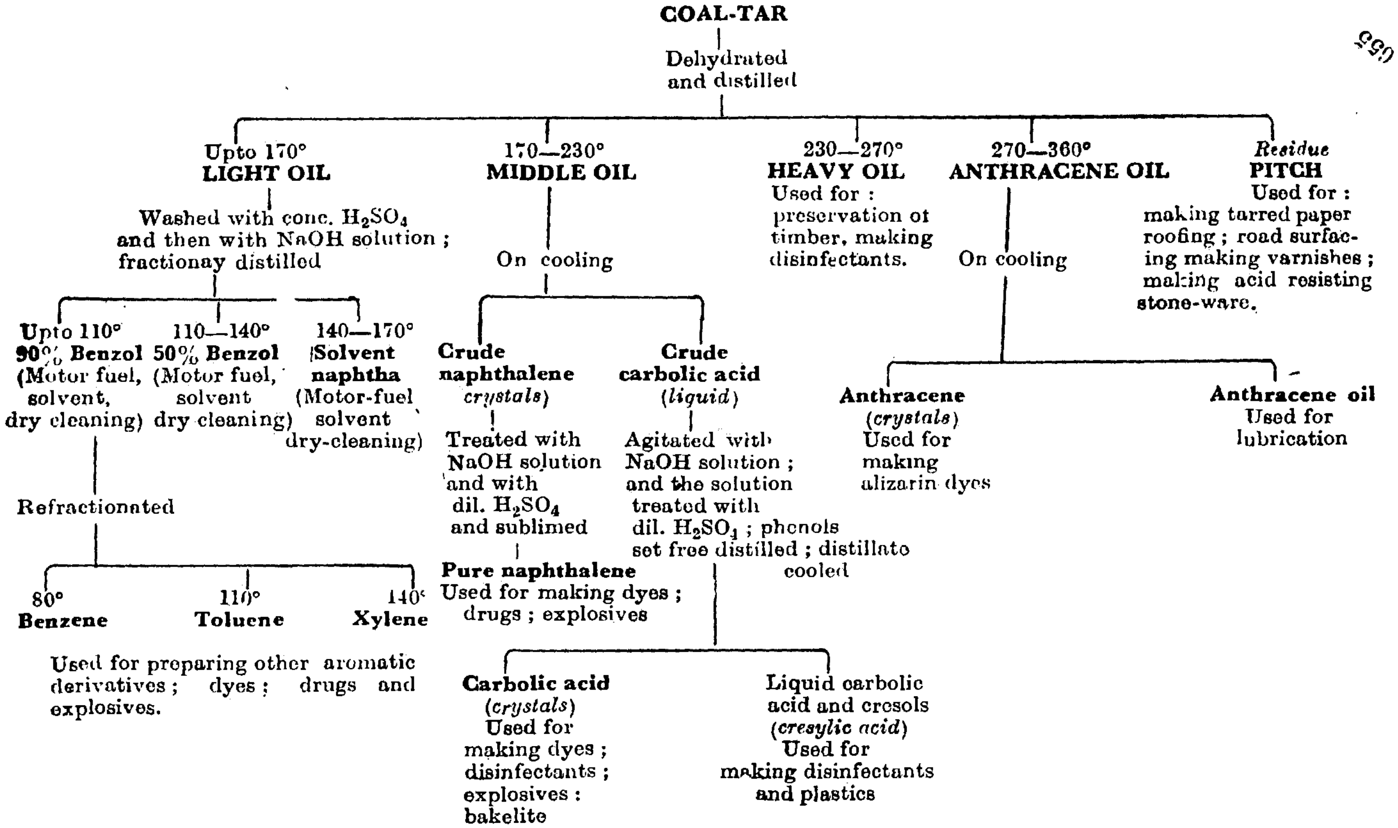
Each fraction is worked and separated into its constituents.

First Fraction, **Light oil** (up to 170°). It is so named because it is lighter than water. It contains benzene, toluene. xylenes along with some phenol and basic substances such as pyridine. The light oil is washed with concentrated sulphuric acid to remove the bases and then with sodium hydroxide which removes the phenol and excess acid. The oil thus purified is fractionally distilled and the following three constituents are collected.

NAME OF FRACTION	TEMPERATURE RANGE	CHIEF CONSTITUENTS
"90% benzol"	Up to 110°	Benzene, toluene and xylene.
"50% benzol"	110 to 140°	Benzene, toluene and xylene.
Solvent naphtha or Benzine	140 to 170°	Xylene, mesitylene, etc.

All the three fractions are used under their commercial names as motor fuel, solvents, and for dry-cleaning. 90% *benzol* is fractionated again to yield benzene (b.p. 80·4%), toluene (b.p. 110°) and xylene (b.p. 140°).

Second Fraction, **Middle oil** (170—230°). The fraction collected in between the light oil and the heavy oil is named as the *Middle*


COAL-TAR
Dehydrated and distilled
Upto 170° **LIGHT OIL**
Washed with conc. H_2SO_4 and then with NaOH solution ; fractionay distilled
Upto 110° **90% Benzol** (Motor fuel, solvent, dry cleaning)
110—140° **50% Benzol** (Motor fuel, solvent dry cleaning)
140—170° **Solvent naphtha** (Motor-fuel solvent dry-cleaning)
Refractionated
80° **Benzene**
110° **Toluene**
140° **Xylene**
Used for preparing other aromatic derivatives ; dyes ; drugs and explosives.
170—230° **MIDDLE OIL**
On cooling
Crude naphthalene *crystals*)
Treated with NaOH solution and with dil. H_2SO_4 and sublimed
Pure naphthalene Used for making dyes ; drugs ; explosives
Crude carbolic acid (*liquid*)
Agitated with NaOH solution ; and the solution treated with dil. H_2SO_4 ; phenols set free distilled ; distillate cooled
Carbolic acid (*crystals*) Used for making dyes ; disinfectants ; explosives : bakelite
Liquid carbolic acid and cresols (*cresylic acid*) Used for making disinfectants and plastics
230—270° **HEAVY OIL** Used for : preservation of timber, making disinfectants.
270—360° **ANTHRACENE OIL**
On cooling
Anthracene (*crystals*) Used for making alizarin dyes
Anthracene oil Used for lubrication
Residue **PITCH** Used for : making tarred paper roofing ; road surfacing making varnishes ; making acid resisting stone-ware.

oil. It consists chiefly of naphthalene and carbolic acid, hence its name **carbolic oil**. On cooling it deposits crystals of naphthalene leaving behind crude liquid carbolic acid. Naphthalene is purified by treatment with sodium hydroxide and then with dilute sulphuric acid, and it is finally sublimed. The crude carbolic acid is agitated with sodium hydroxide solution which dissolves phenols. The solution is run off and treated with dilute sulphuric acid to recover free phenols which on distillation yield crystals of carbolic acid. Naphthalene is used for making dyes, drugs and explosives ; phenol is employed for making dyes, disinfectants, explosives bakelite, etc.

Third Fraction, **Heavy oil** (230—270°). It is heavier than water and is, therefore, named as *Heavy oil*. Its chief ingredients are carbolic acid and cresol. It is not purified further and is used as much under the name of **Creosote oil**, for the preservation of timber and for making disinfectants.

Fourth Fraction, **Anthracene oil**, (270—360°). It bears this name because its chief ingredient is anthracene. Since the oil shows green fluorescence, it is also called **Green oil**. On cooling, it deposits crystals of anthracene which is a starting material for alizarin dyes.

Residue in the still, **Pitch**. It is run out from the still while hot. It contains 92—94% of carbon and is used for making tarred paper, for roofing, for road-surfacing, for preparing varnishes and for making acid-resisting stoneware.

A complete summary of coal-tar distillation products is given on page 656.

Coal-tar industry in India. Our country occupies the ninth position in the world in respect of the annual production of coal. There are numerous coal fields, the more important amongst these being located at Jharia, Raniganj, Bokaro, Giridih, Karanpura and Assam. The carbonisation of coa is being carried out at several places near the coal fields mainly for the manufacture of coke needed for the iron and steel industry. The Tata Iron and Steel Co. Ltd. at Jamshedpur is the biggest concern having one of the larges single coking plants in the world. Recently this company has also installed benzol recovery plant.

Till late India produced about 10,000 tons of coal-tar annually whic was mostly consumed for road-surfacing. and there was hardly any concer carrying out the distillation of coal-tar on a reasonable scale. The coal-t industry received an impetus during the last World War when the annu productions were recorded as : Naphthalene 600 tons ; Phenol 50 tons ; Cres 100 tons ; Benzene 20 lakh tons ; Toluene 4-5 lakh gallons ; and Solve naphtha 1 lakh gallons. Taking into consideration the huge imports of t coal-tar distillation products at present, the Union Government is encouragi the industry in the country and it is anticipated that in due course it will att the necessary importance.

QUESTIONS

1. Discuss fully the significance of the term 'aromatic'. What is fundamental difference between the aliphatic and the aromatic compounds ?

2. What is the composition of coal-tar ? How its important con nents are isolated ?

3. Amplify the statement : "The black obnoxious coal-tar is the parent of beautiful dyes, fragrant perfumes, useful drugs and explosives."

4. Write what you know about the method of coal-tar distillation and the different fractions obtained.

5. Give a brief account of the products obtained by the destructive distillation of coal. How are the important components of coal separated ?

6. What important chemicals are found in coal-tar ? Describe in detail how you would obtain one liquid and one solid component from it.

7. Describe the destructive distillation of coal and name the important commercial products obtained from coal-tar. (*Marathwada B.Sc. III, 1963*)

8. Starting from coal-tar crudes, how would you proceed to prepare (*a*) Dimethylaniline, (*b*) Acetophenone, (*c*) Aspirin, and (*d*) Sulphanilic acid ? (*Calcutta B.Sc., 1964*)

9. How is pure benzene isolated from coal-tar ? (*Banaras B.Sc., 1968*)

10. Describe coal-tar distillation. Give important uses of various products obtained. (*Panjab B.Sc., 1969*)

36

Benzene and its Homologues

F.A. KEKULE
(1829—1867)

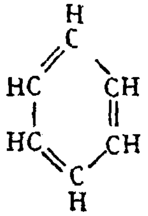
He started his career as a student of architecture at the University of Giessen. Later he turned a Chemist. While Professor in Ghent in 1858, he developed his theory of the Structure of Benzene.

The most important hydrocarbons of this series are benzene C_6H_6 ; toluene, $C_6H_5\,CH_3$; xylene, $C_6H_4.(CH_3)_2$; and mesitylene $C_6H_3(CH_3)_3$ They have the general formula C_nH_{2n-6} and are highly unsaturated. However, owing to their peculiar cyclic structure, they behave like saturated hydrocarbons and yield substitution products readily.

Benzene and its homologues occur chiefly in coal-tar and coal gas. They are also found to be present in petroleum which was formerly thought of as a mixture of aliphatic compounds only.

NOMENCLATURE

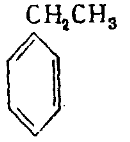
The natural name of the parent hydrocarbon is benzene which has the structural formula :



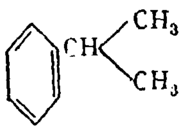
often written as

Other hydrocarbons of the series are to be regarded as the alkyl derivatives of benzene. They are called by their natural names or may be named as *alkyl benzenes.* Thus :

Toluene, Methylbenzene

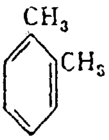


Ethylbenzene

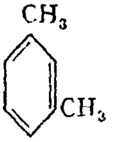


Isopropylbenzene

In higher homologues of benzene having two or more alkyl groups on the benzene ring, the positions of the alkyl groups are indicated by numbering the corners of the ring as 1, 2, 3, 4 etc. in a clockwise direction. Thus :

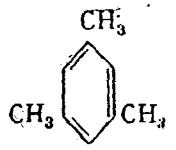


1, 2-dimethyl benzene (o-Xylene)



1, 3-dimethyl-benzene (*m*-Xylene)

1, 4-dimethyl-benzene (*p*-Xylene)



1, 3, 5-trimethyl-benzene (Mesitylene)

In the above hydrocarbons the six-carbon-atom benzene ring is called the **benzene nucleus** and the alkyl groups attached to it as **side-chains**. Further the positions 1, 2 ; 1, 3 ; and 1, 4 respectively are referred to as **ortho, meta** and **para**. The terminology is followed up while naming all derivatives of benzene.

The groups of radicals resulting from aromatic hydrocarbons by removal of H-atoms are called **aryl radicals**. The radicals corresponding to benzene and toluene are given below :

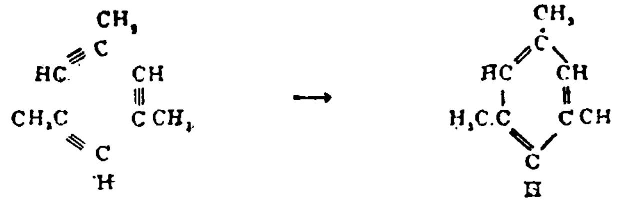
RADICAL	NAME	RADICAL	NAME
C_6H_5—	Phenyl or *Ph*	$C_6H_5CH_2$—	Benzyl
$C_6H_4<$	Phenylene	$C_6H_5CH<$	Benzal
$CH_3.C_6H_4$—	Tolyl		
		$C_6H_5C\lessdot$	Benzol

METHODS OF FORMATION

While the lower benzene hydrocarbons are isolated from coal-tar, the higher members may be synthesised by the following methods.

(1) **Polymerisation of acetylenes.** Benzene and many of its homologues are produced by passing the vapour of the corresponding acetylenic hydrocarbon through a red hot tube (500°). Thus :

$$\underset{\text{Acetylene}}{3C_2H_2} \longrightarrow \underset{\text{Benzene}}{C_6H_6}$$



Methylacetylene Mesitylene

This method is of academic interest as it affords a means of synthesising benzene from elements, as also of passing from aliphatic to aromatic series.

(2) **Wurtz-Fittig reaction** (1864). The homologues of benzene can be obtained by the action of sodium metal on a mixture of alkyl and aryl halides in ether solution. Thus :

$$\underset{\text{Bromobenzene}}{C_6H_5Br} + 2Na + BrC_2H_5 \longrightarrow \underset{\text{Ethylbenzene}}{C_6H_5 \cdot C_2H_5} + 2NaBr$$

This method is, in fact, an extension of Wurtz reaction for the preparation of alkanes.

(3) **Friedel-Crafts reaction.** The homologues of benzene can be best prepared by the action of an alkyl halide on benzene in the presence of anhydrous aluminium chloride as a catalyst. Thus :

$$C_6H_6 + C_2H_5Cl \longrightarrow \underset{\text{Ethylbenzene}}{C_6H_5.C_2H_5} + HCl$$

$$\underset{\text{Toluene}}{C_6H_5.CH_3} + CH_3Cl \longrightarrow \underset{\text{Xylene}}{C_6H_4(CH_3)_2} + HCl$$

By this reaction all the hydrogen atoms of the benzene nucleus may be successively replaced by alkyl radicals. With the various alkyl halides, the ease of reaction is in the order : chloride > bromide > iodide

(4) **Decarboxylation of aromatic acids.** Benzene and its homologues can be prepared by heating the sodium salts of an aromatic carboxylic acid with soda-lime.

$$\underset{\text{Sod. benzoate}}{C_6H_5COONa} + NaOH \longrightarrow C_6H_6 + Na_2CO_3$$

$$\underset{\text{Sod. toluate}}{C_6H_4(CH_3)COONa} + NaOH \longrightarrow C_6H_5CH_3 + Na_2CO_3$$

This method is analogous to the preparation of alkanes by decarboxylation of fatty acids. It was employed for obtaining the first thiophene free sample of benzene.

(5) **Removal of oxygen from phenols.** When distilled with zinc dust, phenols are converted to the parent hydrocarbons.

Thus :

$$\underset{\text{Cresol}}{C_6H_4(OH)CH_3} + Zn \longrightarrow \underset{\text{Toluene}}{C_6H_5.CH_3} + ZnO$$

(6) **Clemmensen reduction of ketones** (Clemmensen, 1913). Higher homologues of benzene can be prepared particularly easily by the reduction of aromatic-aliphatic ketones with zinc amalgam and hydrochloric acid.

$$\underset{\text{Acetophenone}}{C_6H_5COCH_3} + 4[H] \longrightarrow \underset{\text{Ethylbenzene}}{C_6H_5CH_2CH_3} + H_2O$$

The ketone needed for the purpose may be prepared from benzene by Friedel-Crafts reaction.

(7) **From Grignard reagents.** The homologues of benzene can be synthesised by action of an alkyl halide (or alkyl sulphate) on phenylmagnesium bromide.

$$C_6H_5.MgBr + Br|C_2H_5 \longrightarrow \underset{\text{Ethylbenzene}}{C_6H_5.C_2H_5} + MgBr_2$$

(8) **Hydrolysis of sulphonic acids.** Benzene and its homologues can be produced from sulphonic acids by boiling them with dilute hydrochloric or sulphuric acid under pressure.

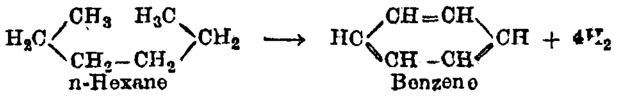
$$\underset{\text{Benzenesulphonic acid}}{C_6H_5{:}SO_3H} + HO{:}H \longrightarrow C_6H_6 + H_2SO_4$$

This method is helpful for the separation of benzene hydrocarbons from aliphatic hydrocarbons which do not undergo sulphonation under similar conditions.

(9) **Reduction of diazonium salts.** Diazonium salts when treated with alcohol, yield the corresponding hydrocarbons. Thus :

$$C_6H_5N_2Cl + CH_3CH_2OH \longrightarrow C_6H_6 + N_2 + HCl + CH_3CHO$$

(10) **Cyclization.** Benzene and its homologues are now prepared by passing the vapour of long-chain alkanes, derived from petroleum, over a chromium catalyst (Cr_2O_3 supported on Al_2O_3) at 500°. Thus :



Similarly n-heptane and n-octane yield toluene and o-xylene respectively.

PHYSICAL CHARACTERISTICS

(1) Benzene and its homologues are colourless, mobile liquids having a characteristic odour.

(2) They are lighter than and insoluble in water but are miscible in all proportions with organic solvents such as alcohol, ether, petrol, etc.

(3) They dissolve fats and many other organic substances which are insoluble in water.

(4) Their boiling points show a gradual rise with **increasing** molecular weight.

	B. Pt.		B.Pt.
Benzene, C_6H_6	80·4°	o-Xylene, $C_6H_4(CH_3)_2$	144°
Toluene, $C_6H_5.CH_3$	110°	m-Xylene, $C_6H_4(CH_3)_2$	139°
Ethylbenzene, $C_6H_5.C_2H_5$	136°	p-Xylene, $C_6H_4(CH_3)_2$	138·5°
Propylbenzene, $C_6H_5.C_3H_7$	159°	Mesitylene, $C_6H_3(CH_3)_3$	165°

(5) They have a pronounced toxic character, the continued breathing of their vapours being attended with danger.

CHEMICAL CHARACTERISTICS

Benzene contains a six-carbon-atom ring having three double bonds in the alternate positions, while its homologues contain one or more alkyl groups attached to a benzene ring. Owing to its unusal stability, the benzene ring gives a variety of substitution reactions, and more readily than do the alkanes. The double bonds of the benzene ring form addition compounds very reluctantly. Any alkyl groups linked to the benzene ring give the usual substitution reactions with halogens, and are readily attacked by oxidising agents.

(1) **Halogenation.** Benzene and its homologues undergo halogenation with chlorine and bromine either in the benzene nucleus or in the side-chain depending upon conditions.

(*i*) In dark and in the presence of a halogen carrier ($FeCl_3$, $AlCl_3$, I_2), they react with chlorine to form nuclear halogen derivatives. Thus :

$$\underset{\text{Benzene}}{C_6H_6} + Cl_2 \longrightarrow \underset{\text{Chlorobenzene}}{C_6H_5Cl} + HCl$$

$$\underset{\text{Toluene}}{H_3C.C_6H_5} + Cl_2 \longrightarrow \underset{\text{o- \& p-chlorotoluene}}{H_3C.C_6H_4.Cl} + HCl$$

(*ii*) When chlorine is passed into boiling toluene, it attacks the side-chain and the hydrogen atoms of the methyl group are successively replaced.

$$\underset{\text{Toluene}}{C_6H_5CH_3} \xrightarrow{Cl_2} \underset{\text{Benzyl chloride}}{C_6H_5.CH_2Cl} \xrightarrow{Cl_2} \underset{\text{Benzal chloride}}{C_6H_5.CHCl_2} \xrightarrow{Cl_2} \underset{\text{Benzotrichloride}}{C_6H_5.CCl_3}$$

Iodine has no direct action on the aromatic hydrocarbons unless with the addition of iodic acid or nitric acid.

(2) **Nitration.** When treated with concentrated nitric acid, or better with a mixture of nitric acid and sulphuric acid, they undergo substitution in the benzene ring yielding nitro compounds.

Thus :

$$\underset{\text{Benzene}}{C_6H_5\boxed{H + HO}NO_2} \longrightarrow \underset{\text{Nitrobenzene}}{C_6H_5NO_2} + H_2O$$

$$\underset{\text{Toluene}}{H_3C.C_6H_5} + HONO_2 \longrightarrow \underset{\text{o- \& p-Nitrotoluene}}{H_3C.C_6H_4.NO_2} + H_2O$$

By using fuming nitric acid at high temperature, it is possible to introduce two or three NO_2 groups in the benzene ring.

(3) **Sulphonation.** The benzene hydrocarbons are readily sulphonated in the benzene nucleus by heating with concentrated sulphuric acid. Thus :

$$\underset{\text{Benzene}}{C_6H_5\boxed{H + HO}SO_3H} \longrightarrow \underset{\text{Benzenesulphonic acid}}{C_6H_5.SO_3H} + H_2O$$

By using fuming sulphuric acid, we can introduce a second sulphonic acid group in the benzene nucleus.

(4) **Friedel-Crafts reaction.** This useful reaction was discovered by the French chemist Friedel and his American collaborator Crafts in 1877. They showed that benzene and other aromatic hydrocarbons react with an alkyl halide in the presence of anhydrous aluminium chloride to form alkylated hydrocarbons.

Thus :

$$\underset{\text{Benzene}}{C_6H_6} + \underset{\text{Alkyl chloride}}{RCl} \xrightarrow{AlCl_3} \underset{\text{Alkylbenzene}}{C_6H_5R} + HCl$$

During later years, this reaction has been extended in scope by varying the aliphatic reagent. Thus at present, Friedel-Crafts reaction may be stated to be a very general reaction taking place between an aromatic hydrocarbon and an aliphatic reagent, which may be a halogen derivative, acyl halide, acid anhydride, alcohol or an alkene, in the presence of anhydrous aluminium chloride as a catalyst. Other less effective catalysts which may be employed in place of aluminium chloride are $FeCl_3$, $SnCl_4$, $ZnCl_2$ and BF_3. The importance of the reaction will be realised by the application for the synthesis of a large variety of aromatic compounds.

(*a*) *Hydrocarbons* :

$$\underset{\text{Benzene}}{C_6H_6} + CH_3Cl \xrightarrow{AlCl_3} \underset{\text{Toluene}}{C_6H_5.CH_3} + HCl$$

$$\underset{\text{Toluene}}{CH_3.C_6H_5} + CH_3Cl \longrightarrow \underset{\text{Xylene}}{CH_3.C_6H_4.CH_3} + HCl$$

$$C_6H_6 + \underset{\text{Alcohol}}{C_2H_5OH} \longrightarrow \underset{\text{Ethylbenzene}}{C_6H_5.C_2H_5} + H_2O$$

$$C_6H_6 + \underset{\text{Ethylene}}{C_2H_4} \longrightarrow \underset{\text{Ethylbenzene}}{C_6H_5.C_2H_5}$$

(*b*) *Ketones* :

$$C_6H_6 + \underset{\text{Acetyl chloride}}{ClCOCH_3} \xrightarrow{AlCl_3} \underset{\text{Acetophenone}}{C_6H_5COCH_3} + HCl$$

$$C_6H_6 + \underset{\text{Benzoyl chloride}}{ClCOC_6H_5} \longrightarrow \underset{\text{Benzophenone}}{C_6H_5COC_6H_5} + HCl$$

$$C_6H_6 + \underset{\text{Propionic anhydride}}{(CH_3CH_2CO)_2O} \longrightarrow \underset{\text{Ethyl phenyl ketone}}{C_6H_5COCH_2CH_3} + CH_3CH_2COOH$$

(*c*) *Aldehydes* :

$$C_6H_6 + (HCl + CO) \xrightarrow{AlCl_3} \underset{\text{Benzaldehyde}}{C_6H_5CHO} + HCl$$

(*d*) *Carboxylic acids* :

$$C_6H_6 + CO_2 \xrightarrow{AlCl_3} \underset{\text{Benzoic acid}}{C_6H_5COOH}$$

(*e*) *Acid chlorides* :

$$C_6H_6 + \underset{\substack{\text{Carbonyl}\\\text{chloride}}}{ClCOCl} \xrightarrow{AlCl_3} \underset{\substack{\text{Benzoyl}\\\text{chloride}}}{C_6H_5COCl} + HCl$$

(*f*) *Acid amides* :

$$C_6H_6 + \underset{\text{Chloroformamide}}{ClCONH_2} \xrightarrow{AlCl_3} \underset{\text{Benzamide}}{C_6H_5CONH_2} + HCl$$

(*g*) *Phenols* :

$$2C_6H_6 + O_2 \xrightarrow{AlCl_3} \underset{\text{Phenol}}{2C_6H_5OH}$$

(5) **Mercuration.** Aromatic hydrocarbons when heated with mercuric acetate undergo '*mercuration*' whereby a hydrogen atom of the benzene nucleus is replaced by —Hg.O.OC.CH$_3$. Thus :

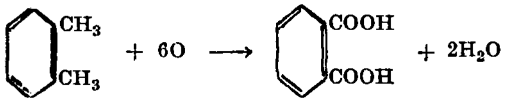
$$C_6H_6 + \underset{\text{Mercuric acetate}}{Hg(O.OC.CH_3)_2} \longrightarrow \underset{\text{Acetoxymercuribenzene}}{C_6H_5.Hg.O.OC.CH_3} + CH_3COOH$$

Mercuration is as characteristic of aromatic hydrocarbons as halogenation and nitration. Since the mercury atom directly linked with carbon can be readily replaced by other elements, this reaction is now becoming increasingly important as a synthetic method as well as serving for the preparation of valuable *mercurial drugs*.

(6) **Oxidation.** Benzene is very stable to oxidising agents and is not attacked by hot chromic acid, alkaline potassium permanganate or dilute nitric acid. The homologues of benzene having an aliphatic side-chain are, however, oxidised by the above reagents *when the entire side-chain is converted to a carboxyl group.*

$$\underset{\text{Toluene}}{C_6H_5.CH_3} + 3O \longrightarrow C_6H_5COOH + H_2O$$

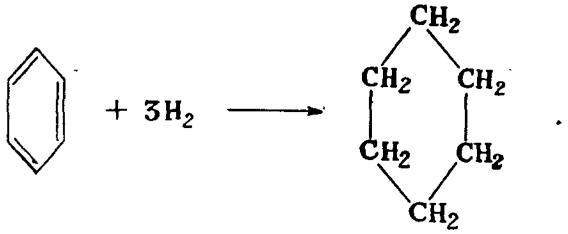
$$\underset{\text{Ethylbenzene}}{C_6H_5.CH_2CH_3} + 6O \longrightarrow C_6H_5COOH + CO_2 + 2H_2O$$



o-Xylene Phthalic acid

The above reactions also point to the stability of the benzene ring which survives oxidation.

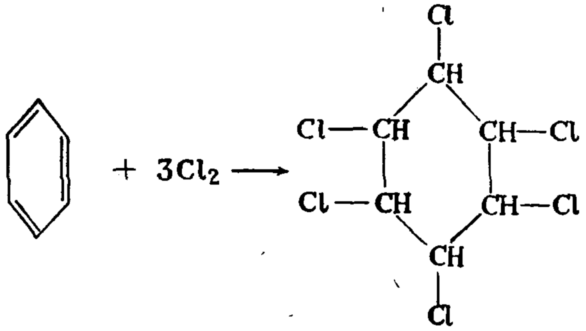
(7) **Addition reactions.** (*i*) *Hydrogenation.* On catalytic hydrogenation with nickel, benzene and its homologues add three molecules of hydrogen to form *hexahydro* compounds. Thus :



BENZENE CYCLOHEXANE

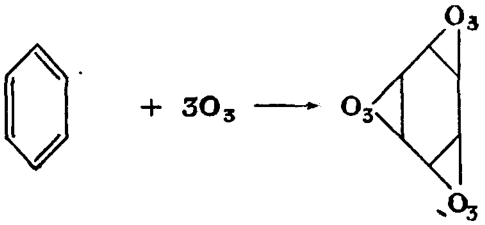
(*ii*) *Addition of halogens.* In bright sunlight and in the absence of a catalyst, benzene and its homologues add three molecules of chlorine or bromine to form hexahalocyclohexane.

Thus :



Benzenehexachloride

(*iii*) *Ozonide formation.* The aromatic hydrocarbons form ozonides by addition of one ozone molecule at each double bond of the benzene ring. Thus :



Benzene triozonide

INDIVIDUAL MEMBERS

BENZENE, C_6H_6

Benzene is the simplest hydrocarbon which heads the series of aromatic hydrocarbons. It was first isolated by Faraday (1825) from oil condensed in cylinders containing compressed *illuminating gas*. In 1845 Hofmann pointed out its presence in coal-tar which is still the main source of benzene. It is also present in coal gas and occurs in certain natural petroleums. Its commercial name is *'benzol'*.

Benzene is an exceedingly important compound not only because it is the parent of all aromatic compounds but because numerous of these are actually prepared from it.

Preparation. Benzene can be produced by the general methods 1, 4, 5, 8 and 10. However, the two important sources of commercial benzene are *light oil* and *coal gas*.

(1) *From Light oil.* The light oil is washed successively with concentrated sulphuric acid and sodium hydroxide solution which removes respectively the basic (*pyridine*) and acid (*phenol*) impurities. The oil is finally washed with water, dried and distilled. The fraction passing up to 110° '90% *benzol*' contains about 70 per cent of benzene and the rest toluene and some thiophene (C_4H_4S, b.p. 82°). Benzene is recovered from it by refractionation, the fraction collected between 80-82° being a most pure benzene. It, however, contains thiophene which may be removed by repeated treatment with cold sulphuric acid. The crude benzene is redistilled.

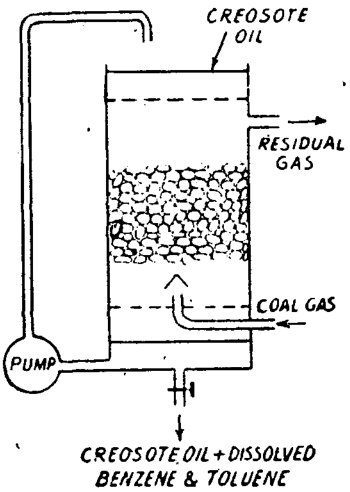


Fig. 36·1. Recovery of benzene from coal gas.

(2) *From Coal gas.* Coal gas contains large amounts of benzene and some toluene. It is passed through towers in which high-boiling *creosote oil* is sprayed from the top. Both benzene and toluene dissolve in the oil from which they are recovered by steam-distillation. The mixture of benzene and toluene thus obtained is fractionally distilled to yield pure benzene.

Laboratory Preparation. Benzene can be prepared conveniently in the laboratory by heating a mixture of sodium and sodalime.

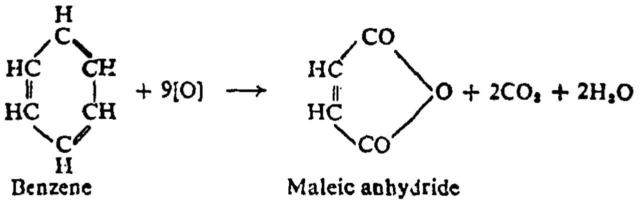
$$\underset{\text{Sod. benzoate}}{C_6H_5COONa} + NaOH \longrightarrow \underset{\text{Benzene}}{C_6H_6} + Na_2CO_3$$

Place a mixture of sodium benzoate (20 g) and soda-lime (30 g) in a round-bottomed flask fitted with thermometer and a delivery tube connected to a water-condenser. As the flask is heated, benzene-water mixture collects in the receiver placed below the other end of the water-condenser. The benzene layer is separated with the help of a tap-funnel, dried over calcium chloride and purified by redistillation.

Properties. (*Physical*). Benzene is a colourless highly refractive, mobile liquid, m.p. 5·4°, b.p. 80·4°, sp. gr. 0·8799 at 20°. It has a burning taste and a peculiar odour which is not unpleasant. It is insoluble in water but is miscible with ether, alcohol and petrol in all proportions. It readily dissolves fats, resins, sulphur and iodine. Benzene is highly inflammable and burns with a smoky, luminous flame which is indicative of its high carbon content.

(*Chemical*). The molecule of benzene is composed of a six-carbon ring with three double bonds in alternate positions, and having one H-atom on each carbon. It undergoes a variety of substitution reactions more comfortably than do the alkanes, which is due to the extremely stable structure of the benzene ring. Unlike the double bonds of alkenes, the double bonds of benzene ring are rather inert and give addition reactions reluctantly.

(1) OXIDATION. Ordinary oxidising agents as potassium permanganate and chromic acid have no effect on benzene. However, when oxidised by air in the presence of heated vanadium pentoxide (V_2O_5), it is converted to maleic anhydride.



Benzene Maleic anhydride

This reaction has been recently employed for the manufacture of maleic acid.

Substitution Reactions

(2) HALOGENATION. Chlorine and bromine react with benzene in the presence of a catalyst (I_2, $FeCl_3$, $AlBr_3$) forming substitution products. Thus :

$$C_6H_6 + Cl_2 \longrightarrow \underset{\text{Monochlorobenzene}}{C_6H_5Cl} + HCl$$

$$C_6H_5Cl + Cl_2 \longrightarrow \underset{o\text{- \& } p\text{-Dichlorobenzene}}{C_6H_4Cl_2} + HCl$$

and so forth till the six H-atoms are replaced by chlorine. Iodine does not react under similar conditions.

(3) NITRATION. Concentrated nitric acid, or better a mixture of nitric acid and sulphuric acid, converts benzene to nitrobenzene.

$$C_6H_6 + HONO_2 \longrightarrow C_6H_5NO_2 + H_2O$$

Fuming nitric acid at high temperature yields *m*-dinitrobenzene, while a mixture of fuming nitric and sulphuric acids gives 1, 3, 5-trinitrobenzene.

(4) SULPHONATION. When heated with concentrated sulphuric acid, benzene is converted to benzene sulphonic acid.

$$C_6H_6 + HO.SO_3H \longrightarrow C_6H_5SO_3H + H_2O$$

By using fuming sulphuric acid, we get *m*-benzenedisulphonic acid.

(5) FRIEDEL-CRAFTS REACTION. In the presence of anhydrous aluminium chloride, benzene reacts with alkyl halides, alkenes, acyl-

halides, a mixture of HCl and CO, CO_2, $COCl_2$, $ClCONH_2$, O_3, etc. to form a variety of products.

$$C_6H_6\left[\begin{array}{lll} + \ CH_3Cl & \longrightarrow & C_6H_5.CH_3 + HCl \\ + \ C_2H_4 & \longrightarrow & C_6H_5.C_2H_5 \\ + \ CH_3COCl & \longrightarrow & C_6H_5COCH_3 + HCl \\ + \ HCl + CO & \longrightarrow & C_6H_5CHO + HCl \\ + \ CO_2 & \longrightarrow & C_6H_5COOH \\ + \ COCl_2 & \longrightarrow & C_6H_5COCl + HCl \\ + \ ClCONH_2 & \longrightarrow & C_6H_5CONH_2 + HCl \\ + \ O_2 & \longrightarrow & C_6H_5OH \end{array}\right.$$

(6) MERCURATION. Benzene is readily mercurated by heating with mercuric acetate in alcoholic solution, to form phenyl mercury acetate, or acetoxymercuribenzene.

$$C_6H_6 + Hg(O.OC.CH_3)_2 \longrightarrow \underset{\text{Phenylmercury acetate}}{C_6H_5.Hg.O.OC.CH_3} + CH_3COOH$$

Addition Reactions

(7) HYDROGENATION. On catalytic hydrogenation with nickel at 180°—200°, benzene adds three molecules of hydrogen and is converted to cyclohexane, C_6H_{12}.

(8) ADDITION OF HALOGEN. In bright sunlight, and in the absence of a catalyst, benzene reacts with chlorine and bromine to form benzenehexachloride, $C_6H_6Cl_6$, and benzene hexabromide, $C_6H_6Br_6$, respectively the former of which is a powerful insecticide and is sold under the name *Gammexane* or 666.

(9) OZONIDE FORMATION. With ozone, benzene yields a tri-ozonide which on hydrolysis yields glyoxal.

$$\underset{\text{Benzene}}{C_6H_6} + 3O_3 \longrightarrow \underset{\text{Benzene triozonide}}{C_6H_6(O_3)_3} \xrightarrow{+3H_2O} \underset{\text{Glyoxal}}{3CHO.CHO} + 3H_2O_2$$

Uses. Benzene is used : (1) as a solvent for the extraction of fats and oils ; (2) for dry-cleaning woollen clothes ; (3) as motor fuel along with petrol ; (4) as a starting material in the synthesis of various derivatives for preparation of dyes, drugs, plastics, perfumes, explosives, etc. ; and (5) for the manufacture of maleic acid by catalytic oxidation.

STRUCTURE OF BENZENE

(1) **Molecular formula.** Elementary analysis and molecular-weight determination shows that the molecular formula of benzene is C_6H_6. Comparison of this formula with that of the corresponding saturated hydrocarbon hexane, C_6H_{14}, at once suggests that benzene is a highly unsaturated compound. Thus, the six carbon atoms in its molecule may be presented to be linked by double or triple bonds so as to form a straight chain or a closed ring.

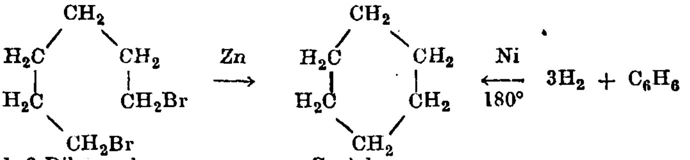
(2) **Open-chain structure untenable.** Benzene could be possibly represented by straight-chain formula containing double and triple bonds, such as

$HC{\equiv}C—CH_2—CH_2—C{\equiv}CH$ (Dipropargyl)

$H_2C{=}CH—C{\equiv}C—CH{=}CH_2$ (Divinylacetylene)

Both these compounds are known. Unlike benzene, they are easily oxidised and form addition products readily. Therefore, any straight-chain structures as given above are incompatible with the behaviour of benzene.

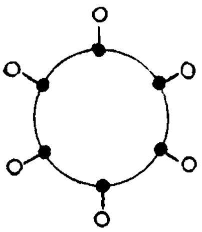
(3) **Evidence in favour of ring formula.** (*i*) Catalytic hydrogenation of benzene yields cyclohexane which is identical with the product synthesised by the action of zinc on 1, 6-dibromohexane.

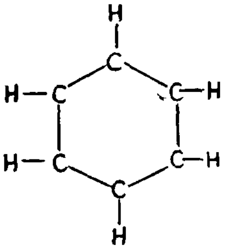


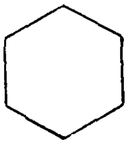
1, 6-Dibromohexane Cyclohexane

This indicates that the six carbon atoms of benzene are joined in a ring.

(*ii*) Benzene forms one and only one monosubstitution product. Thus there is but one chlorobenzene and one nitrobenzene known. This is possible if benzene molecule is made of a symmetrical ring of six carbons each of which carries a hydrogen atom. For the time being, neglecting the fourth valency of carbon atom, we can represent benzene as follows :

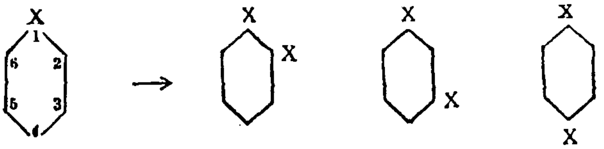






In the last formula, one CH is understood to be occupying each vacant corner of the hexagon.

(*iii*) Benzene froms three di- and three tri-substitution products for similar substituents, which is again explained on the basis of the ring formula. Since the positions 2 and 6 ; 3 and 5 of the mono-substitution product C_6H_5X are identical there are only three different H atoms (2, 3, 4) the replacement of which would yield three disubstitution products.

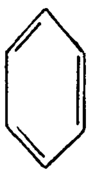


Proceeding similarly it can be shown that the above disubstitution products upon introduction of a third X in the ring would give in all three trisubstitution products.

(*iv*) Now physical methods such as X-ray crystal and electron-diffraction measurements on benzene and its derivatives have proved beyond doubt that benzene has a ring structure.

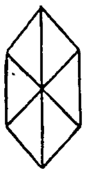
Fig. 36·2. Visible proof of the hexagonal arrangement of carbon atoms in the benzene ring. It is a photograph of a molecule of hexamethyl benzene, $C_6(CH_3)_6$, based on X-ray diffraction. The black spots are carbon atoms. Obviously the inner hexagon is the benzene ring while the outer spots represent the carbons of the six-methyl groups linked to the carbon atoms of the former. Hydrogen atoms of methyl groups are too small to diffract X-rays and hence do not show up in the picture.

(4) **Bond structure of benzene.** In the above ring formula of benzene the fourth valency of all the six carbon atoms was left unaccounted for. For the disposition of the fourth valency of each



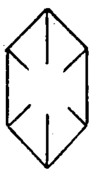
I

Kekule's formula (1865)



II

Diagonal formula of Claus (1867)

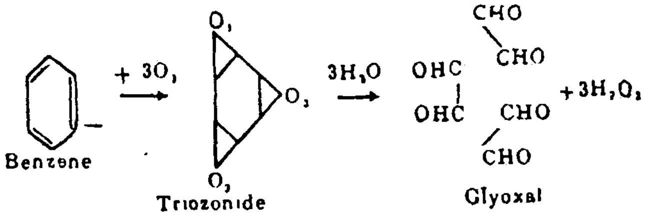


III

Centric formula of Armstrong and Baeyer (1887) carbon consistent with the behaviour of benzene, many alternative arrangements were suggested from time to time by different workers. Of these we mention the three important ones. In formulae II and III the fourth valency of carbon atoms is directed towards the centre of the hexagon. Such molecules should be able to combine chemically with a hexavalent atom like that of sulphur. Since no such reaction between benzene and sulphur is known to take place, the formulae II and III are ruled out.

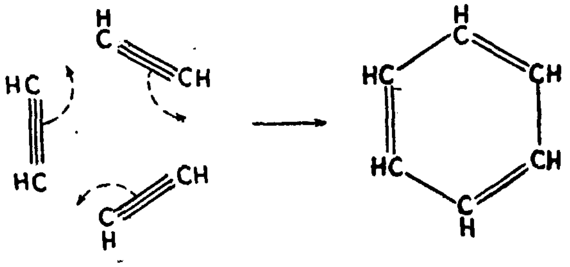
(5) **Facts that support Kekule's formula.** (*i*) Benzene combines with three molecules of hydrogen and of chlorine to form respectively cyclohexane, C_6H_{12}, and benzenehexachloride, $C_6H_6Cl_6$. This proves the presence of three double bonds in the ring.

(*ii*) Benzene forms a triozonide which on hydrolysis yields three molecules of glyoxal.



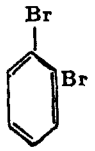
This confirms the presence of double bonds in alternate positions in the benzene ring.

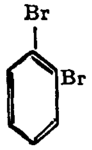
(*ii*) Three molecules of acetylene polymerise to form benzene which may be visualised to take place as follows.



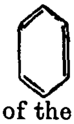
(6) **Objections to Kekule's formula.** The two main objections levelled against Kekule's formula are :

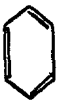
(*i*) *It admits the formation of two ortho disubstitution products for similar substituents.* Thus two *o*-dibromobenzenes possible would be :





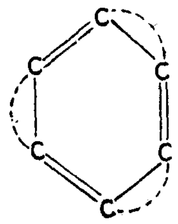
However, actually only *one* dibromobenzene is known. Kekule replied this objection by proposing that the double bonds in benzene ring were continuously oscillating back and forth between two adjacent positions thus



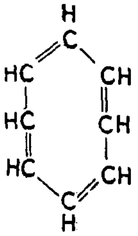


Since the positions of the double bonds were not fixed, the question of formation of two dibromobenzenes did not arise.

(*ii*) *It represents benzene as a highly unsaturated compound, while it actually behaves like a saturated one, forming substitution compounds readily.* Many attempts have been made to meet this objection, including the proposed formulae of Baeyer and Claus. In 1809 Thiele applied his theory of partial valency and pointed out that in benzene we have a system of conjugated double bonds with no ends, and hence all partial valencies are neutralised. Thus, the double bonds of benzene are not able to enter into addition reactions and hence the hydrocarbon becomes predominantly saturated in behaviour. However, Thiele's formula of benzene was open to objection since cyclooctatetrene having analogous structure behaves like alkenes and lacks aromatic character.

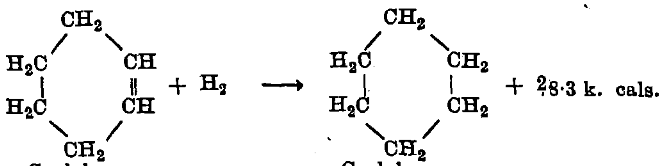


Thiele's formula for benzene



Cyclooctatetrene

(*iii*) From thermochemical data it is observed that "*the heat of hydrogenation* of benzene is much lower than expected from Kekule's formula.*" Cyclohexene (having only one double bond) has heat of hydrogenation of 28·6 k. cals and cyclohexadiene (two double bonds) should have a value twice as large. Accordingly the heat of hydrogenation for Kekule's structure of benzene (hexatriene) should be thrice as large as that of cyclohexene *i.e.*, 3 × 28·6 = 85·8 k.cal/mole. The actual observed values of heats of hydrogenation are given below.



Cyclohexene Cyclohexane

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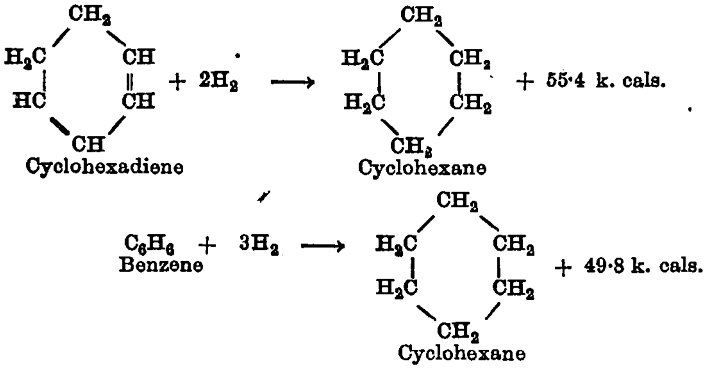
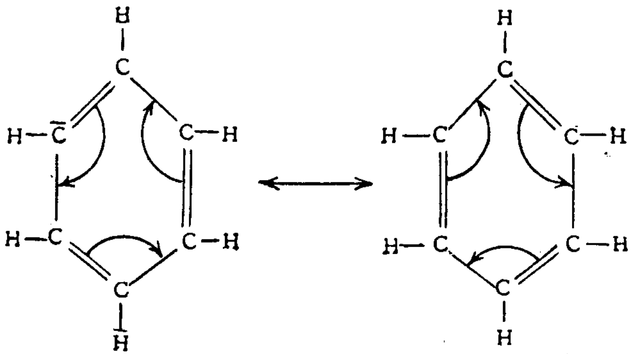
*Heat of hydrogenation is defined as the quantity of heat evolved when one mole of an unsaturated compound is hydrogenated.



It is, therefore, clear from the data given above that the heat of hydrogenation of 'real' benzene is 36 k. cal/mole less than the expected value for Kekule's structure of benzene. This discrepancy cannot be accounted for considering the Kekule structure of benzene as cyclohexatriene.

(7) Present-day position regarding the structure of benzene.

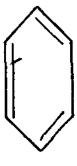
Kekule's suggestion that the double bonds in the benzene ring are continuously oscillating back and forth between two adjacent positions (dynamic equilibrium), meets the first objection satisfactorily—

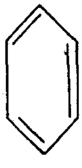


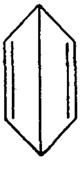
However, Kekule's formula still fails to explain the second and third objections since benzene is still depicted as an unsaturated substance with three double bonds.

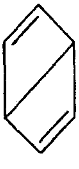
Spectroscopic data, X-ray and electron diffraction studies throw more light on the problem. Accordingly, it is known that all the six C atoms are arranged as a regular hexagon (angle 120°) in one plane and all the carbon-to-carbon bonds are equivalent in length (1·397Å) which is intermediate between that of C—C bond (1·54 Å) and C=C bond (1·33 Å). Hence there are no longer short bonds in benzene structure as erroneously thought of by Kekule.

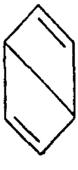
Resonance Structure. According to the resonance concept, benzene molecule is regarded a 'resonance hybrid' of a number of canonical forms such as :

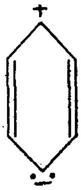

I


II


III

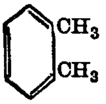

IV


V

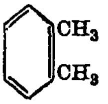

VI

I and II are Kekule structures, III, IV and V are Dewar structures, while there may be many dipolar forms such as structure VI. Kekule structures contribute over 80 per cent to explain the character of the benzene molecule. Since in the resonance hybrid of benzene the carbon-carbon bonds are of equivalent lengths, it is much more stabler than any of the canonical forms. The added stability of benzene ring is due to its resonance stabilisation energy which is 39 k. cal/mole.

Hayman and Wibaut (1939) showed that the products of ozonolysis of *o*-xylene agree with the existence of the two forms :



and



thereby establishing the truth of resonance structure of benzene molecule.

Orbital Model of Benzene. The molecular orbital theory provides, probably the fullest description of the benzene ring. From

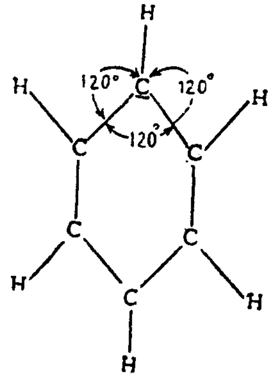


Fig. 36·3. Bond angles in benzene skeleton.

spectroscopic studies and X-ray analysis, it is known that all the C—C—C and C—C—H bond angles are equal to 120° and the carbon atoms are arranged as a regular hexagon lying in one plane.

Therefore, it stands to reason that, each of the six carbon atoms is in a state of sp^2 hybridisation (*trigonal hybridisation*) *i.e.*, it possesses three sp^2 hybrid orbitals inclined at an angle of 120° and a fourth p orbital disposed perpendicularly to the plane of sp^2 orbitals.

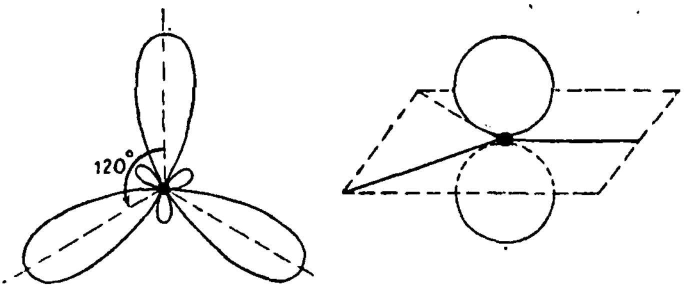


Fig. 36·4. sp^2 hybrids in carbon leaving a pure p orbital.

Two sp^2 orbitals on each of the six carbon atoms are utilised in overlapping orbitals on two adjacent carbon atoms to form σ bonds. The third sp^2 orbital is used in forming σ bond with hydrogen atom. The σ skeleton of benzene is shown below.

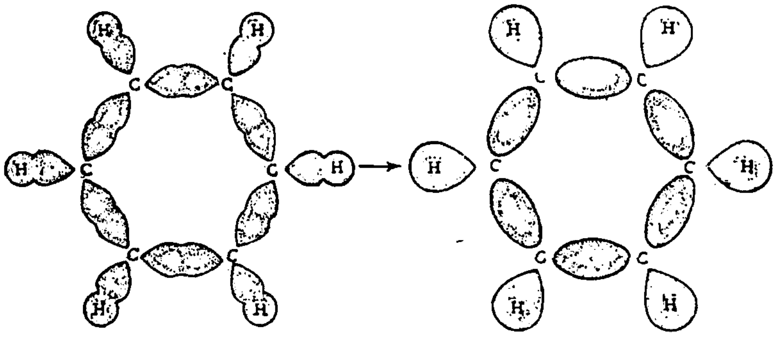


Fig. 36·5. The formation of σ skeleton of benzene.

It may be noted that there remains an unused p-orbital on each carbon atom disposed at right angles to the plane of the ring.

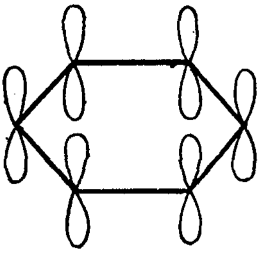


Fig. 36·6. An unpaired 'p' orbital on each carbon atom.

It can be used for π bond formation. The situation may be illustrated as above in Fig. 36·6.

From the geometry of the molecule it is quite clear that *p* orbitals on carbon atoms can overlap in two ways. The *p* orbitals of carbons 1 and 2, 3 and 4, and 5 and 6 will overlap to form three dicentric π molecular orbitals, Fig. 36·7 (*a*). At the same time, three dicentric π M.Os can also be formed if the *p* orbitals of carbons 2 and 3, 4 and 5 and 6 and 1 overlap, Fig. 36·7 (*b*). The molecules resulting from these two modes of orbital overlap are quite analogous to the two Kekule structures. However, actually each *p* orbital overlaps its two neighbours equally thus resulting in the formation of continuous π molecular orbital with six electrons in it, encompassing all the six carbon atoms of the ring. This π M.O. is, therefore, polycentric and electrons in it are very much delocalised just as was the case with Butadiene. The π M.O. comprises two doughnut shaped lobes, one lying above and the other below the plane of atomic nuclei as shown in Fig. 36·8.

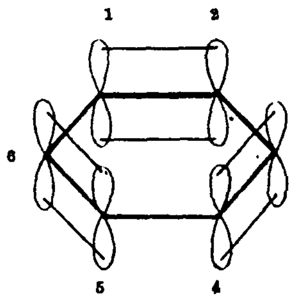


Fig. 36·7 (*a*)

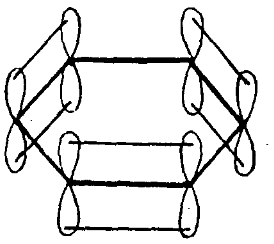


Fig. 36·7 (*b*)

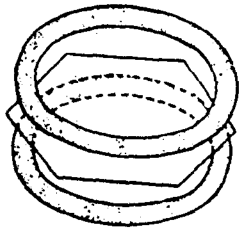


Fig. 36·8. The delocalized π oribal in benzene.

In fact the delocalised π M.O. represents three localised π M.Os. The energy of the six *delocalised* π electrons is less than that of the three pairs of localised π electrons. Thus *delocalisation stabilises the benzene molecule* and its orbital structure, with continuous tubular π orbitals sandwiching the 6-carbon atom ring, stands confirmed.

TOLUENE, METHYLBENZENE, PHENYLMETHANE, $C_6H_5CH_3$

Toluene is the simplest homologue of benzene. It takes its name from *Tolu balsam* from which it was first obtained by distillation. Its industrial name is '*toluol*'.

Preparation. Toluene is prepared industrially from the 'light oil' fraction of coal-tar, and also from coal gas by methods already described under benzene. The mixture of benzene and toluene finally obtained is fractionally distilled to yield toluene. Recently considerable quantities of toluene have been obtained by cyclization of n-heptane and by isolation from certain varieties of petroleum.

Toluene can be prepared in the laboratory : (1) By Friedel-Crafts reaction.

$$\underset{\text{Benzene}}{C_6H_6} + \underset{\substack{\text{Methyl}\\ \text{chloride}}}{CH_3Cl} \xrightarrow{AlCl_3} \underset{\text{Toluene}}{C_6H_5CH_3} + HCl$$

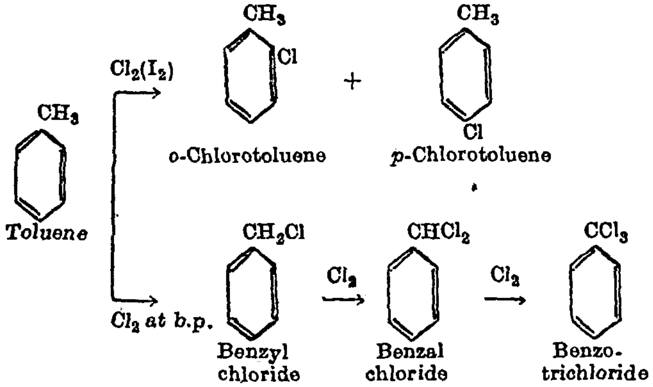
and (2) by Wurtz-Fittig reaction.

$$\underset{\textit{Bromobenzene}}{C_6H_5Br} + \underset{\substack{\text{Methyl}\\ \text{bromide}}}{CH_3Br} + 2Na \xrightarrow{\text{(in ether)}} \underset{\text{Toluene}}{C_6H_5.CH_3} + 2NaBr$$

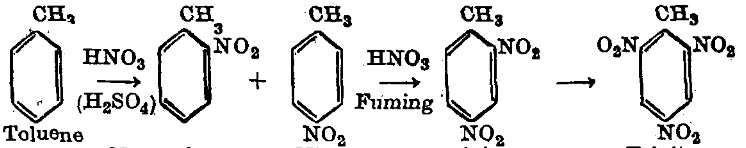
Properties. (*Physical*). Toluene is a colourless, mobile liquid, b.p. 110°, m.p. —95°, sp. gr. 0·867 at 20°. It has an odour similar to that of benzene. It is insoluble in water, but is miscible in all proportions with alcohol, ether and petroleum. It has a high co-efficient of expansion. It is a good solvent for many organic substances.

(*Chemical*). The molecule of toluene is made of a phenyl group linked with a methyl group. Thus, it combines the behaviour of benzene and methane. However, the methyl group is readily attacked by oxidising agents since it is connected to the negative phenyl group.

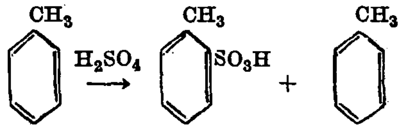
(1) HALOGENATION. *Chlorine and bromine substitute* either in the benzene ring or in the side-chain depending on conditions. Thus : (*a*) In the presence of a catalyst (I_2, $FeCl_3$) chlorine forms *o*- and *p*-chlorotoluenes and (*b*) At boiling point, chlorine reacts with toluene giving benzyl chloride, benzal chloride and benzotrichloride.



(2) NITRATION. A mixture of nitric acid and sulphuric acid nitrates toluene to form *o*- and *p*-nitrotoluenes. Further nitration yields di- and tri-nitro derivatives.


Toluene o-Nitrotoluene p-Nitrotoluene 2, 4-Dinitrotoluene Trinitrotoluene

(3) SULPHONATION. Hot sulphuric acid sulphonates toluene to o- an p-toluenesulphonic acids.


Toluene o-Toluenesulphonic acid p-Toluenesulphonic acid

(4) OXIDATION. (i) Oxidising agents such as dilute nitric acid, potassium permanganate and chromic acid convert toluene into benzoic acid.

$$\underset{\text{Toluene}}{C_6H_5CH_3} + 3[O] \longrightarrow \underset{\text{Benzoic acid}}{C_6H_5COOH} + H_2O$$

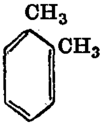
(ii) A mild oxidising agent like chromyl chloride (CrO_2Cl_2) converts toluene to benzaldehyde (*Etard's reaction*).

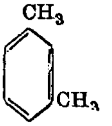
$$\underset{\text{Toluene}}{C_6H_5CH_3} + 2[O] \longrightarrow \underset{\text{Benzaldehyde}}{C_6H_5CHO} + H_2O$$

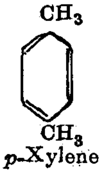
Uses. Toluene is used : (1) for dry-cleaning ; (2) as a solvent and diluent for lacquers ; (3) for blending petrol ; (4) as a starting material for the manufacture of certain dyes and drugs, as also for nitrotoluene (*explosive*), saccharin, benzaldehyde, benzoic acid etc.

XYLENES, DIMETHYLBENZENES, $C_6H_4(CH_3)_2$

They are the next homologues of benzene and are isomeric with ethylbenzene, $C_6H_5.C_2H_5$.


o-Xylene, 1, 2-dimethylbenzene

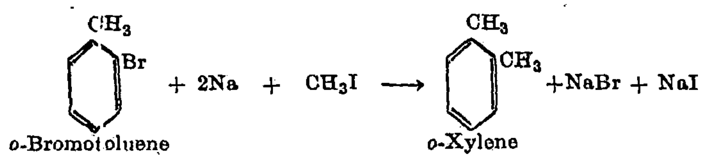

m-Xylene, 1, 3-dimethylbenzene


p-Xylene, 1, 4-dimethylbenzene

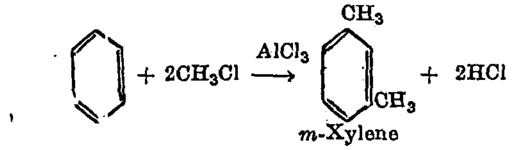
All the three xylenes are present in coal-tar, the meta compound predominating.

Preparation. A mixture of xylenes '*xylol*' is obtained by fractionating "50 per cent benzol" between 138—142°. It contains about 60 per cent of m-xylene along with some o- and p-isomers. Individual xylenes cannot be isolated as their boiling points are too close together. Therefore, if a pure xylene is desired, it is generally prepared by synthesis from other compounds.

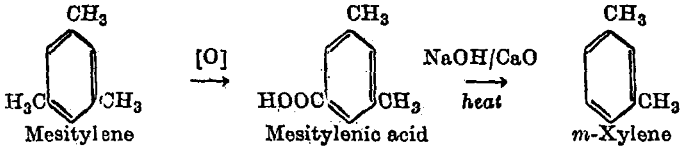
(1) The three xylenes can be obtained by treating the corresponding bromotoluenes with methyl iodide and sodium (*Wurtz Fittig reaction*). Thus :



(2) When methyl chloride is passed into benzene, (or toluene) in the presence of anhydrous aluminium chloride, *m*-xylene admixed with a little *p*-xylene is produced (*Friedel-Crafts reaction*).

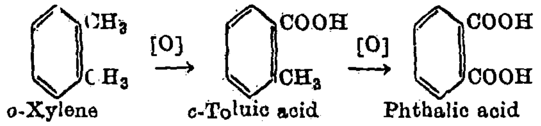


(3) *m*-xylene can be prepared by partial oxidation of mesitylene to form mesitylenic acid and subsequent distillation with soda-lime.



Properties. The three xylenes are colourless, mobile liquids having rather pleasant odours. Their boiling points are : *o*-xylene 142° ; *m*-xylene 139° ; *p*-xylene 138·5°.

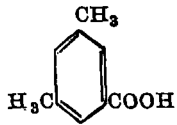
The xylenes form substitution products much in the same way as toluene. On oxidation with dilute nitric acid or potassium permanganate they are converted in the first place to toluic acids and then to phthalic acids. Thus :



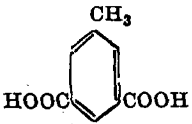
Uses. Xylol is used as a solvent and diluent for making lacquers, *o*-Xylene is employed for the manufacture of Vitamin B_2, and *m*-xylene for making '*Xylene musk*'. The amino derivatives of xylene find use in the dye-stuff industry.

Mesitylene *1, 3, 5-Trimethylbenzene*, $C_6H_3(CH_3)_3$. Mesitylene occurs in coal-tar and is prepared by distilling acetone with sulphuric acid, or by the polymerisation of propyne in the presence of sulphuric acid.

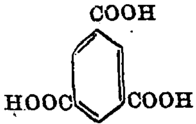
Properties. Mesitylene is a colourless pleasant smelling liquid, b.p. 165°. On oxidation with dilute nitric acid, the three methyl groups are successively converted to carboxylic acid groups, forming



Mesitylenic acid



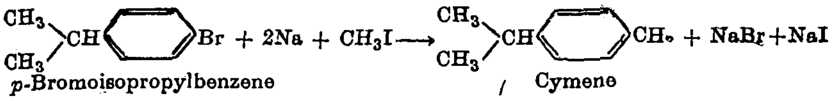
Uvitic acid



Trimesic acid

These acids produce *m*-xylene, toluene and benzene respectively on heating with sodalime.

Cymene, *Methylisopropylbenzene,* $CH_3.C_6H_4.CH(CH_3)_2$. Cymene occurs in oil of thyme and oil of eucalyptus. It may be prepared by heating camphor with phosphorus pentoxide, or by heating turpentine oil with sulphuric acid. It has been synthesised by the action of sodium on *p*-bromoisopropylbenzene and methyl iodide, which proves its constitution.



p-Bromoisopropylbenzene

Cymene

Styrene, *Phenylethylene, Vinylbenzene,* $C_6H_5.CH{:}CH_2$. Styrene occurs in coal-tar and in the plant Storax (hence its name). It can be prepared conveniently in the laboratory by heating cinnamic acid with a little hydroquinol which prevents polymerisation.

$$\underset{\text{Cinnamic acid}}{C_6H_5.CH{=}CH.COOH} \xrightarrow{300^\circ} \underset{\text{Styrene}}{C_6H_5CH{=}CH_2} + CO_2$$

Styrene is manufactured by the catalytic dehydrogenation of ethyl benzene, previously obtained by the alkylation of benzene with ethylene.

$$C_6H_6 + CH_2{=}CH_2 \xrightarrow{AlCl_3} \underset{\text{Ethylbenzene}}{C_6H_5.CH_2CH_3} \xrightarrow[700^\circ]{Al_2O_3} \underset{\text{Styrene}}{C_6H_5.CH{=}CH_2} + H_2$$

Properties. Styrene is a colourless liquid, b.p. 145°. It behaves like ethylene and forms addition products in the side-chain.

$$C_6H_5CH{=}CH_2 + H_2 \xrightarrow{\text{catalyst}} \underset{\text{Ethylbenzene}}{C_6H_5CH_2CH_3}$$

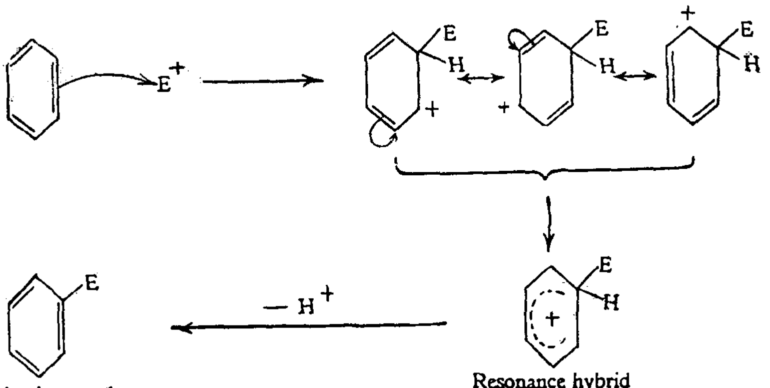
$$C_6H_5CH{=}CH_2 + Br_2 \longrightarrow \underset{\text{Styrene dibromide}}{C_6H_5CHBr.CH_2Br}$$

On oxidation styrene is converted to benzoic acid. On standing or heating it polymerises readily to solid 'metastyrene'. Styrene is used for making plastic and rubber.

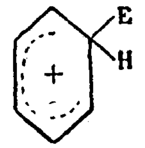
MECHANISM OF SUBSTITUTION IN BENZENE RING

The main feature of benzene ring is the delocalised sextet of π electrons as described above. Benzene ring, therefore, serves as a source of electrons and can readily react with compounds deficient in electrons *i.e., Electrophiles* (E^+). In other words, benzene undergoes Electrophilic substitution while the nucleophilic reagents will be repelled by benzene ring. A high and uniform electron density in the benzene ring offers electrons to electrophiles for bond formation at any carbon atom.

Electrophilic substitution in benzene is believed to take place by first formation of an unstable positive intermediate which readily loses a proton to give the substitution product.



In forming the carbonium ion $\overset{+}{C}_6H_5{<}^{E}_{H}$, two of the six π electrons of the benzene ring are donated to the electrophile to form a new bond and the remaining four π electrons are delocalised over 5 carbon atoms. It involves a loss of delocalisation or resonance energy and restricts the freedom of electrons rendering the system unstable. The intermediate compound then reverts to benzenoid character by expelling a proton in step (*ii*) and thus regaining the resonance energy lost in step (*i*). As discussed above the intermediate compound is, in fact, a resonance hybrid of the three structures.

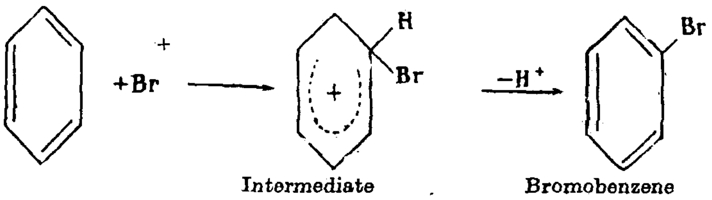


We will now proceed to apply these general principles of substitution to explain the mechanism of bromination, nitration, sulphonation and Friedel-Crafts reaction of benzene.

(*a*) **Bromination.** Bromine in presence of catalyst $AlBr_3$, supplies the necessary electrophile Br^+ for substitution.

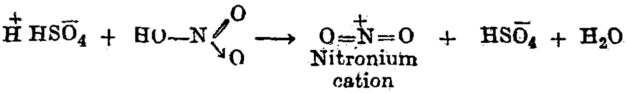
$$:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Br}}}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Br}}}: + \underset{\substack{\cdot\cdot\\ \mathrm{Br}\\ \text{Catalyst}}}{\overset{\substack{\mathrm{Br}\\ \cdot\cdot}}{\mathrm{Al}}}:\mathrm{Br} \underset{\substack{\text{Octet of Al}\\ \text{completed}}}{\overset{\text{Heterolysis}}{\rightleftharpoons}} :\overset{+}{\underset{\cdot\cdot}{\mathrm{Br}}} + \left[\mathrm{Br}:\underset{\substack{\cdot\cdot\\ \mathrm{Br}\\ \text{Base}}}{\overset{\substack{\mathrm{Br}\\ \cdot\cdot}}{\mathrm{Al}}}:\mathrm{Br}\right]^-$$

The Br^+ ion formed by heterolytic fission of Br—Br, attacks benzene to form the intermediate $\overset{+}{C}_6H_5{<}^{H}_{Br}$ which loses a proton ($\overset{+}{H}$) to give bromobenzene. The proton is accepted by the base $[AlBr_4]^-$.



$$\overset{+}{H} + [Al\,Br_4] \longrightarrow AlBr_3 + HBr$$

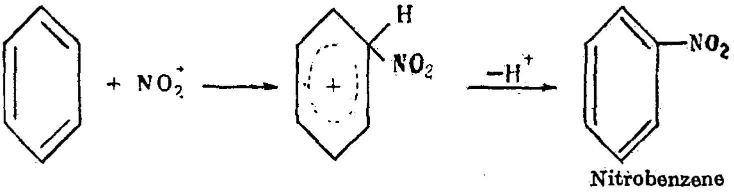
(b) **Nitration.** This reaction is brought about by the electrophile $\overset{+}{N}O_2$ (nitromium ion), which is produced in the nitrating mixture ($HNO_3 + H_2SO_4$) as shown below



$$\overset{+}{H}\,HS\bar{O}_4 + HO{-}N\overset{O}{\underset{O}{\lessgtr}} \longrightarrow O{=}\overset{+}{N}{=}O + HS\bar{O}_4 + H_2O$$

Nitronium cation

The $\overset{+}{N}O_2$ cation reacts with benzene to form the intermediate which loses a proton to the anion HSO_4.

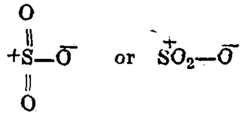


$$\overset{+}{H} + HS\bar{O}_4 \longrightarrow H_2SO_4$$

(c) **Sulphonation.** It is believed that the electrophilic reagent in this case is sulphur trioxide (SO_3) which is produced by the reaction

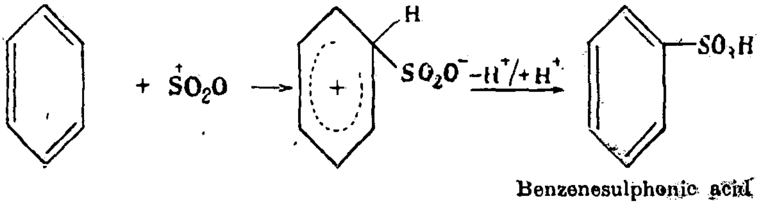
$$2H_2SO_4 \rightleftharpoons \overset{+}{H_3}O + SO_3 + HS\bar{O}_4$$

Sulphur trioxide is a resonance hybrid of many canonical forms of which the following dipolar form predominates.

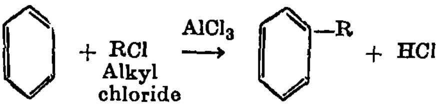


$$+\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}{-}\bar{O} \quad \text{or} \quad \overset{+}{S}O_2{-}\bar{O}$$

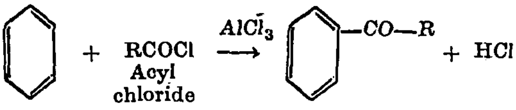
The sulphur trioxide reacts with benzene to form the intermedate which loses a proton to the negative oxygen atom of SO_3.



(*d*) **Friedel-Crafts reaction.** In Friedel-Crafts reaction the hydrogen of the benzene ring is replaced by an alkyl radical (R—) or an acyl radical (RCO—) in the presence of $AlCl_3$ as catalyst.



Benzene Substituted benzene

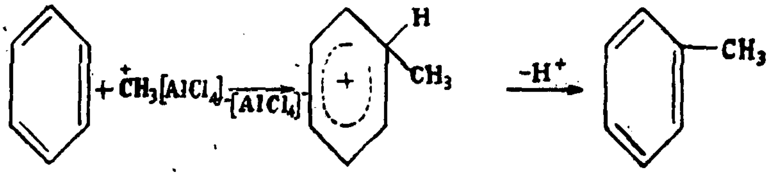


Benzene Aromatic ketone

The mechanism of alkylation may be explained by taking example of formation of toluene ($C_6H_5.CH_3$) by the action of methyl chloride on benzene. Here the electrophile is a positively charged methyl group produced by the influence of the anhydrous aluminium catalyst in the same way as the formation of a positively charged bromine atom in bromination.

$$CH_3—Cl + AlCl_3 \longrightarrow \underset{Complex}{\overset{+}{C}H_3[Al\overset{-}{C}l_4]}$$

The positively charged methyl group, known as a carbonium ion, attacks the benzene ring to form an unstable intermediate which then loses a proton.

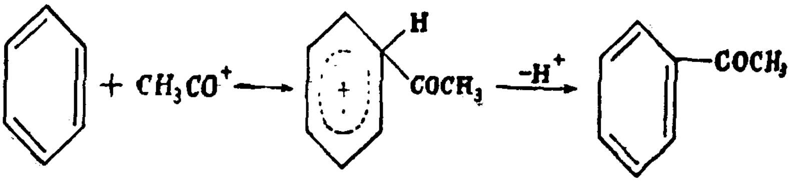


Unstable Intermediate Toluene

$$\overset{+}{H} + Al\overset{-}{C}l_4 \longrightarrow HCl + AlCl_3$$

In acylation of benzene to form a ketone, the acid chloride (say CH_3COCl) reacts with $AlCl_3$ to form the acylium ion $[R—\overset{+}{C}{=}O]$ which acts as electrophile. The acylium ion then attacks the benzene molecule to give an intermediate which loses a proton to yield the corresponding ketone.

$$CH_3COCl + AlCl_3 \longrightarrow \underset{Acylium\ ion}{CH_3\overset{+}{C}O} + Al\overset{-}{C}l_4$$



Intermediate Acetophenone

It may be noted that the mechanism of monosubstitutions described above is true not only for benzene but for all aromatic compounds *containing a benzene ring.*

QUESTIONS

1. Describe the general methods of synthesis and important reactions of benzene and its homologues.

2. Compare the chemical properties of the alkene, alkanes and the aromatic hydrocarbons, illustrating your answer by reference to methane, ethylene and benzene.

3. How can you locate a side chain on the benzene nucleus ? You are given three unlabelled bottles containing benzene toluene and o-xylene. How will you proceed to find which is which ?

4. Describe in detail the action of halogens on benzene and toluene.

5. How does benzene differ from an aliphatic hydrocarbon ? Discuss the constitution of the benzene molecule. *(Dibrugarh B.Sc. III, 1967)*

6. Write notes on the following :—

(*a*) Nuclear and side-chain Halogenat: -

(*b*) Friedel-Crafts reaction.

(*c*) Mechanism of Nitration. *(Agra B.Sc. III, 1967)*

7. Write notes on the following :—

(*a*) Friedel-Crafts reaction.

(*b*) Reimer Tiemann Reaction.

(*c*) Sandmeyer Reaction. *(Allahabad B.Sc. II, 1967)*

8. Discuss the constitution of benzene. What are the merits and demerits of various formulae assigned to it. What are the modern views about its structure ? *(Panjab B.Sc. III, 1968)*

9. Starting from benzene, how will you synthesise the following ? In each case, give the reaction involved

Toluene, Aniline, Benzophenone, Iodobenzene and Benzoic acid. *(Tribhuwan B.Sc., 1968)*

10. Starting from benzene how are the following prepared : (*a*) *p*-nitrophenol (*b*) Benzamide (*c*) *m*-nitroaniline (*d*) *Azo*-benzene. *(Osmania B.Sc., 1968)*

11. What are the distinctions between aliphatic and aromatic compounds ? Discuss with examples. How is pure benzene obtained ? *(Dibrugarh B.Sc., 1968)*

12. Explain the term "aromaticity". What is meant by electrophilic substitution ? Illustrate your answer with reference to reactions of benzene *(Aligarh B.Sc., 1968)*

13. "Aromatic compounds *originally presented a* problem to Organic Chemists because, although they did possess double bonds, they did not display the typical reactions of unsaturated compounds such as olefines." Discuss the

statement briefly in terms of modern theory, and illustrate the difference between aromatic compounds and olefines by comparing the reactions of benzene and ethylene with respect to the following reagents : (*a*) Hydrogen bromide ; (*b*) Chlorine ; (*c*) Concentrated sulphuric acid

With all reactions indicate conditions required. (*Ceylon B.Sc., 1968*)

14. (*a*) Discuss what is meant by aromatic character.

(*b*) Outline the isolation of benzene from coal-tar.

(*Viswa-Bharati B.Sc., 1969*)

15. State the evidence on which the constitution of benzene is based. What are the modern views about its constitution

(*Vanketshwara B.Sc., 1969*)

16. State the evidence on which the constitution of benzene is based. Give modern views on this subject. (*Panjab B.Sc., 1969*)

17. How would you isolate a pure sample of benzene from the light oil fraction of coal-tar distillation. What happens when benzene is

(*i*) Sulphonated ; (*ii*) Chlorinated ; (*iii*) Treated with methyl chloride in the presence of anhydrous aluminium chloride ? (*Kurukshetra B.Sc., 1969*)

37

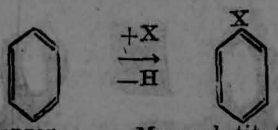
Isomerism and Orientation of Benzene Derivatives

IRVING LANGMUIR
(1881—, American)
His contribution to the theories of aromatic molecular structure have been of great importance in the recent development of organic chemistry. Invented atomic hydrogen flame. Awarded Nobel Prize in 1932. Now Associate Director of the Research Laboratory of the General Electric Company U.S.A.

ISOMERISM

As we have already mentioned, the benzene molecule can be represented by a simple hexagon. It is understood that one carbon atom is occupying each vacant corner of the hexagon or 'ring' and that a hydrogen atom is attached to each carbon. The *mono-*, *di-tri-*substitution products, etc. may be derived by replacing one, two, three or more H atoms of the ring by other atoms or groups. These may be represented in a simple way by introducing the corresponding number of substituted atoms or groups on the hexagon.

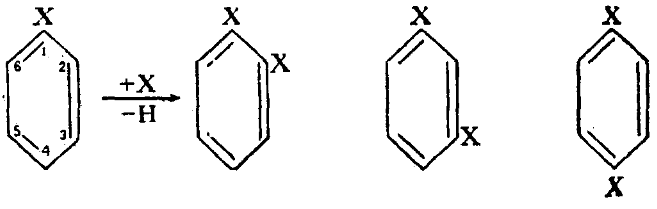
Only one monosubstitution product possible. All the six H atoms of benzene are identical, since they are occupying the corners of a symmetrical hexagon. Therefore, the replacement of any one of them will give the same monosubstitution product.



Benzene Monosubstitution product

Thus there is known only one chlorobenzene, one bromobenzene, and one nitrobenzene.

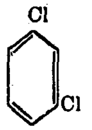
Isomerism of disubstitution products. With the introduction of a second substituent in the benzene ring isomerism appears. In the formula of the monosubstitution product C_6H_5X, the positions 2 and 6 ; 3 and 5 are identical. Thus the replacement of H atoms in positions 2, 3 and 4 by a substituent X will give three different disubstitution products.



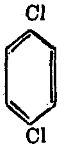
Ortho- (1, 2) *Meta-* (1, 3) *Para-* (1, 4)

It is convenient to designate these derivatives as **ortho** (*o*-), **meta** (*m*-), and **para** (*p*-) according as the two substituents are occupying adjacent, alternate, or opposite positions on the ring. Another way of naming them would be by indicating the number of the positions occupied by the substituted groups of the benzene ring. Actually, three dichlorobenzenes, three dibromobenzenes and three dinitrobenzenes are known to exist. Thus :

o-Dichlorobenzene, 1, 2-dichlorobenzene.

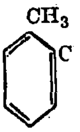


m-Dichlorobenzene, 1, 3-dichlorobenzene.

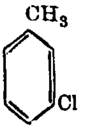


p-Dichlorobenzene, 1, 4-dichlorobenzene.

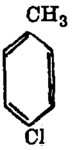
Even when the two substituents are different, *three and only three isomeric disubstitution products are possible.* Thus toluene yields only three chlorotoluenes.



o-Chlorotoluene



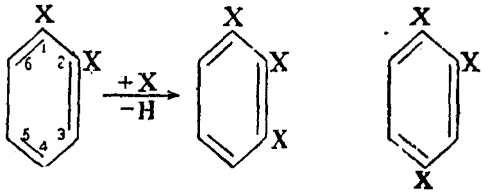
m-Chlorotoluene



p-Chlorotoluene

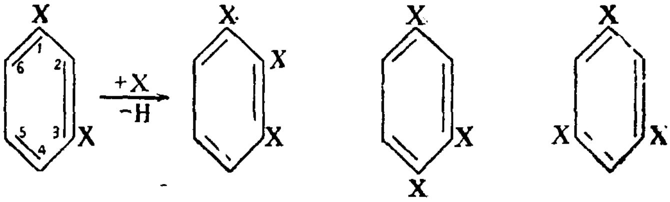
Isomerism of trisubstitution products. In each of the three isomeric disubstitution products (*ortho*, *meta*, *para*) having the formula $C_6H_4X_2$ there are still four vacant corners for further substitution. Thus, in forming a trisubstitution product $C_6H_3X_3$, the third substituent X can be introduced in any of these positions.

(1) In the *ortho* isomer, the positions 3 and 6 ; 4 and 5 are identical. Therefore, it can give two trisubstitution derivatives



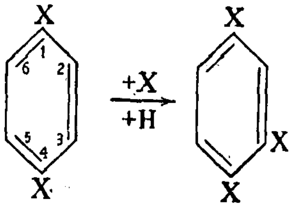
Ortho I II

(2) In the *meta* isomer, the positions 4 and 6 are identical and therefore, the three different positions 2, 4 and 5 are available for introducing the third substituent. Thus it can give three trisubstitution derivatives.



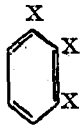
Meta III IV V

(3) In the *para* isomer, all the remaining four positions 2, 3, 5 and 6 are identical and hence it can give only one trisubstitution derivative.

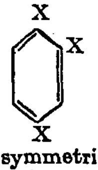


Para VI

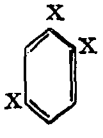
Of the six trisubstituted derivatives (I to VI), I and III ; II, IV and VI are identical. Therefore, in all three trisubstitution products are possible.



Vicinal
(1, 2, 3-)

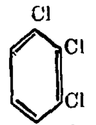


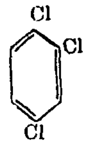
Asymmetrical
(1, 2, 4-)

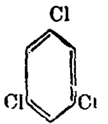


Symmetrical
(1, 3, 5-)

They are often named by indicating the positions of the substituents on the benzene ring, or sometimes by calling them as vicinal (*vic*-), asymmetrical (*as*-) and symmetrical (*s*-) isomers respectively. Thus there are known only three trichlorobenzenes which may be written as


vic-trichlorobenzene,
1, 2, 3-trichloro-
benzene


as-trichlorobenzene,
1, 2, 4-trichlorobenzene


s-trichlorobenzene,
1, 2, 5-trichloro-
benzene

We have seen above that for similar substituents, only three isomeric trisubstitution products are possible. Proceeding in the same manner, it can be proved that if only two of the three substituents are identical, six isomers are possible and if all the three substituents are different the number of isomers is ten. Further it is interesting to note that with the entry of four similar substituents in the benzene ring, the number of isomers is again three, and when five H-atoms are replaced by similar groups there is only one pentasubstitution product possible.

ORIENTATION

We have seen that *di*- and higher substitution products of benzene exist in isomeric forms. Given an unknown isomer, it is often necessary to determine the position of substituents on the benzene ring. *The process of assignment of positions on the benzene ring is known as orientation* (*Orient*, to determine position of). There are two important methods of orientation.

(1) **Korner's Absolute Method.** Korner (1875) gave an elegant method for the orientation of disubstitution products of benzene. It is based on the theory that when a third substituent is introduced in a disubstituted derivative $C_6H_4X_2$, the *o*-isomer gives rise to *two* products, *m*-isomer to *three*, and *p*-isomer to *one* trisubstitution product only. *Thus the position of substituents in an unknown disubstitution compound can be determined by converting it into trisubstitution products and then establishing their number by analysis.* If it yields one trisubstitution product, it was *para* compound ; if it yields two, it was *ortho* ; and if three it was *meta.*

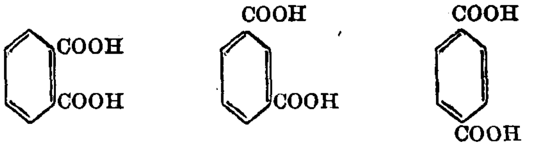
Korner applied his method to the orientation of isomeric dibromobenzenes. He brominated each isomer separately to form tribromobenzenes. One dibromobenzene (m.p. 89°) gave only one tribromobenzene and was, therefore, labelled as *para* ; another (m.p. 2°) gave two tribromobenzenes and was *ortho* ; and the third (m.p. —7°) gave three and was *meta* compound.

The Korner's method of orientation is theoretically absolute (*ideal*) but in actual practice there is considerable difficulty in the separation and identification of the trisubstitution products. Sometimes, an isomer may be formed in very small amount and may escape detection. In view of the other easier methods of orientation now available, Korner's method no longer enjoys an important position.

The converse of Korner's method appears to be more practical *i.e.*, one substituent of the isomeric trisubstitution products is removed. A disubstitution compound thus obtained from three trisubstitution products will be meta ; the one obtained from two trisubstitution products will be ortho ; while that obtained from only one trisubstitution products will be para. Griess (1874) heated each of the six known diaminobenzoic acids with sodalime and thus obtained three phenylenediamines ; three acids gave the same diamine which was, therefore, *m*-isomer ; two acids gave another diamine which was, therefore, *o*-isomer ; and one acid gave one diamine which was, therefore, the *p*-isomer.

(2) **The Indirect Method.** At present time the orientation of benzene derivatives is usually done by the so-called *Indirect method.* In this method, the positions of substituents in an unknown compound are determined indirectly by a study of its reactions, or by converting it into or synthesising from a substance of known orientation

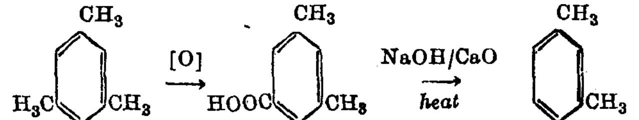
(*a*) *By a study of reactions.* Of the three benzenedicarboxylic acids, phthalic acid, isophthalic acid, terephthalic acid, the first named acid only gives anhydride on heating. Obviously phthalic acid must be the *o*-isomer as the two carboxylic groups in it being nearest readily split out a water molecule to form anhydride.



Phthalic acid Isophthalic acid Terephthalic acid

The COOH groups are too far to react together

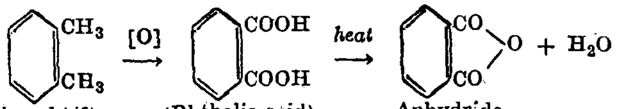
(*b*) *By synthesising from a compound of known orientation.* Of the three isomeric xylenes the one that boils at 139° can be formed by partial oxidation of mesitylene to mesitylenic acid and then heating the latter compound with sodalime.



Mesitylene Mesitylenic acid *m*-Xylene (b.p. 139°)

Since in mesitylene the three methyl groups are meta to each other, the removal of one of them by the above method leaves the remaining two groups intact in the meta position. Therefore the xylene thus produced is the *m*-isomer.

(*c*) *By conversion into a compound of known orientation.* Of the xylenes the one that boils at 144° on oxidation forms a dicarboxylic acid (phthalic acid) which on heating yields anhydride.



(b.p. 144°) (Phthalic acid) Anhydride

10 pe

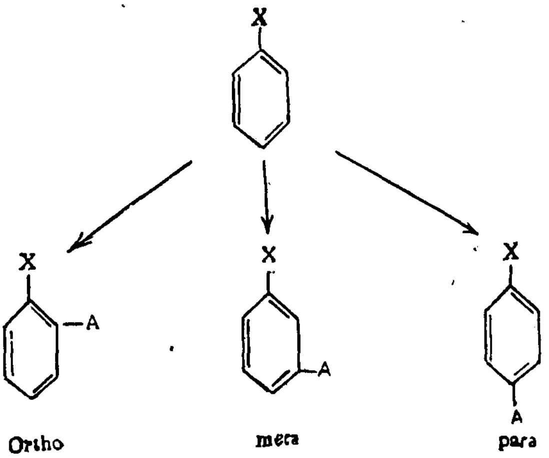
hat this particular xylene must be

ally give the complete orientation
isomer (b.p. 139°) is identified by
he o-isomer (b.p. 144°) is identified
; while the third that boils at 138°

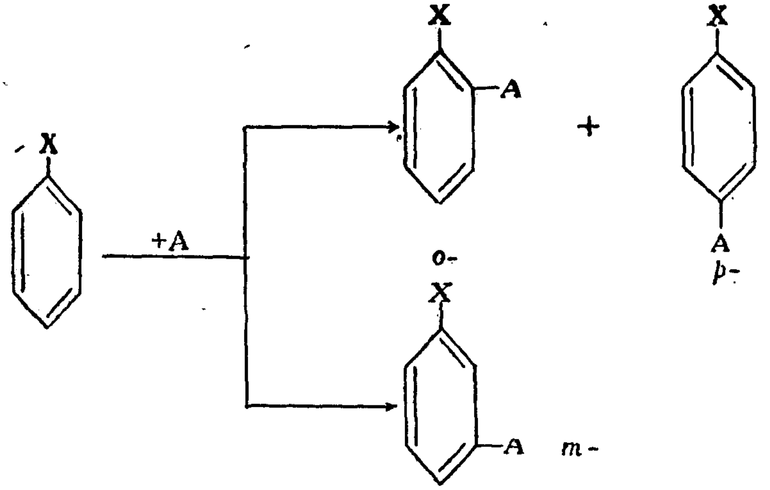
sed on the assumption that the atoms
ound retain or exchange their positions
r orientation. This, however, may not
ce the interpretation of results always
For example, *o*-, *m*-, *p*-bromobenzene
ihydroxybenzene (resorcinol) on fusion
with sodalime.

DIRECTIVE INFLUENCE OF SUBSTITUENTS—ELECTRONIC INTERPRETATION

Substitution is the most characteristic type of reaction of aromatic compounds. It involves the replacement of a hydrogen atom in the ring by another atom or group. It occurs at definite positions with respect to substituents already present on the benzene nucleus The new group (A) may enter the ring at positions ortho, and para, or meta to the group (X) already present.



Which position on the benzene ring, will the new entrant actually occupy, is a pertinent question. It has been found experimentally that the nature of the substituent (X) mainly determines the position of the new substituent on the benzene ring and also governs the ease of substitution. It is also an established experimental fact that when the second group (A) enters the benzene nucleus the chief product is either a mixture of ortho and para isomers, or the meta isomer.



In simple words the substitution in benzene ring can either be *o*- & *p*- or meta. The substituents (X) already present on the benzene ring are, therefore, of two types (*i*) **Ortho para directing groups** (class I) ; (*ii*) **meta-directing groups** (class II).

Class I : —OH, —OR, —SH, —SR, —NH_2, —NHR, —NR_2, —NHCOR —N=N, —CH_3, —CH_2R, —CR_3, —CH_2Cl, —CH_2OH, —CH_2NH_2, —CH_2CN, —CH_2COOH, —CH=CH—COOH, —C_6H_5, —F, —Cl, —Br, —I.

Class II : —SO_3H, —NO_2, —COOH, —COOR, —COCl, —COR, —COCOOH, —CN —CCl_3 —$\overset{+}{N}H_3$, —$\overset{+}{N}H_2R$, $\overset{+}{N}HR_2$, $\overset{+}{N}R_3$, —CHO.

The directive influence of substituents described above can be interpreted in terms of the modern electronic concept. There are three types of substitution reactions of benzenoid hydrocarbons.

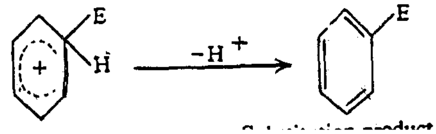
Electrophilic Substitutions. The main feature of benzene ring is the delocalised sextet of π electrons as was described under the 'orbital structure of benzene'. Benzene ring, therefore, serves as a source of electrons and can readily react with compounds deficient in electrons or *electrophiles* (E^+). A high electron density in the benzene ring causes electrophilic substitution. The entering electrophile will be attached to a carbon atom in the ring where electron density is greater.

MECHANISM OF ELECTROPHILIC SUBSTITUTION. Electrophilic substitution involves the following two steps :

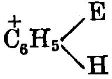
(1)

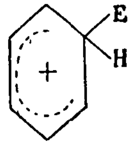
Intermediate compound

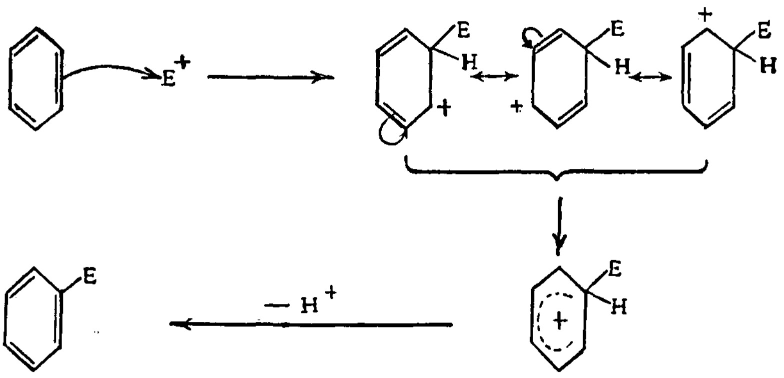
(2)



Substitution product

The electrophile attacks the benzene ring to form an intermediate compound involving a carbonium ion  $\overset{+}{C_6H_5}\langle^{E}_{H}$ In forming a carbonium ion, two of the six π electrons of benzene ring are donated to the electrophile to form a new bond and the remaining four π electrons are delocalised over 5 carbon atoms. This also leaves a delocalised positive charge on these five carbons. The formation of intermediate compound involves a loss of delocalisation or resonance energy rendering the system unstable. The intermediate compound then reverts to benzenoid character by expelling a proton in step (2) and thus regaining the resonance energy lost in step (1). The intermediate compound is, in fact the resonance hybrid of the three structures shown below :

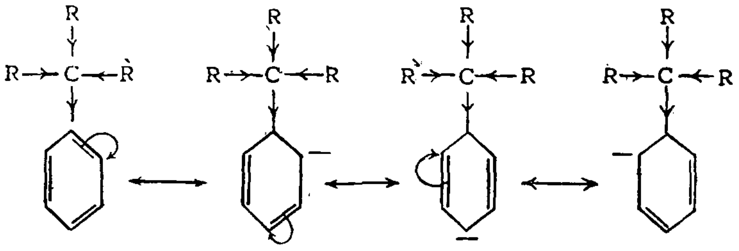




Since the electron density is uniform throughout the benzene ring, the incoming electrophile (E+) has no preferential choice and will occupy any position. However, the presence of a substituent (X) on the benzene ring disturbs its uniform density which increases at specific positions relative to others, thus producing 'charged centres' on the ring. Now the incoming electrophile (E+) would naturally get attached to the carbon atom possessing highest electron density or the 'negative charge centre'. This relative increase of electron density takes place either on the ortho- and para-positions, or on the meta-position.

The type of electronic disturbance caused by the substituent (X) will depend upon its nature whether it 'withdraws' electrons from the ring or 'pumps' electrons into it.

Ortho-para Direction. Let us consider the substituent $—CR_3$, $—NH_2$, $—OH$ etc. of class I to be present on the ring. The $—CR_3$ group increases electron density on the benzene ring as a whole, particularly on the *o*- and *p*-positions due to its electron repelling nature. This causes negative charge-centres on these positions as shown at page 695.



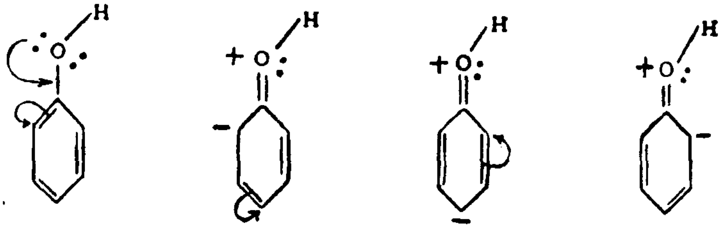
The incoming electrophilic substituent (E^+) is, therefore, directed towards *o*- and *p*-positions.

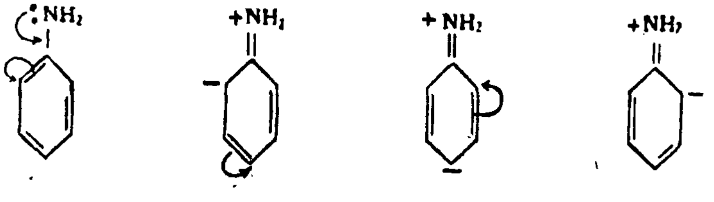
The electron attracting or repelling power of an atom or group in the benzene ring alone does not determine the position taken up by a new entrant. An important characteristic of ortho and para directing substituents is that their 'key atom' has at least one lone pair of electrons *e.g.*,

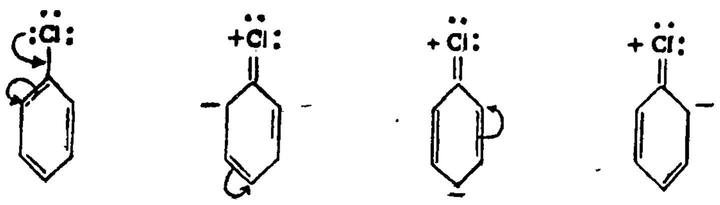
$-\ddot{N}H_2$ $\quad$ $-\underset{\cdot\cdot}{\ddot{O}}-H$ $\quad$ $-\underset{\cdot\cdot}{\ddot{Cl}}:$

(1 lone pair) (2 lone pairs) (3 lone pairs)

The lone pair on the 'key atom' can get conjugated with π electrons of the ring giving rise to the resonance structures as shown below :





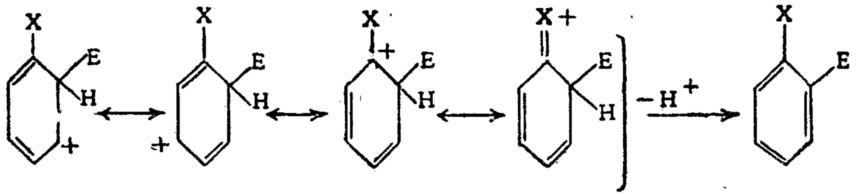


It is interesting to note that the electron density has been increased on the *o*- and *p*-positions only, making these positions susceptible to attack by electrophilic reagents.

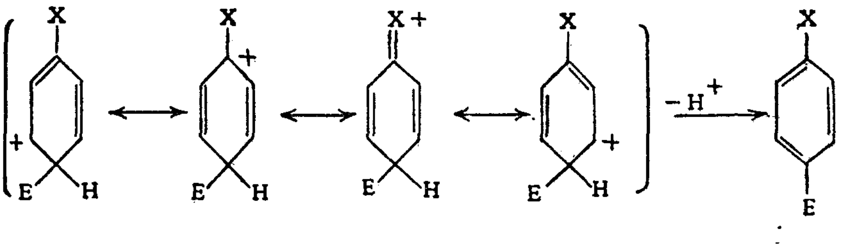
Chlorine atom is different in that it has a pronounced inductive effect, withdrawing electrons from the benzene ring. However, the presence of 3 lone pairs of electrons simultaneously produces a mesomeric effect which opposes the inductive effect. Further a strong electromeric effect is caused in the benzene ring in the presence of the electrophilic attacking reagent (E^+) which raises the electron density on ortho- and para- positions. But this rise of electron density is much smaller as compared to that produced by other groups such as $—NH_2$, $—OH$, $—CR_3$. Consequently, further substitution (say nitration) of chlorobenzene is difficult.

We have already discussed the mechanism of electrophilic substitution. Following the same lines, we will now proceed to show that *o*- and *p*- derivatives are the chief products of substitution when an electrophile E^+ attacks C_6H_5X (where X is a substituent belonging to class I). In the monosubstituted product C_6H_5X, the electrophile E^+ can possibly enter into the *o*-, *p*- or *m*-position. Thus :

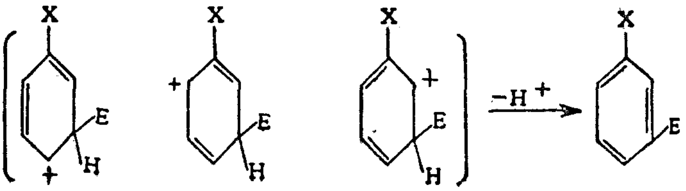
Case I – (E^+ enters Ortho-positions)



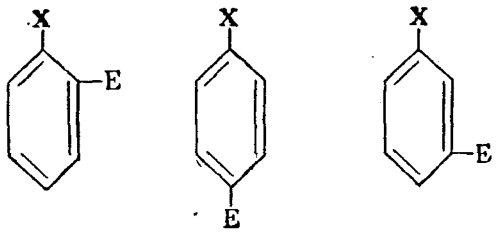
Case II – (E^+ enters para-position)



Case III – (E^+ enters meta-position)

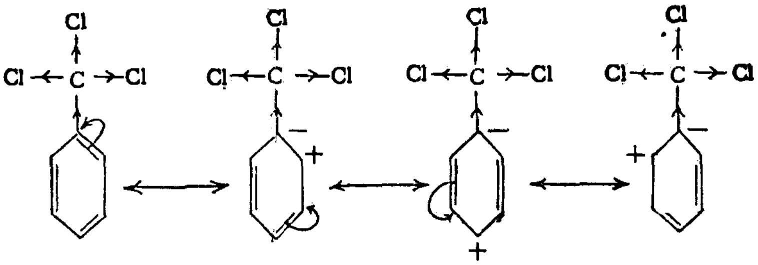


It is the resonance hybrid in each of the above cases that loses a proton and gives rise to the *o*-, *p*-, and *m*-disubstituted products respectively—



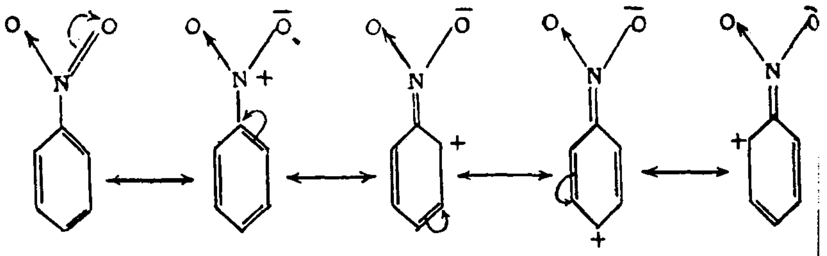
In ortho and para substitutions above, *four* resonance structures are formed in both cases, whereas meta isomer forms *three* resonance structures only. We know that larger the number of resonance structures possible for a substance, the stabler it is. Therefore, the *o*- and *p*-substitution products (giving larger number of resonance structures) are produced predominantly.

Meta Direction. A substituent such as $—CCl_3$, $—NO_2$, —COOH etc. of Class II, withdraws electrons from the benzene ring thus reducing electron density on the latter. The *o*- and *p*-positions to the substituent acquire a positive charge. This naturally implies a high electron density on the meta position. Hence the electrophilic substitution takes place predominantly on the *meta*-position. Let us take the example of substitution in benzene ring with the substituent $—CCl_3$.

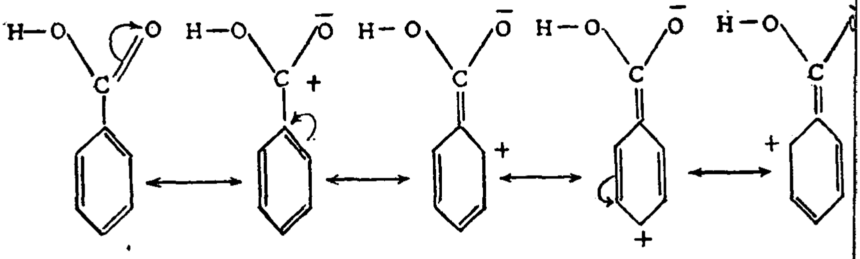


Here the electrophilic attack is at the meta position. The resonating structures in case of meta directing $—NO_2$ and —COOH are given on page 698.

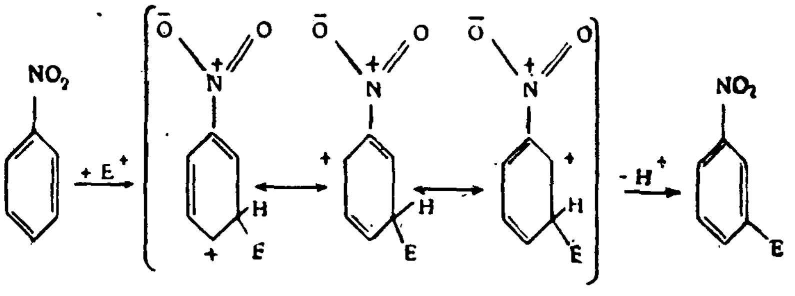
Nitrobenzene



Benzoic acid



Mechanism of an electrophilic attack on nitrobenzene at the meta position is shown below.



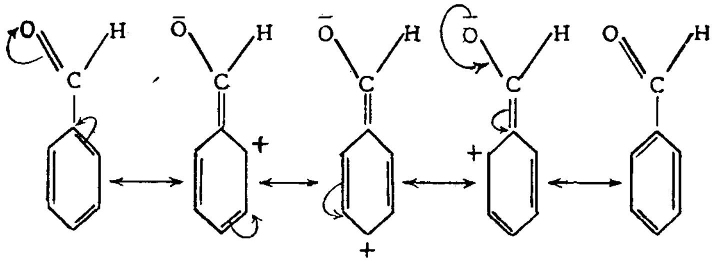
Nucleophilic Substitutions. Benzene ring has already a sextet of π electrons. Therefore, the nucleophilic substituents do not enter the ring readily. Nucleophilic substitution of hydrogen in benzene ring is not very common. It is encountered only when the benzene ring contains electron attracting groups.

$$\text{Nu}: + \text{H}:\vdots\,\text{C}_6\text{H}_4\text{X} \longrightarrow \text{Nu}\,\text{C}_6\text{H}_4\text{X} + \bar{\text{H}}:$$

Since nucleophilic reagents are either anions or neutral molecules with free *p*-electrons, they will attack positions that are deficient in electrons. The charged centres of benzene, therefore, will behave oppositely in nucleophilic substitution than in electrophilic substitution. In the foregoing discussion, we have seen that a *m*-

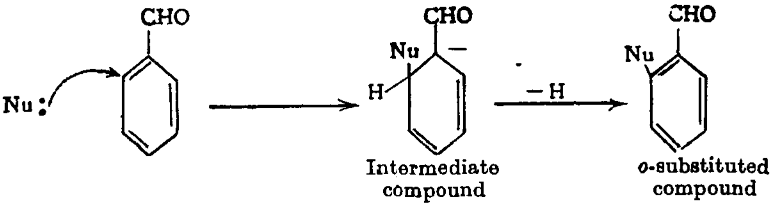
directing group, when present in the benzene ring, creates a deficiency of electrons in the *o*- and *p*-positions producing positive charge centres. These are thus rendered susceptible to attack by nucleophilic reagents.

Let us consider the resonance structures of benzaldehyde with a view to determining the position of the incoming group.

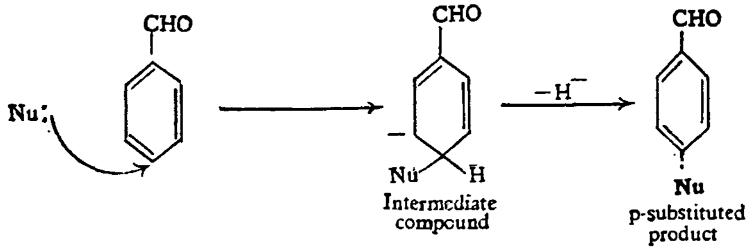


The positive charge lies at *o*- and *p*-positions only, while *m*-position has relatively high electron density. Nucleophilic attack, therefore, takes place at the *o*- and *p*-positions.

Mechanism of Nucleophilic substitution of benzaldehyde :



and



Free Radical Substitution (Homolytic substitution). During this type of substitution of benzene ring, it is attacked by a *free radical* ($\dot{R}$).

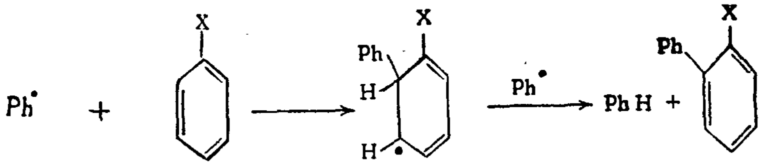
$$\dot{R} + H\cdot/.C_6H_5 \longrightarrow R—C_6H_5 + \dot{H}$$

Since the attacking free radicals are neutral species, polar effects do not influence the substitution reactions here. Majority of these reactions involve substitution by an aryl radical with the formation of *bi* aryls. A few sources of aryl radicals are :

$$\underset{\text{Benzoyl peroxide}}{(C_6H_5CO_2)_2} \longrightarrow 2C_6H_5CO_2 \longrightarrow \underset{\text{Phenyl free radical}}{2\dot{C}_6H_5} + 2CO_2$$

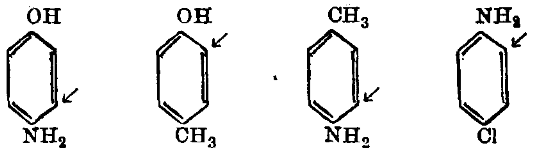
$$\underset{\text{Benzenediazonium chloride}}{C_6H_5\overset{+}{N_2}\bar{Cl}} \xrightarrow{\bar{O}H} C_6H_5{-}N{=}N{-}OH \longrightarrow \dot{C_6H_5} + N_2 + \bar{O}H$$

The presence of substituent (X) in the benzene ring has much smaller effect in aromatic homolytic substitutions than in the other type of aromatic substitutions. Both electron withdrawing and electron-donating groups (class I and II) on the benzene ring have a very mild tendency to *direct* the incoming substituents to the *ortho* position because of two readily available ortho positions. *p*- and *m*-isomers are also formed.



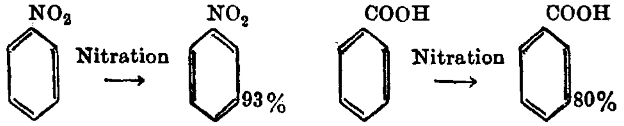
Ph stands for phenyl free radical. These are mainly of theoretical interest rather than of practical importance.

Relative effectiveness of groups. The relative effectiveness of different *o*-*p*-directing groups can be judged by the result of competition between two groups located on the same benzene ring. Thus in *p*-aminophenol substitution occurs preferably in the position ortho to NH_2 which is, therefore, more powerful than OH group. In this way it has been established that NH_2 and OH groups are the most powerful of all *o*-*p*-directing groups.



(*Substitution occurs as indicated by arrows*)

The meta-directing influence of a group can be measured by noting the yield of the *m*-isomer produced by further substitution. Thus :

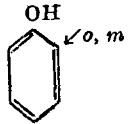


As indicated above, the yields of *m*-nitro derivatives in the two cases are 93 per cent and 80 per cent respectively. Hence, NO_2 group is more powerful than COOH group. The order of effectiveness of some important *m*-directing groups is given below :

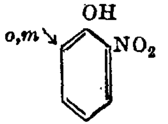
$$NO_2 > SO_3H > CHO > COOH > CONH_2$$

Directive influence in polysubstituted compounds. The course of further substitution in a polysubstituted compound is determined by the combined effect of all the substituents. Thus in *o*- and *p*-nitrophenols, the OH and

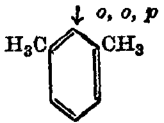
NO_2 add up each other's effect and the substitution takes place as indicated by arrows. In mesitylene the *o*-directing influence of two methyl groups and the *p*-directing influence of the third reinforce at one position and further substitution is guided as shown below :



p-Nitrophenol



o-Nitrophenol



Mesitylene

RULES OF ORIENTATION

The regularities of substitutions observed have been used by certain workers to frame set rules with the help of which one could predict the orientation (*arrangement*) of benzene derivatives. Although these rules are more or less empirical in nature, they have proved fairly accurate in most cases. Two important rules of orientation are :

(1) *Crum Brown–Gibson Rule* ; *and*

(2) *Hammick Illingworth Rule.*

Crum Brown–Gibson Rule (1897). According to this rule, *if a Group X forms a compound HX which can be directly oxidised to HO.X, then X will direct a new incoming group to the meta position otherwise to ortho and para positions.* For example,

X	HX	HOX	DIRECTIVE INFLUENCE
NO_2	HNO_3 Nitrous acid	$HO.NO_2$ Nitric acid.	*Meta*
CH_3	$H.CH_3$ Methane	$HO{\cdot}CH_3$ Methyl alcohol ; *not formed by direct oxidation*	*Ortho-para*
SO_3H	$H.SO_3H$ Sulphurous acid	$HO.SO_3H$ Sulphuric acid	*Meta*
Cl	HCl	HO.Cl Hypochlorous acid ; *not formed by direct oxidation*	*Ortho-para*

The Crum Brown-Gibson Rule applies to most cases but exceptions are known. The OH group forms HOH (water) which is oxidised to HO.OH (hydrogen peroxide) by ultraviolet rays ; therefore, OH group should be *m*-directing while actually it is *o-p*-directing. In fact, the meaning of the words 'direct oxidation' are vague and need clarification.

Hammick-Illingworth Rule (1930). It states that :

If in the benzene derivative C_6H_5*—XY, Y is in a later group of* *the periodic table than X, or if being in the same group, Y is of lower atomic weight than X, then a second atom or group entering the benzene nucleus will go to the meta position ; in all other cases when Y is in an earlier group, or if there is no Y, it goes to o-* and *p-positions.* The rule may be illustrated by the examples given below.

COMPOUND	X AND ITS GROUP	Y AND ITS GROUP	DIRECTIVE INFLUENCE
$C_6H_5.NO_2$	N Group V	O Group VI	*Meta*
$C_6H_5.SO_2H$	S Group VI At. Wt. 32	O Group VI At. Wt. 16	*Meta*
$C_6H_5.NH_2$	N Group V	H Group I	*Ortho-para*
$C_6H_5.Cl$	Cl Group VII	—	*Ortho-para*

Of all the rules of orientation, the Hammick-Illingworth rule is the most satisfactory. It is superior to Crum-Brown's rule as it applied to all cases without any notable exception.

QUESTIONS

1. What type of isomerism you come across in benzene derivatives ? Show from theoretical considerations that benzene can form three *di-* and three *tri-*substitution products for similar substituents.

2. Describe the methods of orientation of disubstituted products of benzene.

3. Explain one method of determining the position of the substituents in the disubstitution products of benzene.

4. Give an account of the methods available for finding out the relative positions of substituents in a disubstituted Benzene derivative.

5. Write a note on orientation in the benzene ring. How would you apply Korner's method to orientate the three chlorotoluenes ?

6. Write an essay on "directive influence of substituents on further substitution on benzene ring".

7. Give a monosubstituted benzene derivative. How far are we in a position to foretell the orientation of a second substituent ?

8. Write an account of the mechanism of aromatic substitution with reference to electrophilic, nucleophilic and free radical mechanisms. *(Poona B.Sc., 1964)*

9. Write what you know of aromatic substitutions and discuss the theory of directing influence in the benzene ring based on the modern electronic theory of valency. *(Nagpur B.Sc., 1964)*

10. Write a note on the directive influence of groups in aromatic substitution giving suitable examples. *(Allahabad B.Sc. II, 1967)*

11. What is meant by the term 'Orientation'? Write an account of the methods of orientation.

Write down the formulae of the six di-aminobenzoic acids and explain the significance of the results obtained on decarboxylation of the acids.
(*Banaras B.Sc. II, 1967*)

12. Describe the rules governing the substitution in mono and disubstituted benzene. Illustrate your answer with suitable examples.
(*Marathwada B.Sc., 1968*)

13. State reasons for the following facts :—

(*a*) $-\ddot{N}H_2$, $-\underset{\cdot\cdot}{\ddot{O}}CH_3$, $-\ddot{N}H.COCH_3$ and $-Cl$ are ortho-para orienting groups.

(*b*) $-CO_2H$, $-NO_2$ are *m*-directing groups. (*Jadavpur B.Sc., 1969*)

14. State the Rules regarding aromatic substitutions with suitable examples. (*Viswa Bharti B.Sc., 1969*)

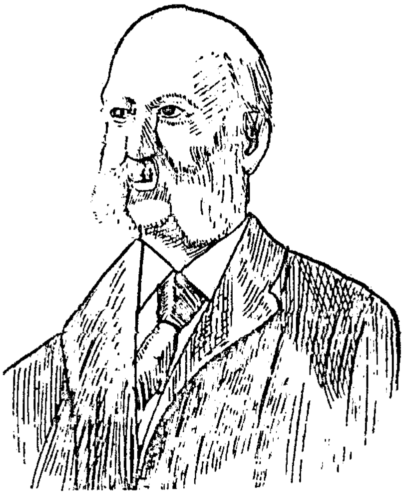
15. Write an essay on the orientation in the benzene ring.
(*Marathwada B.Sc., 1969*)

16. Describe rules that help you to predict the nature of the disubstitution products formed when a monosubstitution benzene derivative is treated with some reagent. What products will be formed when :

(*i*) toluene is sulphonated, (*ii*) benzenesulphonic acid is brominated, (*iii*) benzaldehyde is nitrated and (*iv*) phenol is treated with bromine water ?
(*Tribhuvan B.Sc., 1969*)

38

Aromatic Halogen Compounds



JAMES M. CRAFT
(1839—1897)

American chemist. He developed the well-known Friedl-Craft reaction. He also worked on organic compounds of silicon and the density of halogens at high temperatures.

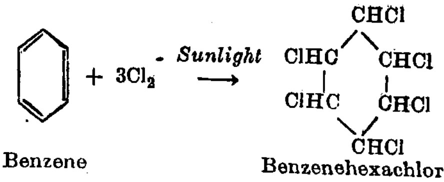
Aromatic halogen compounds are of three types : (1) *Addition compounds* which are obtained by addition of halogens at the double bonds of the benzene nucleus, *e.g.*, benzene hexachloride, $C_6H_6Cl_6$;

(2) *Nuclear substitution products* in which the halogen is attached directly to the benzene nucleus, *e.g.*, chlorobenzene, C_6H_5Cl ; and

(3) *Side-chain substitution products* in which the halogen is attached to the side-chain, *e.g.*, benzyl chloride, $C_6H_5CH_2Cl$.

1. ADDITION COMPOUNDS

When benzene is treated with chlorine or bromine in the presence of sunlight, it forms benzenehexachloride, $C_6H_6Cl_6$, and benzenehexabromide, $C_6H_6Br_6$, respectively. Thus :

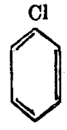


Benzene Benzenehexachloride

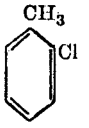
Benzenehexachloride, *Hexachlorohexane* can exist in eight possible stereoisomeric forms due to different arrangements of H and Cl on opposite sides of the benzene ring. Of these, the one known as γ-isomer is a powerful insecticide which acts more quickly than D.D.T. Thus, the product obtained by the action of chlorine on benzene in the presence of ultraviolent light, containing 12—14 per cent of the γ-isomer is sold as insecticide under the name **Gammexane**, or 666.

2. NUCLEAR HALOGEN DERIVATIVES

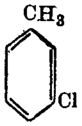
These compounds are obtained by the substitution of one or more hydrogen atoms of the benzene nucleus by halogen atoms. Thus, benzene and toluene form the following monochloro derivatives :



Chlorobenzene



o-Chlorotoluene



m-Chlorotoluene

p-Chlorotoluene

In the nuclear halogen derivatives, we have an aromatic radical linked with a halogen and hence they are named as **Aryl halides**.

METHODS OF FORMATION

The nuclear halogen derivatives of benzene and its homologues may be prepared by the following methods :

(1) **Direct halogenation.** Chloro and bromo derivatives can be obtained conveniently by the direct action of chlorine and bromine on the hydrocarbons in the presence of a catalyst (I, Fe or Al) at room temperature. Thus :

$$\underset{\text{Benzene}}{C_6H_6} + Cl_2 \xrightarrow{Fe} \underset{\text{Chlorobenzene}}{C_6H_5Cl} + HCl$$

$$\underset{\text{Toluene}}{C_6H_5.CH_3} + Br_2 \xrightarrow{Fe} \underset{o\text{-, }p\text{-bromotoluene}}{CH_3.C_6H_4.Br} + HBr$$

If excess of halogen is used, the dihalo derivatives are formed.

Iodo compounds are produced in good yield by the action of iodine on benzene hydrocarbons in the presence of iodic acid or nitric acid. Thus :

$$5C_6H_6 + 2I_2 + \underset{\text{Iodic acid}}{HIO_3} \longrightarrow \underset{\text{Iodobenzene}}{5C_6H_5I} + 3H_2O$$

(2) **Action of phosphorus pentachloride on phenols.** Aromatic chloro derivatives are obtained by the treatment of phenols with phosphorus pentachloride. Thus :

$$\underset{\text{Phenol}}{C_6H_5OH} + PCl_5 \longrightarrow \underset{\text{Chlorobenzene}}{C_6H_5Cl} + POCl_3 + HCl$$

The yield is rather poor.

(3) **Decomposition of diazonium salts.** Nuclear halogen derivatives are prepared most satisfactorily by running the acid solution of a diazonium salt into a solution of cuprous halide dissolved in the corresponding halogen acid. The diazonium salt thus decomposes to yield the respective halogen derivative.

$$\underset{\substack{\text{Benzenediazonium}\\\text{chloride}}}{C_6H_5N_2Cl} \xrightarrow{Cu_2Cl_2} \underset{\text{Chlorobenzene}}{C_6H_5Cl} + N_2$$

$$C_6H_5N_2Cl \xrightarrow{HBr} C_6H_5N_2Br \xrightarrow{Cu_2Br_2} \underset{\text{Bromobenzene}}{C_6H_5Br} + N_2$$

Iodo compounds are obtained by the direct action with potassium iodide, the presence of copper salts being unnecessary.

$$C_6H_5N_2Cl \xrightarrow{KI} C_6H_5N_2I \longrightarrow \underset{\text{Iodobenzene}}{C_6H_5I} + N_2$$

This method is particularly important for the preparation of iodo compounds which cannot be prepared by any other method. Also, the method is useful for introducing a halogen atom at a particular point in the benzene nucleus.

(4) **Decarboxylation of halogenated acids.** The sodium salt of a halogenated acid when heated with soda-lime yields the corresponding halogen derivative. Thus :

$$C_6H_4Br.COONa + NaOH \longrightarrow \underset{\text{Bromobenzene}}{C_6H_5Br} + Na_2CO_3$$

(5) **Action of hypobromous acid.** Bromo compounds can be obtained by treatment of the hydrocarbons with aqueous hypobromous acid.

$$C_6H_6 + HOBr \longrightarrow C_6H_5Br + H_2O$$

PHYSICAL CHARACTERISTICS

(1) Nuclear halogen derivatives are colourless oils or crystalline solids having an agreeable odour.

(2) They are insoluble in water and soluble in organic solvents like alcohol and ether.

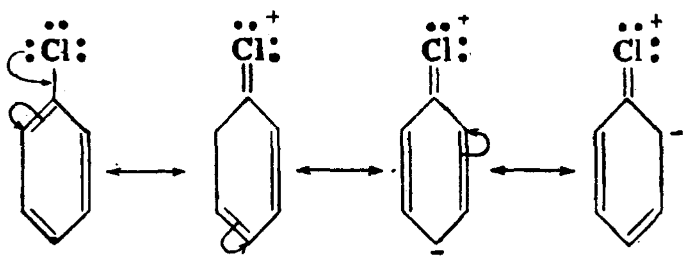
(3) They are all heavier than water.

(4) The boiling points and specific gravities rise gradually as we pass chloro to iodo-compounds. Thus :

	B. PT.	SP. GR. AT 0°
Chlorobenzene, C_6H_5Cl	132°	1·128
Bromobenzene, C_6H_5Br	155°	1·517
Iodobenzene, C_6H_5I	188°	1·857

CHEMICAL CHARACTERISTICS

The molecule of a nuclear halogen derivative is made of (*a*) a hydrocarbon radical, and (*b*) one or more halogen atoms. The hydrocarbon radical gives the usual substitution reactions of the benzene hydrocarbons. The halogen atoms are very firmly attached to the benzene nucleus and cannot be easily replaced by nucleophiles such as $\bar{O}H$, $C\bar{N}$, $\ddot{N}H_3$ etc. This is explained as due to the tendency of the halogen atom to share its lone pair of electrons with benzene and acquire some double bond character. The halogen atom is thus more strongly held with the ring due to shortening of the halogen-carbon linkage. The transference of the lone pair also produces resonance, thereby increasing the stability of the compound. The situation in chlorobenzene is represented as



Thus aryl halides differ very much from the alkyl halides which readily undergo nucleophilic substitution reactions. However, they resemble in properties with vinyl halides due to similarity in their structure. In aryl and vinyl halides the halogen atom is linked with a carbon which is attached to another carbon with a double bond.

The nuclear halogen derivatives, however, give the following reactions :

(1) **Replacement by OH, NH_2 and CN.** The halogen of the nucleus cannot be replaced by OH, NH_2 and CN by aqueous sodium hydroxide, alcoholic ammonia or potassium cyanide. However, under special conditions these replacements may be effected.

Thus :

(*i*) Chlorobenzene when heated with aqueous sodium hydroxide under pressure at 300°, gives phenol.

$$C_6H_5Cl + NaOH \longrightarrow C_6H_5OH + NaCl$$

(*ii*) Chlorobenzene when heated with aqueous ammonia in the presence of cuprous oxide at 200° under pressure, gives aniline.

$$2C_6H_5Cl + 2NH_3 + Cu_2O \xrightarrow[200^\circ]{\text{Pressure}} 2C_6H_5NH_2 + 2CuCl + H_2O$$

(*iii*) Bromobenzene when heated with copper cyanide in the presence of pyridine, gives phenyl cyanide.

$$C_6H_5Br + CuCN \xrightarrow[200^\circ]{\text{Pyridine}} C_6H_5CN + CuBr$$

(2) **Reduction.** When reduced with sodium amalgam and aqueous alcohol in the presence of alkali, aryl halides are converted into the parent hydrocarbon.

$$C_6H_5Cl + 2[H] \longrightarrow C_6H_6 + HCl$$

(3) **Wurtz-Fittig reaction.** Aryl halides give Wurtz-Fittig reaction. Thus a mixture of phenyl bromide and methyl bromide when treated with sodium in ether solution forms toluene.

$$C_6H_5\boxed{Br + 2Na + Br}CH_3 \longrightarrow \underset{\text{Toluene}}{C_6H_5.CH_3} + 2NaBr$$

Mechanism :

The mechanism of the Wurtz-Fittig reaction may be either ionic or free radical, though the former appears more likely.

I. *Ionic mechanism.*

(*i*) $C_6H_5Br + 2Na \longrightarrow C_6\bar{H}_5\overset{+}{Na} + NaBr$

(*ii*) $C_6\bar{H}_5\overset{+}{Na} + CH_3Br \longrightarrow C_6H_5{-}CH_3 + NaBr$

(*iii*) $CH_3Br + 2Na \longrightarrow C\bar{H}_3\overset{+}{Na} + NaBr$

(*iv*) $C\bar{H}_3\overset{+}{Na} + CH_3Br \longrightarrow CH_3{-}CH_3 + NaBr$

(*v*) $C\bar{H}_3\overset{+}{Na} + C_6H_5Br \longrightarrow C_6H_5.CH_3 + NaBr$

II. *Free radical mechanism.*

$$C_6H_5Br + \dot{Na} \longrightarrow C_6\dot{H}_5 + NaBr$$

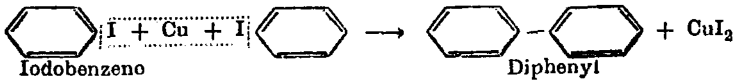
$$2C_6\dot{H}_5 \longrightarrow C_6H_5{-}C_6H_5$$

$$CH_3Br + \dot{Na} \longrightarrow C\dot{H}_3 + NaBr$$

$$2C\dot{H}_3 \longrightarrow CH_3{-}CH_3$$

$$C_6\dot{H}_5 + C\dot{H}_3 \longrightarrow C_6H_5{-}CH_3$$

(4) **Ullmann reaction.** Ullmann discovered that the action of copper powder on aryl iodides at elevated temperature readily gives diphenyl.



Such a condensation of two aryl radicals cannot be done smoothly by the action of sodium on aryl halides.

(5) **Grignard reaction.** Like alkyl halides, aryl halides react with magnesium dissolved in ether to form Grignard reagents.

Thus :

$$\underset{\text{Phenyl bromide}}{C_3H_5Br} + Mg \longrightarrow \underset{\text{Phenylmagnesium bromide}}{C_6H_5MgBr}$$

Individual Members

CHLOROBENZENE, PHENYL CHLORIDE, C_6H_5Cl

Chlorobenzene is prepared by passing chlorine through benzene in the presence of a catalyst ($FeCl_3$, I_2). It is produced industrially by passing a mixture of benzene vapour, air and hydrogen chloride over a copper chloride catalyst (*Raschig process*).

$$C_6H_6 + HCl + \tfrac{1}{2}O_2 \longrightarrow C_6H_5Cl + H_2O$$

Laboratory Preparation. Chlorobenzene is prepared most convoniently in the laboratory by the decomposition of benzenediazonium chloride in the presence of cuprous chloride solution.

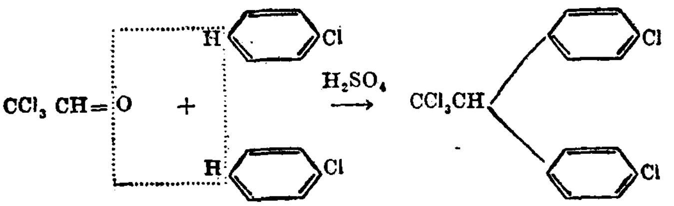
$$C_6H_5N_2Cl \xrightarrow{Cu_2Cl_2} C_2H_5Cl + N_2$$

10 grams of cuprous chloride is dissolved in 100 ml. concentrated hydrochloric acid and the solution placed in a round bottomed flask attached to a reflux condenser fitted with a tap-funnel. 20 grams aniline is diazotised in the manner described later and put in the tap-funnel. The flask is now heated to 60° on water-bath and the diazo solution is allowed to run slowly down the condenser into the cuprous chloride solution. When the whole of it has been added the flask is heated again on the boiling water-bath for about 30 minutes to complete the reaction. The flask is then detached from the condenser and its contents are steam-distilled. The oily liquid (chlorobenzene) is separated from water in the distillate, dried over calcium chloride, filtered and distilled using an air-condenser.

Properties. Chlorobenzene is a colourless, pleasant-smelling liquid, b.p. 132°. It is insoluble in water and soluble in alcohol and ether. It is volatile in steam. It gives all reactions characteristic of nuclear halogen derivatives.

$$C_6H_5Cl \left[\begin{array}{lll} + \textit{Aq}.\,NaOH & \xrightarrow[200^\circ]{\text{Pressure}} & C_6H_5OH + NaCl \\ + \textit{Aq}.\,NH_3 & \xrightarrow{Cu_2O} & C_6H_5NH_2 + HCl \\ + CuCN & \longrightarrow & C_6H_5CN + CuCl \\ + 2[H] & \xrightarrow{Na/Hg} & C_6H_6 + HCl \\ + \quad CH_3Br + 2Na & \xrightarrow{aq.C_2H_5OH} & C_6H_5CH_3 + NaBr + NaCl \\ + \quad Mg & \longrightarrow & C_6H_5MgCl \end{array} \right.$$

When heated with chloral in the presence of concentrated sulphuric acid, chlorobenzene forms **D.D.T.**



p-Dichloro-Diphenyl-Trichloroethane
(D.D.T)

D.D.T. is a solid (m.p. 109—110°) ; it is a powerful insecticide.

Uses. Chlorobenzene is used for the manufacture of phenol, aniline and D.D.T.

BROMOBENZENE, PHENYL BROMIDE, C_6H_5Br

Bromobenzene is readily made by adding bromine to benzene in the presence of iron filings.

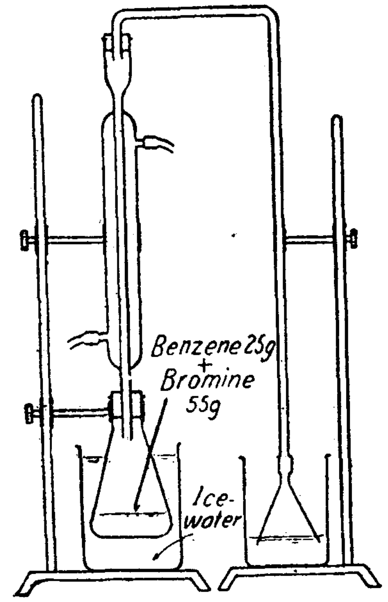


Fig. 38·1. Preparation of bromobenzene.

$$C_6H_6 + Br_2 \xrightarrow{Fe} C_6H_5Br + HBr$$

The apparatus used for the purpose is shown in Fig. 38·1. Benzene (25 g) is placed in a conical flask and two clean iron nails are dropped into it. The flask is immersed in ice-water bath and the condenser fixed firmly. Bromine (55 g) is poured from another flask which has been kept well corked, down the condenser. The exit tube is at once attached to the upper end of the condenser. When the reaction is complete, the dark layer of bromobenzene is separated by means of a separating funnel and washed well with water and dilute sodium hydroxide solution successively. The colourless bromobenzene is then dried over anhydrous calcium chloride and fractionated.

Bromobenzene is a colourless liquid, b.p. 156°. It closely resembles chlorobenzene in behaviour and gives analogous reactions. It forms the Grignard reagent, C_6H_5MgBr, which is a valuable synthetic reagent.

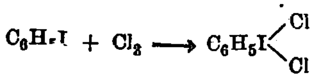
IODOBENZENE, PHENYL IODIDE, C_6H_5I

Iodobenzene is most conveniently prepared by the direct action of potassium iodide on benzenediazonium chloride without the use of a catalyst.

$$C_6H_5N_2Cl + KI \longrightarrow C_6H_5I + N_2 + KCl$$

Aniline (15 mls.) is diazotised as described later on. To the cold diazo solution is then added a concentrated sodium or potassium iodide (35 g. per 55 mls. water) with shaking. The mixture is allowed to stand for 10 minutes and is then heated over the boiling water-bath for 20 minutes. The crude iodobenzene is now present at the bottom of the flask as a dark oil. It is separated by steam-distillation, washed with dilute sodium hydroxide solution, dried and distilled.

Properties. Iodobenzene is a colourless liquid, b.p. 188°. On exposure to light it turns pale yellow. It is insoluble in water and volatile in steam. The chemical behaviour of iodobenzene is, for the most part, closely similar to that of chlorobenzene and bromobenzene. However, it also reacts with chlorine to form iodobenzene dichloride.



$$C_6H_5I + Cl_2 \longrightarrow C_6H_5I\begin{smallmatrix}\diagup Cl \\ \diagdown Cl\end{smallmatrix}$$

Iodobenzene dichloride

Iodobenzene dichloride when treated with sodium hydroxide solution gives iodosobenzene which on boiling with water yields iodoxybenzene.

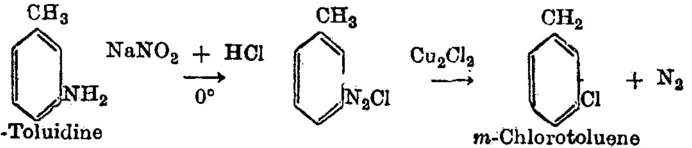
$$\underset{}{C_6H_5ICl_2} + 2NaOH \longrightarrow \underset{\text{Iodosobenzene}}{C_6H_5IO} + 2NaCl + H_2O$$

$$2C_6H_5IO \longrightarrow \underset{\text{Iodoxybenzene}}{C_6H_5IO_2} + C_6H_5I$$

Both iodosobenzene and iodoxybenzene when heated explode without melting.

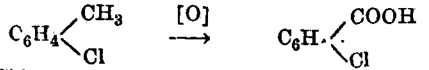
CHLOROTOLUENES, TOLYL CHLORIDES, $CH_3.C_6H_4.Cl$

o- and *p*-chlorotoluenes are prepared by chlorinating toluene in the presence of iodine or iron. All the three isomeric toluenes are, however, often obtained from the corresponding toluidines by Sandmeyer's reaction. Thus :



m-Toluidine *m*-Chlorotoluene

Properties. Chlorotoluenes are heavy, colourless liquids, b.pts. : ortho 159°, meta 162°, para 162°. They are immiscible with water. In chemical behaviour they closely resemble chlorobenzene. On oxidation with alkaline potassium permanganate, they form the corresponding chlorobenzoic acids. This reaction is often used to distinguish chlorotoluenes from the isomeric benzyl chloride.



$$C_6H_4\begin{smallmatrix}\diagup CH_3 \\ \diagdown Cl\end{smallmatrix} \xrightarrow{[O]} C_6H_4\begin{smallmatrix}\diagup COOH \\ \diagdown Cl\end{smallmatrix}$$

Chlorotoluene Chlorobenzoic acid

$$\underset{\text{Benzyl chloride}}{C_6H_5CH_2Cl} \xrightarrow{[O]} \underset{\text{Benzoic acid}}{C_6H_5COOH}$$

3. SIDE-CHAIN HALOGEN DERIVATIVES

These compounds are, in fact, aryl-substituted alkyl halides and behave like the parent alkyl halides.

$$CH_3Cl \xrightarrow[+C_6H_5]{-H} \underset{\text{Benzyl chloride}}{C_6H_5CH_2Cl}$$

The halogen atom is even more reactive than in the corresponding alkyl halides.

The side-chain halogen derivatives can be obtained by the direct action of chlorine and bromine on homologues of benzene. They are also formed by the action of phosphorus halides (PCl_5) on the corresponding oxygenated compounds.

BENZYL CHLORIDE, $C_6H_5CH_2Cl$

Benzyl chloride is a typical example of a compound in which the halogen is present in the side-chain. It is isomeric with the three chlorotoluenes but differs from them widely in many respects.

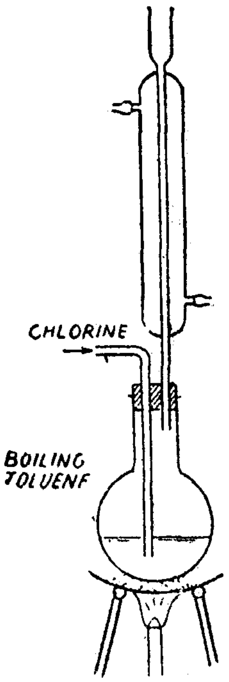


Fig. 38·2. Preparation of benzyl chloride.

Preparation. (1) DIRECT CHLORINATION OF TOLUENE. Benzyl chloride is prepared conveniently by passing chlorine into boiling toluene in sunlight till the theoretical increase in weight is reached.

$$C_6H_5CH_3 + Cl_2 \longrightarrow \underset{\text{Benzyl chloride}}{C_6H_5CH_2Cl} + HCl$$

A weighed quantity of toluene placed in a round bottomed flask fitted with a reflux condenser and a delivery tube (see Fig. 38·2). The flask is heated on a sand-bath while axposed to strong sunlight. A stream of dry chlorine is then passed into the boiling toluene by means of a delivery tube until the theoretical increase in weight has taken place. The benzyl chloride in the product is isolated by fractional distillation.

(2) CHLOROMETHYLATION OF BENZENE. It may be prepared by heating benzene with formalin and hydrochloric acid in the presence of zinc chloride.

$$C_6H_6 + CH_2O + HCl \xrightarrow{ZnCl_2} C_6H_5CH_2Cl + H_2O$$

(3) ACTION OF PCl_5 ON BENZYL ALCOHOL. It is also produced by the action of phosphorus pentachloride on benzyl alcohol.

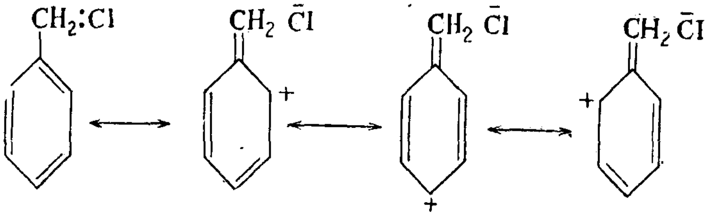
$$C_6H_5CH_2OH + PCl_5 \longrightarrow C_6H_5CH_2Cl + POCl_3 + HCl$$

Properties. (*Physical*). Benzyl chloride is a colourless unpleasant smelling liquid, b.p. 170°. It is insoluble in water, but is miscible with most organic solvents. Its vapours have an irritating action on eyes and nose, causing flow of tears.

(*Chemical*). (1) REPLACEMENT REACTIONS. The chlorine atom of benzyl chloride can be easily replaced by other atoms or groups like the one present in ethyl chloride. Thus :

$$C_6H_5CH_2Cl \begin{cases} + \ \textit{Aq.}\ KOH \longrightarrow \underset{\text{Benzyl alcohol}}{C_6H_5CH_2OH} + KCl \\ + \ \textit{Aq.}\ KCN \longrightarrow \underset{\text{Benzyl cyanide}}{C_6H_5CH_2CN} + KCl \\ + \ \textit{Alc.}\ NH_3 \longrightarrow \underset{\text{Benzylamine}}{C_6H_5CH_2NH_2} + HCl \\ + \ CH_3COOAg \longrightarrow \underset{\text{Benzyl acetate}}{CH_3COOCH_2C_6H_5} + AgCl \end{cases}$$

In fact, the chlorine atom in benzyl chloride is more reactive than in ethyl chloride. The resonance stabilisation of the residual carbonium ion $C_6H_5\overset{+}{C}H_2$, left after the removal of $\overline{Cl}$ ion helps in the easy removal of $\overline{Cl}$.



(2) WURTZ-FITTIG REACTION. Upon treatment with sodium metal, it gives *dibenzyl*.

$$2C_6H_5CH_2Cl + 2Na \longrightarrow \underset{\text{Dibenzyl}}{C_6H_5CH_2C_6H_5} + 2NaCl$$

(3) OXIDATION. When oxidised with dilute nitric acid, the side-chain along with the halogen is converted to carboxyl group forming benzoic acid.

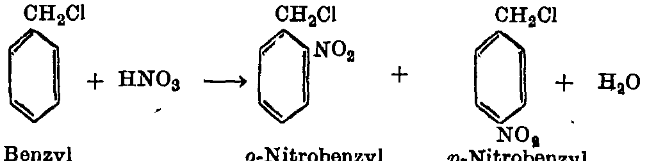
$$C_6H_5CH_2Cl \xrightarrow{[O]} \underset{\text{Benzoic acid}}{C_6H_5COOH} + HCl$$

On mild oxidation with cupric nitrate, it gives benzaldehyde.

$$C_6H_5CH_2Cl + O \longrightarrow C_6H_5CHO + HCl$$

(4) SUBSTITUTION REACTIONS. Benzyl chloride can be nitrated and sulphonated in the benzene nucleus just like toluene.

Thus :



Benzyl chloride o-Nitrobenzyl chloride *p*-Nitrobenzyl chloride

Benzyl chloride also gives Friedel-Crafts reaction and the Grignard reaction.

Uses. Benzyl chloride is used for the introduction of benzyl group in organic compounds. It is the starting material for the manufacture of benzyl alcohol, benzylamine and benzaldehyde.

BENZAL CHLORIDE, BENZILIDENE CHLORIDE, $C_6H_5CHCl_2$

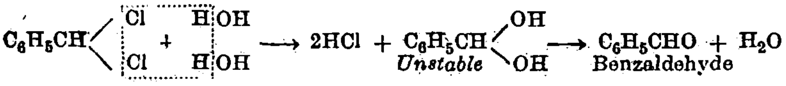
Benzal chloride may be prepared : (1) By passing chlorine into boiling toluene until the required weight increase takes place, *(Commercial).*

$$C_6H_5CH_3 + 2Cl_2 \longrightarrow C_6H_5CHCl_2 + 2HCl$$

(2) By the action of phosphorus pentachloride on benzaldehyde.

$$C_6H_5CHO + PCl_5 \longrightarrow C_6H_5CHCl_2 + POCl_3$$

Properties. Benzal chloride is a colourless liquid, b.p. 207°. It lacks the lachrymatory property that benzyl chloride possesses. When heated with calcium hydroxide solution, it is hydrolysed to benzaldehyde and is used industrially for the purpose.



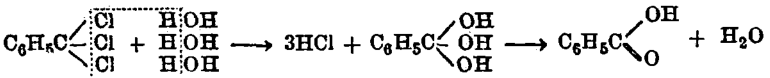
$$C_6H_5CH\begin{matrix}Cl & & H & OH\\ & + & & \\ Cl & & H & OH\end{matrix} \longrightarrow 2HCl + \underset{Unstable}{C_6H_5CH\begin{matrix}OH\\ OH\end{matrix}} \longrightarrow \underset{Benzaldehyde}{C_6H_5CHO} + H_2O$$

BENZOTRICHLORIDE, PHENYLCHLOROFORM, $C_6H_5CCl_3$

It is prepared by passing chlorine into boiling toluene till no further increase in weight takes place.

$$C_6H_5CH_3 + 3Cl_2 \longrightarrow C_6H_5CCl_3 + 3HCl$$

Properties. Benzotrichloride is a colourless liquid, b.p. 214°. Due to the presence of the negative phenyl group, halogen atoms are more reactive than in chloroform. Thus when boiled with calcium hydroxide solution it is hydrolysed to benzoic acid ; it is used industrially for the purpose.



$$\underset{Benzotrichloride}{C_6H_5C\begin{matrix}Cl\\ Cl\\ Cl\end{matrix}} + \begin{matrix}H & OH\\ H & OH\\ H & OH\end{matrix} \longrightarrow 3HCl + \underset{(Unstable)}{C_6H_5C\begin{matrix}OH\\ OH\\ OH\end{matrix}} \longrightarrow \underset{(Benzoic\ acid)}{C_6H_5C\begin{matrix}OH\\ O\end{matrix}} + H_2O$$

COMPARISON OF SIDE-CHAIN AND NUCLEAR DERIVATIVES

The properties of the side-chain halogen derivatives are very much different from those of the nuclear derivatives. The former closely resemble the alkyl halides in behaviour but possess a pungent odour and are lachrymatory. In general, the nuclear halogen derivatives are much less reactive than the side-chain derivatives, since the halogen in them is very tightly attached to the benzene nucleus.

SIDE-CHAIN DERIVATIVES	NUCLEAR DERIVATIVES
Points of Difference :—	
(1) Pungent smelling; lachrymatory.	(1) Agreeable odour; not lachrymatory.
(2) React with aqueous alkali and alcoholic ammonia to form the respective alcohols and amines.	(2) No action with aqueous alkali or alcoholic ammonia.
(3) Give Friedel-Crafts reaction.	(3) Do not give Friedel-Crafts reaction.
(4) On oxidation with alkaline permanganate, the halogen is knocked from the molecule.	(4) On similar oxidation, the halogen remains attached to the benzene nucleus.
Points of Resemblance :—	
(1) Participate in Wurtz-Fittig reaction.	(1) Also participate in Wurtz-Fittig reaction.
(2) Form Grignard reagents.	(2) Also form Grignard reagents.
(3) On reduction with nascent hydrogen form the parent hydrocarbons.	(3) Also reduce with nascent hydrogen to form the parent hydrocarbons.
(4) Give substitution reactions in the benzene nucleus in ortho and para positions.	(4) Give substitution reactions in the benzene nucleus in ortho and para positions.

QUESTIONS

1. Describe the three types of aromatic halogen derivatives, giving two examples of each type.

2. Give the general methods of introducing a halogen atom in the benzene nucleus and the side-chain.

3. Describe the general methods of preparation and properties of nuclear halogen derivatives.

4. Discuss in detail the products obtained by the reaction of chlorine on toluene, and indicate their industrial importance.

5. How does chlorine act upon toluene under different conditions? Indicate how benzyl alcohol, benzaldehyde and benzoic acid are obtained from chlorination products of toluene. Give equations.

6. Mention the conditions under which chlorine reacts with toluene and give formulae of the compounds formed. How would these products of reaction be generally distinguished from one another?

7. How is iodobenzene prepared? Compare and contrast the properties of iodobenzene with those of ethyl iodide.

8. Write the graphic formulae of the isomeric halogen compounds having the molecular formula C_7H_7Cl. What are the chief differences in their chemical behaviour on which you would rely in order to distinguish between them.

9. How may the monochloro derivatives of formula C_7H_7Cl be prepared from toluene ? Compare the properties of chlorine atom in the compounds prepared.

10. Describe the conditions under which nuclear and side-chain halogenation of an organic hydrocarbon is effected. Give an account of the general reactions of these two types of halogen derivatives and point out their differences. (*Allahabad B.Sc., 1961*)

11. Starting from toluene, how would you obtain benzyl chloride, benzal chloride and benzotrichloride ? Give equations.

How does benzyl chloride differ from (*a*) chlorotoluenes and (*b*) benzoyl chloride ? (*Dibrugarh B.Sc., 1967*)

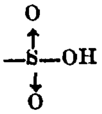
12. Give methods of introducing a halogen group in (*a*) the nucleus (*b*) the side-chain of an aromatic hydrocarbon. Describe both physical and chemical properties to illustrate the differences between the compounds formed. (*Kurukshetra B.Sc., 1969*)

39

Aromatic Sulphonic Acids

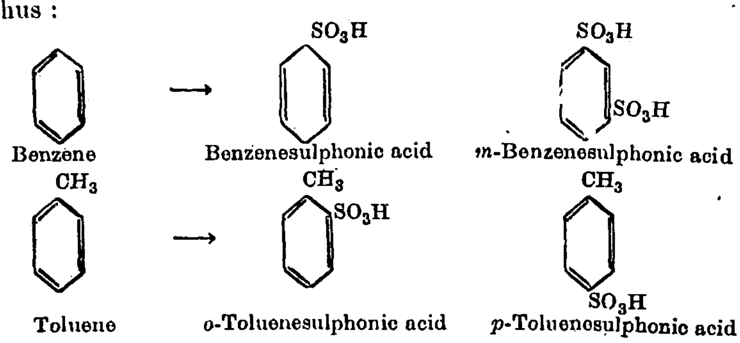
V.N. IPATIEFF
(1867— , American)
His chief interest lies in high pressure catalytic reactions, in which he has made significant contributions both in theory and practice. Author of book 'Catalytic Reactions at High Pressures and Temperatures'.

They are the derivatives of hydrocarbons in which one or more H-atoms of the *nucleus* have been replaced by the sulphonic acid groups.



$$-\overset{\overset{O}{\uparrow}}{\underset{\underset{O}{\downarrow}}{S}}-OH \quad \text{or} \quad -SO_2.OH \quad \text{or} \quad -SO_3H$$

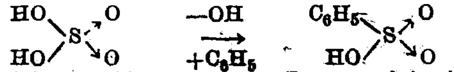
Thus :



Benzene → Benzenesulphonic acid, *m*-Benzenesulphonic acid

Toluene → *o*-Toluenesulphonic acid, *p*-Toluenesulphonic acid

Sulphonic acids could also be regarded as derivatives of sulphuric acid in which one OH group has been replaced by an aryl group.



Sulphuric acid Benzenesulphonic acid

Thus aromatic sulphonic acids are strong acids like sulphuric acid and give many similar reactions.

METHODS OF FORMATION

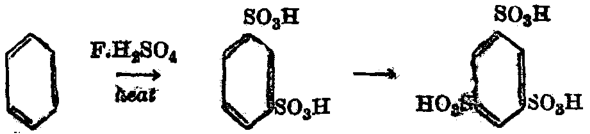
The process of introducing a sulphonic acid group in the benzene nucleus is called **Sulphonation**. It may be carried by the following methods :

(1) **Action of Sulphuric acid.** An aromatic hydrocarbon when heated with concentrated sulphuric acid forms the respective sulphonic acid. Thus :

$$\underset{\text{Benzene}}{C_6H_5{:}H} + HO{:}SO_3H \rightleftharpoons \underset{\text{Benzenesulphonic acid}}{C_6H_5.SO_3H} + H_2O$$

The reaction is reversible and the accumulation of water retards it. Therefore, to get the maximum yield of sulphonic acid, the water may be removed as steam by carrying the reaction at high temperature (170—180°).

(2) **Action of Fuming sulphuric acid.** Fuming sulphuric acid (*oleum*), which contains about 70 per cent dissolved sulphur trioxide, is a more drastic sulphonating agent than concentrated sulphuric acid. The dissolved sulphur trioxide combines with water to form sulphuric acid and thus enhances the rate of reaction. Fuming sulphuric acid is, therefore, employed to introduce two or three sulphonic acid groups in the benzene nucleus.



Benzene *m*-Benzenedisulphonic acid *s*-Benzenetrisulphonic acid

More than three sulphonic acid groups cannot be introduced in the benzene nucleus.

Silver sulphate, mercuric sulphate and iodine act as catalysts for sulphonation.

(3) **Action of chlorosulphonic acid.** Aromatic hydrocarbons when treated with equimolecular quantity of chlorosulphonic acid in carbon tetrachloride solution readily yield sulphonic acids.

Thus :

$$\underset{\text{Benzene}}{C_6H_5{:}H} + \underset{\text{Chlorosulphonic acid}}{Cl{:}SO_3H} \longrightarrow \underset{\text{Benzene sulphonic acid}}{C_6H_5.SO_3H} + HCl$$

No water is produced in the reaction and the HCl gas escapes from solution leaving pure sulphonic acid.

Isolation of Sulphonic acids. The isolation of sulphonic acids from the sulphonating mixture is usually difficult because they are highly soluble in water and non-volatile. This may be done by two methods.

(1) *By 'Salting out'.* The sulphonating mixture is run into a saturated solution of sodium chloride which throws out crystalline sodium sulphonate.

$$C_6H_5SO_3H + NaCl \longrightarrow \underset{\text{Sodium sulphonate}}{C_6H_5SO_3Na} + HCl$$

(2) *By forming soluble Pb-salt.* The sulphonating mixture is diluted and neutralised with lead carbonate. The excess of sulphuric acid is removed as insoluble lead sulphate and filtered. The filtrate containing the soluble barium sulphonate is decomposed with hydrogen sulphide, filtered and the filtrate evaporated to dryness under reduced pressure.

A detailed mechanism of sulphonation reactions has already been explained under benzene

PHYSICAL CHARACTERISTICS

(1) Aromatic sulphonic acids are crystalline, non-volatile solids. They are hygroscopic and tend to form syrups in moist air.

(2) They have seldom a definite melting point and gradually decompose when heated above 200°.

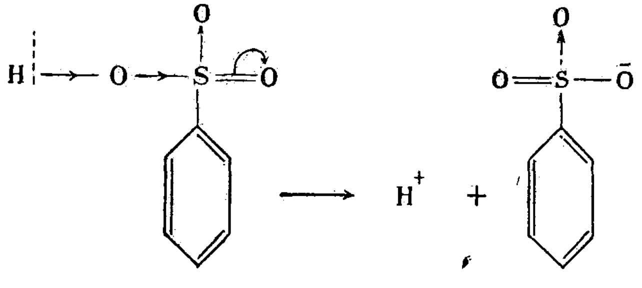
(3) They are highly soluble in water.

(4) They are strong acids, intermediate between HCl and H_2SO_4.

CHEMICAL CHARACTERISTICS

In aromatic sulphonic acids, the sulphonic acid radical is not very tightly attached to the benzene nucleus and it can be readily, replaced by other atoms or groups giving a variety of compounds. The sulphonic acid radical, $-SO_2.OH$, shows analogous behaviour to that of carboxyl group, $-CO.OH$, and forms similar derivatives.

The proton releasing tendency (acidic character) of benzene sulphonic acid molecule is very much enhanced to the presence of a highly electron attracting group, which displaces the electrons as :



Benzenesulphonic acid Proton Sulphonate ion

Moreover the benzene sulphonate ion is very much stabilised by resonance.

Reactions of the SO_2OH group

(1) **Formation of Salts.** Sulphonic acids react with alkalis to form salts known as sulphonates.

$$C_6H_5SO_2.OH + NaOH \longrightarrow C_6H_5SO_2.ONa + H_2O$$

Benzenesulphonic acid — Sodium benzene sulphonate

Their alkali-metal salts are readily soluble in water.

(2) **Formation of Esters.** When heated with alcohols, they form esters. Thus :

$$C_6H_5SO_2.O\boxed{H + HO}C_2H_5 \longrightarrow C_6H_5SO_2.OC_2H_5 + H_2O$$

Benzenesulphonic acid — Ethyl benzenesulphonate

In actual practice, this reaction is never used for the preparation of esters of sulphonic acids.

(3) **Formation of Sulphonyl chlorides.** They react with phosphorus pentachloride to form sulphonyl chlorides, the OH of sulphonic acid being replaced by Cl atom. Thus :

$$C_6H_5SO_3.H + PCl_5 \longrightarrow C_6H_5SO_2Cl + POCl_3 + HCl$$

Benzenesulphonic acid — Benzenesulphonyl chloride

The sulphonyl chloride behaves like the acid chlorides of carboxylic acids ; they react with ammonia to give *sulphonamides* which have definite melting points and are used for identifying sulphonic acids.

(4) **Formation of Sulphones.** Sulphonic acids react with hydrocarbons to form *sulphones* which are neutral substances.

Thus :

$$C_6H_5SO_2\boxed{OH + H}C_6H_5 \longrightarrow C_6H_5SO_2C_6H_5 + H_2O$$

Benzene — Diphenylsulphone

Sulphones are formed as secondary products during sulphonation of hydrocarbons.

Reactions in which SO_3H group is replaced

(5) **Desulphonation.** When sulphonic acids are heated to a high temperature with water, or with solutions of hydrochloric acid or sulphuric acid, the SO_3H group is replaced by H atom to form the parent hydrocarbons. Thus :

$$C_6H_5\boxed{SO_3H + HO}H \longrightarrow C_6H_6 + H_2SO_4$$

The splitting out of sulphonic acid group from the benzene nucleus is termed *desulphonation*.

(6) **Formation of Phenols.** When sodium sulphonates are fused with sodium hydroxide, they form phenols. Thus :

$$C_6H_5\boxed{SO_3Na + Na}OH \xrightarrow{Fuse} C_6H_5OH + Na_2SO_4$$

Sod. benzenesulphonate — Phenol

(7) **Formation of Nitriles.** When sodium sulphonates are fused with sodium cyanide, they form nitriles. Thus :

$$C_6H_5\boxed{SO_3Na + Na}CN \xrightarrow{Fuse} C_6H_5CN + Na_2SO_4$$

Phenyl nitrile

The nitriles upon hydrolysis yield carboxylic acids.

(8) **Formation of Carboxylic acids.** When sodium sulphonates are fused with sodium formate, they form carboxylic acids straightway. Thus :

$$C_6H_5SO_3Na + \underset{\text{Sod. formate}}{HCOONa} \xrightarrow{\text{Fuse}} \underset{\text{Sod. benzoate}}{C_6H_5COONa} + NaHSO_3$$

(9) **Formation of Amines.** When sodium sulphonates are fused with sodamide, they form aromatic amines. Thus :

$$C_6H_5SO_3Na + NaNH_2 \longrightarrow \underset{\text{Aniline}}{C_6H_5NH_2} + Na_2SO_3$$

(10) **Formation of Thiophenols.** When potassium sulphonates are fused with potassium hydrogen sulphide, they form thiophenols.

Thus :

$$\underset{\text{Pot. benzenesulphonate}}{C_6H_5SO_3K} + KSH \longrightarrow \underset{\text{Thiophenol}}{C_6H_5SH} + K_2SO_3$$

In addition to the above reactions, sulphonic acids give the usual substitution reactions in the benzene nucleus with difficulty when the incoming group occupies the meta position.

INDIVIDUAL MEMBERS

BENZENESULPHONIC ACID, $C_6H_5SO_3H$

It is a typical and the most important member of the class. It was first prepared by Mitscherlich in 1934. It is found in the waste products of metabolism.

Preparation. (1) Benzenesulphonic acid is readily prepared by heating benzene with concentrated sulphuric acid at 80°.

$$C_6H_6 + H_2SO_4 \xrightarrow{80^\circ} \underset{\substack{\text{Benzenesulphonic}\\ \text{acid}}}{C_6H_5SO_3H} + H_2O$$

A mixture of benzene (1 part) and concentrated sulphuric acid (2 parts) is placed in a round-bottomed flask fitted with a reflux condenser. It is heated on a sand-bath till the whole of benzene has dissolved. The resulting mixture is poured into a strong solution of sodium chloride when sodium benzenesulphonate separates. This is used as such for most purposes.

If pure benzenesulphonic acid is required, the sulphonating mixture i diluted and neutralised with lead carbonate. The precipitate of lead sulphat is filtered. The filtrate containing lead benzenesulphonate is decomposed b passing H_2S, filtered and the filtrate concentrated to crystallisation.

(2) Benzenesulphonic acid may also be obtained by the actio of chlorosulphonic acid on benzene :

$$\underset{\text{Benzene}}{C_6H_5H} + ClSO_3H \longrightarrow C_6H_5SO_3H + HCl$$

Properties. (*Physical*). Benzenesulphonic acid crystallise from water forming colourless leaflets containing $1\frac{1}{2}H_2O$. Th hydrated compound melts at 46°. It is very hygroscopic and form a syrupy liquid when exposed to moist air. It is highly soluble i water and the solution is strongly acidic (about as strong as sulphur acid).

- (*Chemical*). In benzenesulphonic acid the SO_3H group is rather loosely attached to the benzene ring and can be replaced by other atoms or groups. The sulphonic acid group, $SO_2.OH$, exhibits analogous behaviour to that of COOH group and forms similar derivatives.

The reactions of benzenesulphonic acid have been discussed under the general treatment of sulphonic acids. A summary of these is given below for recapitulation.

Reactions of SO_3H group :

$C_6H_5.SO_3.OH$

$+ NaOH \longrightarrow C_6H_5SO_2.ONa + H_2O$
Sod. benzenesulphonate

$+ C_2H_5OH \longrightarrow C_6H_5SO_2OC_2H_5 + H_2O$
Ethyl benzenesulphonate

$+ PCl_5 \longrightarrow C_6H_5SO_2Cl + POCl_3 + HCl$
Benzenesulphonyl chloride

Reactions in which SO_3H group is replaced :—

$C_6H_5SO_3H$
or
$C_6H_5SO_3Na$

$+ HOH \xrightarrow{Heat} C_6H_6 + H_2SO_4$

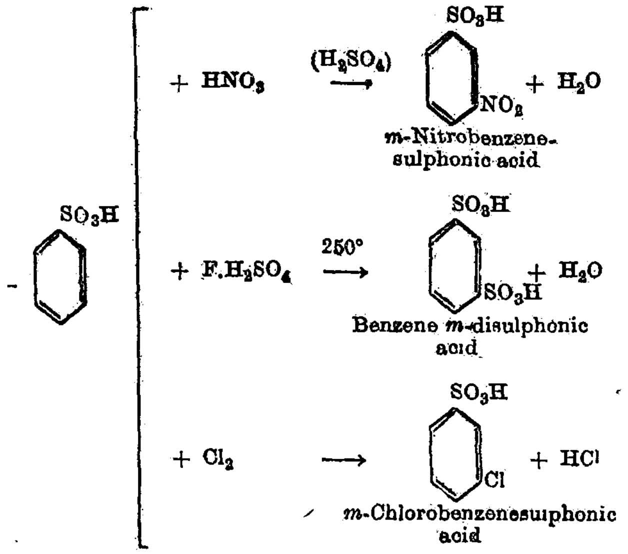
$+ NaOH \xrightarrow{Fuse} C_6H_5OH + Na_2SO_3$
Phenol

$+ NaCN \xrightarrow{Fuse} C_6H_5CN + Na_2SO_3$
Phenyl nitrile

$+ HCOONa \xrightarrow{Fuse} C_6H_5COONa + NaHSO_3$
Sod. benzoate

$+ NaNH_2 \xrightarrow{Fuse} C_6H_5NH_2 + Na_2SO_3$

Reactions of benzene nucleus :



Uses. Benzenesulphonic acid is the starting material for the preparation of many benzene derivatives. It is an important intermediate in the manufacture of certain dyes and drugs. It is also used as a catalyst for the preparation of olefines and ethers ; it has the advantage of not causing charring as does sulphuric acid.

Benzenesulphonyl chloride, $C_6H_5SO_2Cl$

Preparation. (1) It may be obtained by heating sodium benzenesulphonate with phosphorus pentachloride at 170°—180° for several hours.

$$C_6H_5.SO_2ONa + PCl_5 \longrightarrow C_6H_5.SO_2Cl + POCl_3 + NaCl$$

(2) It is best prepared by treating benzene with excess chlorosulphonic acid.

$$C_6H_5H + \underbrace{HO\,SO_2Cl}_{\text{Chlorosulphonic acid}} \longrightarrow C_6H_5SO_2Cl + H_2O$$

Properties and Uses. Benzenesulphonyl chloride is an oily liquid, b.p. 246°. It has a characteristic disagreeable odour and is lachrymatory. It is insoluble in water but soluble in ether.

Benzenesulphonyl chloride behaves like other acid chlorides although it is not as reactive.

(1) It is decomposed by hot water, more rapidly by alkalis, to form benzenesulphonic acid.

$$C_6H_5SO_2Cl + HOH \longrightarrow \underset{\text{Benzenesulphonic acid}}{C_6H_5SO_3.OH} + HCl$$

(2) It reacts with alcohols in the presence of an alkali to form esters.

$$C_6H_5SO_2Cl + HOC_2H_5 \longrightarrow \underset{\text{Ethyl benzenesulphonate}}{C_6H_5SO_2.OC_2H_5} + HCl$$

(3) When shaken with concentrated ammonia, it forms benzenesulphonamide, m.p. 150°.

$$C_6H_5SO_2Cl + 2NH_3 \longrightarrow C_6H_5SO_2NH_2 + NH_4Cl$$

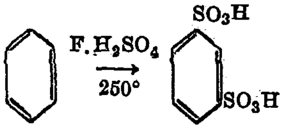
(4) It reacts with primary and secondary amines to form *N*-substituted sulphonamides.

$$C_6H_5SO_2Cl + RNH_2 \longrightarrow C_6H_5SO_2NHR + HCl$$
$$C_6H_5SO_2Cl + R_2NH \longrightarrow C_6H_5SO_2NR_2 + HCl$$

These derivatives are used for the separation of three classes of amines (*see* Hinsberg's method).

BENZENE-*m*-DISULPHONIC ACID, $C_6H_4(SO_3H)_2$

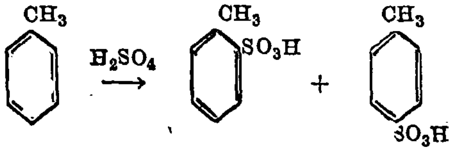
It is prepared by heating benzene with excess fuming sulphuric acid at 250°.



When fused with potassium hydroxide, it forms *m*-dihydroxy benzene (resorcinol).

TOLUENESULPHONIC ACIDS, $C_6H_4(CH_3)SO_3H$

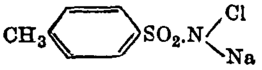
Toluene on sulphonation with concentrated sulphuric acid forms *o*- and *p*-toluenesulphonic acids.



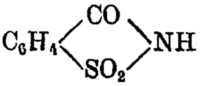
If the reaction is carried above 100° the *p*-isomer predominates in the product, while at room temperature the product is mainly the *o*-isomer.

Both *o*- and *p*-toluenesulphonic acids are crystalline solids, the *o*- melting at 67·5°, and *p*- at 106°.

o-Toluenesulphonic acid is used in the preparation of saccharin; *p*-toluenesulphonic acid is used in the preparation of **Chloramine T**, which is a powerful antiseptic, and has the formula

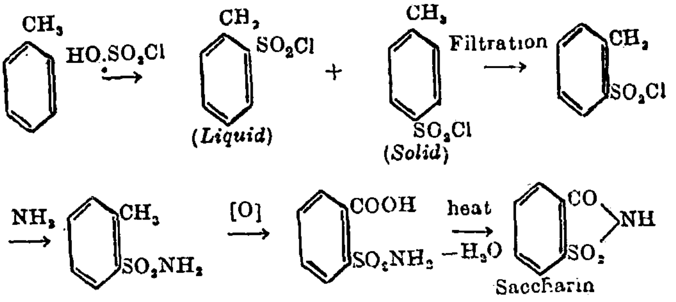


Saccharin, *o-sulphobenzoic imide*,



$$C_6H_4\left\langle\begin{matrix}CO\\SO_2\end{matrix}\right\rangle NH$$

The imide of *o*-sulphobenzoic acid is known as saccharin. It is prepared by treating toluene with excess chlorosulphonic acid when a mixture of *o*-toluenesulphonyl chloride (liquid) and *p*-toluenesulphonyl chloride (solid) is obtained. The *o*-compound is separated by filtration and treated with ammonia to form the amide which is then oxidised with chromic acid. The resulting acid on heating forms saccharin.



Saccharin is a colourless, crystalline solid, m.p. 224°. It is about 500 times as sweet as cane sugar. It is almost insoluble in water and hence it is sold as sodium salt which is very soluble.

Saccharin is used in cheap drinks in place of sugar. It is also used as a sweetening agent by diabetic and obese persons who are not allowed sugar in their diet. However, unlike carbohydrates it has no food value and is excreted unchanged in urine.

QUESTIONS

1. Describe the preparation of aromatic sulphonic acids. Give their important reactions.

2. How are aromatic sulphonic acids prepared ? Give synthetic use of sulphonic acids in replacing H of benzene by OH, CN and Cl. Do you know any technical use of sulphonic acid ?

3. Describe some of the properties of benzenesulphonic acid. Explain how benzene, chlorobenzene, phenol and phenyl cyanide may be obtained from it.

4. How can benzenesulphonyl chloride be prepared, and what are its important properties ? Explain giving necessary equations, how it can be used for the separation of a mixture of a primary, a secondary, and a tertiary amine.

5. Describe the preparation of benzene sulphonic acid. Give its important reactions. How can saccharin be obtained from toluene ? *(Panjab B.Sc. III, 1965)*

6. Give at least three methods for the preparation of benzenesulphonic acid. How can this be converted into (*a*) benzene, (*b*) phenol, (*c*) thiophenol, (*d*) benzene sulphonamide and (*e*) Phenyl cyanide. *(Agra B.Sc. II, 1967)*

7. Write an account of the sulphonating agents used in aromatic chemistry and discuss the uses of aromatic sulphonic acids as synthetic reagents. *(Kalyani B.Sc. Hons., 1967)*

8. What is sulphonation ? Give one method for the preparation of a pure sample of benzenesulphonic acid. Describe the importance of aromatic sulphonic acids in organic synthesis and in industry. *(Allahabad B.Sc. II, 1967)*

9. Discuss the general methods available for obtaining aromatic sulphonic acids. Describe their important properties and industrial uses. *(Bombay B.Sc., 1967)*

10. How would you prepare Hinsberg reagent ? What are its chief uses ? *(Panjab B.Sc. III, 1968)*

11. What is meant by sulphonation ?

How is benzenesulphonic acid prepared ?

How will you obtain the following from benzene sulphonic acid ?

(*i*) Phenol, (*ii*) Phenyl cyanide, (*iii*) Benzoic acid and (*iv*) Benzene sulphonamide ? *(Ujjain B.Sc., 1968)*

12. How is benzenesulphonic acid prepared ? What are its important reactions ? How can it be converted into (*i*) benzene ; (*ii*) benzene sulphonyl chloride ? *(Tribhuvan B.Sc., 1969)*

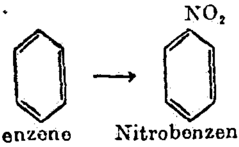
40

Aromatic Nitro-Compounds

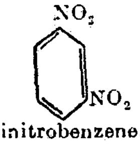
JAMES B CONANT
(1893—)

American. He has been interested in the quantitative side of organic chemistry. Work with oxidation and reduction of organic compounds and chlorophyll is outstanding. Author of several well-known organic chemistry text-books.

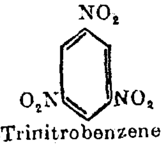
They are the derivatives of aromatic hydrocarbons in which one or more H-atoms of the *nucleus* have been replaced by nitro groups, NO_2. Thus ;



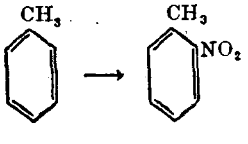
Benzene Nitrobenzene.



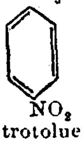
m-Dinitrobenzene, 1, 3-Dinitrobenzene



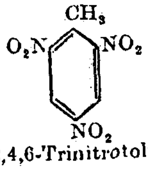
s-Trinitrobenzene, 1,3,5 -Trinitrobenzene



Toluene *o*-Nitrotoluene

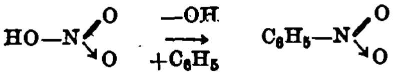


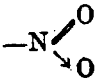
p-Nitrotoluene



2,4,6-Trinitrotoluene

The nitro-compounds could also be regarded as derivatives of nitric acid in which the OH group has been replaced by an aryl radical.



Thus the accepted structure of nitro group is  ,

Aromatic nitrocompounds are of far greater importance than the aliphatic nitrocompounds. This is so because of their easy preparation, and more especially because it is from them that the amino and diazonium compounds are commonly obtained. They are used in large quantities for the preparation of dyes, drugs, perfumes and explosives.

METHODS OF FORMATION

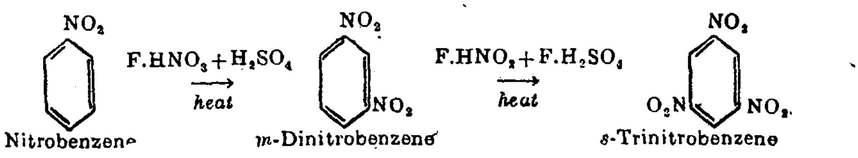
The substitution of a nitro group for hydrogen of the *nucleus* is termed **nitration**. It may be effected by the following methods :

(1) **Action of Nitric acid**. The most common method of nitration is by the direct action of nitric acid on a hydrocarbon. Thus, benzene on treatment with concentrated nitric acid at room temperature forms nitrobenzene.

$$C_6H_5\boxed{H + HO}NO_2 \longrightarrow \underset{\text{Nitrobenzene}}{C_6H_5NO_2} + H_2O$$

In actual practice, a mixture of nitric acid and concentrated sulphuric acid is generally employed. The sulphuric acid promotes the reaction by taking up water and thus protecting the nitric acid from dilution, and also by acting as a catalyst.*

To introduce a second and a third nitro group in the nucleus, it is necessary to use a mixture of fuming nitric acid and concentrated (or fuming) sulphuric acid at elevated temperatures. Thus :



Since all nitro compounds are insoluble in water, they are isolated from the reaction mixture by pouring it into water ; the

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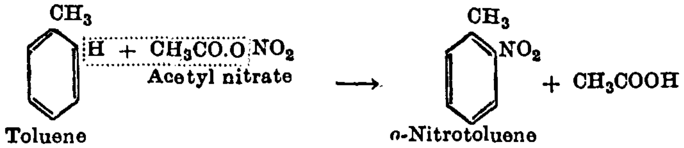
*According to Bennet and Ingold (1946), nitration in sulphuric acid is due to the production of *nitronium ion*, NO_2^+ which, is, in fact, the active nitration agent.

$$HNO_3 + 2H_2SO_4 \longrightarrow NO_2^+ + H_3O^+ + 2HSO_4^-$$

The existence of the nitronium ion has been confirmed by physical methods.

insoluble product being then removed from water by filtration or decantation.

(2) **Action of Acetyl nitrate.** In certain cases, acetyl nitrate* is used as a nitrating agent with advantage, since it introduces only one nitro group in the ortho position. Thus :



Toluene o-Nitrotoluene

The use of acetyl nitrate is somewhat dangerous, since it tends to explode when heated.

(3) **From Diazonium salts.** Nitrocompounds are also produced by the action of nitrous acid on diazonium salts in the presence of cuprous oxide. Thus :

$$\underset{\text{Benzenediazonium chloride}}{C_6H_5N_2Cl} + HNO_2 \longrightarrow \underset{\text{Nitrobenzene}}{C_6H_5NO_2} + HCl$$

This method is of theoretical interest only.

PHYSICAL CHARACTERISTICS

(1) A few nitrocompounds including nitrobenzene, are pale yellow liquids having pleasant sweetish odours. All others are almost colourless crystalline solids with no odour.

(2) They are volatile in steam.

(3) They are heavier than and insoluble in water but dissolve readily in organic solvents such as benzene, alcohol and ether.

(4) The mono-, di-, and trinitro derivatives of benzene and toluene have progressively higher melting and boiling points.

	M.Pt.	B.Pt.		M.Pt.	B.Pt.
Nitrobenzene	5·7°	210°	*o*-Nitrotoluene	—10°	218°
m-Dinitrobenzene	90·8°	303°	*p*-Nitrotoluene	52°	234°
o-Trinitrobenzene	122°	—	*m*-Nitrotoluene	16°	230°
			2, 4, 6-Trinitrotoluene	8·15°	—

(5) When heated strongly, polynitro-compounds detonate with explosive violence and cannot, therefore, be distilled under atmospheric pressure.

CHEMICAL CHARACTERISTICS

The nitro compounds are composed of one or more nitro groups linked to the benzene nucleus. Their chemical behaviour may be summed up as follows :

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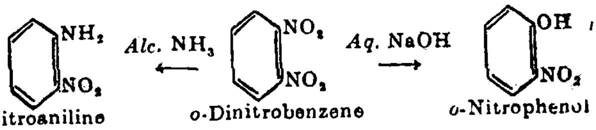
[*] **Acetylnitrate.** Acetyl nitrate needed for nitration is prepared by the reaction between acetic anhydride and nitrogen pentoxide.

$$(CH_3CO)_2O + N_2O_5 \longrightarrow \underset{\text{Acetyl nitrate}}{2CH_3CO.O.NO_2}$$

(1) The nitro group is firmly held by the nucleus and cannot be ordinarily replaced by other atoms or groups. However, in *o*- and *p*-dinitro compounds one of the nitro groups is uncomfortable and may be exchanged for OH, NH_2, etc. Thus :



o-Nitroaniline o-Dinitrobenzene o-Nitrophenol

(2) The nitro groups, being made of nitrogen and oxygen only, show no other reactions except those of reduction.

(3) The benzene nucleus gives the usual electrophilic substitution reactions less readily and in meta position to the original nitro group.

Reduction of Nitro-compounds. The behaviour of nitro-compounds on reduction is of great theoretical and practical interest. The course of reduction in case of nitrobenzene, for example, has been shown to take place as follows through *three* stages.

$$\underset{\text{Nitrobenzene}}{C_6H_5NO_2} \xrightarrow{\text{I}} \underset{\text{Nitrosobenzene}}{C_6H_5NO} \xrightarrow{\text{II}} \underset{\text{Phenylhydroxylamine}}{C_6H_5NHOH} \xrightarrow{\text{III}} \underset{\text{Aniline}}{C_6H_5NH_2}$$

However, the nature of the product actually obtained chiefly depends on whether the reduction is carried in acid, neutral or alkaline solution.

(1) REDUCTION IN ACID SOLUTION. The reduction of nitrobenzene with a metal and acid (Sn+HCl ; Fe+HCl) gives aniline. This is so, because the intermediate compounds nitrosobenzene and phenylhydroxylamine are transitory and the stages I and II are, so to say, skipped over giving straightway the end product.

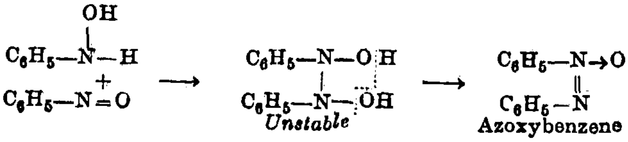
Thus :

$$C_6H_5NO_2 + 6[H] \xrightarrow{Sn/HCl} C_6H_5NH_2 + 2H_2O$$

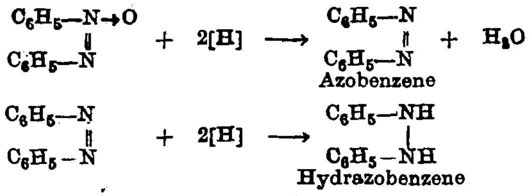
(2) REDUCTION IN NEUTRAL SOLUTION. With a neutral reducing agent (Zinc dust+NH_4Cl solution), the reduction is interrupted after stage II and phenylhydroxylamine is obtained as a stable product. The intermediate nitrosobenzene being transitory is not isolated. Thus :

$$C_6H_5NO_2 + 4[H] \xrightarrow{Zn/H_2O} C_6H_5NHOH + H_2O$$

(3) REDUCTION IN ALKALINE SOLUTION. With alkaline reducing agents (Zn + NaOH ; $SnCl_2$+NaOH, etc.) the reduction is interrupted after stage II due to side reactions. The nitrosobenzene and phenylhydroxylamine react together to form azobenzene and hydrazobenzene. Thus :



$$\begin{array}{c} \overset{OH}{\overset{|}{C_6H_5-N-H}} \\ + \\ C_6H_5-N=O \end{array} \longrightarrow \underset{\textit{Unstable}}{\begin{array}{c} C_6H_5-N-O\,H \\ | \\ C_6H_5-N-\,OH \end{array}} \longrightarrow \underset{\text{Azoxybenzene}}{\begin{array}{c} C_6H_5-N\rightarrow O \\ \| \\ C_6H_5-N \end{array}}$$



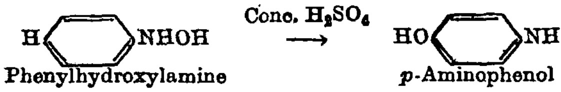
$$\begin{matrix} C_6H_5{-}N{\rightarrow}O \\ \| \\ C_6H_5{-}N \end{matrix} + 2[H] \longrightarrow \begin{matrix} C_6H_5{-}N \\ \| \\ C_6H_5{-}N \end{matrix} + H_2O$$

Azobenzene

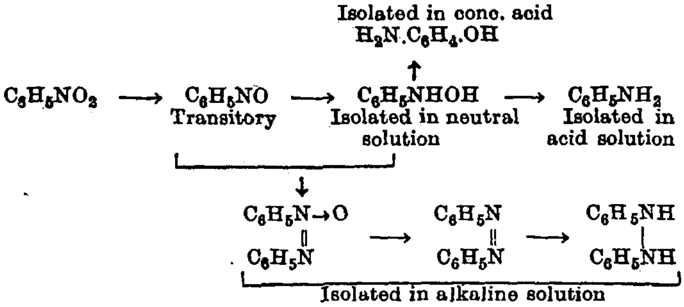
$$\begin{matrix} C_6H_5{-}N \\ \| \\ C_6H_5{-}N \end{matrix} + 2[H] \longrightarrow \begin{matrix} C_6H_5{-}NH \\ | \\ C_6H_5{-}NH \end{matrix}$$

Hydrazobenzene

(4) ELECTROLYTIC REDUCTION. When nitrobenzene is reduced by electrolysis in strong sulphuric acid solution, the reaction is interrupted after stage II since phenylhydroxylamine as soon as it is produced, undergoes an intramolecular rearrangement to give *p*-aminophenol.



The complex behaviour of nitrobenzene on reduction may be summed in the table below.



$$C_6H_5NO_2 \longrightarrow C_6H_5NO \longrightarrow C_6H_5NHOH \longrightarrow C_6H_5NH_2$$

$$\begin{matrix} C_6H_5N{\rightarrow}O \\ \| \\ C_6H_5N \end{matrix} \longrightarrow \begin{matrix} C_6H_5N \\ \| \\ C_6H_5N \end{matrix} \longrightarrow \begin{matrix} C_6H_5NH \\ | \\ C_6H_5NH \end{matrix}$$

All aromatic nitro compounds form similar products to those obtained from nitrobenzene in the above scheme.

Tests for Nitro group. (1) A little given substance is suspended in water and reduced with tin and hydrochloric acid. The solution thus obtained is cooled and a little sodium nitrate solution is added to it, and then a few drops of alkaline solution of β-naphthol are added. A red precipitate of azo-dye shows the presence of NO_2 group in the original substance.

(2) The given substance is boiled with zinc dust and alcohol, and filtered. The filtrate is then heated with Fehling's solution. A red precipitate indicates the presence of NO_2 group. In this reaction the nitro compound is first reduced to arylhydroxylamine which reduces the Fehling's solution to red cuprous oxide.

INDIVIDUAL MEMBERS

NITROBENZENE, OIL OF MIRABANE, $C_6H_5NO_2$

It was first isolated by Mitscherlich in 1834. It is sold as artificial oil of bitter almonds under the name '*Oil of Mirabane*'.

Preparation. LABORATORY METHOD In the laboratory, nitrobenzene is prepared by the action of a mixture of conc. HNO_3 and conc. H_2SO_4 on benzene at ordinary temperature.

$$C_6H_5\vdots H + HO\vdots NO_2 \longrightarrow C_6O_5NO_2 + H_2O$$

Benzene Nitric acid Nitrobenzene

120 ml. concentrated sulphuric acid is slowly mixed with 60 ml. concentrated nitric acid in a round-bottomed flask. 70 ml. benzene is then gradually added to it from a tap funnel. The flask is shaken after each addition and

the temperature of its contents is kept below 60° by immersing the flask in cold water if necessary. This is important as at a higher temperature *m*-dinitrobenzene is formed. When all the benzene has been added, the mixture is heated on a water-bath at 60° for an hour or so to complete the reaction. The contents of the flask are then transferred to a separating funnel and the lower acid layer drawn off. The nitrobenzene left is shaken successively with sodium carbonate solution and water to remove any acid. The lower layer of benzene after washing is drawn off and dried by standing over fused calcium chloride. It is finally distilled using an air condenser (Fig. 40·1). The fraction passing between 208-212° is collected; it consists of almost pure nitrobenzene.

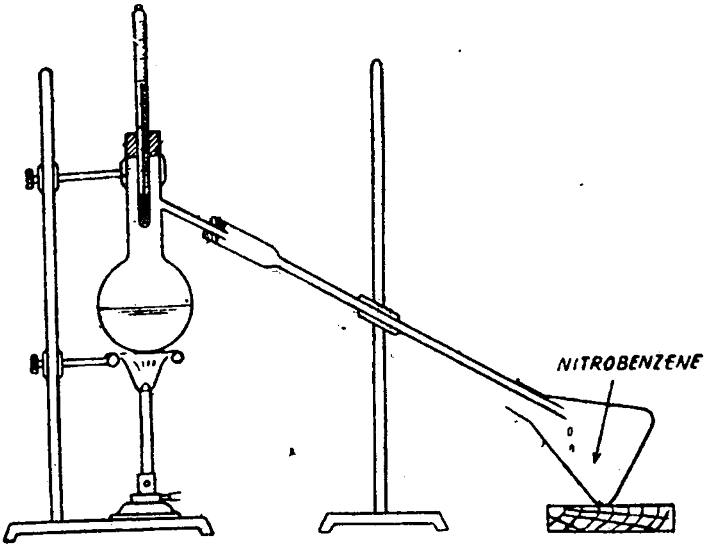


Fig. 40·1. Distillation of Nitrobenzene.

Commercial Method. On a large scale also, nitrobenzene is prepared by the action of a mixture of nitric acid and sulphuric acid on benzene. The working details remain the same as in the laboratory process except that here the nitration is carried in a pan provided with a stirrer and a cold-water pipe. At the end, the spent acids are withdrawn and the nitrobenzene layer given the necessary washings. The product is exposed to a current of steam until free from benzene.

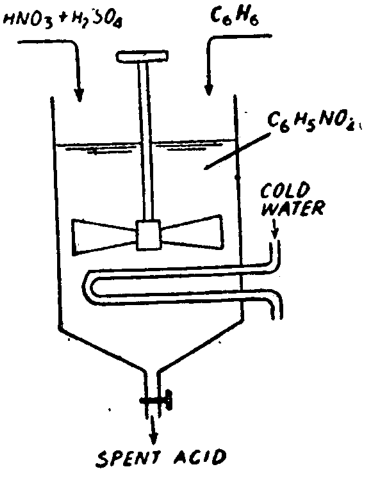


Fig. 40·2. Manufacture of Nitrobenzene.

Properties. (*Physical*). Nitrobenzene is a pale yellow oily liquid (b.p. 210°; sp. gr. 1·087) having odour of bitter almonds. Its colour darkens somewhat with age. It is insoluble in water but dissolves readily in alcohol and ether. It is volatile in steam. Its vapours are poisonous.

(Chemical). The chemical reactions of nitrobenzene are those of a nitro group and a phenyl radical.

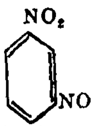
(1) The nitro group is tightly attached to the phenyl radical and cannot be replaced by other atoms or groups. Thus aqueous alkali or alcoholic ammonia has no action on nitrobenzene.

(2) When reduced with tin and hydrochloric acid, it is converted to aniline.

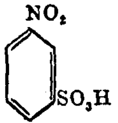
$$C_6H_5NO_2 + 6[H] \longrightarrow C_6H_5NH_2 + 2H_2O$$

The reduction of nitrobenzene in neutral and alkaline solutions gives a variety of products as mentioned earlier.

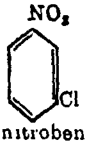
(3) Under suitable conditions nitrobenzene can be nitrated, sulphonated and chlorinated to form meta substitution products.



m-Dinitrobenzene



m-Nitrobenzene sulphonic acid

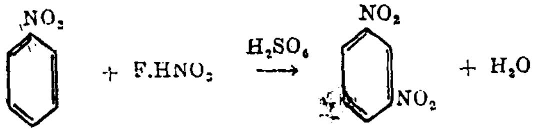


m-Chloronitrobenzene

Uses. Nitrobenzene is used : (1) for scenting cheap soaps : (2) for making shoe polishes, since it is an excellent solvent for the dye and penetrates leather well ; (3) in the manufacture of floor polishes ; (4) as a high boiling solvent ; (5) for the manufacture of aniline and some azo-dyes ; and (6) as an oxidising agent in organic synthesis.

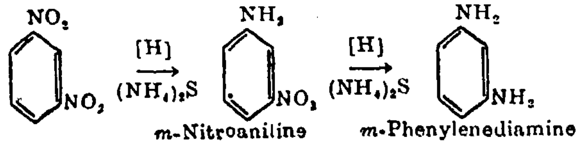
m-DINITROBENZENE, $C_6H_4(NO_2)_2$

Of the three isomeric dinitrobenzenes (*o*-, *m*-, *p*-), the meta derivative is by far the most important. It is prepared by heating benzene with a mixture of fuming nitric acid and sulphuric acid.



About 7 per cent of the *o*-isomer is also obtained which is removed during crystallisation.

m-Dinitrobenzene forms pale yellow crystals, m.p. 90°. It is insoluble in water but is volatile in steam. It is very poisonous. When reduced with alcoholic ammonium sulphide, it is first converted to *m*-nitroaniline and then to *m*-phenylenediamine. Both the nitro groups are tightly held by the nucleus and cannot be replaced by other atoms or groups.

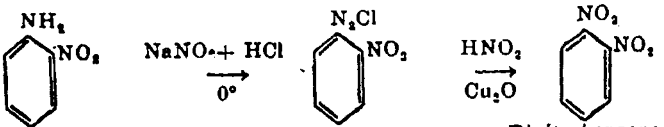


m-Nitroaniline m-Phenylenediamine

It is used in the manufacture of explosive *Roburite* and *Securite*, and for preparing *m*-phenylenediamine.

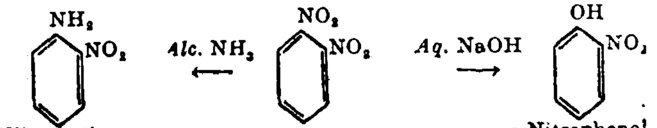
o-DINITROBENZENE, $C_6H_4(NO_2)_2$

It is formed by the direct nitration of nitrobenzene and is recovered from the mother liquor after separating the crystals of the *m*-isomer. It may also be prepared from the corresponding nitro-aniline by replacing the NH_2 by NO_2 by diazotization and treatment with excess nitrous acid and Cu_2O.



o-Nitroaniline *o*-Dinitrobenzene

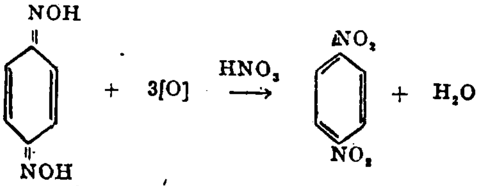
o-Dinitrobenzene is a colourless solid, m.p. 118°. It resembles the *m*-isomer in the behaviour on reduction. It differs from the latter in that one of the NO_2 groups can be replaced by OH or NH_2 by boiling with aqueous sodium hydroxide and alcoholic ammonia respectively.



o-Nitroaniline *o*-Nitrophenol

p-DINITROBENZENE, $C_6H_4(NO_2)_2$

Like the *o*-isomer, it is prepared by diazotization of *p*-nitroaniline and treatment with excess nitrous acid and Cu_2O. It may also be obtained by oxidising *p*-benzoquinone dioxime with nitric acid.

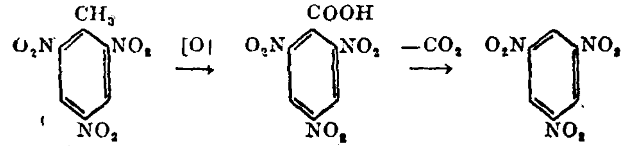


p-Benzoquinone dioxime *p*-Dinitrobenzene

p-Dinitrobenzene is a colourless solid, m.p. 174°. It resembles closely with the *o*-isomer ; (1) it can be reduced in two stages giving *p*-phenylenediamine ; (2) one of the NO_2 groups can be replaced by OH or NH_2 by treatment with alkali or ammonia.

1, 3, 5-TRINITROBENZENE, *s*-TRINITROBENZENE, $C_6H_3(NO_2)_3$

It may be made by heating *m*-dinitrobenzene with a mixture of fuming nitric acid and fuming sulphuric acid for five days. It is more conveniently prepared by oxidising trinitrotoluene and then knocking the COOH group by heating in acetic acid solution.



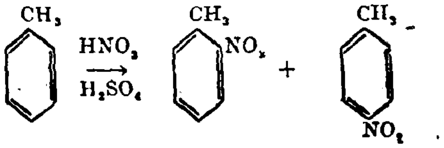
2, 4, 6-trinitrobenzene *s*-trinitrobenzene

s-Trinitrobenzene crystallises in snow-white leaflets, m.p. 122°. It forms well-defined addition compounds with numerous aromatic compounds such as hydrocarbons, phenols, etc. One of the three NO_2 groups can be replaced by OH or NH_2 by the same reagents which attack the *o*- and *p*-dinitrobenzenes.

Trinitrobenzene (T.N.B.) is used in making explosives ; it has a greater explosive power than trinitrotoluene.

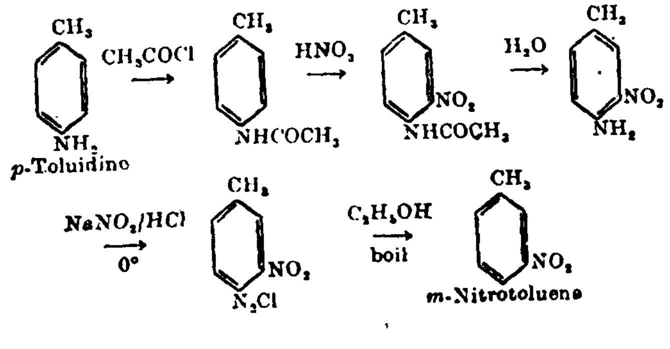
NITROTOLUENES, $CH_3.C_6H_4.NO_2$.

Toluene nitrates readily with a mixture of nitric and sulphuric acids to form a mixture of *o*- and *p*-nitrotoluenes.



These may be separated by fractional distillation under reduced pressure.

About 4 per cent of *m*-nitrotoluene is also obtained by direct nitration of the toluene. When needed in large quantities it is prepared indirectly by acetylating *p*-toluidine, nitrating the acetyl derivative, deacetylating and replacing the amino group by hydrogen.

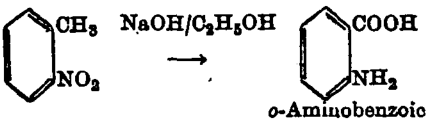


p-Toluidine

m-Nitrotoluene

The NH_2 group in toluidine has to be acetylated to protect it from oxidation and to help ortho orientation.

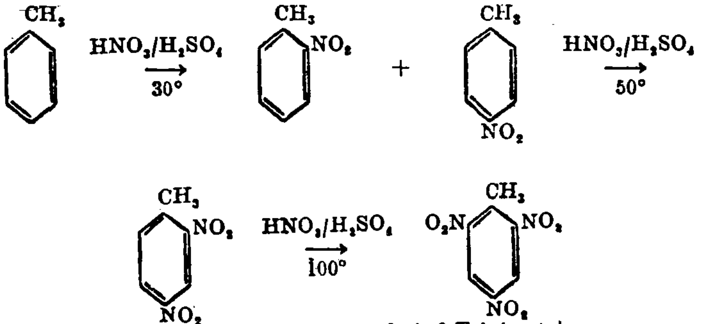
Properties. *o*-Nitrotoluene is a liquid, m.p. —4°, b.p. 222°. *m*-dinitrotoluene is a liquid, m.p. 16°, b.p. 227° ; *o*-nitrotoluene is a solid, m.p. 54°, b.p. 238°. All nitrotoluenes may be reduced in acid solution to give the corresponding toluidines. On oxidation with potassium permanganate, they are converted to nitrobenzoic acids, the CH_3 group being transformed into COOH group, *o*-isomer, when heated with sodium hydroxide and alcohol, undergoes an interesting internal oxidation and reduction to form *o*-aminobenzoic acid.



o-Aminobenzoic acid

2, 4, 6-TRINITROTOLUENE, $CH_3C_6H_2(NO_2)_3$

It may be prepared by nitrating toluene with a mixture of fuming nitric acid and fuming sulphuric acid, but generally it is prepared by carrying the reaction in three independent steps.



2, 4, 6-Trinitrotoluene

The spent acids from the third step are utilised for effecting the second step, and those from the second step for effecting the first step ; thus there is no wastage. The product is run into water washed with sodium sulphite solution to dissolve out any isomers leaving pure trinitrotoluene.

Trinitrotoluene is a faint yellow crystalline solid, m.p. 81°. The molecule being loaded with negative nitro groups is under strain, and has enough oxygen for internal combustion ; it therefore, explodes violently on detonation. On explosion it is believed to decompose as follows, leaving no residue.

$$2CH_3C_6H_2(NO_2)_3 \longrightarrow 14CO + 3N_2 + 5H_2$$

The sudden liberation of large volume of gases lends intensity to the explosion.

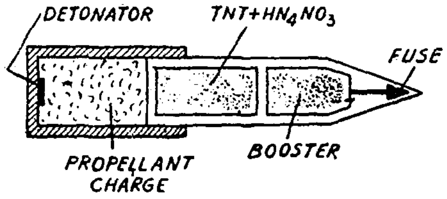


Fig. 40·3. T.N.T. Bomb.

Trinitrotoluene is extensively employed as a high explosive (**TNT**). It is a reasonably safe explosive, requiring strong detonation to set it off. It is used for filling shells, bombs and torpedoes. Mixed with ammonium nitrate, it forms the blasting material **amatol.**

Phenylnitromethane, $C_6H_5.CH_2NO_2$. It is isomeric with nitrotoluenes but has the nitro group in the side-chain instead of the ring. It may be prepared (1) by heating toluene with dilute nitric acid in a sealed tube at 100°.

$$C_6H_5.CH_3 + HNO_3 \longrightarrow C_6H_5CH_2NO_2 + H_2O$$

or (2) by treating benzyl iodide with silver nitrite.

$$C_6H_5CH_2I + AgNO_2 \longrightarrow C_6H_5CH_2NO_2 + AgI$$

Properties. Phenylnitromethane is a yellow oil, b.p. 226°. Like the primary nitroalkanes it exhibits tautomerism and has small amount of the *aci* form in contact.

$$\underset{\textit{nitro form}}{C_6H_5CH_2.N\begin{smallmatrix}\nearrow O\\ \searrow O\end{smallmatrix}} \rightleftharpoons \underset{\textit{aci form}}{C_6H_5CH{=}N\begin{smallmatrix}\nearrow O\\ \searrow OH\end{smallmatrix}}$$

Thus phenylnitromethane (*nitro form*) dissolves in sodium hydroxide to give sodium salt of the *aci form*, which when treated with a mineral acid liberates the *aci form*. The latter is a solid, m.p. 34°, but on standing it soon changes into the liquid phenylnitromethane.

QUESTIONS

1. Describe the various methods commonly used for introducing nitro groups in the benzene ring.

2. Discuss the behaviour of aromatic nitro compounds on reduction, taking nitrobenzene as an example. Indicate the nature of compounds formed under different conditions.

3. By what chemical reactions would you distinguish between nitroethane and nitrobenzene ?

4. How is nitrobenzene prepared in the laboratory ? How would you convert it into aniline ?

5. Write brief notes on T.N.B., T.N.T. and phenylnitromethane.

6. Describe the preparation of nitrobenzene in the laboratory. What products are obtained on reduction of nitrobenzene under acidic and alkaline conditions ? *(Gorakhpur B.Sc., 1967)*

7. How can nitrobenzene be prepared on a large scale ? Give an account of the products obtained from it by reduction under different conditions. *(Indore B.Sc. III, 1967)*

8. Discuss the different methods for the preparation of aromatic nitro-compounds. Discuss their industrial importance. *(Bombay B.Sc., 1967)*

9. Describe the reduction of nitrobenzene under different conditions. *(Bombay B.Sc., 1968)*

10. Describe the method for the preparation of 2, 4, 6-trinitrotoluene. Predict the products of the following reactions with equations.

(*a*) Nitrobenzene is warmed with iron powder and HCl followed by treatment with aqueous solution of sodium hydroxide.

(*b*) *m*-dinitrobenzene is treated with ammonium hydrogen sulphide.

(*c*) The product obtained in (*a*) is purified and treated with conc. H_2SO_4 and heated at 150-160°.

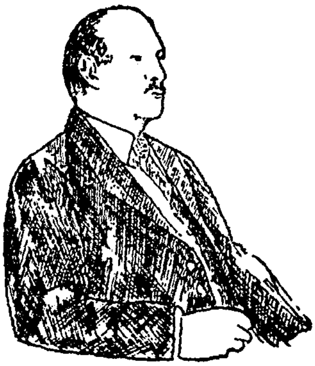
(*d*) The product obtained in (*a*) is purified and treated with chloroform and KOH and warmed. (*Jadavpur B.Sc., 1969*)

11. How is nitrobenzene prepared in the laboratory? Give an account of the products obtained by its reduction under different conditions. (*Marathwada B.Sc., 1969*)

12. How is nitrobenzene obtained on a large scale ? Discuss fully the reduction of nitrobenzene under different conditions. Mention the importance of the reduction products. (*Bombay B.Sc., 1969*)

41

Aromatic Amines



Ludwig Gattermann
(1860—1920)
German. Known for his contributions in synthetic organic chemistry. Several syntheses bear his name (preparation of halogen aromatic compounds, aldehydes)

Just *as* aliphatic amines are the alkyl derivatives of ammonia, *aromatic amines are the aryl derivatives of ammonia*. Thus :

$$NH_3 \xrightarrow[+C_6H_5]{-H} \underset{\text{Aniline}}{C_6H_5.NH_2} \qquad \textit{(First type)}$$

$$NH_3 \xrightarrow[+C_6H_5CH_2]{-H} \underset{\text{Benzylamine}}{C_6H_5CH_2NH_2} \qquad \textit{(Second type)}$$

They are of two types : (1) those in which the amine group is attached to the ring and (2) those in which the amine group is attached to a carbon atom of the side-chain. The derivatives of the first type are true aromatic amines ; they differ considerably in their reactions from the aliphatic amines and are commonly named as **amino compounds**. The derivatives of the second type, however, behave like aliphatic amines and are to be regarded as *aryl-substituted* aliphatic amines.

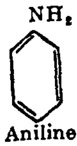
Aromatic amines may be divided into the same three classes as the aliphatic amines : *primary*, *secondary* and *tertiary*. Thus :

$C_6H_5NH_2$	$(C_6H_5)_2NH$	$(C_6H_5)_3N$
Aniline	Diphenylamine	Triphenylamine
(Primary)	*(Secondary)*	*(Tertiary)*

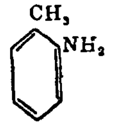
The primary amines are further designated as *monoamines, diamines* and *triamines* according to the number of NH_2 groups present in the ring. The secondary and tertiary amines may be purely aromatic, (Ar_2NH ; Ar_3N) or mixed aliphatic-aromatic ($Ar.NH.R$; $Ar_2N.R$; $Ar.NR_2$).

1. PRIMARY MONOAMINES (*Monoamino Compounds*)

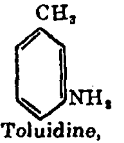
They are primary aromatic amines having one NH_2 group in the ring. They may be regarded as derivatives of hydrocarbons in which one nuclear H atom has been replaced by an amino group; thus they are often named as amino-hydrocarbons. Benzene and toluene give rise to the following monoamines.



Aniline,
Aminobonzene



o-Toluidine,
o-aminotolune



m-Toluidine,
m-aminotoluene

p-Toluidine.
p-aminotoluene

METHODS OF FORMATION

(1) **Reduction of Nitro-compounds.** Monoamines are nearly always prepared by the reduction of the corresponding nitro-compounds with a metal and acid *e.g.*, tin, zinc or iron with hydrochloric acid.

$$\underset{\text{Nitrobenzene}}{C_6H_5NO_2} + 6[H] \xrightarrow{Sn/HCl} C_6H_5NH_2 + 2H_2O$$

$$\underset{\text{Nitrotoluene}}{CH_3.C_6H_4.NO_2} + 6[H] \xrightarrow{Sn/HCl} \underset{\text{Toluidine}}{CH_3.C_6H_4.NH_2} + 2H_2O$$

Nitro-compounds may also be converted to the amines by catalytic reduction at 200°—400°.

(2) **Ammonolysis of Chloro derivatives.** The chloro-derivatives of aromatic hydrocarbons react with ammonia in the presence of a catalyst (copper salts) at high temperature and under pressure to yield the corresponding amino-compounds.

Thus :

$$\underset{\text{Chlorobenzene}}{2C_6H_5Cl} + 2NH_3 + Cu_2O \xrightarrow{200^\circ} 2C_6H_5NH_2 + Cu_2Cl_2 + H_2O$$

(3) **Ammonolysis of Phenols.** Phenols react with ammonia in the presence of zinc chloride at about 300° to form the corresponding amines. Thus :

$$\underset{\text{Phenol}}{C_6H_5OH} + NH_3 \xrightarrow[300^\circ]{ZnCl_2} C_6H_5NH_2 + H_2O$$

(4) **Hofmann's-Method.** Aromatic amides are converted to primary aromatic amines by the action of bromine and alkali.

Thus :

$$\underset{\text{Benzamide}}{C_6H_5CONH_2} \xrightarrow{Br_2/KOH} C_6H_5NH_2$$

(5) **Action of Hydroxylamine on hydrocarbons.** Aromatic hydrocarbons react directly with hydroxylamine in the presence of a catalyst ($FeCl_3$, $AlCl_3$) to give monoamines.

$$C_6H_5\boxed{H + HO}NH_2 \longrightarrow C_6H_5NH_2 + H_2O$$

PHYSICAL CHARACTERISTICS

(1) Monoamino compounds are colourless liquids or solids having a characteristic odour which is not unpleasant. They turn brown in air owing to oxidation.

(2) They are volatile in steam, and can be distilled without decomposition.

(3) They are sparingly soluble in water but dissolve readily in common organic solvents.

(4) They are much weaker bases than alkyl amines and are neutral to litmus.

(5) They are toxic ; their contact with skin destroys red blood corpuscles.

CHEMICAL CHARACTERISTICS

Monoamino compounds are made of one NH_2 group attached to a hydrocarbon nucleus. The negative character of the aromatic nucleus influences the behaviour of the amino group in many ways. Nevertheless, amino-compounds show readily all the reactions of the aliphatic primary amines ; the chief difference is their characteristic behaviour on treatment with nitrous acid. The hydrocarbon parts of the amino-compounds give the usual substitution and other reactions, while the alkyl groups in aliphatic amines are inert.

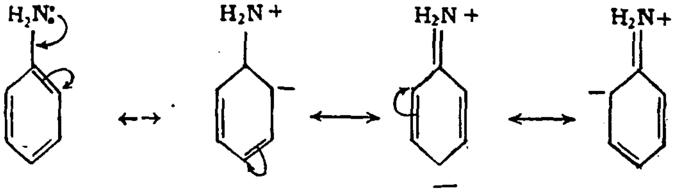
(1) **Action of acids.** Amino compounds combine with strong acids to form crystalline salts. Thus :

$$C_6H_5NH_2 + HCl \longrightarrow \underset{\text{Aniline hydrochloride}}{C_6H_5\overset{+}{N}H_3\overset{-}{Cl}}$$

Aniline hydrochloride is appreciably soluble in water and undergoes hydrolysis to a great extent according to the reversible equation :

$$C_6H_5\overset{+}{N}H_3\overset{-}{Cl} \rightleftharpoons C_6H_5NH_2 + HCl$$

Aniline is a weak base, since the lone pair of electrons on the N atom have a tendency to get paired with the benzene ring. In the absence of the lone pair on N-atom, it will have no tendency to get co-ordinated with a proton. In aniline molecule, the lone pair on N is shared as follows, giving the following resonance structures—



The similar salts of aliphatic amines are not hydrolysed.

(2) **Action with active metals.** The negative aryl radical decreases the basic character of the NH_2 group, and even makes it acidic. Thus amino-compounds when heated with sodium or potassium, form metallic derivatives with the liberation of hydrogen. Thus :

$$C_6H_5NH_2 + K \longrightarrow \underset{\text{Pot. anilide}}{C_6H_5NHK} + \tfrac{1}{2}H_2$$

(3) **Action with alkyl halides.** Amino-compounds react with alkyl halides to form secondary and tertiary amines, the final product being quaternary ammonium salt. Thus :

$$C_6H_5NH_2 + RI \longrightarrow \underset{\text{Secondary amine}}{C_6H_5NHR} + HI$$

$$C_6H_5NHR + RI \longrightarrow \underset{\text{Tertiary amine}}{C_6H_5NR_2} + HI$$

$$C_6H_5NR_2 + RI \longrightarrow \underset{\text{Q. Amm. salt}}{[C_6H_5NR_3]^+I^-}$$

The separation of the mixture may be done by Hofmann's method used in the case of aliphatic amines.

(4) **Action with acyl chlorides : acylation.** They react with acyl chlorides or with acid anhydrides, to form derivatives known as anilides. Thus:

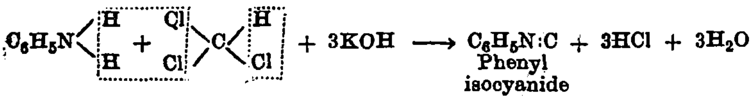
$$C_6H_5NH_2 + \underset{\text{Acetyl chloride}}{CH_3COCl} \longrightarrow \underset{\text{Acetanilide}}{C_6H_5NH.COCH_3} + HCl$$

$$C_6H_5NH_2 + \underset{\text{Benzoyl chloride}}{C_6H_5COCl} \longrightarrow \underset{\text{Benzanilide}}{C_6H_5NH.COC_6H_5} + HCl$$

Dilute alkali is added to neutralise the acid produced during the reaction, and the reaction mixture is shaken or warmed if necessary. The preparation of acid derivatives as above is known as **Schotten Baumann reaction.** The anilides are well-defined crystalline substances and are used for characterising aromatic amines.

Acetylation of amino-compounds is done to protect the NH_2 group during nitration.

(5) **Action with chloroform; Carbylamine reaction.** When heated with chloroform and alcoholic potash amino-compounds form the offensive smelling carbylamines or isocyanides.



$$C_6H_5N\begin{matrix}H\\H\end{matrix} + \begin{matrix}Cl\\Cl\end{matrix}C\begin{matrix}H\\Cl\end{matrix} + 3KOH \longrightarrow C_6H_5N{:}C + 3HCl + 3H_2O$$

Phenyl isocyanide

This reaction forms a test for the aromatic primary amines; it is also given by aliphatic primary amines.

(6) **Action with aldehydes**. They undergo condensation with aromatic aldehydes to form **anils** or **Schiff's bases**. Thus:

$$C_6H_5N\boxed{H_2 + O}{=}HCC_6H_5 \longrightarrow C_6H_5N{=}HCC_6H_5 + H_2O$$

Benzaldehyde Benzalaniline

Schiff's bases are readily hydrolysed to liberate the original amine; their formation, therefore, offers a means for protecting the NH_2 group. These compounds are also used to prepare secondary amines by reduction.

$$C_6H_5N{=}HC.C_6H_5 + 2[H] \longrightarrow C_6H_5NH.CH_2C_6H_5$$

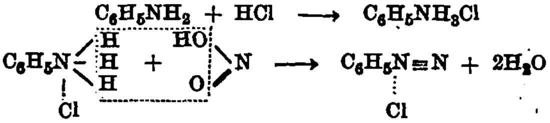
Benzalphenylamine

(7) **Action with Grignard reagents**. Amino-compounds react with Grignard reagents to form hydrocarbons. Thus:

$$R\boxed{MgBr + C_6H_5NH}H \longrightarrow RH + C_6H_5.NH.MgBr$$

(8) **Action of Nitrous acid**. They react with nitrous acid and excess of a mineral acid (HCl or H_2SO_4) at 0°C to form *diazonium salts.*

$$C_6H_5NH_2 + HCl \longrightarrow C_6H_5NH_3Cl$$



$$\underset{Cl}{C_6H_5N}\begin{matrix}H\\H\\H\end{matrix} + \begin{matrix}HO\\O\end{matrix}N \longrightarrow \underset{Cl}{C_6H_5N{\equiv}N} + 2H_2O$$

Benzenediazonium chloride

Aliphatic primary amines do not form diazonium salts under similar conditions; they produce alcohols with liberation of nitrogen. This reaction is used as a test for distinguishing between aliphatic primary amines and amino-compounds.

INDIVIDUAL MEMBERS

ANILINE, AMINOBENZENE, $C_6H_5NH_2$

Aniline was discovered by Unverdorben (1826) who obtained it by the destructive distillation of indigo. It was later isolated from coal-tar by Runge (1834). Fritzsche (1840) also prepared it from indigo and gave it the name aniline (Sanskrit, *nila*=indigo).

Aniline is prepared both in the laboratory and on the commercial scale by the reduction of nitrobenzene.

$$C_6H_5NO_2 + 6[H] \longrightarrow C_6H_5NH_2 + 2H_2O$$

Laboratory Preparation. In the laboratory aniline is prepared by the reduction of nitrobenzene with tin and hydrochloric acid.

$$2C_6H_5NO_2 + 3Sn + 12HCl \longrightarrow 2C_6H_5NH_2 + 3SnCl_4 + 4H_2O$$

Aniline produced by reduction at once combines with stannous chloride and hydrochloric acid to form the soluble salt *aniline stanni-chloride*, $(C_6H_5NH_2)_2.H_2SnCl_6$.

$$2C_6H_5NH_2 + 2HCl + SnCl_4 \longrightarrow \underset{\text{Aniline stannichloride}}{(C_6H_5NH_2)_2.H_2SnCl_6}$$

The salt when decomposed with alkali regenerates aniline which is then removed by steam-distillation.

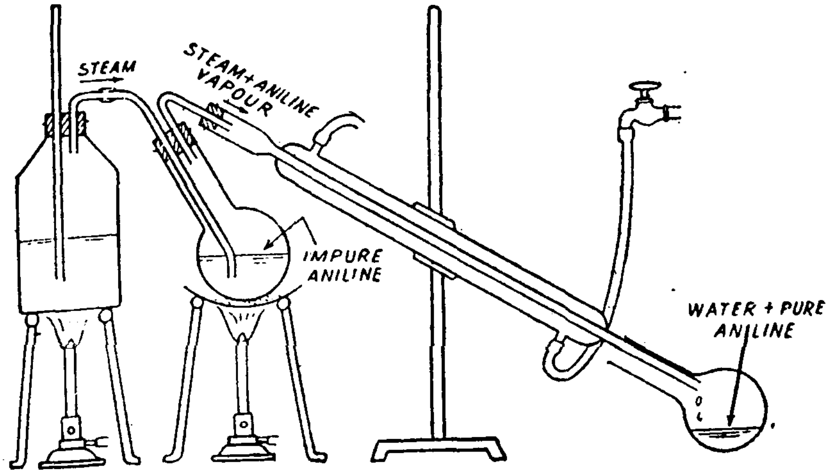


Fig. 41·1. Steam-distillation of aniline.

25 gm. nitrobenzene and 50 gm. granulated tin are placed in a round-bottomed flask fitted with an air condenser. 100 ml. concentrated hydrochloric acid are poured down the condenser in instalments of 20 ml. at a time, the flask being shaken after each addition. A brisk reaction sets in and the flask is cooled by immersing in cold water, in case the reaction becomes too violent. When all the acid has been added, the condenser is removed and the open flask is heated on a water bath until the smell of nitrobenzene has disappeared. At this stage the flask is cooled and a solution of sodium hydroxide in water (20 gm. per 100 ml. water) is added in small quantities. The aniline which is liberated as a dark coloured oil is separated by steam-distillation. The distillate consisting of aniline and water is shaken several times with ether. The ethereal extract is dried over anhydrous caustic potash and then ether removed by distillation The aniline thus obtained is further purified by distillation through an air-condenser.

Industrial Preparation. Aniline is prepared on a large scale by the reduction of nitrobenzene using iron and hydrochloric acid.

$$C_6H_5NO_2 + 3Fe + 6HCl \longrightarrow C_6H_5NH_2 + 2H_2O + 3FeC_3$$

In actual practice about one-fortieth of the amount of hydrochloric acid necessary according to the above equation is used. This is so, because iron acts upon water in the presence of ferrous chloride generating hydrogen which carries on the reduction of nitrobenzene Thus, the overall reaction may be written as

$$C_6H_5NO_2 + 3Fe + 2H_2O \xrightarrow{FeCl_2} C_6H_5NH_2 + Fe_3O_4 + 2H$$

In some modern processes, the reduction of nitrobenzene is effected by means of iron and water in the presence of ferric chloride, thus eliminating the use of hydrochloric acid.

A charge of scrap iron, water and hydrochloric acid is placed in the reducer. Steam is now passed in through the hollow stirrer till boiling sets in. Now nitrobenzene is added gradually so that the charge just keeps boiling. When the reduction is complete steam is again blown in whereby aniline is distilled off. The aniline water mixture coming from the condenser is allowed to separate in a tank. The crude aniline is finally purified by distillation under vacuum.

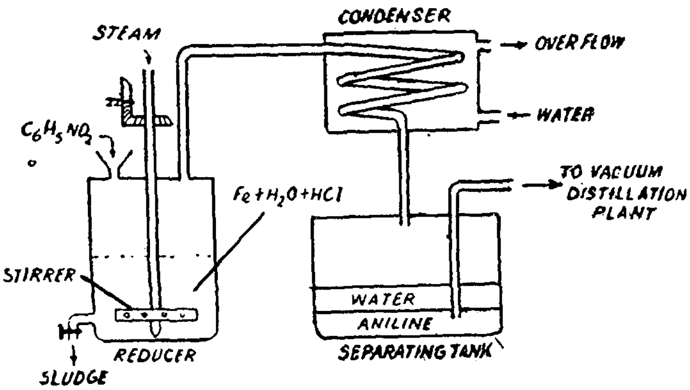


Fig. 41·2. Manufacture of aniline by the reduction of nitrobenzene.

In a more recent American method, aniline is made by the treatment of chlorobenzene with ammonia at 340° and 340 atmos. pressure in the presence of catalyst. In another modern process, nitrobenzene is reduced catalytically with hydrogen or water gas.

Properties. (*Physical*). Aniline, when freshly prepared, is a colourless liquid, b.p. 184°, having *a faint but characteristic odour.* It rapidly darkens in air due to oxidation. It is sparingly soluble in water but is volatile in steam ; it dissolves readily in alcohol and ether. It is poisonous.

(*Chemical*). Aniline molecule is made of one NH_2 group linked to the benzene nucleus. At the NH_2 group it gives all the replacement reactions of the aliphatic primary amines, and differs only in its behaviour towards nitrous acid. The benzene nucleus gives the usual electrophilic substitution reactions in ortho and para positions.

Reactions due to NH_2 group

(1) FORMATION OF SALTS. Aniline forms crystalline salts with strong acids. Thus :

$$C_6H_5NH_2 + HCl \longrightarrow \underset{\text{Aniline hydrochloride}}{C_6H_5NH_2.HCl}$$

$$2C_6H_5NH_2 + H_2SO_4 \longrightarrow \underset{\text{Aniline sulphate}}{(C_6H_5NH_2)_2.H_2SO_4}$$

These salts are readily hydrolysed in water solutions.

(2) Alkylation. Aniline reacts with alkyl halides to yield alkyl-anilines and the quaternary ammonium salts. Thus :

$$\underset{}{C_6H_5NH_2} \xrightarrow{CH_3I} \underset{\text{Methylaniline}}{C_6H_5NHCH_3} \xrightarrow{CH_3I} \underset{\text{Dimethylaniline}}{C_6H_5N(CH_3)_2} \xrightarrow{CH_3I} \underset{\text{Quaternary salt}}{[C_6H_5N(CH_3)_3]^{+}I}$$

(3) Acylation. Aniline, when treated with an acid chloride in the presence of alkali, forms *anilides.*

$$C_6H_5NH_2 + CH_3COCl \longrightarrow \underset{\text{Acetanilide}}{C_6H_5NHOCCH_3} + HCl$$

(4) Formation of Schiff's bases. Aniline reacts with aromatic aldehydes by elimination of water molecule to form *anils* or *Schiff's bases.*

$$C_6H_5N\boxed{H_2 + O}=\underset{\text{Benzaldehyde}}{HC.C_6H_5} \longrightarrow \underset{\text{Benzalaniline}}{C_6H_5N=HCC_6H_5} + H_2O$$

(5) Carbylamine reaction. When heated with chloroform and alcoholic potash, aniline forms phenyl carbylamine or isocyanide which is at once recognised by its offensive smell.

$$C_6H_5NH_2 + CHCl_3 + 3KOH \longrightarrow \underset{\text{Carbylamine}}{C_6H_5NC} + 3KCl + 3H_2O$$

(6) Action with Grignard reagents. Aniline reacts with Grignard reagents to form hydrocarbons.

$$RMgBr + C_6H_5NH_2 \longrightarrow RH + C_6H_5NH.MgBr$$

(7) Diazotization. When treated with nitrous acid in the presence of excess hydrochloric acid at 0°, it forms benzenediazonium chloride.

$$C_6H_5NH_2 + HNO_2 + HCl \xrightarrow{0^\circ} C_6H_5N_2Cl + 2H_2O$$

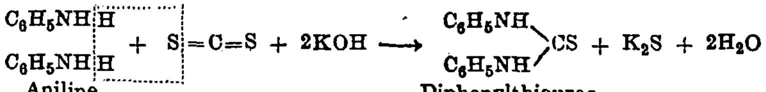
(8) Reaction with Aniline hydrochloride. When aniline is heated with aniline hydrochloride in a closed vessel at 260°, it gives diphenylamine.

$$C_6H_5NH\boxed{H + ClH_3N}C_6H_5 \longrightarrow \underset{\text{Diphenylamine}}{(C_6H_5)_2NH} + NH_4Cl$$

(9) Action with Carbonyl chloride. Aniline reacts readily with carbonyl chloride to form *phenyl isocyanate.*

$$C_6H_5N\boxed{H_2} + CO\boxed{Cl_2} \longrightarrow C_6H_5NCO + 2HCl$$

(10) Action with Carbon disulphide. When heated with alcoholic carbon disulphide and solid potassium hydroxide, aniline yields diphenylthiourea which is used in the vulcanisation of rubber.



$$\begin{matrix} C_6H_5NH\boxed{H} \\ C_6H_5NH\boxed{H} \end{matrix} + \boxed{S}=C=S + 2KOH \longrightarrow \begin{matrix} C_6H_5NH \\ C_6H_5NH \end{matrix}\!\!>CS + K_2S + 2H_2O$$

Aniline
(2 molecules)

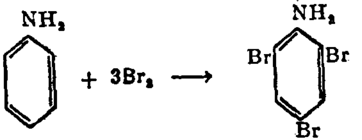
Diphenylthiourea

(11) COUPLING WITH DIAZONIUM SALTS. If aniline is treated with an aqueous solution of benzenediazonium chloride, it gives diazoaminobenzene.

$$C_6H_5N_2\boxed{Cl + H}HNC_6H_5 \longrightarrow \underset{\text{Diazoaminobenzene}}{C_6H_5N{=}N.NHC_6H_5} + HCl$$

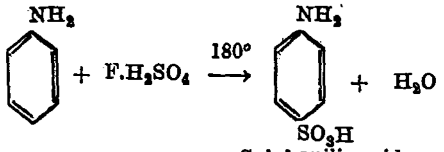
Reactions due to the Nucleus

(12) ACTION WITH HALOGENS. Aniline reacts much more readily with chlorine and bromine than does benzene. Thus when treated with aqueous solutions of chlorine or bromine, it at once forms a precipitate of 2, 4, 6-trihaloanilines.



2, 4, 6-Tribromoaniline

(13) ACTION WITH SULPHURIC ACID. When heated with fuming sulphuric acid, aniline forms sulphanilic acid.



Sulphanilic acid

(14) ACTION WITH NITRIC ACID. Aniline is oxidised and charred with nitric acid. It can be nitrated to a mixture of *o*- and *p*-nitroanilines by employing a large excess of sulphuric acid in the nitrating mixture. However, if aniline is to be nitrated, it is always better to protect the NH_2 group by acetylation before nitration; the $NHCOCH_3$ is restored to NH_2 by hydrolysis.

(15) OXIDATION. Aniline is readily oxidised, the nature of the product depending on the conditions employed. When oxidised with sodium dichromate and sulphuric acid, it forms *aniline black* a black dye of complex structure.

Uses. Aniline is used: (1) for preparing dyes and dye intermediates; (2) for preparing several derivatives such as acetanilide, sulphanilic acid, nitroanilines, and sulpha drugs; and (3) as a solvent in the rubber industry.

Tests for Aniline

(1) Aniline has a characteristic odour.

(2) It gives carbylamine reaction.

(3) On the addition of a few drops of potassium dichromate solution to aniline dissolved in sulphuric acid, a deep blue or black colour is produced.

(4) If bromine water is added to an aqueous solution of aniline, pinkish precipitate is obtained.

(5) If a solution of bleaching powder is added to an aqueous solution of aniline, a purple colour is produced.

(6) If we add a little sodium nitrate to an ice-cold solution of aniline in hydrochloric acid, and then add to it a few drops of an alkaline solution of β-naphthol, a brilliant red precipitate is obtained.

Acetanilide, *N-phenylacetamide*, $C_6H_5.NH.CO.CH_3$. It is conveniently prepared by refluxing aniline with acetic acid, in the presence of anhydrous zinc chloride.

$$C_6H_5NH_2 + CH_3COOH \longrightarrow C_6H_5NH.COCH_3 + H_2O$$

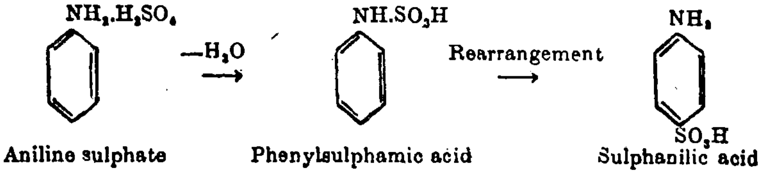
It is obtained rapidly when acetic anhydride or acetyl chloride is added to aniline.

Properties. Acetanilide crystallises from water in small white leaflets, m.p. 114°. When heated with acids or alkalis, it is hydrolysed, giving aniline and acetic acid.

$$C_6H_5NH\boxed{COCH_3 + HO}H \longrightarrow C_6H_5NH_2 + CH_3COOH$$

Uses. Acetanilide has long been used as febrifuge under the name of *antifebrin*, but now it has been replaced by more effective and less toxic medicines. It is a useful intermediate in reactions where the NH_2 group needs to be 'protected'.

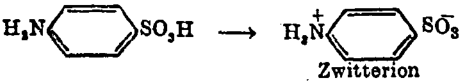
Sulphanilic acid, *p-aminobenzenesulphonic acid*, p-$NH_2.C_6H_4.SO_3H$. It may be prepared by heating aniline with fuming sulphuric acid. It is obtained commercially by 'baking' aniline sulphate to about 200°. The mechanism of the reaction is believed to be as follows :



Aniline sulphate Phenylsulphamic acid Sulphanilic acid

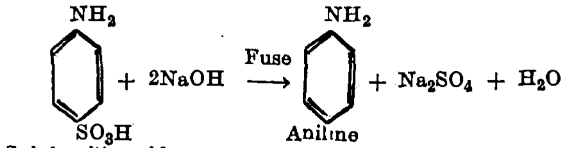
Properties. Sulphanilic acid is a white crystalline solid, m.p. 288° with decomposition. It is almost insoluble in cold water but dissolves fairly readily in hot water.

Since in sulphanilic acid molecule we have an acid and a basic group existing side by side, it forms an internal salt or *zwitterion*.



Zwitterion

Sulphanilic acid forms salts with strong bases but does not do so with acids. This is due to the strong acid nature of the SO_3H group which completely neutralises the basic NH_2 group. However, the SO_3H group is loosened by the presence of amino group in the para position. Thus sulphanilic acid when fused with soda-lime yields aniline, the SO_3H being replaced by hydrogen.

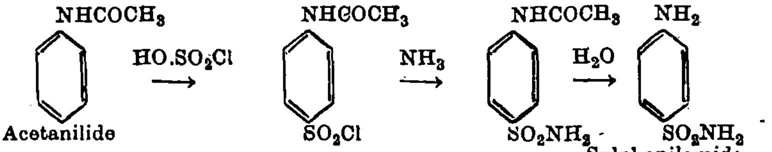


Sulphanilic acid Aniline

The SO_3H group can also be replaced by NO_2 group on treatment with nitric acid. Sulphanilic acid may be diazotized.

Uses. Sulphanilic acid is a valuable dye intermediate. Its substituted amides form the sulphanilamide drugs.

Sulphanilamide, *p-aminobenzenesulphonamide.* It is prepared by reacting acetanilide with chlorosulphonic acid, treating with ammonia to form the sulphonamide, and subsequent hydrolysis of the acetyl group.

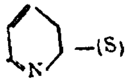


Acetanilide Sulphanilamide

Sulphanilamide is a white crystalline solid, m.p. 166·5°. It has recently come into great prominence in the medical field. Sulphanilamide and its derivatives have a remarkable action in curing bacterial infectious diseases such as pneumonia, meningitus, gonorrhoea, dysentery and typhoid.

Some of its more important derivatives (**Sulpha drugs**) which have revolutionised the treatment of bacterial infections are :

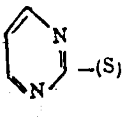
(S) stands for $—NHSO_2.C_6H_4NH_2$



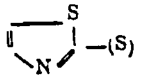
Sulphapyridine
(1914)

$$H_2N—\overset{\overset{NH}{\|}}{C}—(S)$$

Sulphaguanidine
(1940)

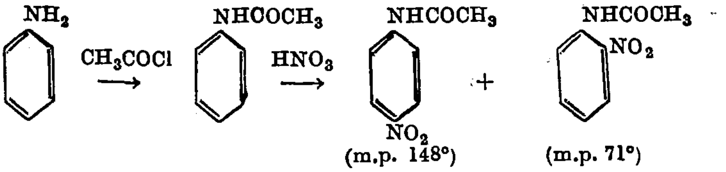


Sulphadiazine
(M & B 693)



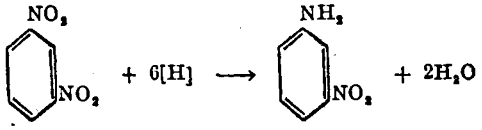
Sulphathiazol
(1942)

Nitroanilines, $C_6H_4(NO_2).NH_2$. *o*-Nitroaniline and *p*-nitroaniline are prepared by nitrating aniline after protecting the NH_2 group.

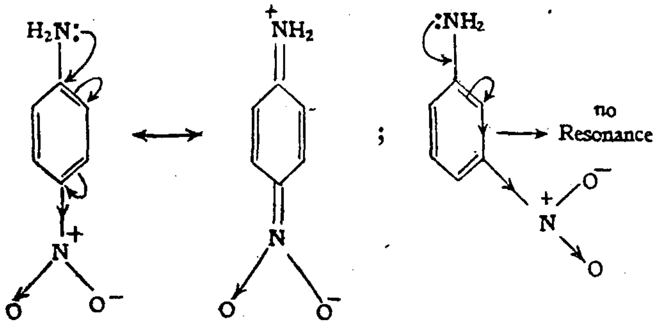


The nitroacetanilides are separated by filtering off the solid isomer, while the *p*-isomer is kept in the liquid state. After separation the nitroanilines are liberated by hydrolysis with alkali.

m-Nitroaniline is prepared by the partial reduction of *m*-dinitrobenzene with ammonium sulphide.

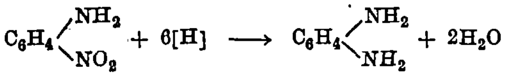


Properties. All the three isomeric nitroanilines are solids. *o*-nitroaniline, m.p. 71° ; *p*-nitroaniline, m.p. 148° ; *m*-nitroaniline, m.p. 114°. They are sparingly soluble in water but dissolve readily in alcohol. The nitro group neutralises the basic character of the amino group almost completely by making the lone pair of N atom less readily available for co-ordination with a proton. The argument extended in favour of the above is that the nitro group is highly electronegative and due to its inductive effect, pulls the lone pair on nitrogen atom into the ring. Nitro group is most effective when present in the ortho and para positions.



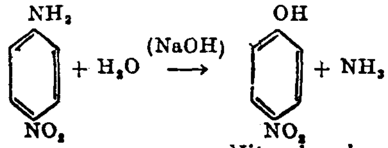
p-Nitroaniline *m*-Nitroaniline

Nitroanilines are weaker bases than aniline. On reduction with a metal and acid, they form the respective phenylenediamines.



$$C_6H_4\begin{matrix}\diagup NH_2\\ \diagdown NO_2\end{matrix} + 6[H] \longrightarrow C_6H_4\begin{matrix}\diagup NH_2\\ \diagdown NH_2\end{matrix} + 2H_2O$$

o- and *p*-Nitroanilines, but not *m*-, when boiled when aqueous sodium hydroxide yield nitrophenols.

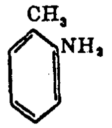


p-Nitrophenol

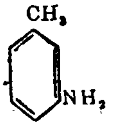
m-Nitroaniline, when nitrated with nitric and sulphuric acids, forms 2, 3, 4, 6-tetranitroaniline which is used as an explosive (T.N.A).

TOLUIDINES, AMINOTOLUENES, $CH_3.C_6H_4.NH_2$

The three aminotoluenes are known as *toluidines*.



o-Toluidine

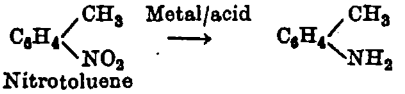


m-Toluidine

p-Toluidine

These are isomeric with benzylamine.

They are prepared by reducing the corresponding nitrotoluenes with a metal and acid.



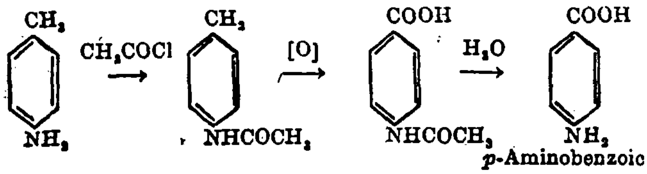
$$C_6H_4\begin{matrix}\diagup CH_3\\ \diagdown NO_2\end{matrix} \xrightarrow{\text{Metal/acid}} C_6H_4\begin{matrix}\diagup CH_3\\ \diagdown NH_2\end{matrix}$$

Nitrotoluene

Properties. o- and m-Toluidines are colourless oily liquids, b.p. 200° and 203° respectively. p-Toluidine is a white crystalline solid, m.p. 45°, b.p. 200·4°. All toluidines are insoluble in water and soluble in most organic solvents. They are poisonous.

The properties of the NH_2 group are not greatly changed by the methyl group in the nucleus, and therefore, toluidines give all the reactions of aniline. They form salts and can be diazotized.

The oxidation of toluidines after protecting the NH_2 group by acetylation, and subsequent hydrolysis yields the corresponding aminobenzoic acids.

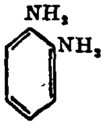


p-Aminobenzoic acid

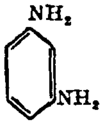
This could be employed to distinguish toluidines from the isomeric benzylamine, which on oxidation forms benzoic acid. o- and p-Toluidines are important dye intermediates.

DIAMINES (*Diaminobenzenes*)

The diaminobenzenes are also called *phenylenediamines*.



o-Phenylenediamine

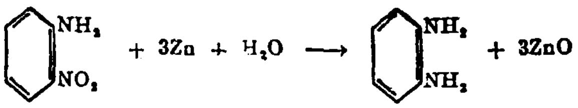


m-Phenylenediamine

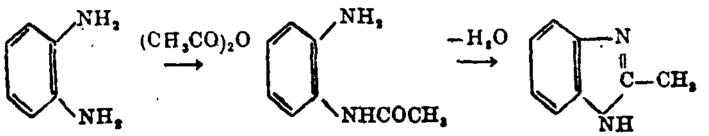
p-Phenylenediamine

o-PHENYLENEDIAMINE, 1, 2-DIAMINOBENZENE

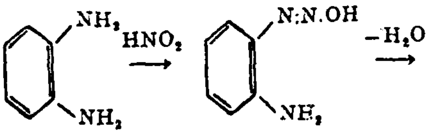
It is prepared by reducing *o*-nitroaniline with zinc dust and sodium hydroxide solution :



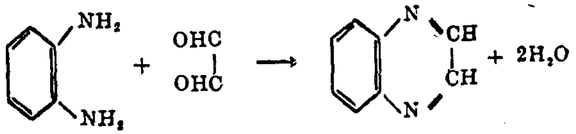
o-Phenylenediamine is a colourless crystalline solid, m.p. 103°. It quickly turns brown in air due to oxidation. It gives all the reactions of the nuclear NH_2 group in duplicate. Owing to the close proximity of the two amino groups, its characteristic reaction is the formation of five and six-membered heterocyclic compounds with suitable reagents. Thus :



Intermediate Methylbenziminazole



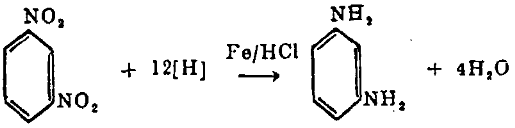
Benztriazole



Glyoxal Quinoxaline

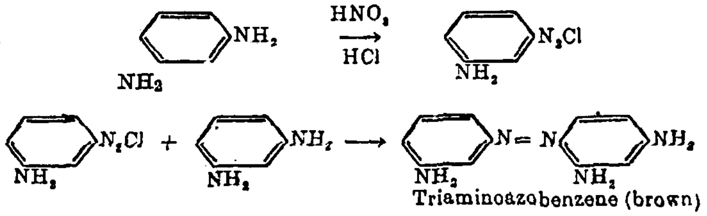
m-PHENYLEZEDIAMINE, 1, 3-DIAMINOBENZENE

It is best prepared by the reduction of *m-dinitrobenzene*, with iron and hydrochloric acid.



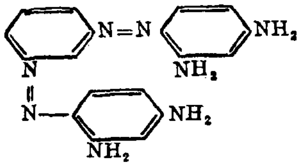
m-Phenylenediamine is a white crystalline solid, m.p. 63°, turning brown in air. It is a diacid base and gives the usual reactions of amino-compounds twice over. Its most characteristic reaction is the formation of the brown dye **Bismarck Brown** by the action of nitrous acid on its aqueous solution. Bismarck Brown is chiefly a mixture of the two brown dyes produced as follows.

(1) *Monoazo dye* : One NH_2 is diazotized which couples with another molecule of the diamine.



Triaminoazobenzene (brown)

(2) *Diazo dye*: Both NH_2 groups are diazotised which couple with two different molecules of the diamine, giving a diazo dye.

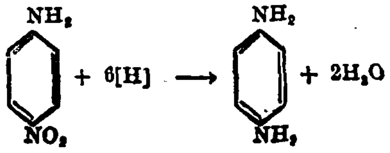


(Brown)

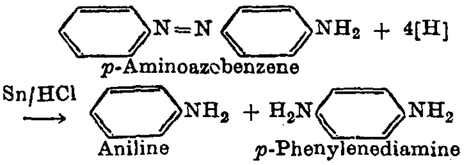
This reaction is used to detect and estimate small amounts of nitrites in drinking water as also a delicate test for nitrites in the laboratory. Bismarck Brown is a dye of considerable merit and is used for making boot polishes.

p-PHENYLENEDIAMINE, 1, 4, DIAMINOBENZENE

Like the *o*-isomer it is obtained by the reduction of the corresponding nitroaniline.



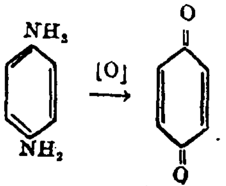
It may also be obtained conveniently by the reduction of *p*-aminoazobenzene.



p-Aminoazobenzene

Aniline *p*-Phenylenediamine

p-Phenylenediamine is a white crystalline solid, m.p. 147°. It is particularly susceptible to oxidation. When oxidised with potassium dichromate and sulphuric acid, it forms *p*-quinone.



p-Quinone

p-Phenylenediamine is an excellent photographic developer. It is also used as a hair dye since it is readily oxidised to a brown-black dye in alkali solution.

SECONDARY AMINES

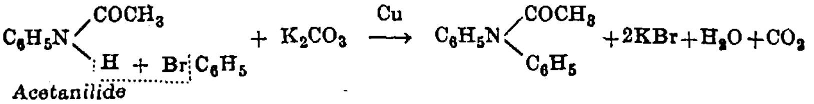
They may be purely aromatic or mixed aliphatic-aromatic according as both the hydrocarbon radicals attached to the N atom are aromatic or one aliphatic and the other aromatic.

DIPHENYLAMINE, $(C_6H_5)_2NH$

Preparation. It may be prepared : (1) By heating phenol with aniline in the presence of zinc chloride at 200°.

$$C_6H_5OH + C_6H_5NH_2 \xrightarrow{ZnCl_2} (C_6H_5)_2NH + H_2O$$

(2) By heating acetanilide with bromobenzene and potassium carbonate in the presence of copper powder.



$$C_6H_5N\begin{matrix}\diagup COCH_3\\ \diagdown H\end{matrix} + Br C_6H_5 + K_2CO_3 \xrightarrow{Cu} C_6H_5N\begin{matrix}\diagup COCH_3\\ \diagdown C_6H_5\end{matrix} + 2KBr + H_2O + CO_2$$

Acetanilide

$$(C_6H_5)_2N\,COCH_3 + HOH \longrightarrow (C_6H_5)_2NH + CH_3COOH$$

(3) By heating aniline and its hydrochloride at 260° under pressure (*Commercial*).

$$C_6H_5NH_3Cl + C_6H_5NH_2 \xrightarrow{260°} (C_6H_5)_2NH + NH_4Cl$$

Properties. Diphenylamine is a white, pleasant-smelling crystalline solid, m.p. 54°. It is practically insoluble in water but dissolves readily in alcohol and ether. In addition to the other usual reactions of aliphatic secondary amines, it shows the following reactions.

(1) It is a weaker base than aniline, since it contains two phenyl groups against one in the latter, it forms salts which are completely hydrolysed in solutions.

(2) When heated with sodium or sodamide, it forms metallic derivatives more readily than does aniline.

$$(C_6H_5)_2NH + Na \longrightarrow (C_6H_5)NNa + \frac{1}{2}H_2$$

(3) It reacts with nitrous acid to form nitrosamine.

$$(C_6H_5)_2N\boxed{H + HO}NO \longrightarrow \underset{\text{Diphenylnitrosamine}}{(C_6H_5)_2N.NO} + H_2O$$

(4) Its solutions in concentrated sulphuric acid give an intense blue colour with a trace of nitric acid or nitrates.

Uses. Diphenylamine is used : (1) as a reagent for testing nitrates as also an internal indicator in oxidation titrations ; (2) as a stabilizer for explosives ; (3) in high-boiling baths ; and (4) for making certain dyes.

METHYLANILINE PHENYLMETHYLAMINE, $C_6H_5.NH.CH_3$

Methylaniline is a mixed aliphatic-aromatic amine It may be obtained by the action of methyl iodide on aniline but it is prepared industrially by the following methods.

(1) By heating aniline and methyl alcohol together with some sulphuric acid under pressure.

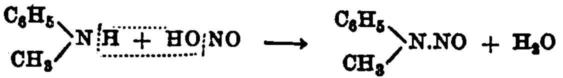
$$C_6H_5NH_2 + CH_3OH \xrightarrow[\text{pressure}]{H_2SO_4} C_6H_5.NH.CH_3 + H_2O$$

(2) By condensing aniline with formaldehyde and reducing the product with zinc and caustic soda. This method gives pure methylaniline and has been introduced recently.

$$C_6H_5N\boxed{H_2 + O}{=}CH_2 \longrightarrow C_6H_5N{=}CH_2 + H_2O$$

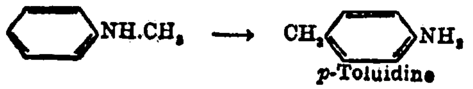
$$C_6H_5N{=}CH_2 + 2[H] \longrightarrow C_6H_5.NH.CH_3$$

Properties. Monomethylaniline is a colourless liquid, b.p. 194° It is a somewhat stronger base than aniline owing to partial aliphatic character. Its reactions are those typical of aliphatic secondary amines except the substitution reactions (in *o*- and *p*-positions) due to the presence of the benzene nucleus. Thus, it reacts with nitrous acid to form a pale-yellow nitrosamine which gives Liebermann's nitroso reaction.



$$\begin{matrix}C_6H_5\\CH_3\end{matrix}\!\!>N\boxed{H + HO}NO \longrightarrow \begin{matrix}C_6H_5\\CH_3\end{matrix}\!\!>N.NO + H_2O$$

When its hydrochloride is heated, the methyl group migrates to the para position of the nucleus giving *p*-toluidine.



p-Toluidine

Methylaniline is used for making certain dyes.

TERTIARY AMINES

They may be purely aromatic or mixed aromatic-aliphatic according as all the hydrocarbon radicals attached to the N atom are aryl, or some are aryl while the remaining are alkyl.

TRIPHENYLAMINE, $(C_6H_5)_3N$

Triphenylamine is a typical purely aromatic tertiary amine. It may be prepared : (1) By heating sodiodiphenylamine and bromobenzene at 300°.

$$(C_6H_5)_2NNa + C_6H_5Br \longrightarrow (C_6H_5)_3N + NaBr$$

(2) By heating diphenylamine with iodobenzene together with potassium carbonate and a little copper. (*Ullmann reaction*).

$$(C_6H_5)_2NH + C_6H_5I \xrightarrow[(K_2CO_3)]{Cu} (C_6H_5)_3N + HI$$

Properties. Triphenylamine is a colourless crystalline solid, m.p. 126·5°. Since the three negative phenyl groups completely neutralise the basic character of the trivalent N atoms, it has no basic properties and does not form salts with acids. It dissolves in warm concentrated sulphuric acid producing an intense blue colour.

DIMETHYLANILINE, PHENYL-DIMETHYLAMINE, $C_6H_5N(CH_3)_2$

It is a mixed aromatic-aliphatic amine and is by far the most important of the alkylanilines.

Preparation. Dimethylaniline may be obtained by the direct methylation of aniline with methyl chloride or with methyl sulphate.

$$C_6H_5NH_2 + 2CH_3Cl \longrightarrow C_6H_5N(CH_3)_2 + 2HCl$$

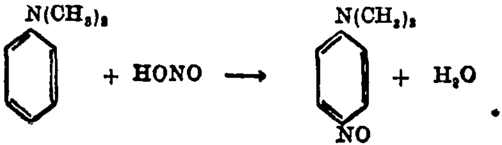
(2) It is prepared industrially by heating aniline with excess of methyl alcohol in the presence of sulphuric acid.

$$C_6H_5NH_2 + 2CH_3OH \xrightarrow{H_2SO_4} C_6H_5N(CH_3)_2 + 2H_2O$$

The excess of methyl alcohol suppresses the formation of monomethylaniline.

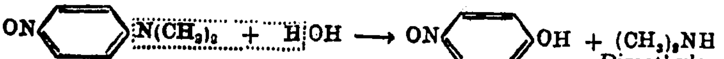
Properties. Dimethylaniline is an oily liquid, b.p. 193°. It is a slightly weaker base than aniline, forms salts with acids, and combines with alkyl halides to give quaternary ammonium salts. The hydrogen atom in the *para*-position of the benzene nucleus is very mobile and can be easily replaced by various groups or atoms.

(1) Dimethylaniline reacts with nitrous acid to form *p*-nitrosodimethylaniline.



p-Nitrosodimethylaniline

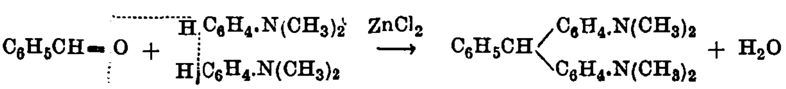
By boiling the nitrosodimethylaniline with alkali, the $N(CH_3)_2$ group is split off with the production of nitrosophenol and dimethylamine.



Dimethylamine

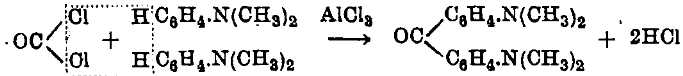
p-Nitrosophenol

(2) It undergoes condensation with benzaldehyde to form *tetramethyldiaminotriphenylmethane* which is an important dye intermediate.



$$C_6H_5CH{=}O + \begin{matrix} H.C_6H_4.N(CH_3)_2 \\ H\,C_6H_4.N(CH_3)_2 \end{matrix} \xrightarrow{ZnCl_2} C_6H_5CH\begin{matrix} C_6H_4.N(CH_3)_2 \\ C_6H_4.N(CH_3)_2 \end{matrix} + H_2O$$

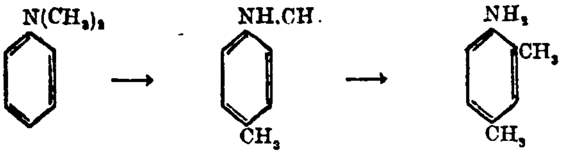
(3) It reacts with carbonyl chloride (*phosgene*) in the presence of aluminium chloride to form *Michler's ketone,* which is an intermediate in the production of dyes of the triphenylmethane class.



$$OC\begin{matrix} Cl \\ Cl \end{matrix} + \begin{matrix} H\,C_6H_4.N(CH_3)_2 \\ H\,C_6H_4.N(CH_3)_2 \end{matrix} \xrightarrow{AlCl_3} OC\begin{matrix} C_6H_4.N(CH_3)_2 \\ C_6H_4.N(CH_3)_2 \end{matrix} + 2HCl$$

Michler's ketone

(4) When its hydrochloride is heated to 300° under pressure, one or both methyl groups wander from the N-atom into the nucleus forming a homologue of aniline.



Uses. Dimethylaniline is used : (1) for preparing dimethylamine, and (2) as a dye intermediate.

AROMATIC AMINES WITH NH_2 IN THE SIDE-CHAIN

BENZYLAMINE, $C_6H_5CH_2NH_2$

It is the simplest member of the class. It is isomeric with toluidines.

Preparation. Benzylamine may be prepared : (1) By the reduction of phenyl cyanide or benzaldoxime with sodium and alcohol.

$$C_6H_5.C{\equiv}N + 4[H] \longrightarrow C_6H_5CH_2NH_2$$

$$C_6H_5CH{=}NOH + 4[H] \longrightarrow C_6H_5CH_2NH_2 + H_2O$$

(2) By heating benzyl chloride with alcoholic ammonia

$$C_6H_5CH_2Cl + NH_3 \longrightarrow C_6H_5CH_2NH_2 + HCl$$

(3) By Hofmann reaction on phenylacetamide.

$$C_6H_5CH_2CONH_2 \xrightarrow{Br_2/KOH} C_6H_5CH_2NH_2$$

Properties. Benzylamine is a colourless liquid, b.p. 185°, having ammoniacal odour. It is freely soluble in water and its aqueous solutions are alkaline to litmus. It gives all reactions of the aliphatic primary amines. Because the amino group is situated in the side-chain and is not under the direct influence of the phenyl group, benzylamine sharply differs from the amino-compounds in that (1) it is strongly basic ; (2) it does not form diazonium salts but gives benzyl alcohol when treated with nitrous acid.

$$C_6H_5CH_2NH_2 + HNO_2 \longrightarrow C_6H_5CH_2OH + N_2 + H_2O$$

and (3) it does not couple with diazonium salts.

On oxidation with potassium permanganate, it is converted to benzoic acid.

COMPARISON BETWEEN AROMATIC AND ALIPHATIC PRIMARY AMINES

AROMATIC AMINES	ALIPHATIC AMINES
1. Colourless liquids or solids having characteristic odour which is not ammoniacal.	1. Colourless gases or liquids, having ammoniacal odour.
2. Sparingly soluble in water giving neutral solutions.	2. Soluble in water giving alkaline solutions.
3. Combine with acids to form salts which are hydrolysed in water.	3. Form salts which are *not* hydrolysed in water.
4. Form metallic derivatives when heated with Na or K.	4. Form metallic derivatives when heated with Na or K.
5. React with alkyl halides to form mixed secondary and tertiary amines.	5. React with alkyl halides to form secondary and tertiary amines.
6. React with acyl chlorides to form *N*-acyl derivatives.	6. React with acyl chlorides to form *N*-acyl derivatives.
7. Give carbylamine reaction.	7. Give carbylamine reaction.
8. React with aromatic aldehydes to form Schiff's bases.	8. React with aromatic aldehydes to form Schiff's bases.
9. React with nitrous acid in cold to form diazonium salts.	9. React with nitrous acid to form alcohols.
10. React with Grignard reagents to produce hydrocarbons.	10. React with Grignard reagents to produce hydrocarbons.
11. Give readily substitution reactions in the benzene nucleus.	11. Do not permit substitution in the hydrocarbon radical.

QUESTIONS

1. Give the general methods of introducing NH_2 group in the benzene nucleus and describe the general characteristics of aromatic amino-compounds.

2. Compare and contrast the properties of aliphatic and aromatic primary amines. What is the action of nitrous acids on : (*a*) monomethylaniline, and (*b*) dimethylaniline ?

3. How are the toluidines prepared ? How can they be distinguished from the isomeric benzylamine ?

4. How would you prepare *o*-phenylenediamine and what are its chief chemical properties ?

5. Give the preparation, properties and uses of diphenylamine and dimethylaniline.

6. Discuss the properties and reactions of aniline from modern point of view. (*Panjab B.Sc. III, 1967*)

7. What is 'Diazotisation' ? Starting with aniline show how you would obtain the following. (Give equations for reactions).

(*i*) Phenol, (*ii*) Iodobenzene, (*iii*) Benzoic acid, (*iv*) Phenyl hydrazine, (*v*) *Sym*—tribromobenzene. (*Poona B.Sc. II, 1967*)

8. How are the primary aromatic amino compounds prepared ? Starting from aniline, how would you obtain the following compounds : (*a*) Phenyl hydrazine, (*b*) Sulphanilic acid, (*c*) *p*-Nitroaniline, (*d*) Sulphanilamide, (*e*) *p*-Amino azobenzene. (*Panjab B.Sc., 1968*)

9. How is aniline prepared in the laboratory ? Describe its important chemical properties and uses. (*Osmania B.Sc., 1968*)

10. Describe the methods of preparation of aromatic primary amines on a large scale.

How will you convert aniline into :—

(*a*) Dimethylaniline, (*b*) Sulphanilic acid, (*c*) Phenylhydrazine ? (*Bombay B.Sc., 1968*)

11. Starting from benzene how would you obtain aniline? Give equations for the reactions involved at different stages. What is diazotization. State its utility. (*Dibrugarh B.Sc., 1968*)

12. How is aniline prepared in the laboratory ? Write its reactions with (*a*) aqueous bromine (*b*) Benzoyl chloride (NaOH) (*c*) sodium nitrite and HCl followed by treatment with alkaline β-naphthol (*d*) chloroform and KOH (*e*) Benzenesulphonic acid in cold (*f*) Benzaldehyde. (*Udaipur B.Sc., 1969*)

13. How is aniline prepared ? Why is aniline weakly basic ? How are (*i*) Sulphanilic acid (*ii*) Benzenediazonium chloride (*iii*) *p*-benzoquinone prepared from aniline ? (*Vankateswara B.Sc., 1969*)

14. Give an account of the preparation of aniline on the laboratory scale. Give the reactions of aniline with (*i*) conc. H_2SO_4 (*ii*) Bromine water (*iii*) Acetly chloride (*iv*) Benzene diazonium chloride. (*Jammu & Kashmir B.Sc., 1969*)

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Diazonium Salts

CARL VON GRAEBE
(1841–1927)
German. Established the structure of alizarin and synthesised it. Verified the Erlenmeyer formula for naphthalene.

When primary aromatic amines are treated with nitrous acid in well-cooled acid solutions, they produce compounds known as *diazonium salts* (Griess, 1860). Thus :

$$\mathrm{Ar.NH_2 + HNO_2 + HCl \xrightarrow{0^\circ} Ar.N_2Cl + 2H_2O}$$

These have been assigned the structure

$$[\mathrm{Ar{-}N{\equiv}\overset{+}{N}}]\ \overset{-}{\mathrm{Cl}} \qquad \mathit{Cf.}\ \underset{\text{Ammonium chloride}}{[\mathrm{H{-}N{\equiv}\overset{+}{H_3}}]\ \overset{-}{\mathrm{Cl}}}$$

which is very much similar to that of ammonium chloride. The name DIAZONIUM was coined from '*di*' meaning two ; '*azo*' meaning nitrogen (French, *azote*=nitrogen ; and '*onium*' from ammonium. It indicates the presence of two nitrogen atoms in the molecule and the marked similarity of these compounds to ammonium salts.

The diazonium salts are among the most useful reagents in the whole field of synthetic organic chemistry. They are important technically in the manufacture of azo dyes.

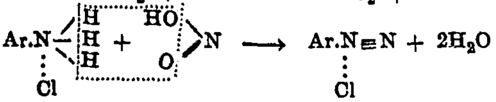
PREPARATION

Diazonium salts are prepared by the interaction of sodium nitrite, and an inorganic acid and a primary aromatic amine at about 0°. This reaction called **Diazotization**, proceeds by the following steps:

(1) $$Ar.NH_2 + HCl \longrightarrow \underset{\text{Hydrochloride}}{Ar.NH_3Cl}$$

(2) $$NaNO_2 + HCl \longrightarrow HNO_2 + NaCl$$

(3)



$$\underset{\underset{Cl}{\vdots}}{Ar.NH_3} + HO.N{=}O \longrightarrow \underset{\underset{Cl}{\vdots}}{Ar.N{\equiv}N} + 2H_2O$$

Diazonium salt

Preparation of Benzenediazonium chloride. Benzenediazonium chloride may be obtained by the addition of concentrated solution of 1 mole of sodium nitrite to 1 mole of aniline dissolved in excess of hydrochloric acid at about 0°.

$$C_6H_5NH_2 + NaNO_2 + HCl \xrightarrow{0°} \underset{\text{Benzenediazonium chloride}}{C_6H_5N_2Cl} + NaCl + 2H_2O$$

Dissolve 2 grams of aniline in 10 ml. of hydrochloric acid in a test tube and cool it by immersing in ice-bath. Then dissolve 2 grams of sodium nitrite in 10 mls. of water and also place it for cooling. When the temperature of both the solutions is about 0°C, add with constant stirring the nitrite solution in small proportions to the aniline solution which is throughout kept in the ice bath. When the reaction mixture on testing with a starch iodide paper gives a blue colour, it means that now there is a slight excess of nitrous acid and the diazotization is complete.

The diazonium salts are unstable and explosive substances and as a rule they are not isolated in the solid state. For synthetic purposes, they are prepared in aqueous solutions and used at once. If desired, the solid diazonium salts may be obtained from their aqueous solutions by addition of alcohol and ether in which they are insoluble.

PHYSICAL CHARACTERISTICS

(1) Diazonium salts are colourless crystalline compounds which turn brown on exposure to air.

(2) Many of them, particularly nitrates, are highly explosive.

(3) They are extremely soluble in water, sparingly soluble in alcohol and glacial acetic acid, and insoluble in ether.

(4) Their aqueous solutions are neutral to litmus and conduct electricity owing to the presence of ions. Thus :

$$C_6H_5N_2Cl \longrightarrow [C_6H_5N_2]^+ + \bar{Cl}$$

CHEMICAL CHARACTERISTICS

Diazonium salts are highly reactive compounds and give two types of reactions :

(i) *those in which the —N_2X group (X=an acid radical) is replaced by a new monovalent substituent with the simultaneous liberation of free nitrogen ; and*

(ii) *those in which the two nitrogen atoms are retained and converted into a more stable grouping.*

A large number of benzene derivatives can be thus prepared via diazonium salts. This will be illustrated by taking example of benzenediazonium chloride.

Reactions in which —N_2X is replaced

(1) **Replacement by H.** When an alcoholic solution of a diazonium salt is heated, the N_2X group is replaced by hydrogen, while the alcohol is oxidised to aldehyde.

$$CH_3CH_2OH \longrightarrow CH_3CHO + 2H$$
$$C_6H_5N_2Cl + 2H \longrightarrow C_6H_5.H + N_2 + HCl$$

Alternatively, the diazonium salts may be reduced with alkaline sodium stannite or formaldehyde.

This reaction provides a method for knocking out nuclear NH_2 or NO_2 groups.

(2) **Replacement by R.** When an alkaline solution of a diazonium salt is treated with aromatic hydrocarbons, N_2X is replaced by an aryl radical. Thus :

$$C_6H_5N_2Cl + C_6H_5H \xrightarrow{NaOH} \underset{\text{Diphenyl}}{C_6H_5.C_6H_5} + N_2 + HCl$$

(3) **Replacement by OH.** When the aqueous solution of a diazonium salt is boiled, a phenol is obtained. Thus :

$$C_6H_5N_2Cl + HOH \longrightarrow \underset{\text{Phenol}}{C_6H_5OH} + N_2 + HCl$$

(4) **Replacement by OR.** When diazonium salts are heated with alcohols, mixed ethers are also produced along with reaction (1).

$$C_6H_5N_2Cl + HOC_2H_5 \longrightarrow \underset{\text{Ethylphenyl ether}}{C_6H_5.O.C_2H_5} + N_2 + HCl$$

(5) **Replacement by Cl and Br.** When a diazonium salt is added to a solution of cuprous chloride or cuprous bromide in the corresponding halogen acid, chloro and bromo derivatives are obtained respectively. (**Sandmeyer's reaction**).

$$C_6H_5N_2Cl \xrightarrow{Cu_2Cl_2/HCl} \underset{\text{Chlorobenzene}}{C_6H_5Cl} + N_2$$

$$C_6H_5N_2Cl + HBr \xrightarrow{Cu_2Br_2/HBr} \underset{\text{Bromobenzene}}{C_6H_5Br} + N_2 + HCl$$

The above reactions can also be carried in cold by using copper powder in place of the cuprous halides (Gattermann, 1890).

Mechanism:

The reaction mechanism in the case of the conversion of aromatic diazonium compounds to aryl halides appears to proceed through aryl radicals since the reaction mixture may be used to initiate the polymerization of arylnitrite. The 'cuprous chloride' is actually $Cu\bar{C}l_2$.

$$CuCl + Cl \longrightarrow Cu\bar{C}l_2$$

$$Ar.\overset{+}{N_2} + CuCl_2^- \xrightarrow{\text{Slow}} N_2 + \dot{Ar} + CuCl_2$$

The final stage is a radical displacement reaction by the aryl radical on the chlorine atom of the cupric chloride.

$$\dot{Ar} + Cl{-}Cu{-}Cl \xrightarrow{\text{Fast}} ArCl + CuCl$$

(6) **Replacement by I.** Iodo-compounds are obtained by boiling diazonium salts with aqueous potassium iodide. Thus :

$$C_6H_5N_2Cl + KI \longrightarrow \underset{\text{Iodobenzene}}{C_6H_5I} + N_2 + KCl$$

This is the best method of introducing an iodine atom in the nucleus.

(7) **Replacement by CN.** When the solution of a diazonium salt is added to a solution of cuprous cyanide dissolved in aqueous potassium cyanide, or treated with aqueous potassium cyanide in the presence of copper powder, cyanides or nitriles are produced.

$$C_6H_5N_2Cl + KCN \longrightarrow \underset{\text{Phenyl cyanide}}{C_6H_5CN} + N_2 + KCl$$

This reaction is a special case of Sandmeyer's and Gattermann's reaction. It is of great importance for synthesising aromatic acids which are obtained by hydrolysing the cyanides.

(8) **Replacement by NO₂.** When a diazonium salt is treated with nitrous acid in the presence of cuprous oxide, nitro compounds are produced.

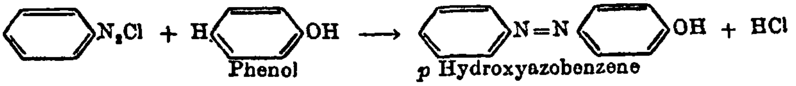
$$C_6H_5N_2Cl + HNO_2 \xrightarrow{Cu_2O} \underset{\text{Nitrobenzene}}{C_6H_5NO_2} + N_2 + HCl$$

Reactions in which N-atoms are retained

(9) **Reduction to Hydrazines.** When reduced with stannous chloride and hydrochloric acid, diazonium salts form hydrazines.

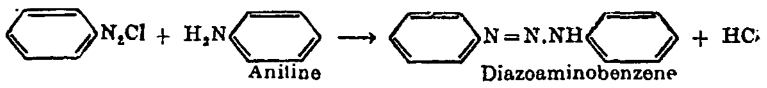
$$\underset{\underset{Cl}{\vdots}}{C_6H_5.N{\equiv}N} \xrightarrow{+2H} \underset{\text{Intermediate}}{\underset{Cl\quad H}{C_6H_5.N{=}NH}} \xrightarrow{+2H} \underset{\text{Phenylhydrazine}}{C_6H_5.NH.NH_2} + HCl$$

(10) **Coupling.** Diazonium salts couple with phenols in the presence of alkali at ice-bath temperature. Thus :



Phenol p Hydroxyazobenzene

Primary and secondary amines when treated with diazonium salts in weakly acid solution, in the presence of sodium acetate, couple as the *N*-atom to form diazoamino-compounds. Thus :



Tertiary amines, such as dialkylanilines, couple directly with nucleus, like the phenols.

STRUCTURE OF DIAZONIUM SALTS

(1) Diazonium salts have been shown to possess the molecular formula $\mathrm{ArN_2.Cl}$.

(2) They dissolve in water giving neutral solutions which conduct electricity. Hence they are ionised salts.

(3) They form a precipitate of silver chloride when treated with silver hydroxide, which shows the existence of chloride ions in their molecule.

(4) From the above considerations, the diazonium salts may be assigned the following structures :

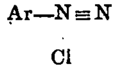
$$\underset{\mathrm{I}}{[\mathrm{Ar{-}N{\equiv}N}]^{+}\overline{\mathrm{Cl}}} \qquad \text{or} \qquad \underset{\mathrm{II}}{[\mathrm{Ar{-}N{=}N}]^{+}\overline{\mathrm{Cl}}}$$

Of these, formula II is untenable as the grouping Ar—N = N has no surplus electrons and is incapable of acting as positive ion. On the other hand, the formula I may represent the correct structure since the grouping $\mathrm{Ar{-}\overset{*}{N}{\equiv}\overset{\bullet}{N}}$ has one surplus electron with the *N*-atom marked by asterisk.

$$\mathrm{Ar} \times \underset{9}{\dot{\mathrm{N}}}\,\vdots\,\vdots\,\dot{\mathrm{N}}: \qquad \mathrm{Ar} \times \underset{8}{\dot{\mathrm{N}}}\,\vdots\,\underset{7}{\dot{\mathrm{N}}}:$$

(The figures indicate the number of electrons in the outermost shell)

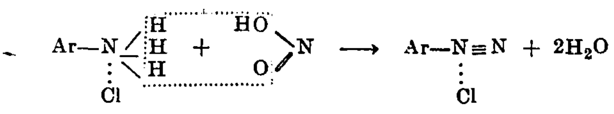
(5) Diazonium salts may, therefore, be written as



$$\underset{\mathrm{Cl}}{\mathrm{Ar{-}N{\equiv}N}} \qquad \text{(Bromstrand, 1869)}$$

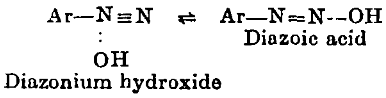
where the dotted line signifies an electrovalent linkage.

(6) The above structure of diazonium salt is supported by its formation from an aromatic-amine hydrochloride and nitrous acid.



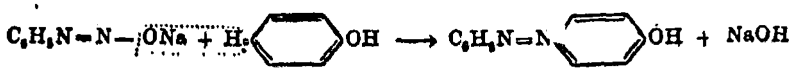
$$\mathrm{Ar{-}N(H)(H)(H)\,:\,Cl} + \mathrm{HO{-}N{=}O} \longrightarrow \underset{\mathrm{Cl}}{\mathrm{Ar{-}N{\equiv}N}} + 2\mathrm{H_2O}$$

(7) This structure, however, fails to explain the formation of diazo-compounds by coupling with phenols and amines. It has been suggested (Hodgson and Marsdon, 1945) that the following equilibrium exists in aqueous solution.

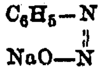


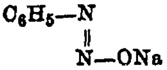
$$\underset{\mathrm{OH}}{\mathrm{Ar{-}N{\equiv}N}} \rightleftharpoons \mathrm{Ar{-}N{=}N{-}OH}$$

In the presence of an acid, the diazonium hydroxide reacts to form the diazonium salt, while in alkali solutions the diazoic acid forms metallic salts (*diazotates*). Thus it is in fact, the diazotates that couple with phenols and amines to give diazo-compounds.

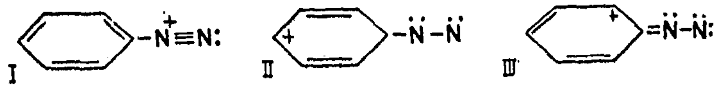


Hantzsch further believes that the diazotates show geometrical isomerism and it is the *syn* form which is reactive.


$$\begin{array}{l} C_6H_5-N \\ \quad\ \ \| \\ NaO-N \end{array}$$
'*Syn*' form


$$\begin{array}{l} C_6H_5-N \\ \quad\ \ \| \\ \quad\ \ N-ONa \end{array}$$
'*Anti*' form

(8) According to modern views, diazonium ion, $C_6H_5\overset{+}{N}_2$, is a resonance hybrid of several forms :



This explains the stability of the aromatic diazonium salts. Aliphatic diazonium ions are incapable of yielding analogous structures and are unstable.

Phenylhydrazine, $C_6H_5NH.NH_2$

It may be regarded as derived from hydrazine, $NH_2.NH_2$, by replacement of one of the hydrogen atoms by the phenyl group.

Preparation. Phenylhydrazine is prepared by reducing benzene diazonium chloride with stannous chloride and hydrochloric acid, or with sodium sulphate.

$$C_6H_5N_2Cl + 4[H] \longrightarrow \underset{\text{Phenylhydrazine hydrochloride}}{C_6H_5.NH.NH_2.HCl}$$

The product on treatment with alkali liberates the free base.

Properties. Phenylhydrazine is a colourless, oily liquid, b.p. 241°. It has an unpleasant odour, suggestive of aniline, and quickly darkens in air owing to oxidation. It is difficultly soluble in water, but dissolves readily in organic solvents. It is very poisonous and attacks skin. Its reactions are given below :

(1) Phenylhydrazine is strongly basic in character and forms well-defined salts such as phenylhydrazine hydrochloride, $C_6H_5NH.NH_2.HCl$.

(2) When warmed with alkaline copper sulphate solution, it splits out nitrogen to form benzene.

$$C_6H_5NH.NH_2 + 2CuSO_4 \longrightarrow C_6H_6 + Cu_2O + N_2 + 2H_2SO_4$$

This is an alternative method of replacing the diazonium group by hydrogen.

(3) When reduced with zinc-dust and hydrochloric acid, the two N-atoms part company to form aniline and ammonia.

$$C_6H_5.NH.NH_2 + 2[H] \xrightarrow{Zn/HCl} C_6H_5.NH_2 + NH_3$$

For the same reason, phenylhydrazine acts as a mild oxidising agent.

(4) It reacts with aldehydes and ketones to form phenylhydrazones and with simple sugars to form osazones ; these derivatives being well defined crystalline substances are used for the identification of the original carbonyl compounds.

Uses. Phenylhydrazine is used : (1) as a reagent for the identification of aldehydes, ketones and sugars ; (2) as a mild oxidising agent ; (3) for making antipyrine and some important dyestuffs.

DIAZOAMINOBENZENE, $C_6H_5N{=}N.NH.C_6H_5$

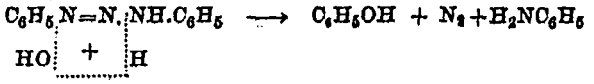
Preparation. It is obtained by the action of benzenediazonium chloride with aniline in weakly acid solution, in presence of sodium acetate.

$$C_6H_5N_2Cl + NH_2.C_6H_5 \longrightarrow C_6H_5.N{=}N.NH.C_6H_5 + HCl$$

It may be prepared conveniently by treating aniline hydrochloride solution with one-half of its equivalent of sodium nitrite, and then adding sodium acetate. Thus one-half of aniline is converted into diazonium salt which then reacts with the remaining half to form diazoaminobenzene as shown above.

Properties. Diazoaminobenzene forms bright yellow crystals, m.p. 98°. It is almost insoluble in water but dissolves readily in alcohol and ether. It is a feeble base and does not form salts with acids.

(1) When boiled with water for a long time, it splits out nitrogen to form phenol and aniline.



$$\underset{HO\ +\ H}{C_6H_5.N{=}N.NH.C_6H_5} \longrightarrow C_6H_5OH + N_2 + H_2NC_6H_5$$

(2) It is converted to benzenediazonium chloride on treatment with nitrous acid and hydrochloric acid.

$$\underset{\text{Diazoaminobenzene}}{C_6H_5N{=}N.NH.C_6H_5} + HNO_2 + 2HCl \longrightarrow 2C_6H_5N_2Cl + 2H_2O$$

(3) It rearranges to *p*-aminoazobenzene on heating with aniline hydrochloride (*catalyst*), $C_6H_5N_2$ group migrating to the para position.

Diazoaminobenzene　　*p*-Aminoazobenzene

QUESTIONS

1. What are the diazonium salts ? Why are they so named ?

2. What is meant by diazotization ? How are diazo compounds prepared in solution ? Derive the constitution of benzenediazonium chloride and outline the reactions in which the compound can be employed.

3. What are the conditions necessary for the preparation of diazonium salts ? Starting with an aqueous solution of diazobenzene chloride how may the following be prepared : benzene, phenol, benzoic acid, phenylhydrazine, and *p*-aminoazobenzene.

4. How is benzenediazonium sulphate prepared ? Give its properties and reactions. Discuss its constitution and give its uses.

5. Describe the action of nitrous acid on aniline salt and compare this with its action upon ethylamine and diethylamine respectively. How would you obtain benzene, phenol and chlorobenzene from aniline through the above reactions.

6. Give the preparation of benzenediazonium chloride. Discuss its constitution. Illustrate the use of this compound in the preparation of (*a*) phenyl hydrazine, (*b*) *p*-aminoazobenzene and (*c*) Phenyl iodide. (*Bombay B.Sc., 1967*)

7. What is diazotisation ? How would you prepare an aqueous solution of benzene-diazonium chloride ? Discuss its synthetic importance. (*Panjab B.Sc. II, 1968*)

8. What is diazotisation ? Describe fully the applications of the reaction in the laboratory and in industry. (*Bombay B.Sc., 1968*)

9. How is aniline diazotized ? Describe the reactions of benzene diazonium chloride. (*Madurai B.Sc., 1968*)

10. How are diazonium salts prepared in the laboratory ? Mention the important synthetic uses of benzenediazonium chloride. (*Utkal B.Sc., 1968*)

11. What are the chief requirements for a compound to be of synthetic value ? Give an account of the preparation and properties of benzene diazonium chloride indicating its synthetic importance. (*Aligarh B.Sc., 1968*)

12. Discuss briefly "Benzenediazonium chloride and its use as a starting point in organic synthesis." (*Ceylon B.Sc., 1968*)

13. How is benzenediazonium chloride prepared ? Discuss briefly the reaction of aromatic diazonium compounds in which the nitrogen (*i*) is retained (*ii*) is replaced by hydrogen, hydroxyl and halogen. (*Viswa Bharati B.Sc., 1969*)

14. Describe the preparation of benzenediazonium chloride. How are the following obtained from it ?

(*a*) Bromobenzene (*b*) Benzoic acid (*c*) phenyl hydrazine. (*Marathwada B.Sc., 1969*)

15. What do you understand by diazotisation. Show how with the help of this reaction various substituents can be introduced into the benzene nucleus. (*Kurukshetra B.Sc., 1969*)

43

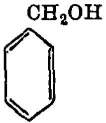
Aromatic Hydroxy Derivatives

STANISLAO CANNIZZARO
(1826—1910)

Italian Organic Chemist. He is best known for developing Cannizzaro Reaction. He did notable work in introducing Avogadro hypothesis to his scientific colleagues.

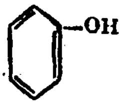
Aromatic hydroxy derivatives are of two types : (1) **phenols**, in which the OH group is attached to the nucleus; and (2) **aromatic alcohols**, in which the OH group is attached to the side-chain.

phenol
(*A phenol*)

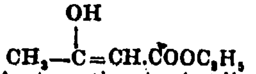


Benzyl alcohol
(An aromatic alcohol)

While aromatic alcohols resemble closely with aliphatic alcohols, phenols differ from them in being acidic and show many characteristic reactions. The peculiar behaviour of phenols is attributed to the fact that the OH in their molecule is linked to a doubly bonded carbon, instead of to a singly bonded carbon in alcohols. This view is supported by the 'phenolic behaviour' of acetoacetic ester which has a similarly linked OH group.



Phenol



$$CH_3-\overset{OH}{\overset{|}{C}}=CH.COOC_2H_5$$

Acetoacetic ester (*enolic*)

CH_3-CH_2-OH

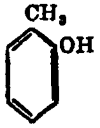
Ethyl alcohol

1. PHENOLS

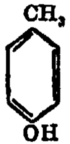
Phenols are derived from aromatic hydrocarbons by replacing one or more H-atoms of the nucleus by hydroxyl groups. They are classified as *mono, di* and *trihydric* phenols according as they contain one, two or three hydroxyl groups. Many phenols bear the names of historic origin.

Monohydric phenols :

Phenol,
Monohydroxybenzene

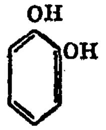


o-Cresol,
o-Hydroxytoluene

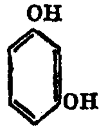


p-Cresol,
p-Hydroxy toluene

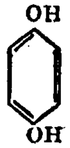
Dihydric phenols :



Catechol,
Dihydroxybenzene

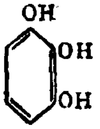


Risorcinol,
m-Dihydroxybenzene



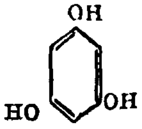
Quinol,
p-Dihydroxybenzene

Trihydric phenols :



Pyrogallol,
1, 2, 3-Trihydroxybenzene

Hydroxyquinone
1, 2, 4-Trihydroxybenzene



Phloroglucinol,
1, 3, 5-Trihydroxybenzene

Phenols are substances of great technical importance as they are used in the manufacture of dyes, drugs, explosives, plastics and disinfectants.

METHODS OF FORMATION

A number of phenols (phenol, cresols) occur in coal tar fractions and are recovered from them industrially by treatment with aqueous sodium hydroxide and then blowing carbon dioxide through the resulting solution. The phenols may be prepared synthetically by the following methods :

(1) **Fusion of sodium sulphonate with sodium hydroxide.** Phenols are commonly obtained by fusing together a mixture

of sodium salt of a sulphonic acid and sodium hydroxide. Thus :

$$\underset{\text{Sod. benzenesulphonate}}{C_6H_5SO_3Na} + 2NaOH \xrightarrow{\text{Fuse}} \underset{\text{Sodium phenolate}}{C_6H_5ONa} + Na_2SO_3 + H_2O$$

The melt is treated with a mineral acid to yield the free phenol.

$$2C_6H_5ONa + H_2SO_4 \longrightarrow 2C_6H_5OH + Na_2SO_4$$

(2) **Hydrolysis of diazonium salts.** Phenols are conveniently prepared by boiling a diazonium sulphate with water. Thus :

$$\underset{\substack{\text{Benzenediazonium}\\ \text{sulphate}}}{C_6H_5.N_2HSO_4} + H_2O \longrightarrow C_6H_5OH + N_2 + H_2SO_4$$

(3) **Hydrolysis of aryl halides.** Phenols may be formed by heating aryl chlorides with aqueous sodium hydroxide under pressure.

$$C_6H_5Cl + NaOH \xrightarrow[\text{pressure}]{300^\circ} C_6H_5OH + NaCl$$

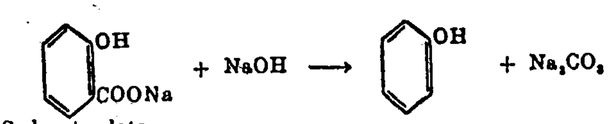
The reaction proceeds readily if an activating group (*nitro*) is present in the nucleus of the chloro compound.

(4) **From Grignard reagents.** Phenols may be formed by treating aryl Grignard reagents with oxygen and subsequent hydrolysis with a mineral acid.

$$\underset{\substack{\text{Phenylmagnesium}\\ \text{bromide}}}{C_6H_5MgBr} + \tfrac{1}{2}O_2 \longrightarrow C_6H_5OMgBr$$

$$C_6H_5OMgBr + H_2O \longrightarrow C_6H_5OH + HO.MgBr$$

(5) **Decarboxylation of phenolic acids.** When phenolic acids are distilled with soda-lime, they split out carbon dioxide to form phenols. Thus :



Sod. salicylate

PHYSICAL CHARACTERISTICS

(1) Phenols are colourless crystalline solids or liquids having a characteristic odour. They darken in air due to oxidation.

(2) They distil without decomposition and are steam-volatile.

(3) Phenols and cresols are sparingly soluble in water, while the *di-* and *trihydric* phenols are fairly soluble. They dissolve readily in alcohol and ether.

(4) Phenols are weekly acidic, their aqueous solutions showing a distinct acid reaction to litmus.

$$Ar.OH \longrightarrow Ar\bar{O} + \overset{+}{H}$$

(5) All phenols are toxic and have antiseptic properties.

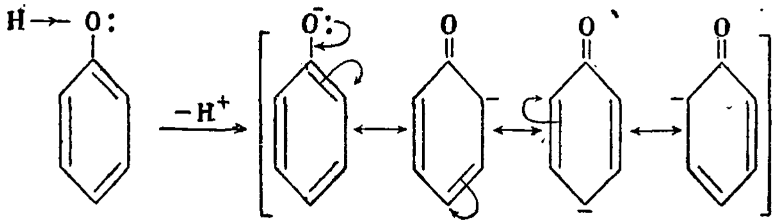
CHEMICAL CHARACTERISTICS

Phenols are made of one or more OH groups attached to the aromatic nucleus. At the OH groups, they give the usual replacement reactions of aliphatic alcohols. Phenols differ from alcohols in having a weakly acid character, which is attributed to the effect of the negative aromatic nucleus. The OH groups exert a reciprocal activating effect on the nucleus and hence phenols give substitution reactions (ortho and para to OH) much more readily than the parent hydrocarbons.

Phenols are acidic because of two reasons :

(*i*) Oxygen atom of the hydroxyl group linked with the benzene ring has a pronounced tendency to share its lone pair of electrons with the benzene ring.

(*ii*) Greater stability of the phenolate ion by resonance, got after the proton release.



Resonance stabilisation of phenolate ion.

Reactions of the OH Group

(1) **Action with Alkalis.** Phenols dissolve in sodium hydroxide or potassium hydroxide solutions forming salts known as **phenolates**, *phenates* or *phenoxides.*

$$C_6H_5OH + NaOH \longrightarrow \underset{\text{Sodium phenolate}}{C_6H_5ONa} + H_2O$$

Phenols do not decompose sodium carbonate or sodium bicarbonate showing that they are weaker bases than carbonic acid. For the same reason, phenols are liberated from phenolates by blowing carbon dioxide through their aqueous solutions. The non-reactivity of phenols with sodium bicarbonate may be made use of for the separation of mixture of phenols and carboxylic acids.

(2) **Action with Ferric chloride.** Many phenols give characteristic colorations with neutral ferric chloride solution due to the formation of complex iron salts. Thus, phenol gives *violet* ; resorcinol, *violet* ; catechol, *green* ; pyrogallol, *red* ; phloroglucinol, *dark violet* ; and so on.

(3) **Reduction with Zinc dust.** When distilled with zinc dust, phenols yield the parent hydrocarbons. Thus :

$$C_6H_5OH + Zn \longrightarrow C_6H_6 + ZnO$$

The reaction is employed to get the first clue to the structure of an unknown complex phenol.

(4) **Action with Alkyl halides.** Phenolates react with alkyl halides to form mixed aliphatic ethers. Thus :

$$\boxed{C_6H_5O\,\vdots\,Na + I\,\vdots}\,CH_3 \longrightarrow \underset{\text{Phenetole}}{C_6H_5OCH_3} + NaI$$

This reaction is an extension of Williamson's method for the synthesis of aliphatic ethers.

(5) **Action with Acyl halides and Acid anhydrides.** Phenols react with acid chlorides and acid anhydrides to form esters.

$$\boxed{C_6H_5O\,\vdots\,Na + Cl\,\vdots}\,OCCH_3 \longrightarrow \underset{\text{Phenyl acetate}}{C_6H_5OOCCH_3} + NaCl$$

Phenolic esters are not obtained by the direct reaction with acids themselves, as for alcohols. They are well-defined crystalline substances and their formation is used for the identification of phenols.

(5) ***Action with PCl_5.*** Phenols react readily with phosphorus pentachloride to form aryl chlorides but owing to the formation of esters of phosphoric acid the yield is very poor.

$$C_6H_5OH + PCl_5 \longrightarrow \underset{\text{Chlorobenzene}}{C_6H_5Cl} + POCl_3 + HCl$$

$$3C_6H_5OH + PCl_5 \longrightarrow \underset{\text{Triphenyl phosphate}}{(C_6H_5)_3PO_4} + 3HCl \ (\textit{main reaction})$$

The hydroxyl group of phenols cannot be replaced by Cl through the action of hydrogen chloride, as for alcohols.

(7) **Action with Ammonia** When heated with ammonia in the presence of zinc chloride, phenols give aromatic amines.

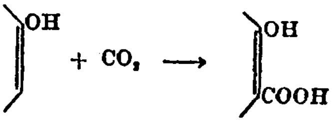
$$C_6H_5OH + NH_3 \xrightarrow[300°]{ZnCl_2} C_6H_5NH_2 + H_2O$$

Polyhydric phenols undergo this reaction even more readily.

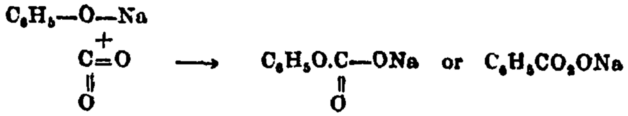
Reactions of the aromatic nucleus

(1) **Substitution reactions.** Phenols undergo nitration, sulphonation, halogenation, mercuration, etc. readily in the ortho and para positions to OH.

(2) **Kolbe reaction.** The carboxylation of a phenol can be carried by direct combination with carbon dioxide (Kolbe, 1850).

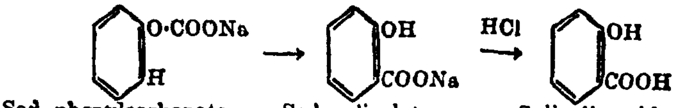


Thus salicylic acid is obtained by heating sodium phenolate with carbon dioxide at 130°. It is believed that sodium phenolate first combines with carbon dioxide to form sodium phenylcarbonate which then rearranges to sodium salicylate. This on acidification gives the free salicylic acid.



$$C_6H_5{-}O{-}Na + \underset{\underset{O}{\|}}{C{=}O} \longrightarrow \underset{\underset{O}{\|}}{C_6H_5O.C{-}ONa} \text{ or } C_6H_5CO_2ONa$$

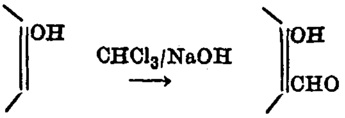
Sodium phenylcarbonate



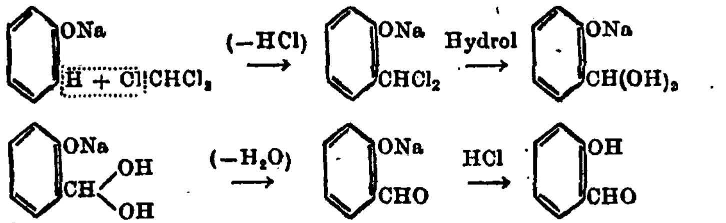
Sod. phenylcarbonate Sod. salicylate Salicylic acid

Kolbe reaction is given by all phenols. It is, however, a remarkable fact that if potassium phenolate is used in place of sodium phenolate, the COOH enters the nucleus in para position.

(3) **Reimer-Tiemann reaction.** A phenol can be converted into phenolic aldehyde by heating with chloroform and alkali (Reimer and Tiemann, 1876).



Thus, phenol when heated with chloroform and alkali at 60° gives *o*- and *p*-hydroxybenzaldehyde, the *o*-isomer predominating. The chloroform molecule first condenses with the nucleus of phenol o form the dichloride which on hydrolysis and subsequent acidification gives the phenolic aldehydes.



Unstable *o*-Hydroxybenzaldehyde

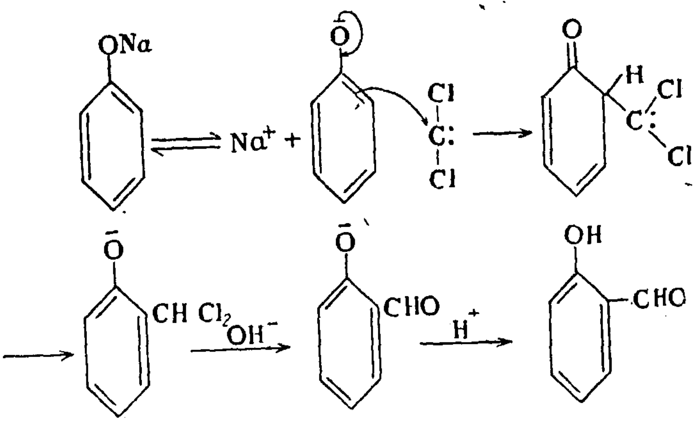
The mixture of phenolic aldehydes thus obtained is then separated by steam-distillation, only the *o*-isomer being steam-volatile.

Reimer-Tiemann reaction is a useful general method for the preparation of phenolic aldehydes. If, however, we take carbon tetrachloride in place of chloroform, the reaction yields phenolic acid.

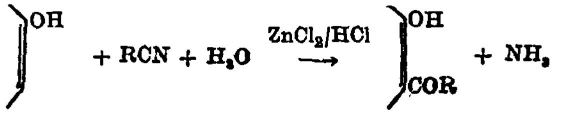
Mechanism :

The mechanism of this reaction is rather uncertain. On the basis of kinetic studies of the reaction by Hine, Wynberg (1954) proposed that the reactive species in the reaction is carbon dichloride (: CCl_2) rather than chloroform : CCl_2) is said to be formed during the alkaline hydrolysis of chloroform.

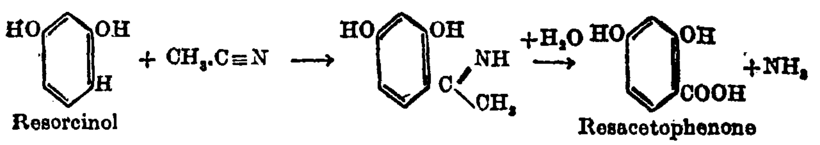
$$CHCl_3 + \bar{O}H \rightleftharpoons H_2O + \bar{C}Cl_3 \longrightarrow \bar{C}l + :CCl_2$$



(4) **Houben-Hoesch reaction.** Polyhydric phenols on condensation with alkyl nitriles in the presence of zinc chloride and hydrogen chloride yield phenolic ketones (Houben and Hoesch, 1927).



Thus, resorcinol gives resacetophenone by the following steps :



Resorcinol Resacetophenone

Houben-Hoesch reaction is given particularly readily by those phenols in which OH groups are meta to each other. Phenol does not respond to this reaction.

(5) **Coupling.** In alkaline solutions, phenols couple with diazonium salt to form hydroxyazo compounds. Thus :

(6) **Oxidation.** Phenols are much more easily oxidised than aromatic hydrocarbons. On oxidation with alkaline permanganate the nucleus is ruptured giving oxalic acid, tartaric acid, CO_2, etc. Cresols can be oxidised to the respective phenolic acids, provided the OH group is protected by alkylation or acylation.

TESTS FOR PHENOLS

(1) *Solubility Test.* If the substance is more soluble in sodium hydroxide than in water, but insoluble in sodium bicarbonate, it is probably a phenol.

(2) *Ferric chloride Test.* To the aqueous or alcoholic solution of the substance is added a neutral solution of ferric chloride ; the production of an intense colour—red, green or black—confirms the presence of a phenol.

(3) *Bromine water Test.* Aqueous solution of the substance is treated with bromine water until the yellow colour of bromine persists ; the formation of a precipitate (substitution product) confirms the presence of a phenol.

(4) *Liebermann's Test.* The substance is warmed with a little concentrated sulphuric acid and sodium nitrate and the dark-coloured product thus obtained is treated with dilute sodium hydroxide solution ; the production of intense blue or green colour confirms the presence of phenol.

MONOHYDRIC PHENOLS

PHENOL, HYDROXYBENZENE, C_6H_5OH

It was discovered by Runge in 1834 in coal-tar and he named it **carbolic acid** (*carbo*=coal ; *oleum*=oil). It is also present in wood-tar.

Preparation. Phenol can be obtained by the general methods discussed before. The more important ones are given below.

(1) FROM COAL-TAR. The *middle oil* fraction of coal-tar contains phenol along with cresols. It is agitated with sodium hydroxide solution when phenols pass into solution as phenolates and are recovered by blowing carbon dioxide through the solution. Phenol is finally isolated from the resulting mixture by fractional distillation.

Formerly phenol was exclusively obtained from coal-tar but with the development of the newer synthetic processes, this method now furnishes less than 10 per cent of the total production needed for industry.

(2) ALKALI FUSION METHOD. The oldest synthetic method consists in fusing sodium benzenesulphonate with sodium hydroxide and decomposing the resulting sodium phenolate with sulphuric acid.

$$C_6H_5SO_3Na + 2NaOH \longrightarrow C_6H_5ONa + H_2O + Na_2SO_3$$
$$2C_6H_5ONa + H_2SO_4 \longrightarrow 2C_6H_5OH + Na_2SO_4$$

This method has been superseded to a great extent by the other methods given below :

(3) CHLOROBENZENE METHOD (**Dow process**). In a recent process, phenol is produced technically by heating chlorobenzene with dilute sodium hydroxide at 350° under pressure.

$$C_6H_5Cl + 2NaOH \longrightarrow C_6H_5ONa + NaCl + H_2O$$

The sodium phenolate is acidified with hydrochloric acid to liberate phenol which is purified by distillation.

According to another more recent process, chlorobenzene is converted to phenol by direct action with steam in the vapour phase.

$$C_6H_5Cl + H_2O \xrightarrow[(SiO_2)]{500^\circ} C_6H_5OH + HCl$$

(4) BENZENE OXIDATION METHOD. This is the newest method of preparing phenol on a large scale. Benzene vapour and air are exposed to high temperature (800°) in a fire brick chamber when benzene is oxidised to phenol.

$$C_6H_6 + \tfrac{1}{2}O_2 \longrightarrow C_6H_5OH$$

$$2C_6H_6 + \tfrac{1}{2}O_2 \longrightarrow \underset{\text{Diphenyl}}{C_6H_5.C_6H_5} + H_2O$$

Diphenyl is obtained as a by-product.

(5) LABORATORY METHOD. If desired, phenol may be obtained conveniently in the laboratory by heating an aqueous solution of benzenediazonium chloride.

$$C_6H_5N_2Cl + H_2O \longrightarrow C_6H_5OH + N_2 + HCl$$

Properties. (*Physical*). Phenol forms colourless needle-like, deliquescent crystals (m.p. 41°, b.p. 182°), which turn pink when exposed to air and light. It has a strong 'carbolic odour' and a burning taste. It is sparingly soluble in water but dissolves readily in alcohol, ether and benzene. It is a violent poison when taken internally, and produces painful blisters in contact with skin.

(*Chemical*). The reactions of phenols are those of the hydroxyl group and the phenyl group. Either group exerts an activating influence on the other so that (*a*) phenol is feebly acid in character in comparison to alcohols which are neutral and (*b*) phenyl group gives the substitution reactions much more readily than does benzene.

Reactions of the OH group

(1) ACTION WITH ALKALIS. Phenol reacts with caustic alkalis to form phenolates which are decomposed by carbon dioxide.

$$C_6H_5OH + NaOH \longrightarrow C_6H_5ONa + H_2O$$

$$C_6H_5ONa + CO_2 + H_2O \longrightarrow C_6H_5OH + NaHCO_3$$

(2) ACTION WITH $FeCl_3$. It gives a violet colour with ferric chloride due to the formation of a complex salt.

(3) REDUCTION WITH ZINC DUST. When distilled with zinc dust, phenol is reduced to benzene.

$$C_6H_5OH + Zn \longrightarrow C_6H_6 + ZnO$$

(4) ACTION WITH ALKYL HALIDES. Its sodium salt reacts with alkyl halides to form alkyl-phenyl ethers.

$$C_6H_5OH + CH_3I \longrightarrow \underset{\substack{\text{Methyl phenyl ether} \\ \text{(anisole)}}}{C_6H_5OCH_3} + HI$$

(5) ACTION WITH ACYL CHLORIDES. It reacts with acyl chlorides (also acid anhydrides) to form phenyl esters.

$$C_6H_5OH + ClOCCH_3 \longrightarrow \underset{\text{Phenyl acetate}}{C_6H_5O.OCCH_3} + HCl$$

(6) ACTION WITH PCl_5. It is decomposed by phosphorus pentachloride to form chlorobenzene, the yield being poor due to the conversion of phenol to triphenyl phosphate.

$$C_6H_5OH + PCl_5 \longrightarrow C_6H_5Cl + POCl_3 + HCl$$

$$3C_6H_5OH + PCl_5 \longrightarrow (C_6H_5)_3PO_4 + 3HCl$$

(7) ACTION WITH AMMONIA. When heated with ammonia in the presence of zinc chloride, it is converted to aniline.

$$C_6H_5OH + NH_3 \xrightarrow[ZnCl_2]{300^\circ} C_6H_5NH_2 + H_2O$$

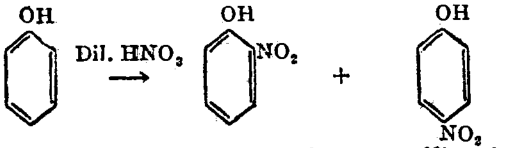
(8) ACTION WITH P_2S_5. It reacts with phosphorus pentasulphide to form thiophenol.

$$5C_6H_5OH + P_2S_5 \longrightarrow \underset{\text{Thiophenol}}{5C_6H_5SH} + P_2O_5$$

Reactions of the Phenyl group

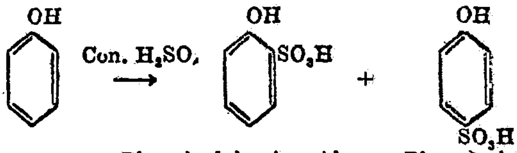
(1) SUBSTITUTION REACTIONS. Phenol readily undergoes nitration, sulphonation and halogenation in the ortho and para positions to OH group. Thus :

(*a*) It reacts with dilute nitric acid to form *o*-, *p*-nitrophenols.



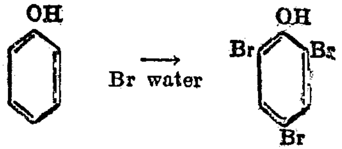
o-Nitrophenol *p*-Nitropheno.

(*b*) It reacts with concentrated sulphuric acid to form *o*-, *p*-phenolsulphonic acids.



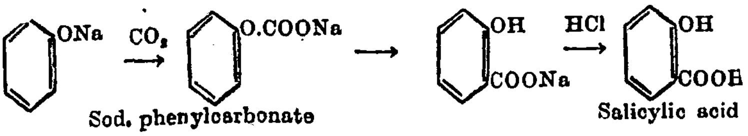
o-Phenolsulphonic acid *p*-Phenolsulphonic acid

(*c*) When shaken with bromine water, it gives a white precipitate of 2, 4, 6-tribromophenol.

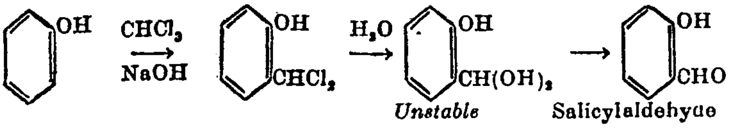


2, 4, 6-Tribromophenol

(2) KOLBE REACTION. When its sodium salt is heated with carbon dioxide at 130° under pressure, phenol gives salicylic acid.

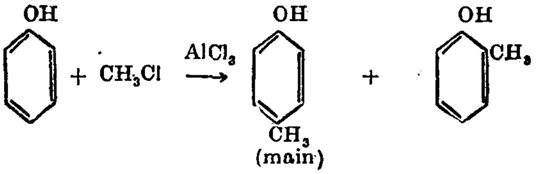


(3) REIMER-TIEMANN REACTION. When heated with chloroform and alkali, phenol is converted into salicyl aldehyde.



Some *p*-isomer is also produced.

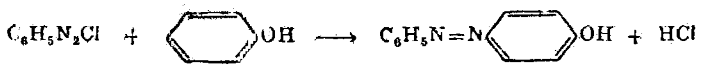
(4) FRIEDEL-CRAFTS REACTION. Phenol undergoes the Friedel-Crafts reaction to form mainly the *p*-derivatives. Thus :



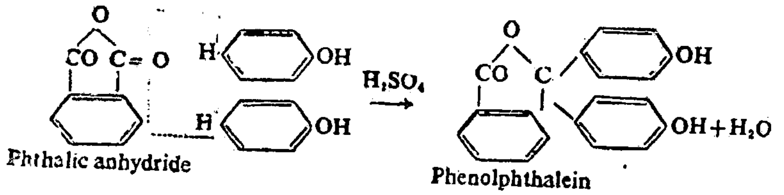
(5) CONDENSATION WITH CH_2O. When treated with formalin in the presence of dilute acid or alkali, phenol condenses to form *p*-hydroxybenzyl alcohol, together with a small amount of the *o*-isomer.

Under suitable conditions, phenol condenses with formaldehyde to give *Bakelite*, which is a poly-condensation product of complex structure.

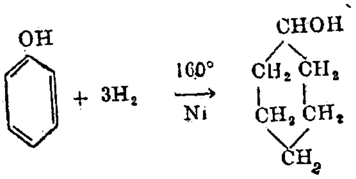
(6) COUPLING. In alkaline solutions, it couples with diazonium salts to form *p*-hydroxyazobenzene which is a red dye.



(7) ACTION WITH PHTHALIC ANHYDRIDE. When heated with phthalic anhydride and a little concentrated sulphuric acid, it forms phenolphthalein



(8) REDUCTION. When hydrogenated in the presence of nickel at 160°, it forms cyclohexanol.



(9) OXIDATION. When phenol is oxidised with alkaline permanganate, the ring is broken to form tartaric acid, oxalic acid and CO_2.

Uses. Phenol is used : (1) as an antiseptic in soaps, lotions and ointments ; (2) as a preservative for inks ; (3) in making *bakelite* ; (4) as starting material for drugs such as salol, aspirin, salicylic acid, etc. ; (5) in the manufacture of picric acid ; (6) for making phenolphthalein and certain other dyes ; (7) for manufacturing cyclohexanol needed as solvent for rubber and lacquers.

Tests. (1) Phenol has a characteristic 'carbolic' smell.

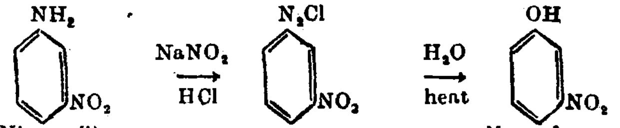
(2) It gives a violet colour with neutral ferric chloride solution.

(3) When its aqueous solution is treated with bromine water, a white precipitate of tribromophenol is quickly formed.

(4) When solid phenol (·5 g) is heated with phthalic anhydride (·5 g) and a drop or two of concentrated sulphuric acid and then alkalified, a pink colour is produced.

(5) It gives Liebermann's test.

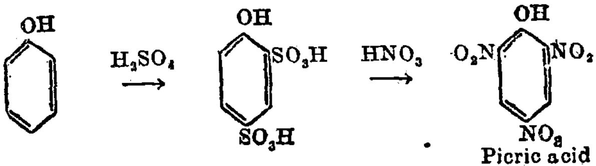
Nitrophenols, $C_6H_4(NO_2)OH$. *o*- and *p*-nitrophenols are obtained by the direct nitration of phenol with dilute nitric acid. The mixture is separated by steam-distillation, the *o*-isomer passing over leaving behind the *p*-isomer. *m*-Nitrophenol is prepared from *m*-nitroaniline by diazo reaction and heating the resulting solution.



m-Nitroaniline *m*-Nitrophenol

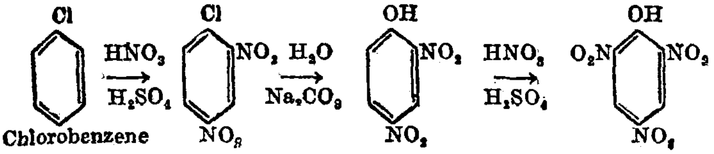
Properties. *s*-Nitrophenol is a yellow solid, m.p. 45°, having a powerful odour ; the *m*- and *p*-isomers are colourless solids m.pts. 90° and 114° respectively. They are all sparingly soluble in water ; the *o*-isomer only is steam-volatile. Owing to the presence of a negative nitro group, they are stronger acids than phenol and dissolve in alkalis and also in alkali carbonates forming coloured salts ; the salts of *o*- and *m*-nitrophenols are red while those of *p*-isomer are yellow. They are all readily reduced to the respective aminophenols. When treated with bromine water, they spilt out the nitro group giving 2, 4, 6-tribromophenol.

Picric acid, *2, 4, 6-Trinitrophenol.* It is obtained by nitrating phenol with a mixture of concentrated nitric acid and concentrated sulphuric acid. Since phenol is partially destroyed by oxidation with nitric acid, picric acid is prepared industrially by first sulphonating phenol (the presence of negative SO_3H groups protecting the OH group from oxidation) and then nitrating the product, when the SO_3H groups are replaced by NO_2 groups giving picric acid.



Picric acid

A more economical and *modern method* is as follows :



Chlorobenzene

Properties. Picric acid is a yellow crystalline solid, m.p. 122° having a bitter taste (hence its name; Greek, *pikros* = bitter). It is sparingly soluble in cold water giving intensely yellow solutions. It dissolves readily in alcohol and benzene. It is poisonous.

Owing to the presence of three negative nitro groups, picric acid is a much stronger acid than phenol (as strong as acetic acid) and behaves like carboxylic acids.

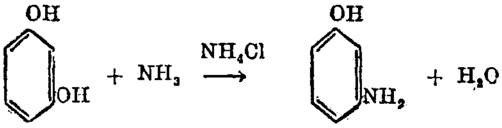
(1) It reacts with alkalis and decomposes carbonates to form salts. Potassium and ammonium salts explode violently when struck, so does dry picric acid.

(2) It reacts readily with PCl_5 to form *picryl chloride* which like acid chlorides is hydrolysed back to picric acid when boiled with water and gives *picramide* on shaking with concentrated ammonia.

(3) It forms well-defined crystalline compounds (*picrates*) with aromatic hydrocarbons, phenols and amines, *e.g.*, benzene picrate $C_6H_6.C_6H_2(NO_2)_3.OH$, ethylamine picrate, $C_6H_5NH_2.C_6H_2(NO_2)_3OH$, etc.

Uses. Picric acid is used : (1) for making explosives (*Lyddite* or *Melinite*) ; and (2) as a reagent for the isolation and identification of aromatic hydrocarbons, phenols and amines. It was formerly used : (1) as a yellow dye for wool and silk ; and (2) as an antiseptic and analgesic in the treatment of burns

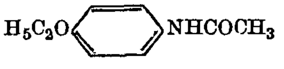
Aminophenols, $C_6H_4(NH_2)OH$. They are produced by reducing the corresponding nitrophenols. The *m*-isomer is obtained by heating resorcinol with ammonia and ammonium chloride at 200°.



p-Aminophenol, the most important of the three isomers, is prepared by the electrolytic reduction of nitrobenzene in strong acid solution.

Properties. All the three aminophenols are colourless solids (m.pts. *o*-, 137° ; *m*-, 123° ; *p*-, 186°), turning yellow or brown in air. The basic amino group annuls the acid character of the hydroxyl group so that aminophenols do not react with alkalis to form phenolates. They, however, form salts with acids.

o-and *p*- aminophenols are used as photographic developers. A derivative of the *p*-isomer is used in medicine as a febrifuge and analgesic under the name phenacetin



CRESOLS, HYDROXYTOLUENES, $CH_3.C_6H_4.OH$

The three hydroxytoluenes (*o*, *m*, *p*) are the next homologues of phenol and are called *cresols*. They are isolated from the *middle oil* fraction of coal-tar much in the same way as phenol. The mixture of the three cresols thus obtained (*cresylic acids* or *creosole*) is used as such for industrial purposes. The individual cresols may be obtained : (1) diazatisation of the corresponding toluidines and warming the resulting aqueous solutions ; and (2) by the fusion of the corresponding toluenesulphonic acids with potash.

$$\underset{\text{Toluidine}}{CH_3.C_6H_4.NH_2} \xrightarrow[HCl]{NaNO_3} CH_3.C_6H_4.N_2Cl \xrightarrow{H_2O} CH_3.C_6H_4.OH$$

$$\underset{\text{Toluenesulphonic acid}}{CH_3.C_6H_4SO_3OH} \xrightarrow[\text{Fuse}]{KOH} CH_3.C_6H_4.OK \xrightarrow{HCl} \underset{\text{Cresol}}{CH_3.C_6H_4.OH}$$

Properties. Cresols are colourless substances having phenolic odour, b. pts. *o*-, 100° ; *m*-, 203° ; *p*-, 202°. They resemble phenol in most of their properties. They are less toxic than phenol but have a greater germicidal value. They give violet colours with ferric chloride and react with bromine. However, they are stable to chromic acid but can be oxidised to the corresponding carboxylic acids if the OH group is blocked by alkylation or acylation.

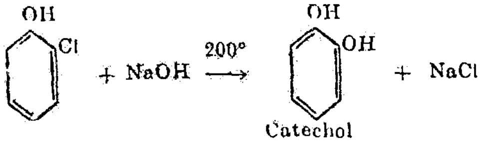
Uses. Mixed cresols are used : (1) for making liquid disinfectants (*lysol*), which are its emulsions with soap ; (2) as a preservative for timber, railway sleepers, etc. ; and (3) for the manufacture of synthetic resins, plasticisers, dyes and explosives :

DIHYDRIC PHENOLS

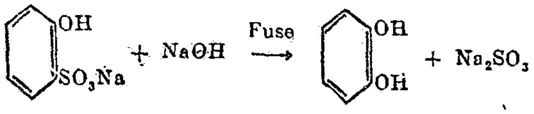
CATECHOL, PYROCATECHOL, *o*-DIHYDROXYBENZENE

Catechol occurs in Indian *catechu* (obtained from *Acacia catechu* tree) and was first obtained by distillation of this product (hence its name).

Preparation. (1) Catechol is prepared by heating *o*-chlorophenol with aqueous sodium hydroxide at 200° under pressure in the presence of copper sulphate.



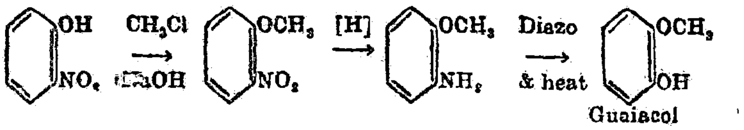
(2) It may also be obtained by fusing *o*-phenolsulphonic acid with sodium hydroxide.



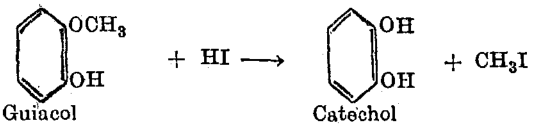
Properties. Catechol is a white crystalline solid, m.p. 105°, readily soluble in water, alcohol and ether. It gives a green colour with ferric chloride It is readily oxidised ; its aqueous solution darkens in air due to oxidation. It reduces cold silver nitrate and warm Fehling's solution. A characteristic reaction of catechol is the formation of the white precipitate on addition of lead acetate solution (distinction from other isomers) to its aqueous solution. On oxidation with silver oxide, it is converted to *o*-benzoquinone.

Uses. Catechol is used : (1) as a photographic developer ; (2) for the manufacture of alizarin and adrenaline, a valuable drug, and (3) as antioxidant in gasoline.

Guaiacol, *the monomethyl ether of catechol* occurs in beechwood tar from which it may be obtained by fractional distillation. It is prepared synthetically from o-nitrophenol as follows :



Guaiacol is a pleasant smelling substance, m.p. 32°, b.pt, 205°. With ferric chloride it gives a blue colour. When heated with concentrated hydriodic acid, it is converted to catechol.

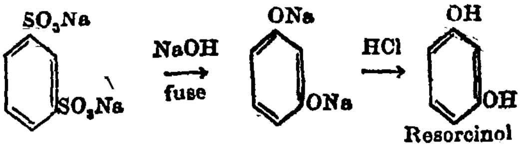


It is used in medicine because of its antiseptic, antipyretic and analgesic action. It is starting material for the manufacture of vanillin.

RESORCINOL, *m*-DIHYDROXYBENZENE

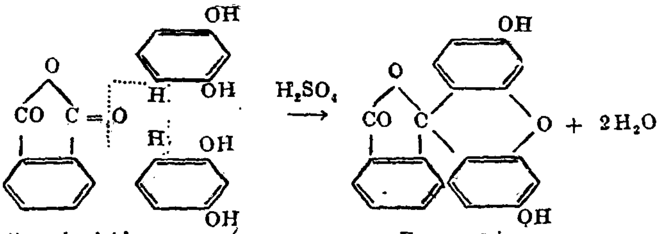
It gets its name from the fact that it was originally obtained by the fusion of certain resins with alkalis.

Preparation. Resorcinol is prepared by fusing sodium *m*-benzenedisulphonate with sodium hydroxide and acidification of the melt.



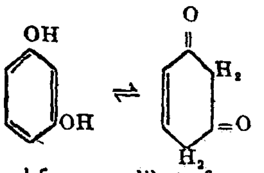
Properties. Resorcinol forms white needle-like crystals, m.p. 118°, turning grey in air due to oxidation. It is very soluble in water, alcohol and ether. It gives a deep violet coloration with ferric chloride and forms a precipitate of 2, 4, 6-tribromoresorcinol with bromine water.

Resorcinol is not as active a reducing agent as either catechol or quinol, but it reduces ammoniacal silver nitrate solution and Fehling's solution slowly on warming. It couples with diazonium salts to form azo-dyes and condenses with phthalic anhydride to form *fluorescein* (delicate test) which shows intense green fluorescence in dilute alkali solution.



Phthalic anhydride Fluorescein

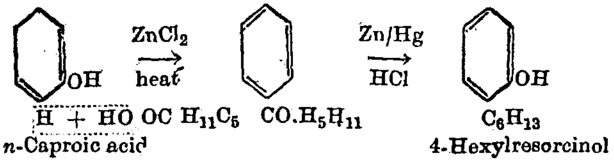
Resorcinol exhibits keto-enol tautomerism which is shown by the fact that it forms a dioxime and a bisulphite compound.



dienol form diketo form

Uses. Resorcinol is used : (1) as antiseptic in ointments for the treatment of eczema ; (2) for manufacturing numerous dyestuffs (azodyes, fluorescein, eosin) ; (3) as starting material for 4-hexylresorcinol, and (4) for making aldehyde condensation resins for bonding plywood.

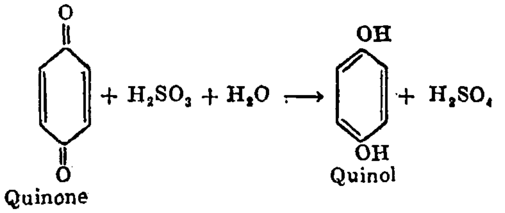
4-n-Hexylresorcinol, *Carprokol*, is prepared by heating resorcinol and *n*-caproic acid with zinc chloride and reducing the resulting ketone by the Clemmensen method.



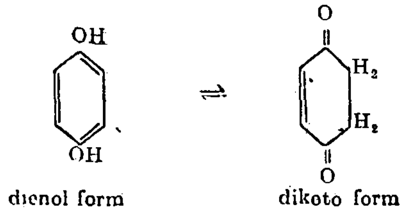
Hexylresorcinol is about 45 times as strong an antiseptic and germicide as phenol. It is widely used as urinary antiseptic and as a remedy for hookworm.

QUINOL, HYDROQUINONE, *p*-DIHYDROXYBENZENE

Preparation. As its name implies, it is prepared by reducing quinone with sulphurous acid.



Properties. Quinol is a white crystalline solid, m.p. 169°, very soluble in water, alcohol and ether. Its aqueous solutions turn brown in air due to oxidation. It is a powerful reducer ; thus even a mild oxidising agent like ferric chloride converts it into quinone (a green solid). It forms a bisulphite addition compound, since, like resoncinol, it exhibits tautomerism.

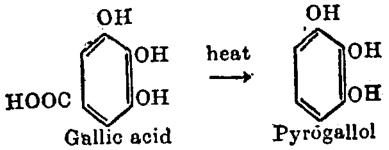


Uses. Quinol is used : (1) as a photographic developer ; (2) as antioxidant or inhibitor in auto-oxidation and polymerisation reactions ; (3) as antiseptic solution in the treatment of conjuctivitus.

TRIHYDRIC PHENOLS

PYROGALLOL, 1, 2, 3-TRIHYDOXYBENZENE

Preparation. It is prepared by heating gallic acid in a steam of carbon dioxide, hence its name.

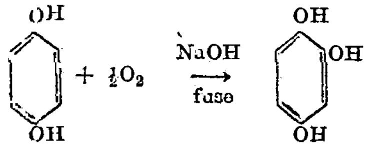


Properties. Pyrogallol is a white crystalline solid, m.p. 134° very soluble in water but less so in alcohol and ether. With ferric chloride it gives a red coloration. Alkaline solution of pyrogallol absorbs oxygen rapidly from air and turns brown. It is the most powerful reducing agent of the group of phenols, reducing ammoniacal silver nitrate and Fehling's solutions in cold.

Uses. Pyrogallol is used : (1) as a photographic developer ; (2) in antiseptic ointments for skin diseases ; (3) as a hair dye ; and (4) in alkaline solution for absorbing oxygen in gas analysis.

HYDROXYQUINOL 1, 2, 4-TRIHYDROXYBENZENE

It may be prepared by fusing quinol with alkali in air,

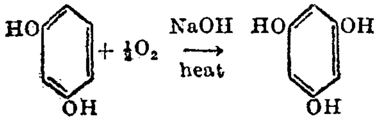


Hydroxyquinol is a white crystalline solid, m p. 140°, very soluble in water. With ferric chloride it gives a greenish brown coloration. It is relatively unimportant.

PHLOROGLUCINOL 1, 3, 5-TRIHYDROXYBENZENE

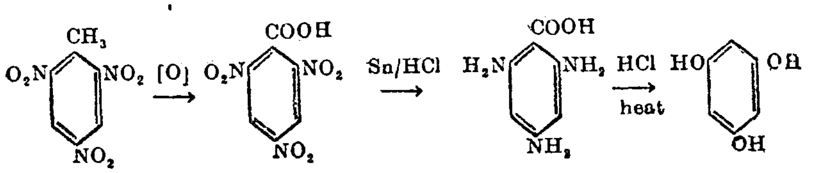
It was first obtained by the decomposition of a glucoside *phlorizin* occurring in the bark of apple trees, hence its name.

Preparation. (1) Phloroglucinol may be obtained by fusing resorcinol with alkali in air.



Phloroglucinol

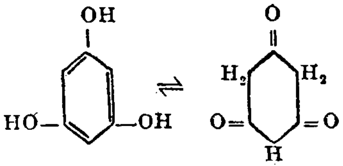
(2) It is prepared most satisfactorily from T.N.T. as follows.



In the last step, 2,4,6-triaminobenzoic acid decarboxylates and the NH_2 groups are simultaneously replaced by OH groups.

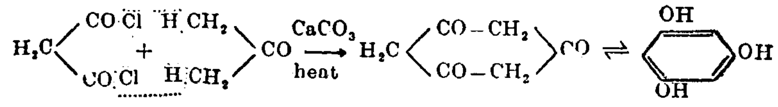
Properties. Phloroglucinol is a white solid, m.p. 219° readily soluble in water, its aqueous solutions tasting sweet. With ferric chloride it gives a bluish violet coloration. Its alkali solutions darken in air due to oxidation.

Phloroglucinol presents a pronounced case of keto-enol tautomerism. It forms a tripotassium derivative, tri-ethers and triesters. On the other hand, it gives a trioxime. These reactions show that it is a tautomeric mixture of the following two forms.



trienol form *triketo-form*

The existence of the above equilibrium is supported by the following synthesis of phloroglucinol from malonyl chloride and acetone.



Malonyl chloride Acetone *triketo form* *trienol form*

Phloroglucinol has no industrial applications. It is used for detecting carbohydrates, giving a red coloration with them in the presence of sulphuric acid.

2. Aromatic Alcohols

Aromatic alcohols contain the OH group in the alkyl side-chain and may well be regarded as aryl-substituted aliphatic alcohols. They closely resemble the latter both in properties and mode of formation.

Aromatic alcohols are pleasant-smelling, neutral, substances. They can be oxidised to the corresponding aldehydes and carboxylic acids ; they form alcoholates, ethers and esters ; react with halogen acids and PCl_5 to replace hydroxyl group by halogen ; and also give substitution reactions of the benzene nucleus. Unlike phenols, they do not form salts with alkalis and do not give colorations with ferric chloride.

BENZYL ALCOHOL, PHENYLCARBINOL, $C_6H_5.CH_2OH$

It is the simplest member of the class and is isomeric with cresols. It occurs in Peru and Tolu balsams as free alcohol and as esters (acetate, benzoate) in oil of jasmine and other essential oils.

Preparation. (1) Benzyl alcohol is prepared industrially by the hydrolysis of Benzyl chloride with aqueous sodium carbonate.

$$2C_6H_5CH_2Cl + Na_2CO_3 + H_2O \longrightarrow 2C_6H_5CH_2OH + 2NaCl + CO_2$$

(2) It is prepared conveniently in the laboratory with concentrated potash solution. (*Cannizzaro s reaction*).

$$2C_6H_5CHO + KOH \longrightarrow \underset{\text{Benzyl alcohol}}{C_6H_5CH_2OH} + \underset{\text{Pot. benzoate}}{C_6H_5COOK}$$

(3) It may also be obtained : (*i*) by the reduction of benzaldehyde with sodium amalgam and water ; (*ii*) from paraformaldehyde and phenylmagnesium bromide.

$$C_6H_5CHO + 2[H] \longrightarrow C_6H_5CH_2OH$$

$$CH_2{=}O + C_6H_5MgBr \longrightarrow C_6H_5CH_2OMgBr \xrightarrow{H_2O} C_6H_5CH_2OH$$

Properties. Benzyl alcohol is a colourless liquid, b.p. 206°, having a faint pleasant odour. It is slightly soluble in water, but dissolves freely in alcohol and ether.

Chemically it behaves like the aliphatic primary alcohols and also gives substitution reactions in the nucleus. Some of its reactions common with aliphatic alcohols are given below for illustration.

(1) On oxidation with dilute nitric acid, it first forms benzaldehyde and then benzoic acid.

$$C_6H_5CH_2OH \xrightarrow{[O]} C_6H_5CHO \xrightarrow{[O]} C_6H_5COOH$$

(2) It is decomposed by sodium to form sodium benzoxide with the liberation of hydrogen.

$$2C_6H_5CH_2OH + 2Na \longrightarrow 2C_6H_5CH_2ONa + H_2$$

(3) It reacts with PCl_5 and halogen acids to form benzyl halides.

$$C_6H_5CH_2OH + PCl_5 \longrightarrow \underset{\text{Benzyl chloride}}{C_6H_5CH_2Cl} + POCl_3 + HCl$$

$$C_6H_5CH_2OH + HBr \longrightarrow \underset{\text{Benzyl bromide}}{C_6H_5CH_2Br} + H_2O$$

(4) When treated with acid chlorides and anhydrides, it forms esters.

$$C_6H_5CH_2OH + ClOCCH_3 \longrightarrow \underset{\text{Benzyl acetate}}{C_6H_5CH_2OOCCH_3} + HCl$$

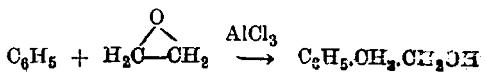
Uses. Benzyl alcohol and its esters are largely used in the perfumery industry. Being a local anaesthetic and antiseptic, it is used in making ointments for relieving itching. Benzyl benzoate is a remedy for asthma and whooping cough.

PHENYLETHYL ALCOHOL, BENZYL CARBINOL, $C_6H_5CH_2CH_2OH$

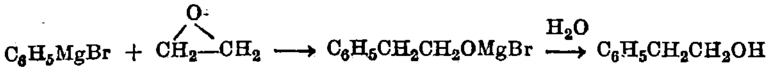
It occurs in the oil of roses and the synthetic product is now used for making artificial '*attar of roses*'. It is prepared : (1) by reducing ethyl phenylacetate with sodium and alcohol.

$$C_6H_5CH_2COOC_2H_5 + [H] \longrightarrow C_6H_5CH_2CH_2OH + C_2H_5OH$$

(2) by action of ethylene oxide with benzene in presence of aluminium chloride, or with phenylmagnesium bromide.



$$C_6H_6 + H_2C\overset{O}{—}CH_2 \xrightarrow{AlCl_3} C_6H_5.CH_2.CH_2OH$$



$$C_6H_5MgBr + \overset{O}{CH_2-CH_2} \longrightarrow C_6H_5CH_2CH_2OMgBr \xrightarrow{H_2O} C_6H_5CH_2CH_2OH$$

Phenylethyl alcohol is a colourless liquid, b.p. 221°, having a strong rose-like odour. It is only slightly soluble in water but freely miscible with alcohol and ether.

COMPARISON OF PROPERTIES OF PHENOLS AND ALCOHOLS

As already stated phenols and aliphatic alcohols have many common reactions *e.g.*, (1) formation of esters with acyl chlorides; (2) formation of ethers with alkyl halides; (3) formation of amines with ammonia; and (4) formation of hydrocarbons on reduction. However, the two classes of compounds show striking differences which are mentioned in the table below.

PHENOLS	ALCOHOLS
1. Have characteristic 'phenolic' odour.	1. Have pleasant odour.
2. Are acidic and dissolve in alkalis to form salts.	2. Are neutral and have no action with alkalis.
3. On oxidation give complex coloured products.	3. Oxidise smoothly to aldehydes or ketones.
4. Give characteristic colours with ferric chloride.	4. No action with ferric chloride.
5. Do not react with halogen acids.	5. Give alkyl halides.
6. React with PCl_5 to form mainly triaryl phosphates.	6. Give alkyl chlorides.
7. Couple with diazonium salts to form azo dyes.	7. Do not form dyes.
8. Readily give substitution reactions with HNO_3, H_2SO_4 and halogens.	8. Do not give substitution reactions but instead form esters with acids.

QUESTIONS

1. What are the general methods for introducing a hydroxyl group into benzene nucleus? In what respects do they differ from aliphatic hydroxy compounds?

2. Give an account of the general methods of preparation, chemical properties and important uses of phenols.

3. What is resorcinol? How has it been synthetically prepared? Explain the use of the compound in the preparation of the organic dye 'Fluorescene'

4. Name and formulate trihydroxybenzenes. How are they prepared? Outline their chief chemical properties.

5. Describe briefly the reactions associated with the name of any four of the following :—(*a*) Wurtz-Fittig, (*b*) Friedel-Crafts, (*c*) Reimer-Tiemann, (*d*) Perkin, (*e*) Sandmeyer, (*f*) Fischer-Tropsch.

6. What are phenols ? How do they differ from the alcohols ? How can phenol be obtained from (*i*) benzene and (*ii*) aniline ? How can it be converted into (*i*) benzene, and (*ii*) aniline ?

7. Give the general methods of the preparation of phenols. How would you convert phenol into :—(*a*) Aniline, (*b*) Anisol, (*c*) Picric acid, (*d*) Phenolphthalein, (*e*) Salicyl aldehyde ? (*Panjab B.Sc. III, 1965*)

8. How is phenol obtained industrially ? What is the action of (*a*) nitric acid, (*b*) alkali, (*c*) bromine water on phenol. (*Gorakhpur B.Sc., 1967*)

9. How is phenol obtained from coal-tar ? Describe giving equations at least four reactions to distinguish between phenol and ethyl alcohol. (*Dibrugarh B.Sc., 1968*)

10. How is phenol prepared on an industrial scale. Give the chemical reactions where phenol differs from benzylalcohol. (*Marathwada B.Sc., 1969*)

11. How is phenol obtained from coal tar ? How is phenol converted into benzene, picric acid and salicyl aldehyde. (*Vankateswara B.Sc., 1969*)

12. How is phenol isolated from coal-tar ? How are the following compounds obtained from phenol?

(*i*) *Aspirin*, (*ii*) Phenolphthalein, (*iii*) Picric Acid. Mention the uses of the above compounds. (*Bangalore B.Sc., 1969*)

13. Describe the preparation and important reactions of phenol. In what ways phenol differs from ethanol. (*Jammu & Kashmir B.Sc., 1969*)

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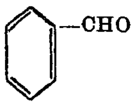
Aromatic Aldehydes and Ketones

ADOLPH W.H. KOLBE
(1818—1884)

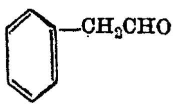
He is best known for his synthesis of aliphatic hydrocarbons by the electrolysis of organic acids. He is credited with : synthesis of acetic acid, of acids from alcohols, synthesis of salicylic acid. He was author of several texts in chemistry.

1. AROMATIC ALDEHYDES

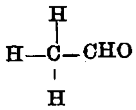
Aromatic aldehydes are of two types : (1) those in which the aldehyde group (CHO) is directly attached to the nucleus *e.g.*, benzaldehyde ; and (2) those in which it is attached to the side chain *e.g.*, phenylacetaldehyde. The former are, in fact, the true aromatic *aldehydes*, while the latter, which are aliphatic in character, may be regarded as aryl-substituted aliphatic aldehydes.



Benzaldehyde
(No H-atom available
with α-carbon)



Phenylacetaldehyde
(H.atoms available
with α-carbon)



$$H-\overset{H}{\underset{H}{C}}-CHO$$

Acetaldehyde
(H-atoms available
with α-carbon)

Aromatic aldehydes have many reactions in common with aliphatic aldehydes. They differ from the latter in that : (1) the —CHO group is more reactive and also gives some characteristic reactions ; (2) they do not show such reactions in which the H atoms attached to a α-carbon are involved (polymerisation, condensation) ; and (3) they show the usual substitution reactions of the benzene nucleus.

Benzaldehyde is by far the most important and typical aldehyde ; it will be used for illustrating the preparation and properties of this class of compounds.

BENZALDEHYDE, PHENYLFORMALDEHYDE, C_6H_5CHO

It occurs in nature as the glucoside amygdalin, in the seeds of bitter almonds, and may be produced from it by hydrolysis with dilute acids or the enzyme *emulsase*

$$\underset{\text{Amygdalin}}{C_{20}H_{26}O_{12}N} + 2H_2O \longrightarrow \underset{\text{Benzaldehyde}}{C_6H_5CHO} + \underset{\text{Glucose}}{2C_6H_{12}O_6} + HCN$$

On this account benzaldehyde is also named as the *'oil of bitter almonds'*.

Preparation. Benzaldehyde is prepared from toluene or benzene by various methods.

(1) *Oxidation of toluene.* This is done with manganese dioxide and sulphuric acid at 40° using copper sulphate as a catalyst. (*Commercial*).

$$C_6H_5CH_3 + 2[O] \longrightarrow \underset{\text{Benzaldehyde}}{C_6H_5CHO} + H_2O$$

Some benzoic acid is also produced. A better method is to oxidise toluene with chromyl chloride, CrO_2Cl_2 (*Etard reaction*) ; in this case, oxidation proceeds no further than aldehyde. In U.S.A. benzaldehyde is also manufactured by oxidation of toluene in the vapour phase with air at 500° using vanadium pentoxide as a catalyst.

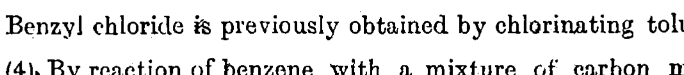
(2) By boiling benzyl chloride with aqueous copper or lead nitrate. This involves the hydrolysis of benzyl chloride to benzyl alcohol which is then oxidised to benzaldehyde.

$$C_6H_5CH_2Cl + HOH \longrightarrow C_6H_5CH_2OH + HCl$$

$$C_6H_5CH_2OH + [O] \longrightarrow C_6H_5CHO + H_2O$$

This is a convenient method for preparing benzaldehyde in the laboratory and in industry. Benzyl chloride is made cheaply by chlorination of toluene.

(3) By boiling benzyl chloride with lime-water (*Commercial*).



$$C_6H_5CH\begin{smallmatrix}\diagup Cl \\ \diagdown Cl\end{smallmatrix} \xrightarrow{+2H_2O} \underset{\textit{Unstable}}{C_6H_5CH\begin{smallmatrix}\diagup OH \\ \diagdown OH\end{smallmatrix}} \longrightarrow C_6H_5CHO + H_2O$$

Benzyl chloride is previously obtained by chlorinating toluene.

(4). By reaction of benzene with a mixture of carbon monoxide and hydrogen chloride in the presence of anhydrous aluminium and cuprous chlorides as a catalyst. (**Gettermann-Koch synthesis**).

$$CO + HCl \longrightarrow \underset{\text{Formyl chloride}}{HCOCl}$$

$$C_6H_6 + HCOCl \xrightarrow{AlCl_3} C_6H_5CHO + HCl$$

Benzaldehyde is also produced on a large scale by the direct carbonylation of benzene in the presence of aluminium chloride.

$$C_6H_6 + CO \xrightarrow{AlCl_3} C_6H_5CHO$$

Other Methods. Benzaldehyde may also be synthesized by other methods, analogous to those used for aliphatic aldehydes :

(1) By oxidation of benzyl alcohol with dilute nitric acid

$$C_6H_6CH_2OH + [O] \longrightarrow C_6H_5CHO + H_2O$$

(2) By distilling a mixture of calcium benzoate and calcium formate

$$C_6H_5COOCa/2 + HCOOCa/2 \longrightarrow C_6H_5CHO + CaCO_3$$

(3) By reducing benzoyl chloride with hydrogen in presence of finely divided palladium.

$$C_6H_5COCl + H_2 \xrightarrow{Pd} C_6H_5CHO + HCl$$

(4) By reducing phenyl cyanide with stannous chloride and hydrolysis of the product.

$$C_6H_5C{\equiv}N \xrightarrow{+2H} C_6H_5CH{=}NH \xrightarrow{+H_2O} C_6H_5CHO + NH_2$$

(5) By reaction of phenylmagnesium bromide with excess of ethyl formate.

$$C_6H_5MgBr + HCOOC_2H_5 \longrightarrow C_6H_5CHO + BrMgOC_2H_5$$

Laboratory Preparation. Benzaldehyde is prepared conveniently in the laboratory by boiling benzyl chloride with an aqueous solution of copper nitrate.

$$C_6H_5CH_2Cl \xrightarrow{H_2O} C_6H_5CH_2OH \xrightarrow{[O]} C_6H_5CHO$$

A mixture of benzyl chloride (*1 part*), water (*5 parts*) and copper nitrate (*1 part*) is boiled for 6·8 hours in a round-bottomed flask fitted with a reflux condenser. A stream of carbon dioxide is passed into the liquid all the time to sweep out nitrogen oxides, which would otherwise oxidise benzaldehyde to benzoic acid. The resulting mixture is extracted with ether which dissolves benzaldehyde. To the ethereal extract is then added a saturated solution of $NaHSO_3$ when crystals of the bisulphite compound separate. These are filtered, washed with ether and decomposed with dilute sulphuric acid. Benzaldehyde thus obtained is again extracted with ether, the ethereal solution dried over anhydrous calcium chloride, the ether removed by heating on water-bath, and the residual benzaldehyde is finally distilled.

Properties. (*Physical*). Benzaldehyde is a colourless, highly refractive liquid, b.p. 179°, with a pleasant odour of almonds It is only slightly soluble in water but dissolves readily in alcohol and ether. It is steam-volatile.

(*Chemical*). The reactions of benzaldehyde are those of the CHO group and the benzene nucleus. The CHO group being linked to a negative phenyl radical is extremely reactive and readily gives most of the reactions typical of aliphatic aldehydes. However, since the CHO group is attached to a tertiary carbon with no available H-atoms, benzaldehyde fails to undergo polymerisation or aldol condensation, but instead gives several characteristic reactions.

A. Reactions of CHO group common with aliphatic aldehydes

(1) *Oxidation.* Benzaldehyde is readily oxidised to benzoic acid, even on mere exposure to air. Thus when a few drops of it are allowed to stand on a watch-glass, crystals of benzoic acid soon appear.

$$C_6H_5CHO + [O] \longrightarrow \underset{\text{Benzoic acid}}{C_6H_5COOH}$$

For the same reason, benzaldehyde is a strong reducing agent. It reduces ammoniacal silver nitrate forming a mirror. Strangely enough, it does not reduce Fehling's solution, which is probably due to the fact that it is rapidly converted to benzyl alcohol and potassium benzoate by alkaline solution (Cannizzaro Reaction).

(2) When reduced with sodium amalgam or with zinc and hydrochloric acid, it forms benzyl alcohol.

$$C_6H_5CH{=}O + 2[H] \longrightarrow C_6H_5CH_2OH$$

(3) It adds on hydrogen cyanide and sodium bisulphite to form the cyanohydrin and the bisulphite compound respectively.

$$C_6H_5CH{=}O + HCN \longrightarrow \underset{\text{Mandelonitrile}}{C_6H_5CH(OH)CN}$$

$$C_6H_5CH{=}O + NaHSO_3 \longrightarrow \underset{\text{Bisulphite compound}}{C_6H_5CH(OH)SO_3Na}$$

Benzaldehyde may be purified via the bisulphite compound.

(4) It condenses with hydroxylamine and phenylhydrazine to form benzaldoxime and the phenylhydrazone.

$$C_6H_5CH{=}O + H_2NOH \longrightarrow \underset{\text{Benzaldoxime}}{C_6H_5CH{=}NOH} + H_2O$$

$$C_6H_5CH{=}O + H_2N.NHC_6H_5 \longrightarrow \underset{\text{Phenylhydrazone}}{C_6H_5CH{=}N.NH.C_6H_5} + H_2O$$

Similarly it reacts with hydrazine and semicarbazide giving hydrazone and semicarbazone respectively.

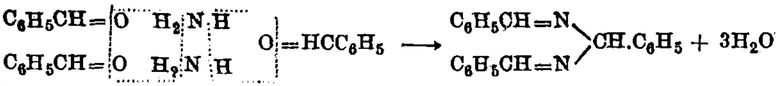
(5) It reacts with PCl_5 to form benzal chloride.

$$C_6H_5CHO + PCl_5 \longrightarrow C_6H_5CHCl_2 + POCl_3$$

(6) It restores the pink colour of Schiff's reagent.

B. Reactions of CHO group not given by aliphatic aldehydes

(1) Benzaldehyde reacts with ammonia to form a complex product *hydrobenzamide*, while aliphatic aldehydes give aldehyde-ammonias.



$$\begin{array}{l} C_6H_5CH{=}O \quad H_2N{:}H \\ \qquad\qquad\qquad\qquad O{=}HCC_6H_5 \\ C_6H_5CH{=}O \quad H_2N{:}H \end{array} \longrightarrow \begin{array}{l} C_6H_5CH{=}N \\ \qquad\qquad\quad >CH.C_6H_5 \\ C_6H_5CH{=}N \end{array} + 3H_2O$$

(3 moles of benzaldehyde & 2 of ammonia) Hydrobenzamide

(2) It reacts with primary aromatic amines to form Schiff's bases, while aliphatic aldehydes do not give similar compounds.

$$C_6H_5CH{=}O + H_2NC_6H_5 \longrightarrow \underset{\text{Benzalaniline}}{C_6H_5CH{=}NC_6H_5} + H_2O$$

(3) **Cannizzaro reaction.** When benzaldehyde is treated with a concentrated solution of sodium hydroxide or potassium hydroxide, one molecule of it is oxidised to benzoic acid and another is reduced to benzyl alcohol. Thus :

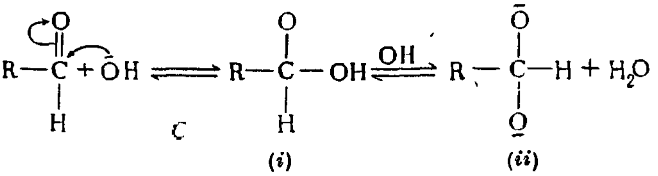
$$2C_6H_5CHO + H_2O \longrightarrow \underset{\text{Benzoic acid}}{C_6H_5COOH} + \underset{\text{Benzyl alcohol}}{C_6H_5CH_2OH}$$

The peculiar reaction was named *Cannizzaro reaction* after its discoverer.

Cannizzaro reaction is shown by all aromatic aldehydes and certain aliphatic aldehydes (formaldehyde, trimethylacetaldehyde) which do not have α-hydrogen atoms and are thus incapable of undergoing aldol condensation.

Mechanism:

One mechanism proposed for the Cannizzaro reaction is the following :



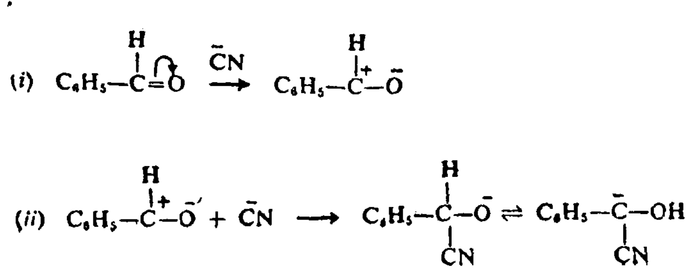
Then proton transfer occurs :

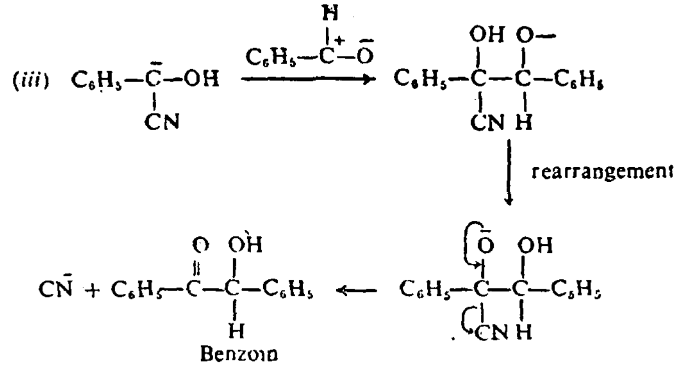
In further agreement with this general mechanism, it has been shown that 'electron-withdrawing' substituents increase the reactivity of aldehydes in the reaction.

(4) **Benzoin condensation.** When heated with alcoholic potassium cyanide, benzaldehyde undergoes self-condensation forming *benzoin* (a keto-alcohol).

$$C_6H_5CHO + OHCC_6H_5 \xrightarrow{(KCN)} \underset{\text{Benzoin}}{C_6H_5.CH(OH).CO.C_6H_5}$$

Mechanism :



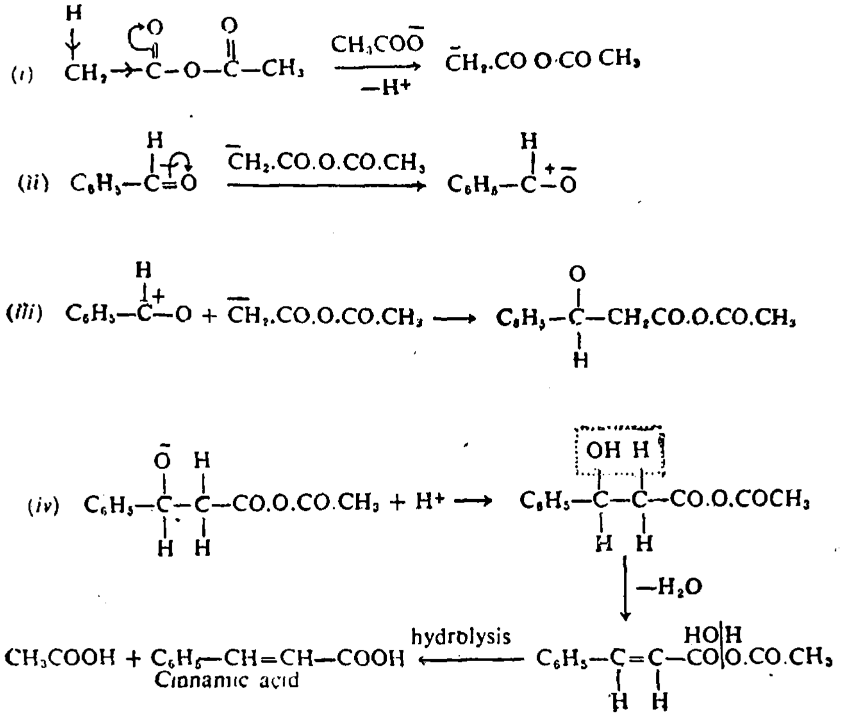


This reaction known as *Benzoin condensation* is also given by formaldehyde.

(5) **Perkin's reaction.** When aromatic aldehyde is heated with the anhydride of an aliphatic acid in the presence of the sodium salt of the same acid, an unsaturated acid results. Thus with acetic anhydride and sodium acetate it gives cinnamic acid.

$$C_6H_5CHO + (CH_3CO)_2O \xrightarrow{CH_3COONa} \underset{\text{Cinnamic acid}}{C_6H_5CH{:}CH.COOH} + CH_3COOH$$

Mechanism : *The mechanism of this reaction may be as follows* :

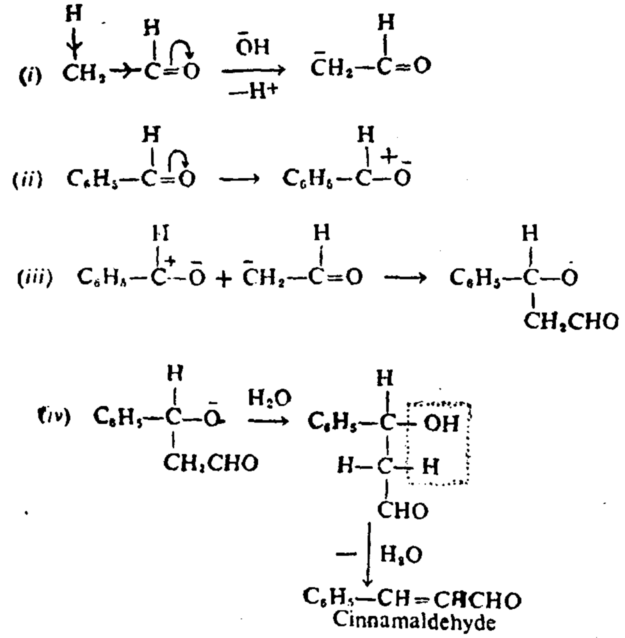


This reaction known as Perkin's reaction (W.H. Perkin, 1868) is *given by all aromatic aldehydes and is a valuable method for the* synthesis of αβ-unsaturated acids.

(6) Benzaldehyde condenses with acetaldehyde in the presence of dilute alkali, to form cinnamaldehyde (*Claisen Condensation*).

$$C_6H_5CHO + CH_3CHO \xrightarrow{NaOH} C_6H_5.CH{:}CH.CHO + H_2O$$

Mechanism : Mechanism of this reaction is similar to that of aldol condensation.



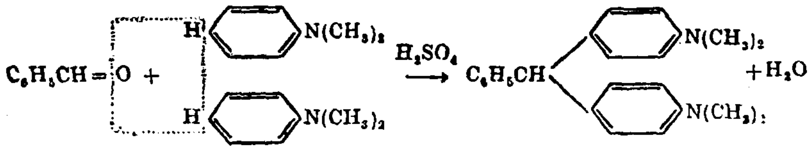
$$(i)\quad H-CH_2-\overset{H}{C}=O \xrightarrow[-H^+]{\bar{O}H} \bar{C}H_2-\overset{H}{C}=O$$

$$(ii)\quad C_6H_5-\overset{H}{C}=O \longrightarrow C_6H_5-\overset{H}{\overset{+}{C}}-\bar{O}$$

$$(iii)\quad C_6H_5-\overset{H}{\overset{+}{C}}-\bar{O} + \bar{C}H_2-\overset{H}{C}=O \longrightarrow C_6H_5-\underset{CH_2CHO}{\overset{H}{C}}-\bar{O}$$

$$(iv)\quad C_6H_5-\underset{CH_2CHO}{\overset{H}{C}}-\bar{O} \xrightarrow{H_2O} C_6H_5-\underset{H-\underset{CHO}{C}-H}{\overset{H}{C}}-OH \xrightarrow{-H_2O} C_6H_5-CH=CHCHO$$

(7) Benzaldehyde condenses with tertiary aromatic amines and phenols in the presence of sulphuric acid or zinc chloride to form derivatives of triphenylmethane. Thus with dimethylaniline it gives *malachite green.*

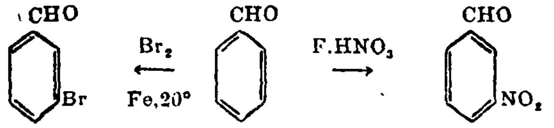


(8) It reacts with chlorine at the boil to form benzoyl chloride.

$$C_6H_5C\Big\langle^{H}_{O} + Cl_2 \longrightarrow C_6H_5C\Big\langle^{Cl}_{O} + HCl$$

C. Reactions of the benzene nucleus

Benzaldehyde gives the usual substitution reactions of the nucleus in the meta position. Thus with fuming nitric acid it gives *m*-nitrobenzaldehyde and with bromine it gives *m*-bromobenzaldehyde.



Uses. Benzaldehyde is used : (1) as a flavouring agent in perfumery ; (2) in the manufacture of dyes (malachite green) ; (3) as starting material for several derivatives *e.g.*, cinnamaldehyde, cinnamic acid, benzoyl chloride, etc.

COMPARISON OF PROPERTIES OF BENZALDEHYDE AND ACETALDEHYDE

Benzaldehyde gives most of the reactions of acetaldehyde. Thus both aldehydes restore pink colour of Schiff's reagent ; form corresponding acids on oxidation ; reduce ammoniacal silver nitrate solution ; form alcohols on reduction ; add on HCN and $NaHSO_3$ to form cyanohydrins and bisulphite compounds ; condense with hydroxyl amine and phenylhydrazine to form oximes and phenylhydrazones ; and react with PCl_5 to form dichloro derivatives in which the O atom is replaced by two Cl atoms. They differ from one another in the following respects :—

BENZALDEHYDE	ACETALDEHYDE
(1) Does not reduce Fehling's solution.	(1) Reduces Fehling's solution.
(2) With ammonia forms hydrobenzamide, $(C_6H_5CH : N)_2 : CH.C_6H_5$.	(2) Forms aldehyde-ammonia.
(3) Condenses with aromatic primary amines to form Schiff's bases.	(3) Does not form Schiff's bases.
(4) In presence of strong alkali, yields benzyl alcohol and benzoic acid.	(4) Gives a resin.
(5) When warmed with alcoholic KCN solution, it forms benzoin.	(5) Does not undergo benzoin condensation ; with a mild alkali undergoes aldol condensation.
(6) With chlorine at the boil, it gives benzoyl chloride.	(6) Does not form acetyl chloride under similar conditions.
(7) Does not polymerise.	(7) Polymerises in contact with H_2SO_4 to form *paraldehyde.*
(8) Condenses with aliphatic aldehydes and acid anhydrides to form unsaturated aldehydes and acids.	(8) Does not undergo similar condensation reactions.
(9) Reacts with HNO_3 and halogens to form substitution products	(9) Nitration in the hydrocarbon radical is not possible. However, reacts with chlorine to form trichloroacetaldehyde.

SOME IMPORTANT AROMATIC ALDEHYDES

CINNAMALDEHYCE, CINNAMIC ALDEHYDE, $C_6H_5.CH{:}CH.CHO$

It is the pleasant smelling constituent of *cinnamon oil* and can be obtained from it through the bisulphite compound. It is prepared by the action of dilute sodium hydroxide upon a mixture of benzaldehyde and acetaldehyde.

$$C_6H_5CHO + CH_3CHO \xrightarrow{NaOH} \underset{\text{Cinnamaldehyde}}{C_6H_5CH{=}CH.CHO} + H_2O$$

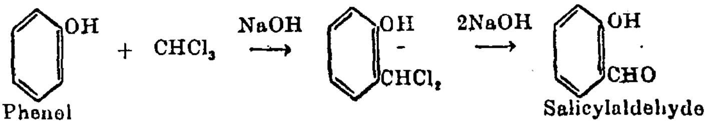
Cinnamaldehyde is a colourless oil, b.p. 252°. On mild oxidation with silver nitrate, it is converted to cinnamic acid.

$$C_6H_5CH{=}CH.CHO + [O] \longrightarrow \underset{\text{Cinnamic acid}}{C_6H_5CH{=}CH.COOH}$$

On vigorous oxidation with acid permanganate, the molecule is split out at the double bond, giving benzoic acid.

SALICYLALDEHYDE, *o*-HYDROXYBENZALDEHYDE

It occurs in oil of *spirea*, and may be made from phenol with the help of Reimer-Tiemann reaction.

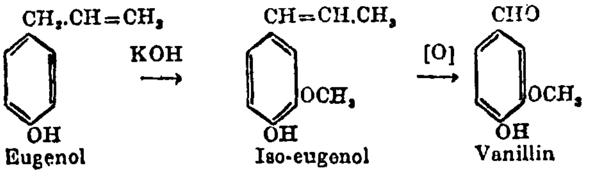


Some *p*-isomer is also obtained which can be removed by steam-distillation, only salicylaldehyde being steam-volatile.

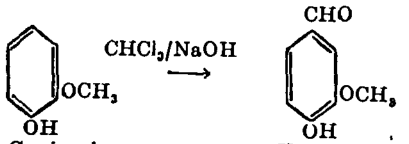
Properties. Salicylaldehyde is a colourless oil, b.p. 196°, with a pleasant smell. It gives the reactions of both aldehydes and phenols. *It produces a violet coloration with ferric chloride.* It may be oxidised to salicylic acid or reduced to *o*-hydroxybenzyl alcohol. It is used for the preparation of coumarin by Perkin's reaction.

VANILLIN, 3-METHOXY-4-HYDROXYBENZALDEHYDE

It is the sweet-smelling principle of vanilla bean and is extracted from it by means of alcohol. It is prepared from *eugenol*, which is obtained from oil of cloves, as follows :



During oxidation the OH group must be protected by temporary acetylation. It may also be prepared from guaiacol by Reimer-Tiemann reaction.



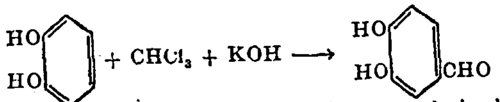
Guaiacol Vanillin

Much of our present-day supply of vanillin is obtained by the hydrolysis of *lignin*, which is a by-product of the paper industry.

Properties. Vanillin is a white pleasant smelling solid, m.p. 81°. It gives a blue coloration with ferric chloride solution. On hydrolysis with hydrochloric acid it forms protocatechuic aldehyde.

2½ per cent alcoholic solution of vanillin is much used for flavouring confectionery.

Protocatechuic aldehyde, *3, 4-dihyldroxybenzaldehyde*, may be synthesised from catechol by Reimer-Tiemann reaction.

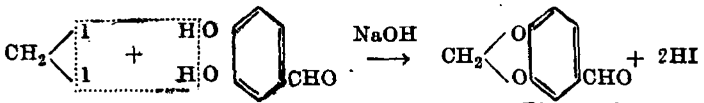


Protocatechuic aldehyde

It is also prepared by the hydrolysis of vanillin with hydrochloric acid.

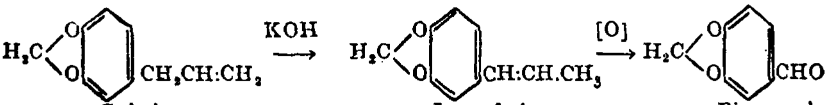
Properties. Protocatechuic aldehyde is a crystalline solid, m.p. 153°. It produces a green coloration with ferric chloride and reduces ammoniacal silver nitrate. On oxidation it forms protocatechuic acid.

Piperonal, *3, 4-methyldioxybenzaldehyde*, was so named as it is produced by oxidation of piperic acid (from alkaloid piperine). It may be synthesised by treating protocatechuic aldehyde with methyl iodide and alkali.



Piperonal

It is made industrially from *safrole* by the same steps as for vanillin from eugenol.



Safrole Iso-safrole *Piperonal*

Properties. Piperonal is a white solid, m.p. 137°, with the smell of *helitrope.* It may be oxidised to piperonylic acid and reduced to piperonyl alcohol. When heated with dilute hydrochloric acid, piperonal is decomposed to form protocatechuic aldehyde together with formaldehyde or methyl alcohol.

2. Aromatic Ketones

Ketones in which either or both the hydrocarbon radicals attached to the carbonyl group are aromatic and are classified as aromatic ketones. Thus :

$C_6H_5.CO.C_6H_5$	$C_6H_5.CO.CH_3$
Benzophenone	Acetophenone

Benzophenone is an example of a purely aromatic ketone, while acetophenone represents a mixed aromatic aliphatic ketone.

Although aromatic ketones may be prepared by any of the methods used for aliphatic ketones, they are generally prepared by means of Friedel-Crafts reaction between a hydrocarbon and acyl chloride or acid anhydride. They give all reactions of the aliphatic ketones in which CO group participates. However, they decline to form the bisulphite compounds, and in addition give the usual substitution reactions of the nucleus.

ACETOPHENONE, METHYL PHENYLKETONE, $C_6H_5.COCH_3$

It is the best known aromatic aliphatic ketone.

Preparation. (1) Acetophenone is best prepared by the Friedel-Crafts reaction from benzene and acetyl chloride.

$$C_6H_6 + ClOCCH_3 \xrightarrow{AlCl_3} C_6H_5.CO.CH_3 + HCl$$

(2) It may also be obtained by heating a mixture of calcium acetate and calcium benzoate but the yield is poor.

Properties. Acetophenone is a colourless crystalline solid, m.p. 20·5°, b.p. 202°, having a smell of hay. It is sparingly soluble in water but dissolves readily in alcohol and ether. It is steam-volatile. When administered by mouth, it produces a natural type of sleep.

Acetophenone gives all the reactions of aliphatic ketones, except that it does not form a bisulphite compound, probably owing to strict hindrance by the phenyl group. It also gives the substitution reactions of the benzene nucleus in the meta position. Its more important reactions are :

(1) On oxidation with strong nitric acid or potassium permanganate, it forms benzoic acid.

$$C_6H_5CO.CH_3 + 4[O] \xrightarrow{HNO_3} C_6H_5COOH + CO_2 + H_2O$$

(2) On reduction with sodium and alcohol, it gives phenylmethyl carbinol.

$$C_6H_5COCH_3 + 2[H] \xrightarrow{Na/C_2H_5OH} C_5H_5.CHOH.CH_3$$

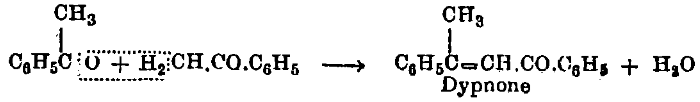
When reduced with amalgamated zinc and hydrochloric acid, it forms ethylbenzene.

$$C_6H_5COCH_3 + 4[H] \xrightarrow[HCl]{Zn/Hg} C_6H_5CH_2CH_3 + H_2O$$

(3) On chlorination it readily forms *phenacyl chloride* which is a relatively harmless but powerful lachyrmator and is used by police as "*mob gas*".

$$C_6H_5COCH_3 + Cl_2 \longrightarrow C_6H_5COCH_2Cl + HCl$$

(4) In the presence of catalyst it undergoes condensation to form *dypnone.*



$$C_6H_5\overset{CH_3}{C}{:}O + H_2{:}CH.CO.C_6H_5 \longrightarrow \underset{\text{Dypnone}}{C_6H_5\overset{CH_3}{C}{=}CH.CO.C_6H_5} + H_2O$$

Uses. Acetophenone is used in perfumery. It was formerly used as a hypnotic under the name "hypnone" but has been replaced by more effective drugs.

BENZOPHENONE, DIPHENYL KETONE, $C_6H_5.CO, C_6H_5$

It is the simplest purely aromatic ketone.

Preparation. (1) Benzophenone is prepared by Friedel-Crafts reaction between benzene and either benzoyl chloride or carbonyl chloride.

$$C_6H_6 + ClOCC_6H_5 \xrightarrow{AlCl_3} C_6H_5.CO.C_6H_5 + HCl$$

$$2C_6H_6 + COCl_2 \longrightarrow (C_6H_5)_2CO + 2HCl$$

(2) It is frequently prepared by Friedel-Crafts reaction between benzene and carbon tetrachloride and hydrolysis of the product.

$$2C_6H_6 + CCl_4 \xrightarrow{AlCl_3} \underset{\substack{\text{Benzophenone}\\ \text{dichloride}}}{(C_6H_5)CCl_2} \xrightarrow{H_2O} (C_6H_5)_2CO$$

(3) It may also be obtained by heating calcium benzoate.

$$(C_6H_5COO)_2Ca \longrightarrow (C_6H_5)_2CO + CaCO_3$$

Properties. Benzophenone exists in two crystalline forms – a metastable monoclinic form, m.p. 27°, and a stable rhombic form, m.p. 48°. It boils at 306°. It has an agreeable odour and is used in making artificial perfumes.

Like acetophenone, it gives all the reactions of aliphatic ketones except that it does not form a bisulphite compound.

(1) On reduction under suitable conditions, it forms benzhydrol and diphenylmethane.

$$C_6H_5.CO.C_6H_5 + 2[H] \xrightarrow[C_6H_5OH]{Na/Hg} \underset{\text{Benzhydrol}}{C_6H_5.CHOH.C_6H_5}$$

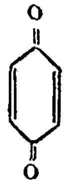
$$C_6H_5.CO.C_6H_5 + 4[H] \xrightarrow[HCl]{Zn/Hg} \underset{\text{Diphenylmethane}}{C_6H_5.CH_2.C_6H_5} + H_2O$$

(2) On fusion with potash, its molecule splits into benzene and benzoic acid.

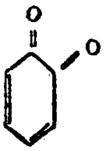
$$C_6H_5.CO.C_6H_5 + KOH \longrightarrow C_6H_5 + \underset{\text{Pot. benzoate}}{C_6H_5COOH}$$

QUINONES

Quinones are unsaturated cyclic diketones. They may be regarded as derived from benzene by replacement of two H atoms by two oxygen atoms. Thus only two quinones, *viz.* *p*-benzoquinone and *o*-benzoquinone are possible.



p-Benzoquinone



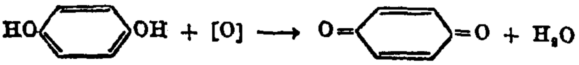
o-Benzoquinone

A similar formula for the *m*-quinone cannot be constructed and it is not known to exist.

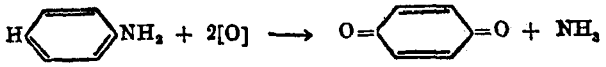
p-BENZOQUINONE

Being the most important member of the class, it is frequently referred to as simply *quinone*.

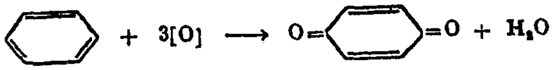
Preparation. (1) Quinone may be readily prepared by the oxidation of quinol with ferric chloride, or with manganese dioxide and sulphuric acid.



(2) It is generally prepared by the oxidation of aniline with sodium dichromate and sulphuric acid in cold.



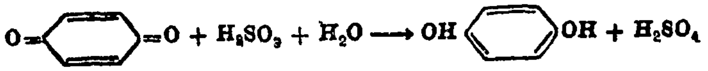
(3) It is also produced technically by the electrolytic oxidation of benzene in the presence of sulphuric acid.



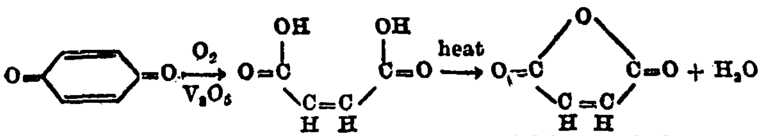
Properties. Quinone forms deep yellow needle-like crystals, m.p. 116°. It has a characteristic pungent smell and causes sneezing. It is only slightly soluble in water but dissolves readily in alcohol and ether. It is steam-volatile.

Quinone lacks the conjugate structure characteristic of aromatic compounds and behaves more as aliphatic than aromatic. Thus it shows the reactions of both ketones and alkenes. It forms an oxime and a bisulphite compound.

(1) REDUCTION. On reduction with sulphurous acid, quinone is converted into hydroquinone.

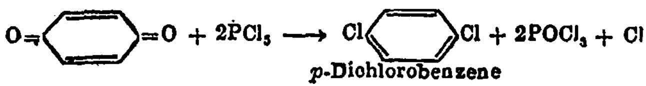


(2) OXIDATION. When oxidised with air in the presence of vanadium pentoxide, it gives maleic acid and finally maleic anhydride.



Maleic acid Maleic anhydride

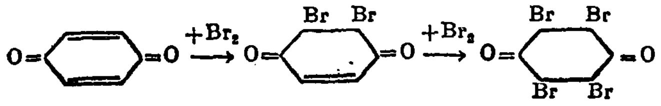
(3) ACTION WITH PCl_5. When treated with phosphorus pentachloride quinone forms *p*-dichlorobenzene.



p-Dichlorobenzene

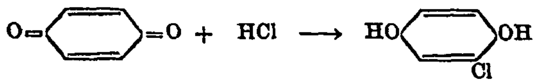
In this reaction, the carbonyl oxygen atoms are replaced by only one atom of chlorine, and not by two as is the case with normal ketones.

(4) ADDITION OF BROMINE. It adds first one and then two molecules of bromine to form a dibromide and tetrabromide respectively.

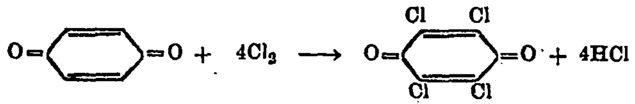


Quinone dibromide Quinone tetrabromide

(5) ADDITION OF HCl. With hydrochloric acid, it undergoes 1, 4-addition forming chlorohydroquinone.



(6) CHLORINATION. With chlorine it yields the substitution product **chloranil**, which is used as a fungicide and as an oxidising agent.

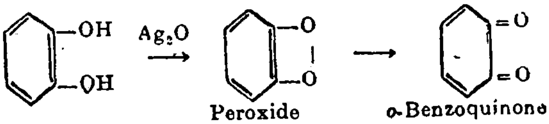


Chloranil

(7) Quinone adds a molecule of hydroquinone to form **quinhydrone**, $C_6H_4O_2.C_6H_4(OH)_2$, which has an important practical use in the measurement of hydrogen-ion concentration by the potentiometric method (*quinhydrone electrode*).

o-BENZOQUINONE, *o*-QUINONE

It is prepared by oxidising catechol with silver oxide in dry ether.



The colourless substance first produced is probably the peroxide which soon changes to the red *o*-quinone.

Properties. *o*-Quinone forms light-red needles, m.p. 60-70° with decomposition. It has no odour and is not volatile with steam. When reduced with sulphurous acid, it gives catechol.

QUESTIONS

1. Point out the structural difference between aliphatic and aromatic aldehydes and bring out clearly the difference between their properties.

2. Give the preparation and important properties of benzaldehyde.

3. Give the properties and uses of benzaldehyde. Compare its properties with those of acetaldehyde.

4. Give an account of the methods used for the preparation of aromatic aldehydes. Compare their properties with those of the aliphatic aldehydes.

5. Write notes on : Etard reaction, Cannizzaro reaction, Benzoin condensation, Perkin reaction.

6. Write notes on : Cannizzaro's reaction, benzoin condensation, Reimer Tiemann reaction, aldol condensation, Gabriel's synthesis.

7. Give a brief account of salicylaldehyde, protocatechuic aldehyde, aniline, and piperonal.

8. How would you prepare vanillin and what are its chief chemical properties ?

9. Give the preparation and properties of acetophenone and benzophenone.

10. How would you distinguish by simple chemical means between any three of the following :

(*i*) Acetaldehyde and benzaldehyde ;
(*ii*) Ethylamine and *p*-toluidine ;
(*iii*) Benzamide and acetanilide ;
(*iv*) Nitroethane and nitrobenzene.

11. How are the quinones prepared ? In what respects do they differ from the ketones ? Discuss the constitution of *p*-benzo-quinone.

12. What are quinones ? Describe *two* methods of preparing *p*-benzoquinone. Discuss its important physical and chemical properties. Would you include these compouds under aromatic class ? Give reasons.

13. Describe two methods for the preparation of a pure sample of benzaldehyde. In what respects does it resemble and differ from benzophenone ; explain these reactions giving equations. (*Allahabad B.Sc. II, 1967*)

14. Outline the structural differences between acetaldehyde and benzaldehyde. In what respect these compounds differ chemically ? Give suitable examples in support of your answers. (*Agra B.Sc. II, 1967*)

15. Give methods of preparation, properties and uses of salicylic acid. Name its important derivatives. (*Indore B.Sc. III, 1967*)

16. What are quinones ? How are they prepared ? Give an account of their important reactions. (*Kalyani B.Sc. Hons. III, 1967*)

17. Give the synthesis of acetophenone. What is the action of (*i*) HNO_3 van NaBrO on acetophenone ? (*Poona B.Sc. II, 1967*)

dric

18. How would you prepare Vanillin ? What are its chief uses ? (*Panjab B.Sc. III, 1968*)

19. How is benzaldehyde prepared commercially ? Compare and con- its properties with those of aliphatic aldehydes. (*Tribhuwan B.Sc., 1968*)

20. How is benzaldehyde prepared in the laboratory ? In what respects its properties differ from those of acetaldehyde ? (*Sambalpur B.Sc., 1968*)

21. How is benzaldehyde prepared from toluene ? Compare the pro- erties of acetaldehyde with those of benzaldehyde. (*Poona B.Sc., 1968*)

22. State the methods by which benzaldehyde can be prepared. State the reactions which bring out the similarities and differences between aromatic and aliphatic aldehydes. (*Viswa Bharati B Sc., 1969*)

23. Describe the laboratory method of preparation of benzaldehyde from benzoyl chloride. Compare its reaction with those of acetaldehyde. (*Marathwada B.Sc., 1969*)

24. Describe the preparation, chemical properties and uses of acetophenone. (*Kurukshetra B.Sc., 1969*)

25. How is benzaldehyde prepared ? Compare its properties with those of acetaldehyde. (*Delhi B.Sc., 1969*)

45

Aromatic Carboxylic Acids

WILLIAM H. PERKIN
(1838—1907)
English Organic Chemist. His chief contribution was the well-known Perkin Reaction, the synthesis of coumarin, and synthesis of alizarin.

They are compounds in which one or more COOH groups are directly attached to the nucleus. Those acids in which the COOH group is attached to the side-chain may be regarded as aryl-substituted aliphatic acids. However, there are no characteristic differences in the behaviour of nuclear and side-chain acids and the term 'aromatic acids' is rather loosely extended to include both classes of compounds.

Aromatic acids may be prepared by the same general methods as used for aliphatic acids. In addition, they may be obtained by oxidation of aromatic hydrocarbons with a side-chain. It will suffice to list below the reactions by means of which aromatic acids can be prepared.

$$(1)\qquad \underset{\text{Benzaldehyde}}{C_6H_5CHO} + (O) \xrightarrow{KMnO_4} \underset{\text{Benzoic acid}}{C_6H_5COOH}$$

$$(2)\qquad \underset{\text{Benzotrichloride}}{C_6H_5CCl_3} + 3H_2O \xrightarrow{NaOH} \underset{\text{Benzoic acid}}{C_6H_5COOH} + 3HCl + H_2O$$

(3) $$\underset{\text{Phenyl cyanide}}{C_6H_5CN} + 2H_2O \xrightarrow{H_2SO_4} \underset{\text{Benzoic acid}}{C_6H_5COOH} + NH_3$$

(4) $$\underset{\text{Phenylmagnesium bromide}}{C_6H_5MgBr} \xrightarrow{CO_2} C_6H_5.CO.OMgBr \xrightarrow{HCl} \underset{\text{Benzoic acid}}{C_6H_5.COOH}$$

(5) $$\underset{\text{Benzene}}{C_6H_6} + COCl_2 \xrightarrow{AlCl_3} C_6H_5COCl \xrightarrow{H_2O} \underset{\text{Benzoic acid}}{C_6H_5.COOH}$$

(6) $$\underset{\text{Toluene}}{C_6H_5.CH_3} \xrightarrow{[O]} \underset{\text{Benzoic acid}}{C_6H_5COOH}$$

Aromatic acids are white crystalline solids. They are generally slightly soluble in cold water but fairly so in hot water and organic solvents. They are somewhat stronger acids than those of the aliphatic series. Aromatic acids show exactly similar reactions to those of aliphatic acids. They differ from the latter chiefly in the substitution reactions of the nucleus.

MONOCARBOXYLIC ACIDS

BENZOIC ACID, BENZENECARBOXYLIC ACID, C_6H_5COOH

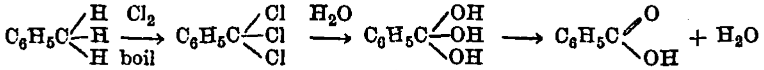
It is the simplest and the most familiar aromatic acid. It was first obtained by Scheele (1775) from *gum benzoin* (whence its name), a natural resin got from trees in Java and Sumatra. It occurs as benzyl ester in Peru and Tolu balsams and as benzoyl glycine in the urine of horses and oxen.

Preparation. Benzoic acid may be obtained by the general methods mentioned earlier. Technically it can be prepared by the following methods :

(1) By the oxidation of toluene with air at 300° in the presence of vanadium pentoxide as catalyst.

$$2C_6H_5CH_3 + 3O_2 \xrightarrow[300^\circ]{V_2O_5} 2C_6H_5COOH + 2H_2O$$

(2) By chlorinating toluene to benzotrichloride and hydrolysing the latter by boiling with lime water, or with water in the presence of iron.



$$C_6H_5C\begin{cases}H\\H\\H\end{cases} \xrightarrow[\text{boil}]{Cl_2} C_6H_5C\begin{cases}Cl\\Cl\\Cl\end{cases} \xrightarrow{H_2O} C_6H_5C\begin{cases}OH\\OH\\OH\end{cases} \longrightarrow C_6H_5C\begin{cases}O\\OH\end{cases} + H_2O$$

Toluene Benzotrichloride *Unstable* Benzoic acid

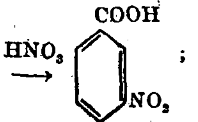
Properties. (*Physical*). Benzoic acid crystallises from water in white, pearly flakes, m.p. 121·4°. It is sparingly soluble in cold water but dissolves readily in hot water, ether, alcohol and benzene. It is volatile in steam and may be sublimed. Its vapours have a peculiarly pungent odour which causes coughing and sneezing. Benzoic acid is a slightly stronger acid than acetic acid.

(*Chemical*). The reactions of benzoic acid are those of the carboxyl group and the benzene nucleus.

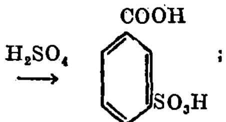
(1) *Reactions of COOH.* Benzoic acid closely resembles the fatty acids in the reactions of the carboxyl group ; that is, it forms salts, esters, amide, and chloride etc. Thus :

$$C_6H_5COOH \left[\begin{array}{l} + NaOH \longrightarrow \underset{\text{Sod. benzoate}}{C_6H_5COONa} + H_2O \\ + C_6H_5OH \xrightarrow{H_2SO_4} \underset{\text{Ethyl benzoate}}{C_6H_5COOC_2H_5} + H_2O \\ + NH_3 \longrightarrow C_6H_5COONH_4 \xrightarrow{\text{heat}} C_6H_5CONH_2 + H_2O \\ + PCl_5 \longrightarrow \underset{\text{Benzoyl chloride}}{C_6H_5COCl} + POCl_3 + HCl \\ + \text{Sodalime} \xrightarrow{\text{heat}} C_6H_6 + Na_2CO_3 \end{array}\right.$$

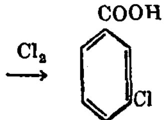
(2) *Reactions of C_6H_5* The benzene nucleus of benzoic acid gives the usual substitution reactions. The COOH group is *meta-directing*, so that such substitution reactions take place less readily than with benzene. Thus :



m-Nitrobenzoic acid ;



m-Sulphobenzoic acid ;



m-Chlorobenzoic acid

Uses. Benzoic acid is used : (1) in medicine as urinary antiseptic and in vapour form for disinfecting bronchial tubes ; (2) in the dye industry for making *aniline blue* ; and (3) as a preservative. Sodium benzoate, being less toxic, is used for preserving food products such as *tomato kechup* aud fruit juices.

Tests. (1) Benzoic acid dissolves in hot water but separates in shining flakes on cooling.

(2) When treated with sodium bicarbonate solution, it evolves carbon dioxide gas.

(3) When fused with soda-lime, inflammable vapours of benzene are given out.

(4) A neutralised solution of benzoic acid reacts with freshly prepared ferric chloride solution to form a light brown precipitate of ferric benzoate.

(5) When warmed with alcohol and concentrated sulphuric acid, it gives a characteristic sweet smell of ethyl benzoate.

BENZOYL CHLORIDE, BENZENECARBONYL CHLORIDE, C_6H_5COCl

It is a typical aromatic acid chloride and occupies the same position in the aromatic series that acetyl chloride occupies among aliphatic compounds.

Preparation, (1) It is prepared most conveniently in the laboratory by distilling benzoic acid with phosphorus pentachloride or with thionyl chloride.

$$C_6H_5COOH + PCl_5 \longrightarrow C_6H_5COCl + POCl_3 + HCl$$
$$C_6H_5COOH + SOCl_2 \longrightarrow C_6H_5COCl + SO_2 + HCl$$

(2) It is also produced by the action of carbonyl chloride on benzene in the presence of anhydrous aluminium chloride (*Friedel-Crafts reaction*).

$$C_6H_6 + \underset{\text{Phosgene}}{ClCO.Cl} \xrightarrow{AlCl_3} C_6H_5.COCl + HCl$$

(2) It is made commercially by chlorination of boiling benzaldehyde.

$$C_6H_5CHO + Cl_2 \longrightarrow C_6H_5COCl + HCl$$

Properties. Benzoyl chloride is a colourless liquid, b.p. 198°, fuming in moist air. It has a pungent odour and its vapour cause profuse watering of eyes and nose. It is practically insoluble in water.

Benzoyl chloride gives all the reactions of acetyl chloride, although much less readily. Thus, it is slowly hydrolysed by hot water to form benzoic acid ; it reacts with alcohols and phenols to form esters, with ammonia and amines to form benzoyl derivatives, and so on

$$C_6H_5COCl \left[\begin{array}{lll} + H_2O & \xrightarrow{\text{boil}} & C_6H_5COOH + HCl \\ & & \text{Benzoic acid} \\ + C_6H_5OH & \longrightarrow & C_6H_5COOC_2H_5 + HCl \\ & & \text{Ethyl benzoate} \\ + \textit{Aq.}\ NH_3 & \longrightarrow & C_6H_5CONH_2 + HCl \\ & & \text{Benzamide} \\ + RNH_2 & \longrightarrow & C_6H_5CO.NHR + HCl \\ + C_6H_6 & \xrightarrow{AlCl_3} & C_6H_5COC_6H_5 + HCl \\ & & \text{Benzophenone} \end{array}\right.$$

Uses. Benzoyl chloride is used : (1) in tear gases to disperse mobs ; and (2) for introducing benzoyl radical, C_6H_5CO-, in hydroxy and amino-compounds. To this end, the substance to be benzoylated is shaken with benzoyl chloride in dilute aqueous sodium hydroxide solution.

$$ROH + ClOCC_6H_5 + NaOH \longrightarrow RO.OCC_6H_5 + NaCl + H_2O$$
$$RNH_2 + ClOCC_6H_5 + NaOH \longrightarrow RNH.OCC_6H_5 + NaCl + H_2O$$

The benzoyl derivative separates as a solid and excess benzoyl chloride dissolves as sodium benzoate. This method of benzoylation is known as the **Schotten-Baumann reaction**. Dry pyridine is also employed as a medium (in place of aqueous alkali) to conduct benzoylation of phenols.

Benzamide, $C_6H_5CONH_2$. It may be prepared by the action of benzoyl chloride on concentrated aqueous ammonia or ammonium carbonate

$$C_6H_5COCl + 2NH_3 \longrightarrow C_6H_5CONH_2 + NH_4Cl$$

It may also be produced by Friedel-Crafts reaction between benzene and carbamyl chloride.

$$C_6H_5H + ClCONH_2 \longrightarrow C_6H_5CONH_2 + HCl$$

Properties. Benzamide is a white crystalline solid, m.p. 130°. It is insoluble in cold water but dissolves in hot. It undergoes most of the usual reactions of aliphatic amines. It is readily hydrolysed to benzoic acid and, ammonia on boiling with dilute acid or alkali ; it forms benzonitrile on heating with P_2O_5.

$$C_6H_5CONH_2 + HOH \longrightarrow C_6H_5COOH + NH_3$$

$$C_6H_5.CONH_2 \longrightarrow C_6H_5CN + H_2O$$

The negative benzoyl group confers acidic properties to the H atom attached to nitrogen atom ; thus benzamide dissolves in alkalis to form salts *e.g.* $C_6H_5CONHNa$. With mercury oxide, it gives mercury benzamide, $(C_6H_5CONH)_2Hg$.

Benzoic anhydride, $(C_6H_5CO)_2O$. It may be prepared by heating benzoyl chloride with sodium benzoate.

$$C_6H_5COONa + ClOCC_6H_5 \longrightarrow \underset{\text{Benzoic anhydride}}{C_6H_5CO.O.COC_6H_5} + NaCl$$

A better method is to boil a mixture of benzoic acid and acetic anhydride.

$$2C_6H_5COOH + (CH_3CO)_2O \longrightarrow (C_6H_5CO)_2O + 2CH_3COOH$$

Properties. Benzoic anhydride is a white crystalline solid, m.p. 42°. Its reactions are those of acetic anhydride, but it is much less reactive. It is only slowly decomposed by water. It may be used for benzoyltion, but benzoyl chloride is more convenient for the purpose.

Benzoyl peroxide, $C_6H_5CO.O.O.COC_6H_5$. It is prepared by adding peroxide to stirred mixture of benzoyl chloride, ice and water.

$$2C_6H_5COCl + Na_2O_2 \longrightarrow \underset{\text{Benzoyl peroxide}}{C_6H_5CO.O.O.COC_6H_5} + 2NaCl$$

Benzoyl peroxide is a relatively stable, colourless solid, m.p. 108°. It acts as an oxidising and disinfecting agent. Hence, it is a harmless bleaching agent and is often used for bleaching wheat flour.

Phenyl cyanide, ***benzonitrile,*** C_6H_5CN. It can be prepared by boiling benzamide with phosphorus pentoxide.

$$C_6H_5.CONH_2 \xrightarrow{P_2O_5} C_6H_5CN + H_2O$$

It may also be produced by fusing sodium benzenesulphonate with sodium cyanide or by Sandmeyer's reaction by treating benzenediazonium chloride with potassium cyanide.

Benzonitrile is a colourless oil, b.p. 191°, having a smell of bitter almonds. It forms benzoic acid on hydrolysis, and benzylamine on reduction.

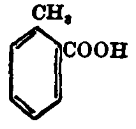
$$C_6H_5C{\equiv}N \xrightarrow{+H_2O} \underset{\text{Benzamide}}{C_6H_5CONH_2} \xrightarrow{+H_2O} \underset{\text{Benzoic acid}}{C_6H_5COOH} + NH_3$$

$$C_6H_5C{\equiv}N + 4[H] \longrightarrow \underset{\text{Benzylamine}}{C_6H_5CH_2NH_2}$$

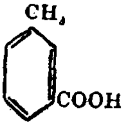
SUBSTITUTED BENZOIC ACIDS

TOLUIC ACIDS, METHYLBENZOIC ACIDS, $C_6H_4(CH_3)COOH$

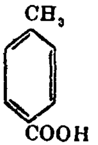
o-, *m*- and *p*-toluene carboxylic acids are called ***toluic acids.***



o-Toluic acid



m-Toluic acid



p-Toluic acid

These are isomeric with phenylacetic acid.

Preparation. The toluic acids may be prepared by oxidation of one of the methyl groups of the corresponding xylenes by dilute nitric acid. They are conveniently made from toluidines by converting them *via* the diazonium salts into nitriles and hydrolysis.

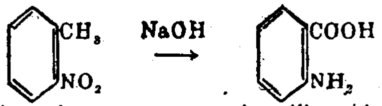
$$CH_3.C_6H_4.NH_2 \xrightarrow[\text{reaction}]{\text{Diazo}} CH_3.C_6H_4.N_2Cl \xrightarrow[\text{reaction}]{\text{Sandmeyer-}} CH_3.C_6H_4.CN \xrightarrow{H_2O} CH_3.C_6H_4.COOH$$

Properties. The toluic acids are white solids, m.pts. *o*- 104°, *m*- 111°, *p*- 178°. Since the methyl groups are almost unreactive, they behave very similar to benzoic acid. However, on oxidation they yield the phthalic acids.

ANTHRANILIC ACID, o-AMINOBENZOIC ACID, $C_6H_4(NH_2)COOH$

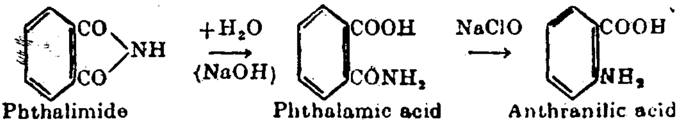
Of the three isomeric aminobenzoic acids, the ortho derivative is the most important. It was first obtained by the fusion of indigo (*anil*) with alkali and hence its name. It occurs as methyl ether in jasmine and organic blossoms.

Preparation. Anthranilic acid may be prepared by reducing *o*-nitrobenzoic acid, or by boiling an alkaline solution of *o*-nitrotoluene in alcohol (*internal oxidation*).



o-Nitrotoluene Anthranilic acid

Technically, it is best made from phthalimide by action with concentrated aqueous alkali and sodium hypochlorite (*Hofmann reaction*).



Phthalimide Phthalamic acid Anthranilic acid

Properties. Anthranilic acid is a white solid, m.p. 45°, having a sweet taste. It is readily soluble in water and alcohol. On heating, it is decarboxylated to form aniline. It gives all other normal reactions of nuclear NH_2 and COOH groups.

Uses. Anthranilic acid is used as an intermediate in the synthesis of indigo and methyl red. Methyl anthranilate is used in perfumery.

p-Aminobenzoic acid, m.p. 187°, may be prepared by reducing p-nitrobenzoic acid. It is a vitamin and has been shown to cure quickly Rocky Mountain spotted fever, a disease spread by fleas. It is of importance in the preparation of novocaine, or procaine, which is the hydrochloride of its diethylaminoethyl ester.

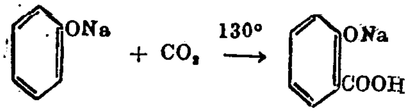
Novocaine

Novocaine is much used as local anaesthetic as it is less toxic and is not habit forming.

SALICYLIC ACID, o-HYDROXYBENZOIC ACID, HO.C_6H_4.COOH

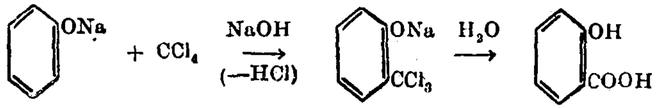
It takes its name from *salicin*, the glucoside of the corresponding alcohol, from which it was first obtained (Piria, 1838) by hydrolysis and oxidation. It occurs as its methyl ester in many essential oils.

Preparation. (1) Salicylic acid is prepared commercially by heating dry sodium phenolate with carbon dioxide at 130° in an autoclave under six to seven atmosphere pressure (*Kolbe reaction*).



The fused mass from the autoclave is dissolved in water and the solution acidified to liberate free salicylic acid. This is then recrystallised from hot water.

(2) It may be made by heating phenol with carbon tetrachloride in alkali solution (*Reimer-Tiemann reaction*).



Salicylic acid is also produced by the oxidation of o-cresol with potassium hydroxide and lead peroxide, or from anthranilic acid *via* diazonium salt.

Properties. (*Physical*). Salicylic acid crystallises from hot water in fine colourless needles, m.p. 159°. It is difficultly soluble in cold water but dissolves readily in hot water, alcohol and ether. It sublimes below its melting point and is steam-volatile. It is a stronger acid than benzoic acid. Salicylic acid is somewhat poisonous and has powerful antiseptic properties.

(*Chemical*). Salicylic acid behaves both like an acid and a phenol. Thus :

(1) It forms salts, esters and other acid derivatives.

$$2C_6H_4(OH)COOH + Na_2CO_3 \longrightarrow \underset{\text{Sod. salicylate}}{2C_6H_4(OH)COONa} + H_2O + CO_2$$

$$C_6H_4(OH)COOH + 2NaOH \longrightarrow \underset{\text{Disodium salicylate}}{C_6H_4(ONa)COONa} + 2H_2O$$

$$C_6H_4(OH)COOH + CH_3OH \xrightarrow{H_2SO_4} \underset{\text{Methyl salicylate}}{C_6H_4(OH)COOCH_3} + H_2O$$

(2) Like most phenols, it gives a violet coloration with $FeCl_3$, couples with diazonium salts, and forms acetyl derivatives at the OH group.

$$C_6H_4(OH)COOH + CH_3COCl \longrightarrow \underset{\text{Acetylsalicylic acid}}{C_6H_4(O.OC.CH_3)COOH} + HCl$$

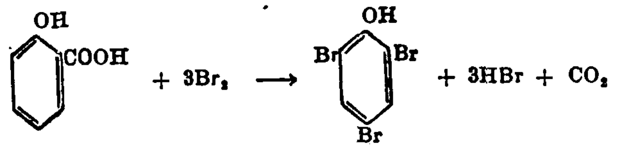
(3) When heated slowly, it decarboxylates to phenol.

$$C_6H_4(OH)(COOH) \longrightarrow C_6H_5OH + CO_2$$

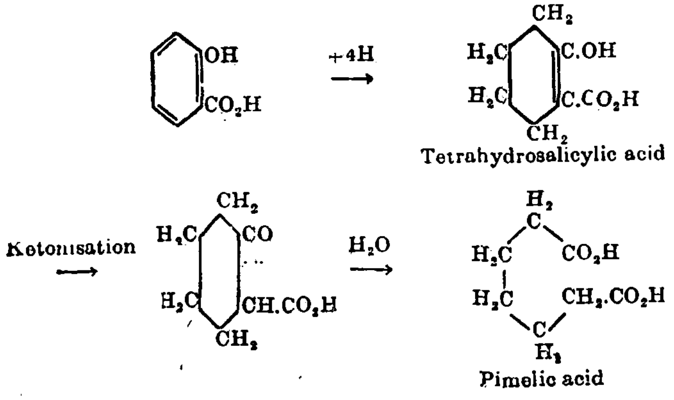
When heated to about 200°, it gives phenyl salicylate. Possibly the phenol first produced combines with unreacted salicylic acid to form the ester.

$$2C_6H_4(OH)COOH \longrightarrow C_6H_4(OH)COOC_6H_5 + CO_2 + H_2O$$

(4) When treated with bromine water, it gives *s*-tribromophenol, the COOH group being replaced by Br atom.

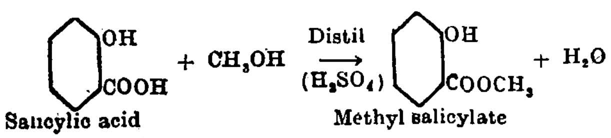


(5) When reduced with sodium and boiling amyl alcohol, the ring hydrogenates and cleaves to form pimelic acid.



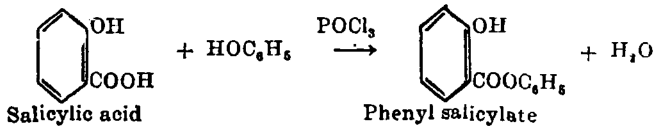
Uses. Salicylic acid is used : (1) as antiseptic and disinfectant ; (2) for making azo-dyestuffs ; (3) for preparing aspirin, salol, methyl salicylate, and (4) as medicine, when it is given as sodium salicylate in rheumatic conditions.

Methyl salicylate. It is the principal constituent of the oil of wintergreen It is prepared by distilling a mixture of salicylic acid and methyl alcohol in the presence of sulphuric acid.



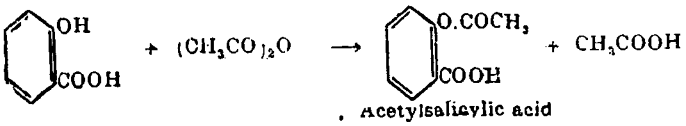
Methyl salicylate is a colourless, pleasant smelling liquid, b.p. 224°. It is used as a flavour and perfume. It possesses a simulating action on the skin and is, therefore, used in hair tonics, and in liniments for treating aches, sprains and bruises.

Phenyl salicylate. It is prepared by heating salicylic acid with phenol in the presence of phosphorus oxychloride.



It is a white solid, m.p. 42°. It is used as an intestinal antiseptic under the name *salol.*

Acetylsalicylic acid. It is prepared by heating salicylic acid with acetic anhydride, in the presence of a trace of sulphuric acid.

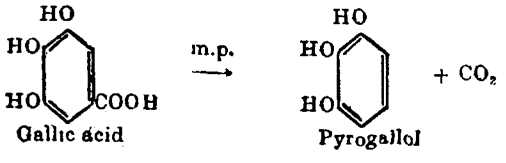


It is a white solid, m.p. 134°. It is used in medicine, under the name *aspirin*, as an analgetic, for relieving toothache, headache and colds.

GALLIC ACID, 3, 4, 5-TRIHYDROXYBENZOIC ACID, $C_6H_2(OH)_3COOH$

It occurs widely in galls, tea, oak, bark, *kikar* bark etc., in the free state and as a unit of *tannin** molecule. It is best prepared by boiling tannin with a dilute acid and extracting the gallic acid with ether.

Properties. Gallic acid forms white needles, m.p. 222°; readily soluble in hot water, alcohol and ether. When heated at its melting point, it breaks down into pyrogallol and carbon dioxide.



Gallic acid is a strong reducing agent. It reduces ammoniacal silver nitrate, and its alkaline solution readily absorbs oxygen from

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***Tannin** or *tannic acid,* is a complex glucoside of gallic acid. It is a colourless solid, dissolves in water to solutions of astringent taste. It is used for tanning hides and making inks.

the air and turns brown. With ferric chloride, it gives a blue-black precipitate ; this property is used in making inks

Gallic acid is used for making pyrogallol, some dyes, and blue-black inks.

Blueblack Inks. The blue-black writing inks consist chiefly of an aqueous solution of gallic acid, ferrous sulphate and a little blue dye. Some gum (protective agent), a little sulphuric acid (to retard oxidation of ferrous sulphate), and a trace of phenol (preservative) is also added. When the ink flows from the pen on the paper, the sulphuric acid is neutralised by alumina of the paper. The ferrous sulphate is then rapidly oxidised to ferric sulphate and this forms a deep black precipitate with gallic acid. Hence, the ink writes blue but becomes intensely black on drying.

PHENYLACETIC ACID, $C_6H_5.CH_2COOH$

It is a typical aromatic acid with the COOH group attached to the side chain. It is isomeric with toluic acids.

Preparation. Phenylacetic acid is prepared easily by boiling benzyl chloride with alcoholic potassium cyanide and hydrolysing the resulting nitrile by boiling with dilute sulphuric acid.

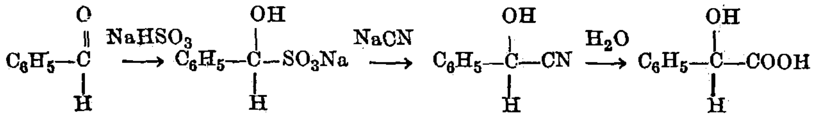
$$\underset{\text{Benzyl chloride}}{C_6H_5CH_2Cl} \xrightarrow{KCN} \underset{\text{Benzyl nitrile}}{C_6H_5\,CH_2CN} \xrightarrow{H_2O} \underset{\text{Phenylacetic acid}}{C_6H_5CH_2COOH}$$

Properties. Phenylacetic acid is a while crystalline solid, m.p. 77°, with an unpleasant odour. It is a stronger acid than acetic acid, which is due to the acid character of the phenyl group. When oxidised with chromic acid, phenylacetic acid is converted to benzoic acid. The isomeric toluic acids on oxidation yield phthalic acids.

MANDELIC ACID, PHENYLHYDROXLACETIC ACID, $C_6H_5.CHOHCOOH$

It occurs naturally as the glucoside, *amygdalin*, in bitter almonds from which source it may be obtained by hydrolysis with concentrated hydrochloric acid.

Preparation. Mandelic acid is prepared by the hydrolysis of benzaldehyde cyanohydrin (mandelonitrile) which in turn is obtained by treating the bisulphite compound of benzaldehyde with concentrated solution of sodium cyanide



$$C_6H_5-\overset{O}{\overset{\|}{C}}-H \xrightarrow{NaHSO_3} C_6H_5-\overset{OH}{\underset{H}{C}}-SO_3Na \xrightarrow{NaCN} C_6H_5-\overset{OH}{\underset{H}{C}}-CN \xrightarrow{H_2O} C_6H_5-\overset{OH}{\underset{H}{C}}-COOH$$

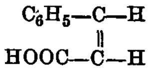
Benzaldehyde Mandelonitrile Mandelic acid

Properties. Mandelic acid is a white crystalline solid moderately soluble in water. It exhibits optical activity, the alcoholic C-atom being asymmetric. The acid obtained by hydrolysis of *amgydalin* is the *l*-form melting at 133° while the *dl*-acid melts at 118°.

Mandelic acid behaves like a hydroxy acid. When heated with hydriodic acid, it is reduced to phenylacetic acid. Upon vigorous oxidation it is converted to benzoic acid. Mandelic acid is used as an internal antiseptic.

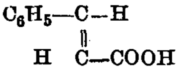
CINNAMIC ACID, β-PHENYLACRYLIC ACID, $C_6H_5.CH:CH.COOH$

It is the most important unsaturated aromatic acid. It occurs free and as benzyl ester in the oil of cinnamon and in Peru and Tolu balsams. Owing to the presence of a double bond in the molecule, cinnamic acid exhibits geometrical isomerism.



$$\begin{matrix} C_6H_5-C-H \\ \| \\ HOOC-C-H \end{matrix}$$

Cis form



$$\begin{matrix} C_6H_5-C-H \\ \| \\ H\quad C-COOH \end{matrix}$$

Trans form

Ordinary acid is the *trans* form, and the *cis* form is also known to exist.

Preparation. (1) It may be prepared by heating a mixture of benzaldehyde, acetic anhydride and sodium acetate for about 6 hours (*Perkin's reaction*). The overall reaction is

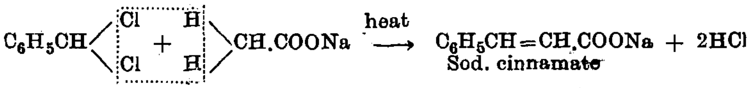
$$C_6H_5CHO + (CH_3CO)_2O \xrightarrow{CH_3COONa} C_6H_5CH{=}CH.COOH$$

(2) It is also produced by the condensation of benzaldehyde with ethyl acetate in the presence of sodium ethoxide (*Claisen reaction*) and hydrolysis of the resulting ester.

$$C_6H_5CH{=}\boxed{O + H_2}C{:}CH.COOC_2H_5 \xrightarrow{C_2H_5ONa} C_6H_5CH{=}CH.COOC_2H_5 + H_2O$$

$$\xrightarrow{H_2O} C_6H_5CH{=}CH.COOH$$

(3) It is made commercially heating sodium acetate with benzal chloride, and acidification of the product.



$$C_6H_5CH\begin{matrix} \diagup \\ \diagdown \end{matrix}\boxed{\begin{matrix} Cl & & H \\ & + & \\ Cl & & H \end{matrix}}\begin{matrix} \diagdown \\ \diagup \end{matrix}CH.COONa \xrightarrow{heat} \underset{\text{Sod. cinnamate}}{C_6H_5CH{=}CH.COONa} + 2HCl$$

(4) It is usually manufactured from benzalacetone by oxidation with alkaline sodium hypochlorite (*Cf.* haloform reaction of acetone).

$$C_6H_5CH{=}CH.CO.CH_3 \xrightarrow{NaClO} C_6H_5CH{=}CH.COOH$$

Properties. Cinnamic acid is a white solid; m.p. 133°, having a persistent sharp odour. It is a very sparingly soluble in water. Its reactions are those of an unsaturated acid and the phenyl radical.

(1) When reduced with sodium amalgam and water, it gives dihydrocinnamic acid (β-phenylpropionic acid).

$$C_6H_5CH{=}CH.COOH + 2[H] \xrightarrow[H_2O]{Na/Hg} C_6H_5CH_2.CH_2.COOH$$

(2) On oxidation with cold potassium permanganate, the double bond cleaves to give benzaldehyde, while vigorous oxidation yields benzoic acid.

$$C_6H_5CH{=}CH.COOH \xrightarrow{KMnO_4} C_6H_5CHO \longrightarrow C_6H_5COOH$$

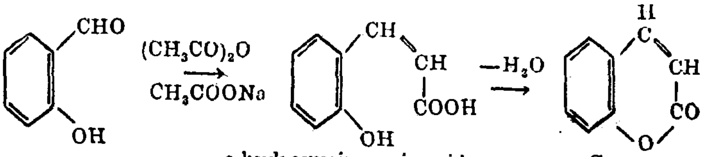
(3) The COOH group gives the usual reaction with alkalis to form salts and with alcohols to form esters. On heating above its melting point, or on heating with soda-lime, cinnamic acid decarboxylates to styrene.

$$C_6H_5CH{=}CH.COOH \xrightarrow{heat} C_6H_5CH{=}CH_2 + CO_2$$

(4) Nitration with mixed acids yields a mixture of *o*- and *p*-nitrocinnamic acids.

Various esters of cinnamic acid are used in the perfumery industry.

Coumarin. It is the odoriferous principle of woodruff, hay and tonka beans. It is prepared from salicylaldehyde by Perkin reaction. The free *o*-hydroxycinnamic acid first produced at once forms the internal ester, coumarin.



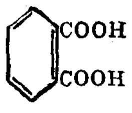
o-hydroxycinnamic acid Coumarin

Coumarin is a white crystalline solid, m.p. 67°, having the flavour resembling that of vanillin. When warmed with sodium hydroxide, the ester ring opens up to form the sodium salt of coumarinic acid.

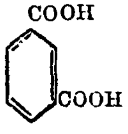
It is used as a cheap substitute of vanillin, in making artificial perfumes.

DICARBOXYLIC ACIDS

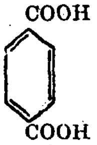
All the three possible benzenedicarboxylic acids are known.



Phthalic acid



Isophthalic acid



Terephthalic acid

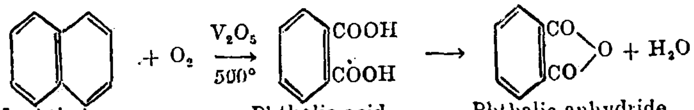
Of these, *o*-dicarboxylic acid, phthalic acid is the most important.

Phthalic acids can be prepared either by oxidation of the respective xylenes or of toluic acids. They can also be obtained from the corresponding toluidines via nitriles and subsequent hydrolysis. Phthalic acids are white crystalline solids. They give all the usual reactions of dicarboxylic acids, forming acid and normal derivatives. *Phthalic acid* is distinguished from the meta and para isomers as it forms an inner anhydride on heating.

PHTHALIC ACID, *o*-BENZENEDICARBOXYLIC ACID, $C_6H_4(COOH)_2$

It was discovered by Laurent (1836) as an oxidation product of naphthalene. It is produced by the oxidation of any benzene derivative having carbon-substituents in ortho positions.

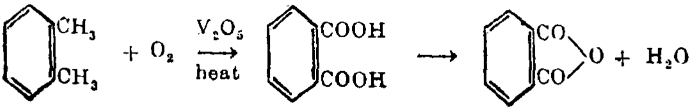
Preparation. (1) Phthalic acid is manufactured by passing a mixture of naphthalene vapour and air over a vanadium pentoxide catalyst at 500°. (*Gibbs Process*)



Naphthalene Phthalic acid Phthalic anhydride

Formerly the above oxidation was carried with fuming sulphuric acid and mercuric sulphate but that method is now obsolete.

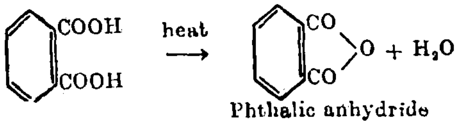
(2) In a newer method, introduced in U.S.A., phthalic acid is produced on a large scale by the catalytic oxidation of *o*-xylene obtained from petroleum.



The phthalic acid first formed in the above methods, loses a molecule of water at high temperature of the reaction and the product is phthalic anhydride. This may be converted to phthalic acid by boiling with water.

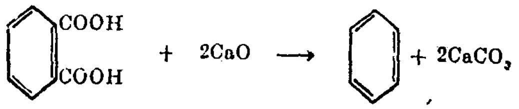
Properties. Phthalic acid is a white crystalline solid melting at 231° on rapid heating. It is sparingly soluble in cold water but dissolves fairly rapidly in hot.

Phthalic acid gives all the usual reactions of a dicarboxylic acid. It decomposes on heating at the melting point to form the anhydride, just like succinic acid.



Phthalic anhydride

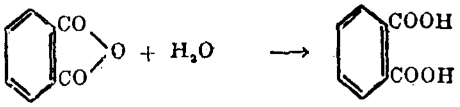
Like benzoic acid, it yields benzene when heated wich soda-lime.



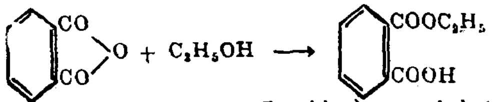
The chief importance of phthalic acid is in the formation of its anhydride which is of great technical value. Benzoic acid is now manufactured by decarboxylating phthalic acid.

Phthalic anhydride, $C_6H_4(CO)_2O$. It is made commercially by the catalytic oxidation of naphthalene and toluene as described under phthalic acid. Phthalic anhydride gives all the normal reactions of acetic anhydride, though less readily.

(1) It is slowly decomposed with cold but quickly with boiling water to form phthalic acid.



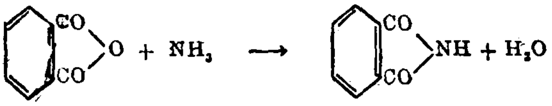
(2) When heated with alcohols, it gives acid esters.



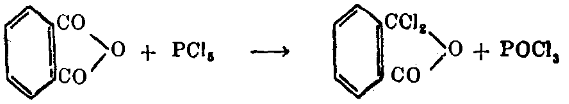
Ethyl hydrogen phthalate

These acid esters may be converted into the normal diesters by the usual method of heating with excess of alcohol and sulphuric acid.

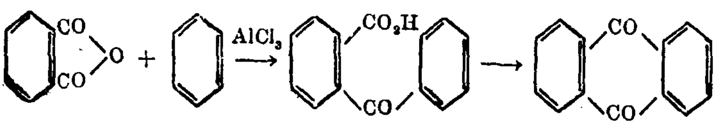
(3) It reacts with dry ammonia, forming straightway phthalimide.



(4) It reacts with PCl_5 to form phthaloyl chloride.



(5) When heated with benzene in presence of anhydrous aluminium chloride, it yields anthraquinone. *(Friedel-Crafts reaction).*

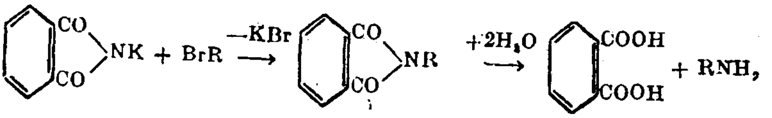


Benzoylbenzoic acid Anthraquinone

(6) It condenses to form phenolphthalein and fluorescein, when heated respectively with phenol and resorcinol, after adding a little sulphuric acid.

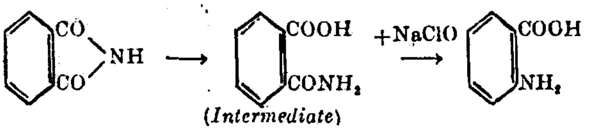
Uses. Phthalic anhydride is used for manufacturing resins, plasticisers (dibutyl phthalate), insect repellants (dimethyl phthalate), perfumes (diethyl phthalate), anthraquinone, phthalimide, phenolphthalein, fluorescein, etc. The production of phthalic anhydride in United States exceeds two hundred million pounds a year (1951).

Phthalimide, $C_6H_4(CO)_2NH$. It is prepared most conveniently by passing dry ammonia gas overheated phthalic anhydride (see above). It is a white crystalline solid, m.p. 238°, insoluble in water. It is definitely acidic in character and forms N-potassium salts when treated with alcoholic potash.



The potassium phthalimide reacts with alkyl halides to form alkyl derivatives which on hydrolysis yield primary amines (Gabriel's synthesis of primary amines).

When treated with alkaline sodium hypochlorite, it is converted into anthranilic acid (*Hofmann's method*).



Phthalimide is used for the synthesis of aliphatic primary amines and for the manufacture of anthranilic acid.

QUESTIONS

1. Give two ways by which benzoic acid may be prepared from benzene. Describe the reactions by which the following may be obtained from benzoic acid : (*a*) benzamide, (*b*) ethyl benzoate, (*c*) silver benzoate, (*d*) benzonitrile.

2. Give the methods by which benzoic acid may be prepared from toluene. How may benzoic acid be converted into (*a*) benzene, (*b*) ethyl benzoate, (*c*) benzoyl chloride, (*d*) silver benzoate? (*Cambridge University*)

3. Indicate by means of formulae and reactions how you would distinguish between benzamide and acetamide.

4. Compare and contrast the properties of benzoic acid and acetic acid.

5. How is salicylic acid prepared ? Describe the action of heat upon the acid and compare its behaviour in this respect with lactic acid. How could it be converted into phenol ? State the uses of salicylic acid.

6. Describe the preparation of salicylic acid. By what tests would you distinguish between (*a*) salicylic acid and benzoic acid ; (*b*) salicylic acid and phenol ?

7. Write short notes on salicylic acid and its derivatives, indicating chiefly their structural formulae and physiological properties and uses. (*Cape Town University*)

8. Give the preparation and important properties of salicylic acid.

9. What is mandelic acid ? How can this be prepared ? What are its properties ? Compare mandelic acid with the lactic acid so far as the reaction of (*i*) HNO_3, (*ii*) HI, (*iii*) HCl on both these compounds is concerned.

10. Describe the preparation of salicylic acid. By what tests would you distinguish between (*a*) Salicylic acid and benzoic acid, (*b*) Salicylic acid and phenol ?

11. Give briefly the preparation, properties and uses of

(*a*) Anthranilic acid. and

(*b*) Phthalic acid. (*Banaras B.Sc. II, 1964*)

12. Give synthesis of the medicinally important substitutes of salicylic acid. (*Vallabhbhai B.Sc. III, 1964*)

13. Describe the manufacture of salicylic acid and give its important reactions. Name two of its derivatives used in medicine, also giving their methods of preparation. (*Nagpur B.Sc. III, 1964*)

14. How is phthalic acid prepared in commerce ? How is it converted into—

(*a*) Anthranilic acid.
(*b*) Phenolphthalein.
(*c*) Fluorescein.
(*d*) Phthaloyl chloride.
(*e*) Anthraquinone. (*Panjab B.Sc. III, 1967*)

15. Give the preparation of salicylic acid from phenol. Mention its uses. What procedure is adopted for its conversion to (*a*) Aspirin and (*b*) Oil of winter green. (*Marathwada B.Sc., 1968*)

16. Describe the various methods of introducing carbonyl group in the benzene nucleus. Starting with benzoic acid how do you prepare :—

(1) Benzamide, (2) Phenyl cyanide (3) Benzoyl chloride and (4) Benzoic acid. (*Poona B.Sc., 1968*)

17. Describe three methods of preparation of cinnamic acid. State the characteristic chemical properties of the acid. (*Viswa-Bharati B.Sc., 1969*)

18. Assuming that the properties of three Phthalic acids are known, devise a procedure to determine the orientation of (*i*) three nitroanilines ; (*ii*) three nitrotoluenes. (*Allahabad B.Sc., 1969*)

46

Colour and Constitution. Dyes

RICHARD WILLSTATTER
(1872—1942)
German Chemist. Famous for his studies of alkaloids, quinones, flower pigments, chemistry of enzymes, and chlorophyll. He won the Nobel Prize in 1915.

ORIGIN OF COLOUR

We know that white light is made of seven colours : violet, indigo, blue, green, yellow, orange and red. If an object reflects or transmits all the light falling on it, it appears to be white ; if it absorbs all the light, it looks black. An object appears coloured when it absorbs only a portion of the white light and reflects or transmits the rest. The colour of this residual light, which escapes absorption and enters our eyes, determines the colour of the object. Thus an object looks blue because it is able to absorb the yellow colour (complementary colour). Similarly, an object appears purple, since it has absorbed the complementary green colour.

Light consists of waves that are produced by the vibrations of electrons, and these waves in turn can cause the vibrations of electrons elsewhere. The absorption of light by a compound is akin to the phenomenon of resonance noted with sound. We know very well that a vibrating string of a piano or a vibrating tuning fork causes the vibrations of any other object which has the same vibration rate. Exactly similarly, the light falling on a compound, sets the electrons of the latter vibrating provided, of course, they can vibrate or resonate in harmony. In doing so, a part of light is absorbed or used up by resonating electrons, and the remaining portion of it determines the colour of the compound. The presence of certain unsaturated groups in a molecule, makes a compound coloured, because such groups provide loosely bound electrons that are available for harmonic vibrations. The saturated compounds like methane, ethyl alcohol etc., having completely paired or firmly bound electrons, are colourless.

WITT'S THEORY OF COLOUR AND DYES

Dyes are coloured compounds capable of being fixed to fabrics and which do not wash out with soap and water or fade on exposure to light. Therefore, *a coloured organic substance is not necessarily a dye.* For illustration, both picric acid and trinitrotoluene are yellow, but only the former can fix to a cloth and is a dye, while the latter does not fix to a cloth and is not a dye.

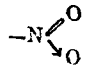
From the study of facts as above, Otto Witt propounded his theory of dyes as early as 1876. This so-called **Chromophore theory** may be summed up in the following points :

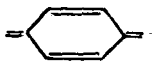
(1) The dye is derived from a parent coloured compound termed **chromogen** (*meaning colour generator*).

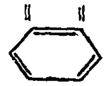
(2) The colour of chromogen is due to the presence of certain groups of atoms called **chromophores** (*meaning colour bearing groups*).

The more important chromophoric groups are :

$C=O$	$-N=N-$	$-N=O$
Carbonyl	Azo	Nitroso


Nitro


p-Quinoid


o-Quinoid

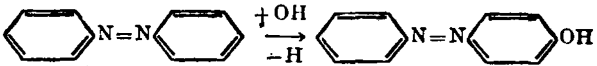
(3) The dye takes its fixing property from certain acid or basic groups present in the molecule. These groups not only increase the solubility of the dye and help in fixing it to a fabric, but also enhance the intensity of the colour and are termed **auxochromes** (meaning, *colour-aiding groups*). For instance, nitrobenzene is pale-yellow but the introduction of the auxochrome NH_2 imparts to it fixing property and also makes it orange in colour. The most important auxochromic groups are OH, COOH, SO_3H, NH_2, NHR, and NR_2.

The postulates of the Witt's theory may be stated as

Dye = Chromogen + Auxochrome

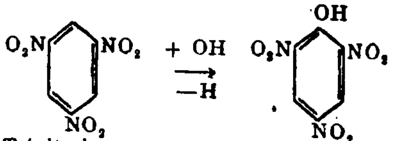
Chromogen = Chromophore bearing compound

This may be illustrated by taking example of *p*-hydroxyazobenzene, which is a bright red dye.


Azobenzene (*Chromogen*) p-Hydroxyazobenzene (*Dye*)

In this case the chromogen is azobenzene which has a red colour ; it contains azo group, —N : N—, as the chromophore. The auxochrome is the phenolic OH group.

Again, picric acid serves as a yellow dye. It contains : (1) the chromogen trinitrobenzene which owes its yellow colour to the three chromophoric nitro groups ; and (2) the OH as the auxochromic group.


Trinitrobenzene (*Chromogen*) Picric acid (*Yellow dye*)

CLASSIFICATION OF DYES

Dyes may be classified according to their molecular structure or by their dyeing procedures.

(1) **Chemical Classification.** Dyes may be divided into groups according to their chemical constitution, more particularly according to chromophores they contain. Thus we have : (*a*) Nitro and nitroso dyes ; (*b*) Azo dyes ; (*c*) Triphenylmethane dyes ; (*d*) Phthalein dyes ; (*e*) Anthraquinone dyes ; (*f*) Indigo dyes ; (*g*) Vat dyes ; (*a*) Sulphur dyes, etc.

(2) **Classification according to dyeing procedures.** The chemical classification of dyes is of theoretical interest to the chemist but the dyer is concerned mainly with application of dyes to fibres. The dyes are often grouped according to the procedure of their application.

(*a*) *Acid dyes.* These contain acidic groups *e.g.*, OH, SO_3H and are applied in acidic solution. They dye wool and silk directly.

(*b*) *Basic dyes.* These contain amine groups and are applied in basic solutions. They dye wool and silk directly and cotton after mordanting.

(*c*) *Direct dyes* ((substantive dyes). These usually contain a number of acidic or basic groups. They dye animal and vegetable fibres directly.

(*d*) *Mordant dyes* (adjective dyes). They contain two or more acidic or basic groups. They dye neither animal nor vegetable fibres directly, but do so when applied to mordanted cloth. For acidic dyes, the mordants used are metallic hydroxides, while for basic dyes, tannic acid is used as a mordant. For *metal mordanting* the cloth is soaked in a solution of the metallic salt (aluminium acetate) and then into the basic solution of the dye. The dye combines with the freshly precipitated metallic hydroxide to form an insoluble pigment called a *lake*, which is fast to washing. For tannin mordanting, the cloth is soaked in tannin solution and then in the dye solution ; this produces insoluble lakes.

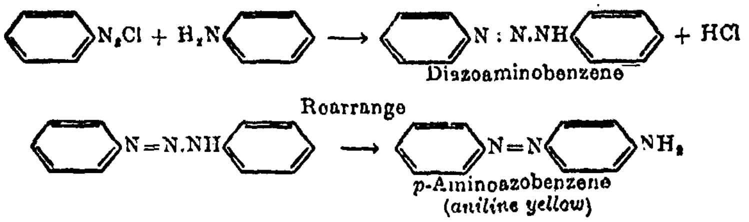
(*e*) *Vat dyes*. These are insoluble in water but are reduced to colourless derivatives (*leuco compounds*) by alkaline reducing agents. The cloth is soaked in the solution of reduced dye and then spread in the air so that the leuco-compound is oxidised back to the original dye. Indigo is an important vat dye.

(*f*) *Ingrain dyes*. There are dyes which are produced in the fibre itself. For example, the cloth is first soaked in the solution of a diazonium salt and then in the solution of a phenol or amine. The coupling takes place in the fibres of the cloth giving a fast colour.

AZO DYES

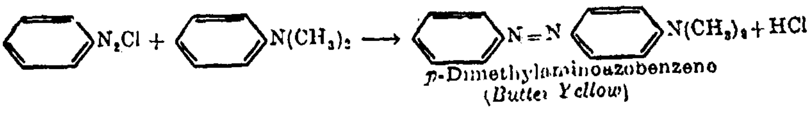
Azo dyes contain the common chromophore the azo group, $-N{=}N-$ and the auxochromes such as $-NH_2$, $-NR_2$, $-OH$, and $-SO_3H$ These dyes are prepared by diazotizing an amino-compound and coupling the resulting diazonium salt with a phenol in alkaline solution, or with an amine in neutral or slightly acidic solution.

Aniline yellow. It is the simplest basic azo dye and is obtained by coupling diazotized aniline with aniline.



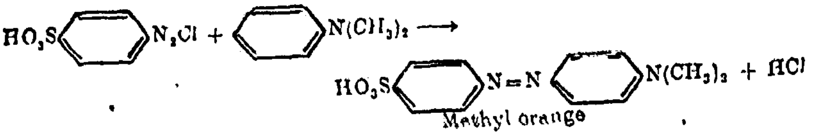
It is used to colour fats and cheese.

Butter yellow. It is prepared by coupling diazotized aniline with dimethylaniline.

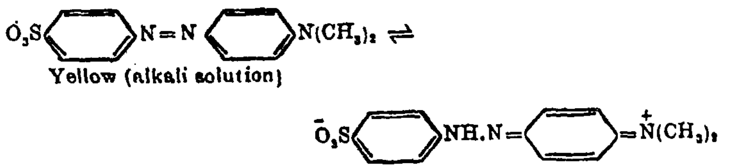


It is used to colour butter and oils.

Methyl Orange. It is made by diazotizing sulphanilic acid and coupling with dimethylaniline.



Methyl orange imparts an orange colour to wool and silk, but t has little importance as a dye because it is not fast to sunlight or washing. It is well known as an indicator for acid-alkali titrations, since it is yellow in alkali solution but becomes *red in acid solution.* [he indicator owes its colour change to a change in the structure of ts ion.

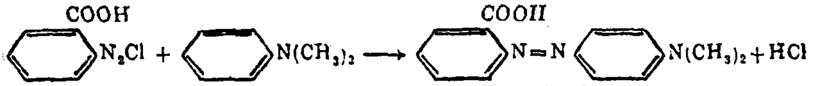


Yellow (alkali solution)

Red acid (solution)

The yellow form contains the *azo* chromophore, while the red form contains the *p*-quinoid chromophore.

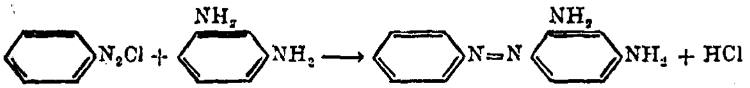
Methyl Red. It is made by coupling diazotized *o*-amino benzoic acid with dimethylaniline.



Methyl red

It is indicator in acid alkali titrations.

Chrysoidine. It is prepared by coupling benzenediazonium chloride with *m*-phenylenediamine.

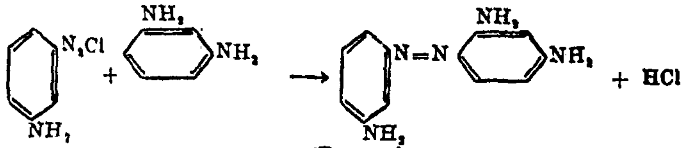


Chrysoidine

It is an orange-red dye and is used for dyeing silk and wool directly, and cotton after tannin mordanting.

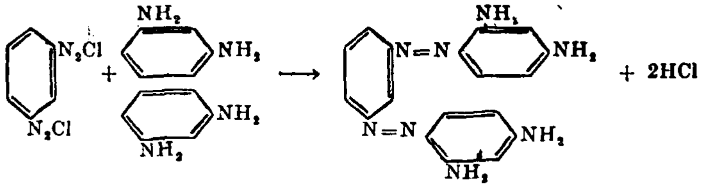
Bismarck Brown. It is prepared by action of nitrous acid on excess *m*-phenylenediamine in hydrochloric acid. It is a mixture of two brown dyes obtained by diazotization of one or both the NH_2 groups of the diamine and subsequent coupling with unchanged diamine.

(*a*) *When only one NH_2 is diazotized :*



(Brown dye)

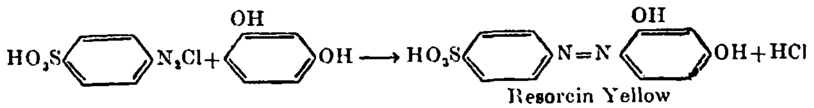
(*b*) *When both NH_2 groups are diazotized* :



(Brown dye)

Bismarck Brown consists of mostly the second dye. It is used for making boot polishes, and for dyeing wool and mordanted cotton. It is also used to stain wood before applying varnish in the production of immitation mahogany furniture.

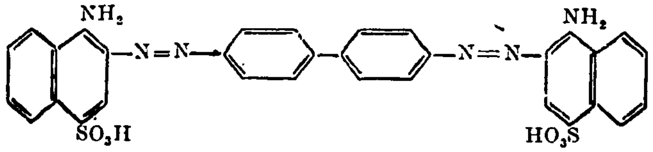
Resorcin Yellow It is made by coupling diazotized sulphanilic acid with resorcinol.



Resorcin Yellow

It is golden yellow dye used for dyeing silk.

Congo Red. It is obtained by coupling diazotized benzidine with 1-aminonaphthalene-4-sulphonic acid. It has the structure



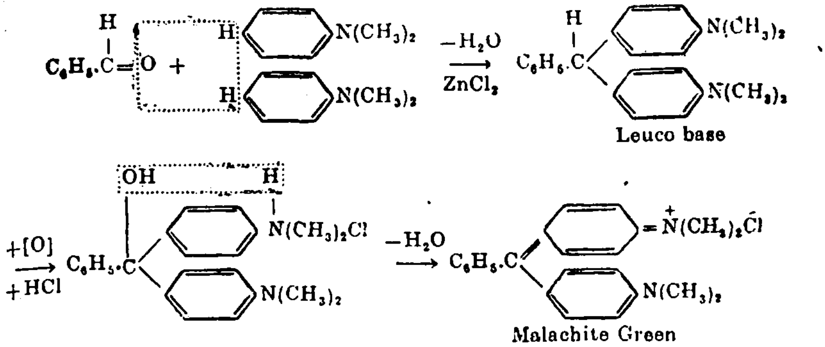
It is a dark red dye used for direct dyeing of cotton. It is also used as indicator—*red in alkali, blue in acid.*

TRIPHENYLMETHANE DYES

Triphenylmethane, $(C_6H_5)_3CH$, is the *chromogen* of a large number of dyes. The common chromophore is the *p*-quinoid structure and the auxochromes are OH, NH_2 and NR_2.

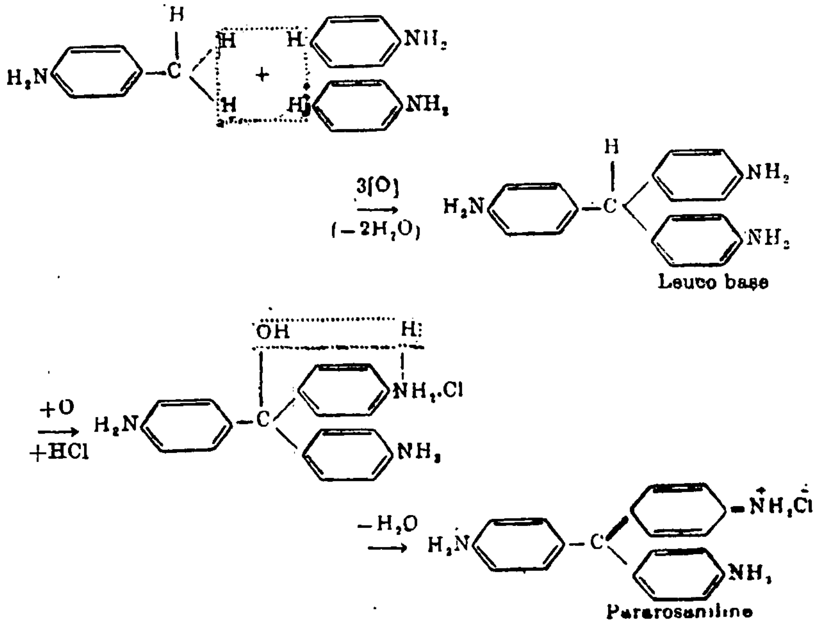
Triphenylmethane dyes are very brilliant intense colours but fade quickly in light. Therefore, they are no longer much used on textiles. However, they are used in large quantities for colouring paper and typewriter ribbons where fastness to light is not so important.

Malachite Green (O. Fischer, 1877). It is the simplest triphenylmethane dye and is prepared by heating benzaldehyde with dimethylaniline in the presence of fused zinc chloride and oxidising the leuco base (Gr., *leuke* = colourless) first produced to the dye with lead dioxide and excess hydrochloric acid.



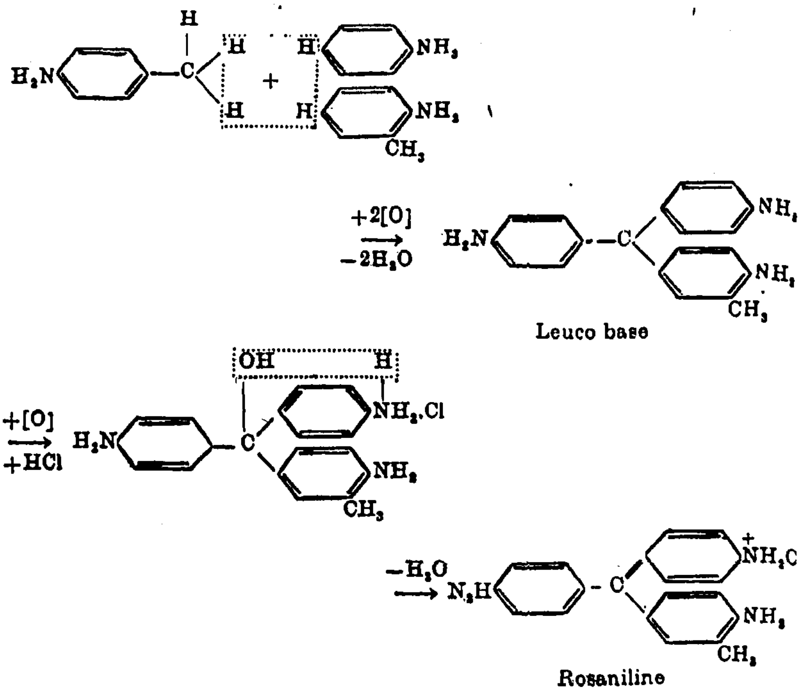
Malachite Green takes its name from the fact that it has a deep blue-green colour resembling that of the *malachite* (copper ore). It is used as a direct dye for silk and wool, and for cotton after mordanting with tannin. It is a basic dye and is marketed in the form of its oxalate.

Pararosaniline (Verguin, 1859). It is made by the oxidation of aniline (2 mols.) and *p*-toluidine (1 mol.) with nitrobenzene and treatment with hydrochloric acid.



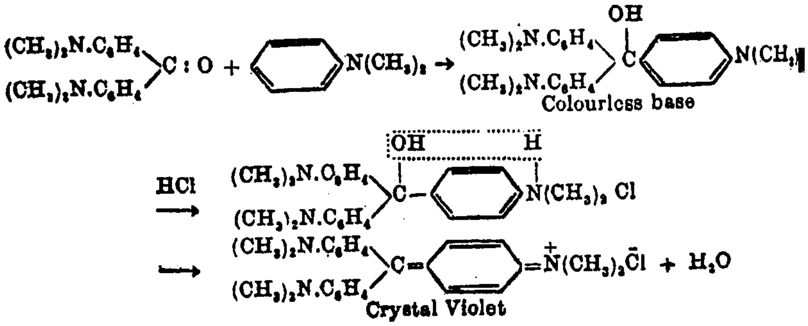
Pararosaniline dyes wool and silk a rose red colour, and cotton after mordanting with tannin.

Rosaniline, *Magenta, Fuschine.* It differs from pararosaniline in the substitution of a methyl radical ortho to one of the amino groups. It is made by oxidising a mixture of aniline (1 mol.), *o*-toluidine (1 mol.) and *p*-toluidine (1 mol.) and treatment of the leuco base thus produced with hydrochloric acid.



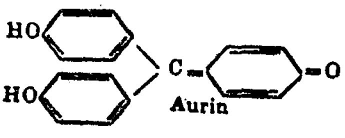
Rosaniline forms bright green crystals which dissolve in water giving crimson solutions. It dyes wool and silk a bright rose red directly, but cotton after mordanting with tannin. It is also used for colouring foods. The aqueous solutions of the dye are rendered colourless by sulphur dioxide owing to the formation of a new leuco base, yielding the **Schiff's reagent** ; it is reddened by aldehydes but not by ketones. (*Test*).

Crystal Violet (Kern, 1883). This is the most important triphenylmethane dye at present. It is usually prepared by heating Michler's ketone with dimethylaniline in the presence of $POCl_3$. The product when treated with hydrochloric acid, gives the dye.



The solid dye consists of bronzy-green crystals which dissolve water to give deep violet solutions (hence, the name). It is an xcellent dye for wool and silk but needs a mordant with cotton. s it fades in light, the dye is used in large quantities for colouring aper and typewriter ribbons where fastness to light is not a great onsideration.

Aurin, *pararosalic acid.* It is made by boiling diozotized ararosaniline with water



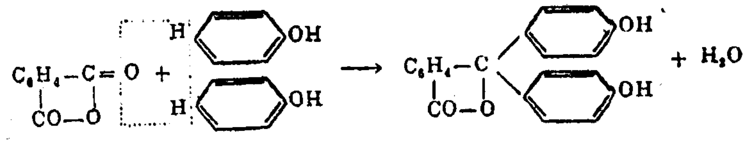
Aurin

Aurin produces yellowish-red solutions which become intense ed on the addition of alkalis. It is used as an indicator and for rinting of wall-paper.

HTHALEINS

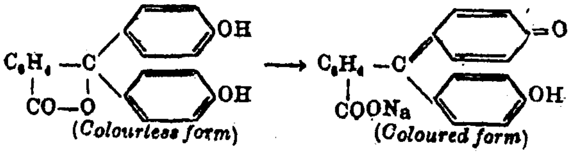
These are triphenylmethane derivatives and are made by heating phthalic anhydride with phenols in the presence of a dehydrating agent (H_2SO_4 or $ZnCl_2$). The phthaleins are colourless but react vith alkalis to form dyes having a qunoid structure.

Phenolphthalein (Baeyer, 1871). It is the simplest member f this class, and is prepared by heating phthalic anhydride (1 mol.) nd phenol (2 mols.) in the presence of concentrated sulphuric acid.



Phthalic anhydride Phenolphthalin

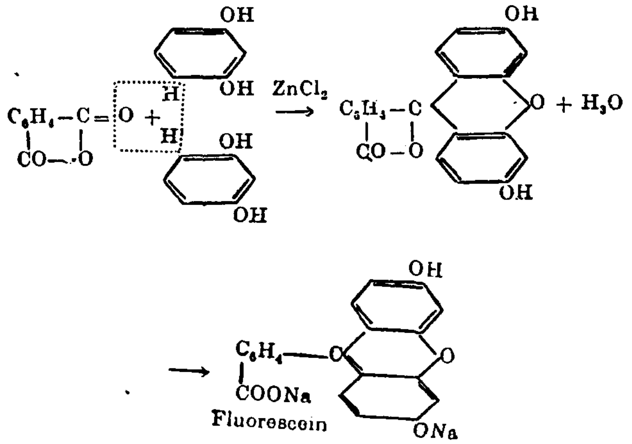
Phenolphthalein is a white crystalline solid. It is insoluble in vater but dissolves in alcohol giving colourless solutions which turn ink on addition of alkalis.



(*Colourless form*) (*Coloured form*)

Phenolphthalein is used as indicator for acid base titrations nd in medicine as a laxative.

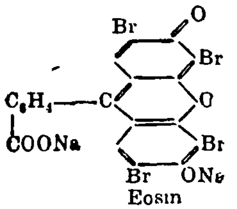
Fluorescein. It is prepared by heating phthalic anhydride 1 mol.) with resorcinol (2 mols.) in the presence of zinc chloride.



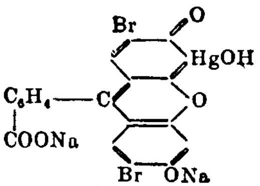
Fluorescein

Fluorescein is an orange powder. Its alkaline solutions show beautiful yellow green fluorescence. It is used for decoration purposes and for tracing the course of water supplies.

Eosin. Direct bromination of fluorescein yields the dye eosin. It is used for dyeing wool and silk yellowish red. It is used in large amounts for making red inks.



Eosin



Mercurochrome

Mercurochrome. It is made by mercuration of dibromofluorescein and action with sodium hydroxide. It is an intense red dye and is used as an antiseptic in the form of a two per cent solution in water.

QUESTIONS

1. Describe the Chromophore theory of dyes. Indicate clearly the meaning of the terms : Chromophore, Auxochrome and Chromogen.

2. Write an essay on colour and constitution.

3. Explain the term 'chromophore', 'chromogen' and 'auxochrome'. How would you prepare malachite green in the laboratory ?

4. What are azo dyes ? Give a short account of Butter Yellow, Methyl Orange, Bismarck Brown, and Congo Red.

5. Classify the various dyestuffs. What is meant by an acid dye, a basic dye and mordant ?

6. Write short explanatory notes on :—

(a) Substantive dye ;

(b) Chromophore ;

(*c*) Auxochrome ;
(*d*) Chromogen ;
(*e*) Mordant ;
(*f*) Lakes.

Give examples.

7. Give the preparation and uses of the following :—
   (*i*) Flourescein.
   (*ii*) Congo Red.
   (*iii*) Malachite green.
   (*iv*) Methyl orange.

8. What are triphenylmethane dyes ? How would you prepare malachite green and pararosaniline ?

9. Give an account of the theories of colour and constitution. (*Baroda B.Sc. III, 1964*)

10. What makes an organic compound coloured ? Discuss the method of preparation and constitution of Alizarin. (*Kurukshetra B.Sc. III, 1967*)

11. Give a short account of 'colour and constitution'. (*J & K B.Sc., 1967*)

12. Give a brief account of the chemistry of triphenylmethane dyes. (*Kalyani B.Sc. Hons., 1967*)

13. How would you prepare fluorescein ? What are its chief uses ? (*Panjab B.Sc., 1968*)

14. Give an elementary account of the relation between colour and constitution. (*Vankateswara B.Sc., 1969*)

15. What are azo and hydrazo compounds ? How are they prepared ? Discuss the factors responsible for the different shades in the azo dyes. (*Kurukshetra B.Sc., 1969*)

16. Describe the synthesis of three important azo dyes and two important triphenylmethane dyes. (*Berhampur B.Sc., 1969*)

47

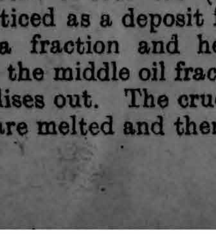
Naphthalene and its Derivatives

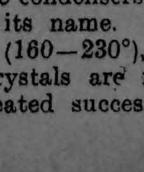
R.A.C. EMIL ERLENMEYER
(1825—1909)

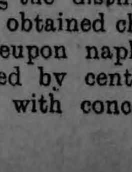
German. Much interted in the structural theories of Organic Chemistry. Best known through naphthalene formula and the conical flask named after him.

NAPHTHALENE, $C_{10}H_8$

Naphthalene is an aromatic hydrocarbon in which two benzene rings are fused in ortho positions. For the purposes of naming its derivatives, the positions are indicated by figures or by the Greek letters.





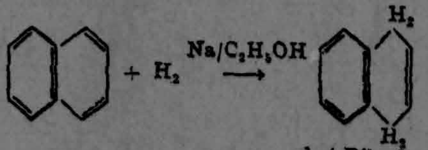


Isolation from Coal-tar. Naphthalene is the largest single component of coal tar (6 to 11 per cent). The hydrocarbon was first noticed as a deposit in the condensers during the distillation of naphtha fraction and hence its name. It is obtained chiefly by cooling the middle oil fraction (160—230°), whereupon naphthalene crystallises out. The crude crystals are removed by centrifuging. These are melted and then treated successively with concentrated sulphuric acid (to remove basic impurities), water, and sodium hydroxide solution (to remove phenols). Finally the naphthalene is sublimed to give the pure product.

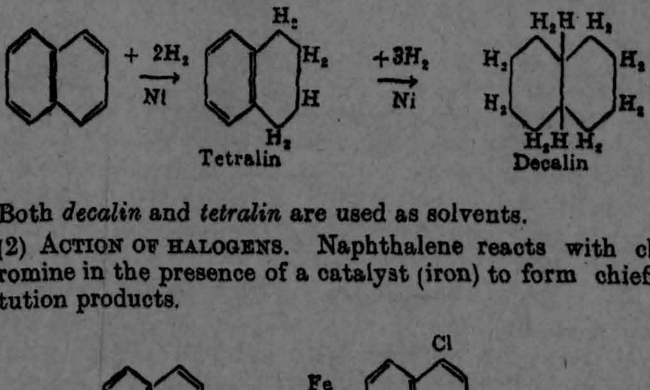
Properties. (*Physical*). Naphthalene is a white solid which crystallises in shining plates, m.p. 80°, b.p. 218°, having a strong odour (familiar in moth balls). It is very volatile and sublimes readily on warming. Naphthalene is insoluble in water, but dissolves easily in organic solvents, particularly ether and benzene.

(*Chemical*). The reactions of naphthalene are essentially the same as those of benzene ; it undergoes substitution readily and forms addition products. However, it is somewhat less aromatic than benzene. Thus the double bonds in naphthalene exhibit in part the reactivity of alkenes and it forms addition compounds more readily than does benzene. As soon as one of the rings is fully saturated by addition of hydrogen or halogens, or is destroyed by oxidation, the second ring at once assumes the stability of benzene.

(1) ADDITION OF HYDROGEN. Naphthalene when reduced with sodium and alcohol, forms 1, 4-dihydro derivative. Catalytic reduction with hydrogen in the presence of nickel may be carried to yield the tetrahydro and under more drastic conditions the decahydro products.



1, 4-Dihydronaphthalene

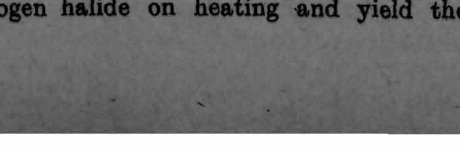


Tetralin

Decalin

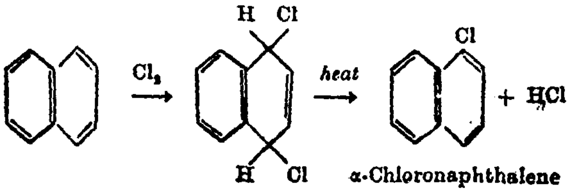
Both *decalin* and *tetralin* are used as solvents.

(2) ACTION OF HALOGENS. Naphthalene reacts with chlorine and bromine in the presence of a catalyst (iron) to form chiefly the substitution products.



α-Chloronaphthalene

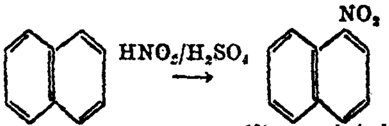
At room temperature and in the absence of a catalyst, naphthalene reacts with halogens to form addition compounds, which lose halogen halide on heating and yield the substitution products.



α-Chloronaphthalene

The action of bromine on naphthalene is so rapid that it is frequently used as a convenient laboratory method for preparing hydrogen bromide.

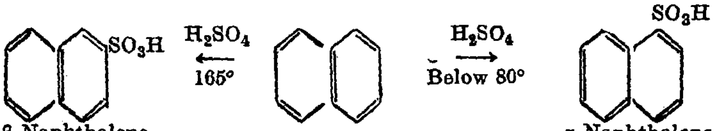
(3) NITRATION. Naphthalene nitrates with a mixture of nitric acid and sulphuric acid at low temperature to form mainly the α-nitronaphthalene.



α Nitronaphthalene

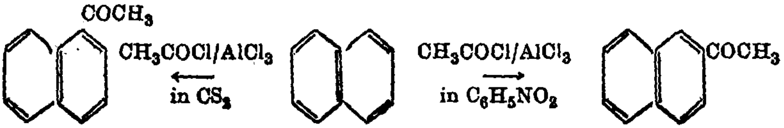
At higher temperatures, a second NO_2 group may be introduced in one of α-positions of the other benzene ring.

(4) SULPHONATION. Sulphonation of naphthalene with concentrated sulphuric acid below 80° forms mainly α-sulphonic acid, and at 165° the β-sulphonic acid.



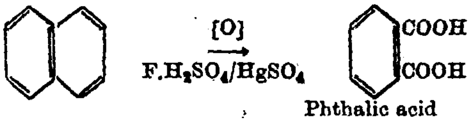
β-Naphthalene-sulphonic acid α-Naphthalene-sulphonic acid

(5) FRIEDEL-CRAFTS REACTION. Naphthalene undergoes Friedel-Crafts reaction with acetyl chloride to form the α or β products depending on conditions.



Methyl α-naphthylketone Methyl β-naphthylketone

(6) OXIDATION. When naphthalene is oxidised with fuming sulphuric acid in the presence of mercuric sulphate, one of the rings is broken resulting in the formation of phthalic acid.



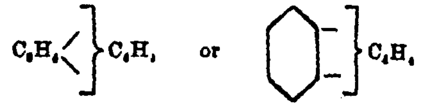
Phthalic acid

The above oxidation is now carried industrially by passing naphthalene vapour mixed with air over vanadium pentoxide (catalyst) at high temperature.

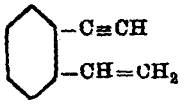
Uses. Naphthalene is used : (1) as a starting material for the manufacture of phthalic anhydride and numerous derivatives which are valuable dye intermediates ; (2) for adding to 'burning gases' to confer luminosity upon the flame ; and (3) as a moth repellant in the form of 'moth balls' ; it has little value for the purpose and is being replaced by new insecticides such as *p*-dichlorobenzene and D.D.T.

Structure. (1) The analysis and the determination of the molecular weight of naphthalene shows that its molecular formula is $C_{10}H_8$.

(2) The oxidation of naphthalene yields phthalic acid which proves that the molecule must contain a benzene nucleus with two ortho side-chains ($C_{10}H_8 - C_6H_4 = C_4H_4$).

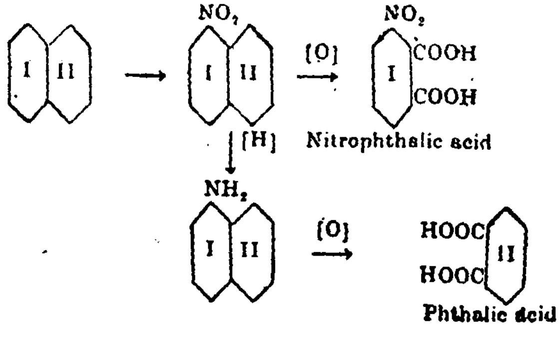


(3) Two independent unsaturated side-chains could be built as *follows but such a formula is antagonistic with the aromatic character of* naphthalene and is at once ruled out.

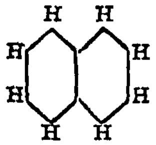


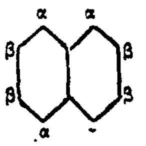
(4) Based on Kekule's formula for benzene, Erlenmeyer (1866 proposed that naphthalene molecule is made of two benzene ring fused in ortho positions. This was further proved by Nolting a follows.

Nitration of naphthalene produces nitronaphthalene whi when oxidised gives 3-nitrophthalic acid, while the oxidation of t amino-compound obtained by reducing the nitro compound yiel only phthalic acid. Thus naphthalene must contain two benze rings one of which, of course, is substituted on nitration. T oxidation of the nitro-compound destroys the unsubstituted r forming nitrophthalic acid, and the oxidation of the amino co pound destroys the substituted ring to yield only phthalic acid.



(5) With a symmetrical distribution of the H atoms as in benzene, the formula for naphthalene may be written as



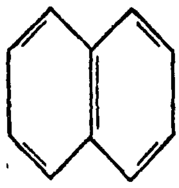


which is supported by the number of substitution products actually formed by naphthalene.

On careful examination of the above formula, it will be noticed that it contains two types of H atoms, marked α and β. Hence, theoretically it would give two monosubstitution products and we know that two isomeric naphthols and naphthylamines are known to exist. Similarly, the existence of 10 isomeric dichloronaphthalenes is justified by the above formula.

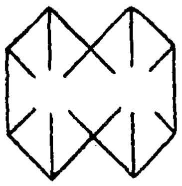
(6) Many structural formulae for naphthalene were put forth to account forthe fourth valency of the carbon atoms constituting the two benzene rings. Two of them are given below.

I



Erlenmeyer

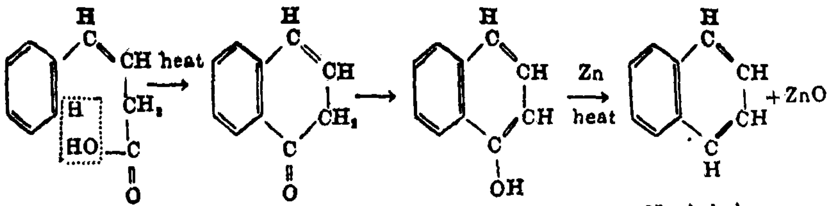
II



Bamberger

Formula II is ruled out on the same ground as the similar formula for benzene, and the formula I represents the accepted structure of naphthalene which explains the largest number of facts.

(7) The structure of naphthalene is finally confirmed by the following synthesis due to Fittig. β-Benzalpropionic acid on heating produces α-naphthol which on distillation with zinc dust yields naphthalene.



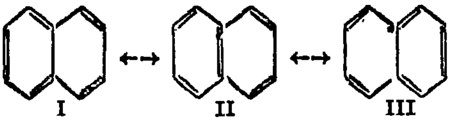
β-Benzalpropionic acid

(*keto form*)

(*enolic form*) α-Naphthol

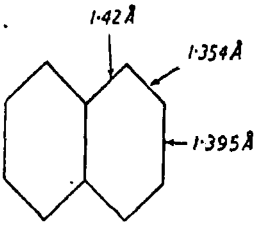
Naphthalene

(8) According to the Physico-chemical evidence, it is now believed that naphthalene bond structure is resonating between the forms I, II and III, and the form II makes the largest contribution.



This explains why the double bond character of linkages between 1, 2-positions is greater than those in benzene

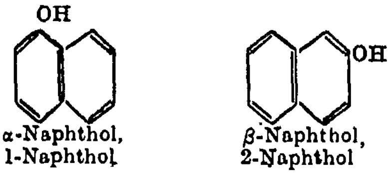
As a matter of general principle, there are $(n+1)$ principal resonating structures for a polynuclear hydrocarbon containing n benzene rings fused together in a linear fashion. The resonance stabilisation energy of naphthalene is 75 k. cals./mole — a value larger than that for benzene since the latter has only two principal resonating structures contributing to the resonance hybrid. The carbon-carbon bond lengths (determined by X-ray methods) are indicated as



DERIVATIVES OF NAPHTHALENE

NAPHTHOLS, $C_{10}H_7OH$

The monohydroxy derivatives of naphthalene are known as naphthols.



α-Naphthol,
1-Naphthol

β-Naphthol,
2-Naphthol

Both naphthols occur in coal-tar.

Preparation. (1) Both α-naphthol and β-naphthol are best prepared by fusing the corresponding sodium naphthalene sulphonate with sodium hydroxide at about 300°.

$$C_{10}H_7SO_3Na + NaOH \xrightarrow[300^\circ]{\text{Fuse}} C_{10}H_7OH + Na_2SO_3$$

(2) α-Naphthol may be obtained from α-naphthylamine by diazotization followed by hydrolysis.

$$C_{10}H_7.NH_2 \xrightarrow[HCl]{NaNO_2} C_{10}H_7.N_2Cl \xrightarrow{H_2O} C_{10}H_7OH$$

(3) Pure α-naphthol is made by heating α-naphthylamine with dilute sulphuric acid at 200° under pressure.

$$C_{10}H_7NH_2 + H OH \xrightarrow[\text{Pressure}]{200^\circ} C_{10}H_7OH + NH_3$$

The production of β-naphthol by methods (1) and (2) is of little value because of the difficulty of obtaining β-nitronaphthalene and, therefore, of the corresponding amine

Properties. Both naphthols are colourless crystalline substance m. pts. α-naphthol 95° ; β-naphthol 122°, having a faint phenolic odour. They are only slightly soluble in water but dissolve readily in alcohol and ether.

The naphthols resemble phenols in chemical behaviour, but the OH group in them is more readily replaced by other groups.

(1) They dissolve in alkali to form naphthoxides.

$$C_{10}H_7OH + NaOH \longrightarrow \underset{\text{Sod. naphthoxide}}{C_{10}H_7ONa} + H_2O$$

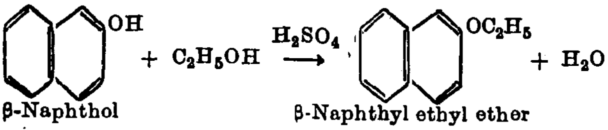
(2) They produce characteristic colours with ferric chloride : α-naphthol, *violet precipitate* ; β-naphthol, *green precipitate*.

(3) When treated with aqueous ammonia and ammonium sulphite they give naphthylamines (Bucherer reaction, 1904).

$$C_{10}H_7OH + NH_3 \xrightarrow{(NH_4)_2SO_3} C_{10}H_7NH_2 + H_2O$$

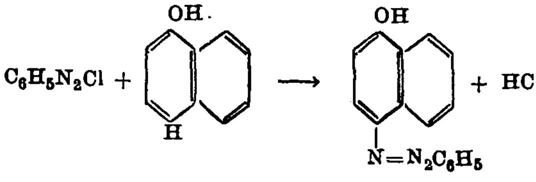
The reaction may also be carried by reaction between naphthol and ammonia in the presence of zinc chloride.

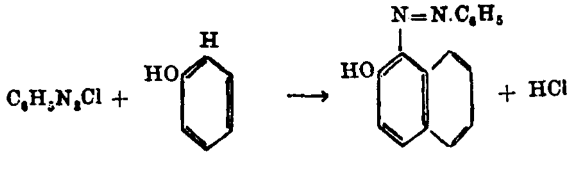
(4) In contrast to phenols, they form ethers when heated with alcohol and sulphuric acid.



β-Naphthol β-Naphthyl ethyl ether

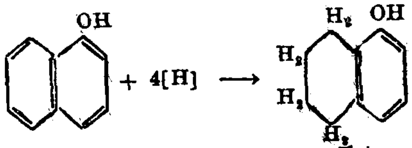
(5) They couple with diazonium salts ; α-naphthol does so at position 4, while β-naphthol at position 1 or 3.





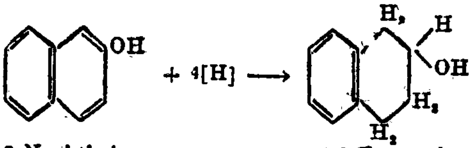
The dyes obtained from β-naphthol are highly coloured and those obtained from β-naphthol are of dull colour.

(6) When reduced with sodium and alcohol, the hydrogenation takes place in the unsubstituted ring with α-naphthol and in the substituted ring with β-naphthol.



α-Naphthol

ar-α-Tetronal (A phenol)



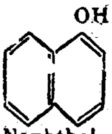
β-Naphthol

ac-β-Tetronal (Cyclic alcohol)

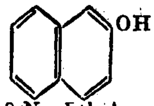
Uses. β-Naphthol is more important of the two naphthols and is used : (1) for making dyes, (2) as a mild antiseptic in the treatment of the skin diseases, (3) for preparing its methyl and ethyl ethers, which are extensively used in perfumery, and (4) as antioxidants, for fats and oils.

NAPHTHYLAMINES, $C_{10}H_7NH_2$

The two aminonaphthalenes or naphthylamines are :



α-Naphthol,
1-Naphthol



β-Naphthol,
2-Naphthol

Preparation. (1) α-Naphthylamine is prepared by reducing α-nitronaphthalene with iron and hydrochloric acid

$$C_{10}H_7NO_2 + 6[H] \xrightarrow{Fe/HCl} C_{10}H_6NH_2 + 2H_2O$$

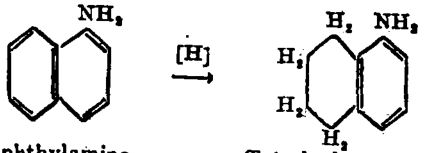
(2) β-Naphthylamine is prepared by treating β-naphthol with aqueous ammonia and ammonium sulphate (Bucherer process).

$$C_{10}H_7OH + NH_3 \xrightarrow{(NH_4)_2SO_4} C_{10}H_7NH_2 + H_2O$$

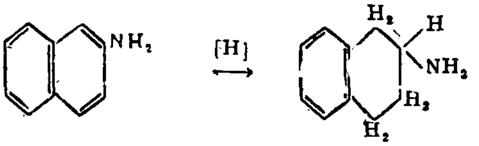
Of course, the above two methods can be applied for the preparation of both the naphthylamines, provided the starting compound is readily available.

Properties. Naphthylamines are colourless solids, m. pts. : α-naphthylamine 50°, β-naphthylamine 112° Both are insoluble in water but dissolve readily in alcohol and ether. α-Naphthylamine has an unpleasant odour while β-naphthylamine is odourless.

Naphthylamines give practically the same reactions as those of aniline. They are slightly weaker bases than aniline and dissolve in acids to form salts. They yield the diazonium salts which may be coupled with amines and phenols in the usual way. When reduced with sodium and amyl alcohol, hydrogenation takes place in different rings in the two naphthylamines.

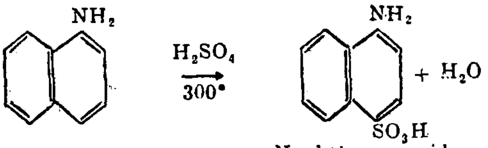


α-Naphthylamine ar-Tetrahydro-α-naphthylamine



ar-Tetrahydro-β-naphthylamine

The sulphonation of α-naphthylamine with concentrated sulphuric acid at 130° yields naphthionic acid which is used in the preparation of Congo Red.

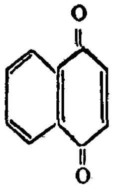


Naphthionic acid

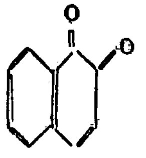
Naphthylamines are used in the manufacture of several dyes.

NAPHTHOQUINONES, $C_{10}H_6O_2$

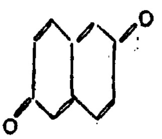
Only three naphthoquinones are known.



α-Naphthoquinone,
1, 4-naphthoquinone

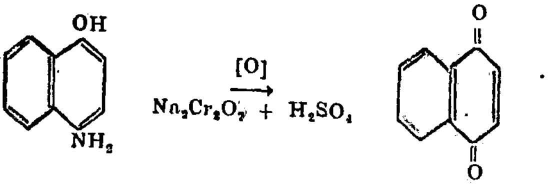


β-Naphthoquinone,
1, 2-naphthoquinone



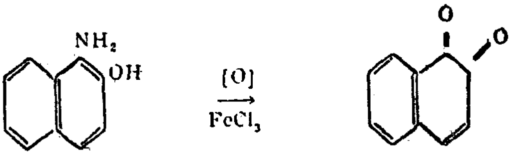
Amphi-naphthoquinone
2, 6-naphthoquinone

α-**Naphthoquinone** is prepared by oxidation of 4-amino-1-naphthol with sodium dichromate and sulphuric acid



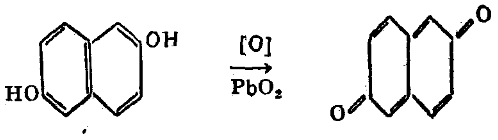
It is a yellow crystalline solid, m.p. 125°, having a pronounced odour. Vitamin K is its derivative.

β-Naphthoquinone is prepared by oxidising 1-amino-2-naphthol with ferric chloride.



It crystallises in red needles and decomposes at 115—120°.

Amphi-naphthoquinone is obtained by oxidising 2, 6-dihydroxynaphthalene with lead peroxide.



It is an orange solid, m.p. 135°.

The chemical reactions of naphthoquinones are the same as *those of quinones.*

QUESTIONS

1. From what sources is naphthalene obtained ? What products does it yield (*a*) on oxidation, (*b*) with H_2SO_4, (*c*) with HNO_3 ?

2. How is naphthalene manufactured ? Describe how it is synthesised and prove its constitution. What do you know about the isomerism of its derivatives ?

3. How are α-naphthol and β-naphthol prepared ? Show that the formula assigned to naphthalene is in agreement with its behaviour.

4. Describe the preparation of naphthalene from coal-tar and indicate how the following compounds could be obtained from naphthalene.

(*a*) β-Naphthol, (*b*) Indigo, and (*c*) Anthraquinone.

5. Discuss the structure of naphthalene. Show that alpha and beta naphthols could be prepared from naphthalene.

6. How is the structure of naphthalene determined ? Give the synthesis of naphthalene. How are β-naphthylamine and α-naphthol obtained from naphthalene ? (*Bombay B.Sc., 1964*)

7. Discuss the constitution of naphthalene. Give its synthesis. How are the following prepared from naphthalene : (*i*) Tetralin, (*ii*) Beta-nitronaphthalene, (*iii*) Anthranilic acid and (*iv*) Beta-naphthol ?
(*Poona B.Sc. II, 1964*)

8. Discuss the structure of naphthalene. How will you convert naphthalene to (1) phenolphthalein, and (2) anthranilic acid ?
(*Marathwada B.Sc. III, 1964*)

9. Establish the constitution of naphthalene. How would you prepare naphthols from it ? what is the action of chlorine on Naphthalene.
(*Panjab B.Sc. III, 1965*)

10. What are the polynuclear hydrocarbons ? Discuss the reactions and structure of Naphthalene. (*Agra B.Sc. III, 1967*)

11. How is Naphthalene prepared on a large scale ? How will you prepare the following starting with Naphthalene ? (*a*) Alpha Naphthol, (*b*) Beta Naphthol, (*c*) Decalin, (*d*) Beta Naphthalene sulphonic acid, and (*e*) Beta Naphthylamine. (*Banaras B.Sc. II, 1967*)

12. Discuss the constitution of Naphthalene. How is it possible to convert it into (*a*) α-naphthol, (*b*) β-naphthol and (*c*) β-naphthylamine ?
(*J and K B.Sc., 1967*)

13. How would you establish the structural formula of Naphthalene ? What are naphthols ? How would you prepare them ? State their properties.
(*Dibrugarh B.Sc. III, 1967*)

14. Give a short account of the structure of Naphthalene.
(*Kaylani B.Sc. Hons. III, 1967*)

15. Indicate the steps of synthesis of Naphthalene, using benzene and acetic anhydride. Starting from Naphthalene show how you would obtain the following : (*i*) Salicylic acid, (*ii*) β-nitro-naphthalene. (*Poona B.Sc. II, 1967*)

16. Discuss evidences in support of the structure of naphthalene.
(*Allahabad B.Sc., 1968*)

17. Discuss the structure of naphthalene with special reference to the nature of the carbon skeleton and the bonds. (*Visva Bharti B.Sc., 1969*)

18. How is naphthalene prepared ? Discuss its constitution
(*Panjab B.Sc., 1969*)

48

Anthracene and its Derivatives

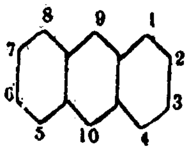
J.B.A. Dumas
(1800—1884)

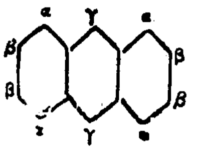
In 1831 Dumas isolated anthracene from coal-tar. He determined the structure of camphor and borneol. Dumas obtained cinnamic aldehyde, cinnamic acid, and methyl nitrate.

ANTHRACENE, $C_{14}H_{10}$

Anthracene is present in coal-tar to the extent of 0·3 to 3·5 per cent, hence its name from Greek *anthrax*—meaning coal. On distillation of tar, it passes over in the high boiling fractions '*anthracene oil*.'

The molecule of anthracene is made of three benzene nuclei fused in ortho positions for purposes of naming its derivatives, the various positions are numbered as follows :





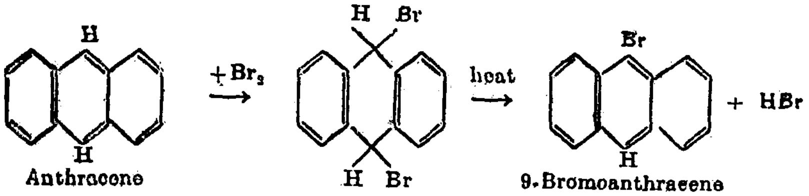
Isolation from Anthracene oil. Anthracene oil is chilled, whereupon a crystalline mass separates which is pressed free from the liquid. The press-cake contains anthracene, phenanthrene (an isomeric hydrocarbon, and carbazole), $(C_6H_4)NH$. This is powdered and washed with *solvent naphtha* which dissolves the phenanthrene, and then with pyridine which dissolves the carbazole. The crude anthracene left behind is purified by crystallising from benzene.

Alternatively, the mass left after removing phenanthrene is distilled with potash. The non-volatile potassium carbazole, $(C_6H_4)_2NH$, thus produced is left behind and the anthracene distils over.

Properties. (*Physical*). Anthracene crystallises in lustrous white flakes, m.p. 217°, which show a fine blue fluorescence. It is insoluble in water, sparingly so in ether and alcohol, but dissolves readily in hot benzene. It forms a picrate, melting at 138°.

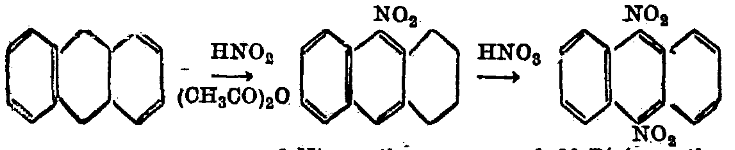
Chemically anthracene behaves in most respects like typical aromatic hydrocarbons, benzene and naphthalene. However, the positions 9 and 10 are extraordinarily reactive and anthracene readily forms derivatives in which the substituents enter these positions.

1. HALOGENATION. Chlorine and bromine react with anthracene to form addition products which at once decompose on heating to form 9, 10 substituted products.



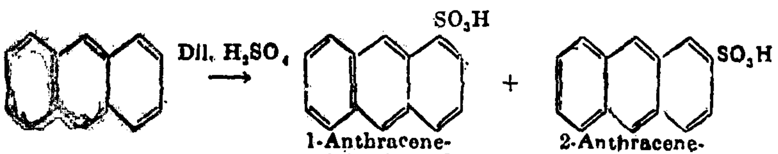
Anthracene 9-Bromoanthracene

2. NITRATION. When nitrated with concentrated nitric acid in acetic anhydride, 9-nitroanthracene and 9, 10-dinitroanthracene is produced.



9-Nitroanthracene 9, 10-Dinitroanthracene

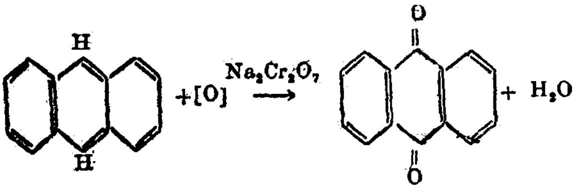
3. SULPHONATION. The sulphonation of anthracene with dilute sulphuric acid, gives 1-anthracene sulphonic acid, and 2-anthracene sulphonic acid.



1-Anthracene-sulphonic acid 2-Anthracene-sulphonic acid

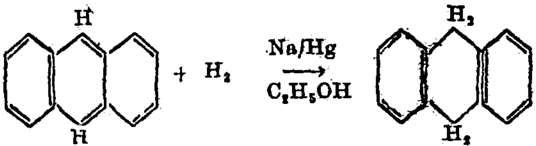
When sulphonated with concentrated sulphuric acid, anthracene forms 1, 5- and 1, 8-anthracene sulphonic acids.

4. OXIDATION. The oxidation of anthracene with concentrated nitric acid or with chromic acid yields anthraquinone.



Anthraquinone

5. REDUCTION. Anthracene when reduced with sodium amalgam and aqueous alcohol readily yields 9, 10-dihydroanthracene.



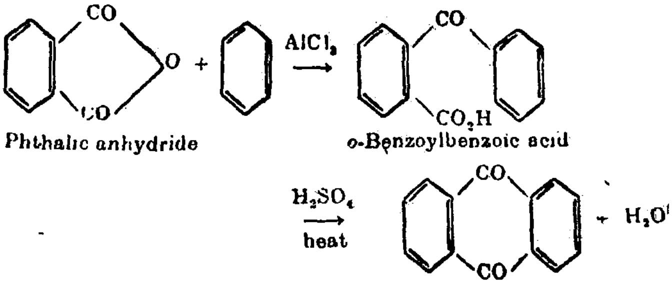
9, 10-Dihydroanthracene

Uses. Anthracene is principally used in the production of anthraquinone and several important dyes, including alizarin and the newer anthraquinone dyes.

Structure. (1) Anthracene has the molecular formula $C_{14}H_{10}$ which at once suggests that this hydrocarbon is related to benzene (C_6H_6) and naphthalene ($C_{10}H_8$).

(2) Like other aromatic hydrocarbons, it gives the addition and substitution reactions (halogenation, sulphonation, nitration) under suitable conditions. This indicates that the anthracene is possibly made of three condensed benzene nuclei.

(3) On mild oxidation, anthracene yields anthraquinone, whose structure has been established by synthesis from phthalic anhydride and benzene as follows:

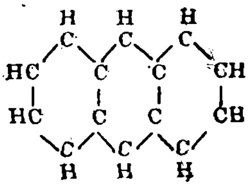


Phthalic anhydride

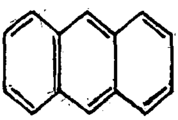
o-Benzoylbenzoic acid

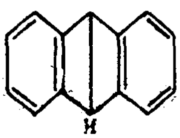
Anthraquinone

This indicates that anthracene must contain the same carbon skeleton as of anthraquinone, and leaving the question of valencies, of the C-atoms open its formula may be written as



(4) To dispose of the fourth valency of the C-atoms many alternative bond structures have been suggested, out of which only three are given.





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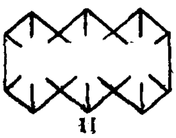
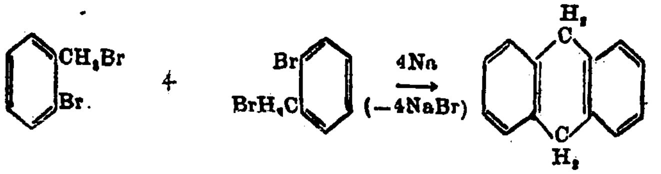


II

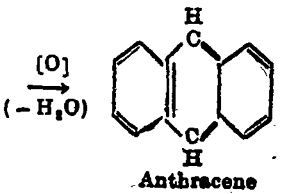
The formula III is ruled out straightway on the same ground, as the similar formula of benzene. The formula II has also been recently discarded since according to the X-ray analysis (Robertson, 1933), the distance between the middle carbon atoms is surely too great for the sharing of a pair of electrons to form a covalent link. The formula I which is analogous to the accepted structure of benzene and naphthalene is at present considered to be correct.

(5) The structure of anthracene has been confirmed by synthesis from *o*-bromobenzyl bromide as follows :-



o-Bromobenzyl bromide (2-*molecules*)

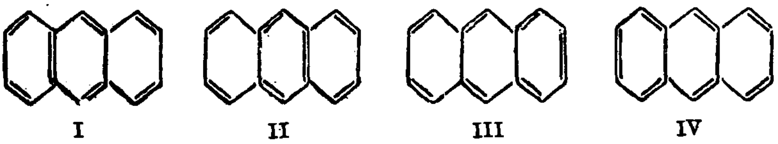
10-Dihydroanthracene



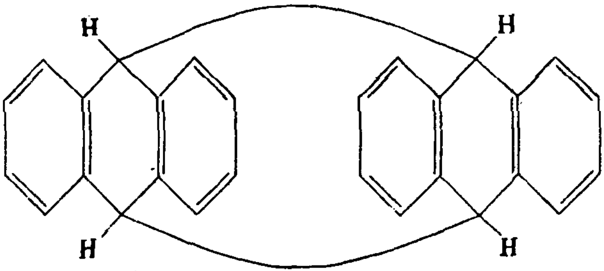
Anthracene

This synthesis also disproves the presence of a bridge between the middle (8, 9) carbon atoms.

(6) All the latest evidence available shows that like other aromatic hydrocarbons, anthracene is a resonance hybrid of the following bond structures of which I and II are most stable.



The resonance stabilisation energy of anthracene is 105 k. cals. mole., greater than both benzene and naphthalene. X-ray analysis studies have however revealed that two anthracene molecules are linked in the 9, 9′; 10, 10′-positions to give the structure.



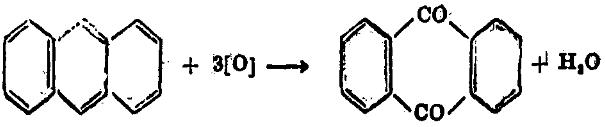
This structure has been confirmed by the ultraviolet spectrum of dianthracene by Weiss (1955).

DERIVATIVES OF ANTHRACENE

ANTHRAQUINONE

Anthraquinone is important because it is the parent substance of the well-known dye alizarin and of the purgative principles of rhubarb, aloes, senna and cascara. It was first obtained by Laurent (1840) by the action of nitric acid on anthracene.

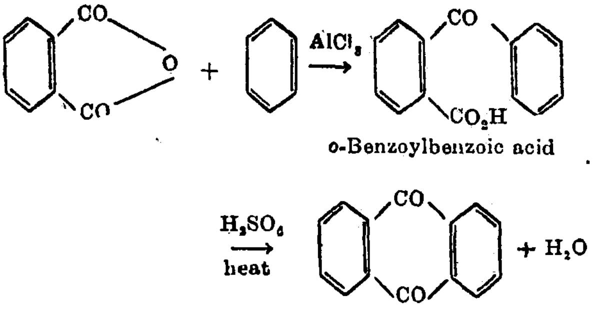
Preparation. (1) Anthraquinone was formerly prepared by the oxidation of pure anthracene with sodium dichromate and sulphuric acid.



Anthraquinone

Now the above oxidation is done cheaply by passing the vapour of crude anthracene containing carbazole, mixed with air over vanadium pentoxide at 400°. The carbazole is removed automatically, being oxidised completely to CO_2 and H_2O.

(2) At present most of the industrial anthraquinone is made by interaction of phthalic anhydride and benzene in the presence of aluminium chloride (*Friedel-Crafts reaction*), and treating the *o*-benzoylbenzoic acid formed with concentrated sulphuric acid.



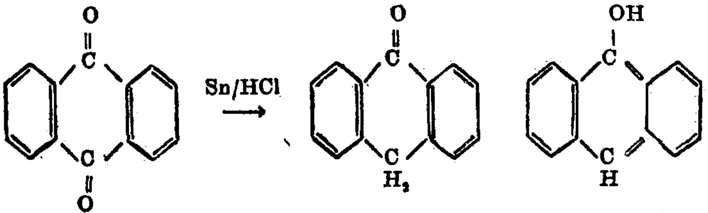
o-Benzoylbenzoic acid

Anthraquinone

The above synthesis of anthraquinone also proves its structure.

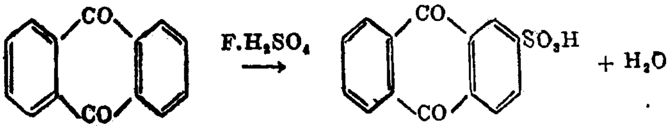
Properties. (*Physical*). Anthraquinone is a pale yellow-crystalline solid, m.p. 285°, having little odour. It sublimes when heated above its melting point. It is insoluble in water but dissolves only difficultly in glacial acetic acid and benzene.

(*Chemical*). Anthraquinone lacks the oxidising properties of quinones and rather behaves as a diketone. Thus it reacts with hydroxylamine to form a dioxime. When reduced with tin and hydrochloric acid, anthraquinone is converted to *anthrone* which is tautomeric with *anthranol*.



Anthrone Anthranol

The benzene rings in anthraquinone are deactivated by the carbonyl groups and, therefore, are substituted only with difficulty. Thus anthraquinone can be sulphonated with fuming sulphuric acid to form anthraquinone-2-sulphonic acid, which is of value as an intermediate in the manufacture of alizarin.



Anthraquinone-2-sulphonic acid

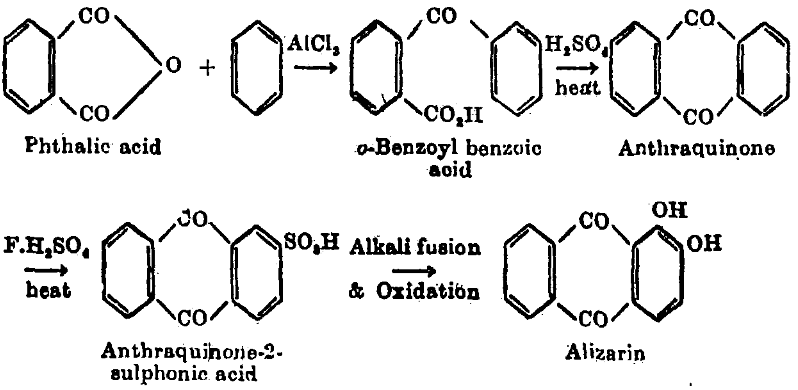
ALIZARIN, 1, 2-DIHYDROXYANTHRAQUINONE

It is a dye of splendid red colour and ranks with indigo as the most valuable of all dye-stuffs, whether synthetic or natural. It occurs in madder root (hence its name from Arabic 'alizari' = *madder*) as the glucoside *ruberythric acid*, which when hydrolysed by enzymes or dilute acids liberates alizarin.

$$\underset{\text{Ruberythric acid}}{C_{26}H_{28}O_{14}} + 2H_2O \longrightarrow 2C_6H_{12}O_6 + \underset{\text{Alizarin}}{C_{14}H_6O_2(OH_2)}$$

Preparation. Alizarin was originally obtained in large quantities by the hydrolysis of ruberythric acid as indicated above. Now it is exclusively made synthetically by the following method (Graebe and Liebermann, 1869).

(1) Anthraquinone is obtained by Friedel-Crafts reaction between phthalic anhydride and benzene to form o-benzoylbenzoic acid and heating the latter with conc. H_2SO_4; (2) The anthraquinone is then sulphonated with fuming sulphuric acid to give anthraquinone-2-sulphonic acid ; (3) The sulphonic acid is finally fused with sodium hydroxide and potassium chlorate, and acidified ; the SO_3H is replaced by OH and another OH is introduced in 2-position giving alizarin.



Phthalic acid

o-Benzoyl benzoic acid

Anthraquinone

Anthraquinone-2-sulphonic acid

Alizarin

Phthalic anhydride needed in the process is obtained by the catalytic oxidation of naphthalene.

Properties. Alizarin forms ruby red crystals, m.p. 289°. It is insoluble in water and sparingly soluble in alcohol. It sublimes on heating and can thus be readily purified. It dissolves in caustic alkalis to give purple solutions of alizarates. Mild oxidation of alizarin introduces a third OH group in the 4-position, giving another dye *purpurin*. When reduced with zinc dust and ammonia, alizarin yields dihydroxyanthranol known as *anthrarobin*, which is a valuable medicine for skin diseases. Alizarin itself is also used as a purgative.

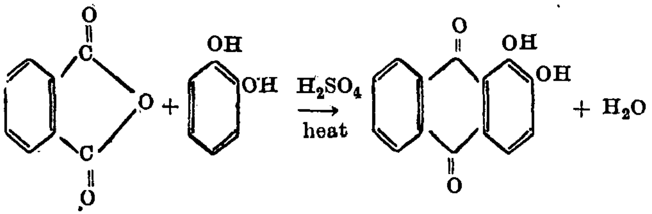
Alizarin is a typical mordant, yielding different colours with different mordants. Thus an aluminium mordant gives a bright-red colour (*Turkey red*), chromium a brown violet, iron (ferric) a violet black and barium a blue colour. Aluminium mordants are usually employed for dyeing cotton fabrics. The cloth is soaked in a solution of aluminium acetate and steam heated, when aluminium hydroxide is deposited in the fibres. The fabric is then steeped in a solution of sodium salt of alizarin, which reacts with aluminium hydroxide to form insoluble 'red lakes' and the fabric is dyed red. Prior to mordanting, the fabric is impregnated with *Turkey-red oil* (sulphated castor oil). The action of the oil is not clearly understood but without it the bright-red shade cannot be obtained.

Structure. (1) By elementary analysis and the molecular weight determination it has been shown that molecular formula of alizarin is $C_{14}H_8O_4$.

(2) When reduced with zinc dust, alizarin is converted to anthracene, which indicates that it has the same carbon skeleton as that of anthracene.

(3) With acetic anhydride it forms a diacetate showing the presence of the two OH groups in the molecule. It may, therefore, be assumed that alizarin is possibly dihydroxy-derivative of anthraquinone.

(4) Alizarin is produced by heating phthalic anhydride and catechol to 150° with sulphuric acid.



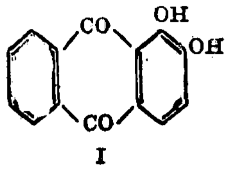
Phthalic anhydride

Catechol

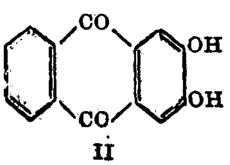
Alizarin (1, 2-dihydroxy anthraquinone)

From this we conclude that alizarin is a dihydroxy derivative of anthraquinone and that both the OH groups are present in the same benzene ring.

(5) The above facts limit our choice to two structural formulae for alizarin.



I

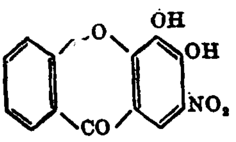


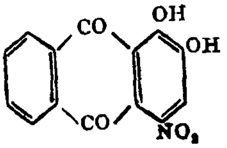
II

(6) Alizarin on nitration yields two isomeric mono-nitroderivatives, both of which on oxidation give phthalic acid and hence contain the NO_2 group in the hydroxylated benzene ring. Writing

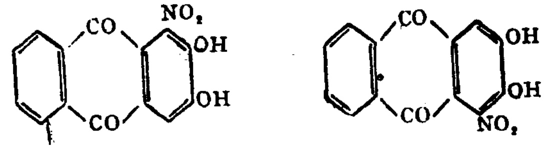
the possible derivatives from formula I and from formula II, we have

From formula I :





From formula II :

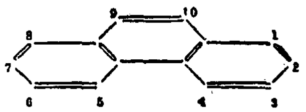


Identical

Since only formula I admits the formation of two isomeric mono-nitro-derivatives, it represents the correct structure of alizarin.

PHENANTHRENE, $C_{14}H_{10}$

It occurs to the extent of 4 per cent in coal-tar along with anthracene, with which it is isomeric. Its structural formula may be written as

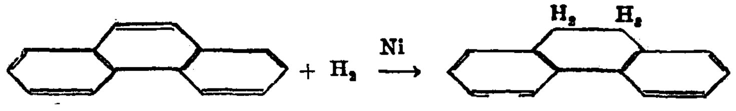


Isolation. Phenanthrene is isolated from anthracene oil fraction of coal-tar which on cooling deposits a solid mass consisting of this hydrocarbon, anthracene and carbazole. It is removed from the solid mixture by dissolution in solvent naphtha in which the other two components are insoluble.

Properties. Phenanthrene is a white crystalline solid, m.p. 99°. It is insoluble in water but dissolves readily in alcohol, benzene and ether. Its alcoholic solutions show blue fluorescence.

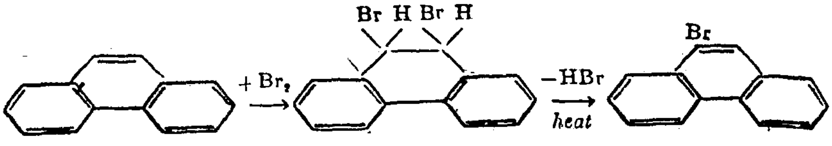
Phenanthrene essentially behaves like other aromatic hydrocarbons giving addition and substitution reactions under suitable conditions. The 9, 10-positions are particularly reactive.

(1) When hydrogenated in the presence of nickel, it forms 9, 10-dihydrophenanthrene.



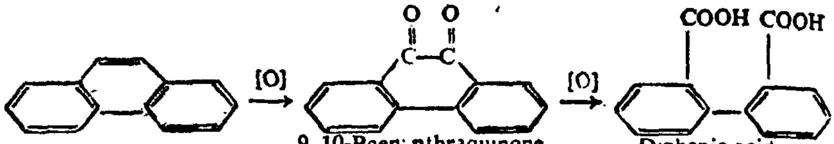
9, 10-Dihydrophenanthrene

(2) It readily adds bromine at the 9, 10-double bond to form a dibromide, which splits out hydrogen bromide on heating and gives 9-bromophenanthrene.



Phenanthrene-9, 10-dibromide 9-Bromophenanthrene

(3) When oxidised with chromic acid in acetic acid, phenanthrene yields a diketone, phenanthraquinone, which upon further oxidation gives diphenic acid.



9, 10-Phenanthraquinone Diphenic acid

Phenanthrene has no commercial applications. Nevertheless, it is important theoretically since a phenanthrene nucleus is a part of the structure of many natural products such as sex hormones, bile acids, chlorosterol, and morphine alkaloids.

QUESTIONS

1. How is anthracene prepared? Give the important uses to which this compound is put and discuss its constitution.

2. How is anthracene prepared in a state of purity? Indicate how you would prepare from it a sample of alizarin.

3. Describe the preparation of anthraquinone from commercial sources. How may it be synthesised and what are its chief uses?

4. How is anthracene isolated from coal-tar and purified? How is it converted into alizarin? Discuss the constitution of alizarin.

5. How would you prepare alizarin in the laboratory? Derive its constitution.

6. Give an account of the hydrocarbon phenanthrene. What are its most important oxidation products and how are they obtained?

7. How are naphthalene and anthracene obtained? How is naphthalene converted into indigo and how is anthracene converted into alizarin?
(*Andhra B.Sc.* 1961)

8. How is anthracene obtained from coal-tar? Describe the preparation of alizarin from anthracene. (*Vankateswara B.Sc.*, 1962)

9. What are multinuclear compounds? How is anthracene prepared? Give its properties. (*Marathwada B.Sc. III*, 1963)

10. How does alizarin occur in nature and how is it isolated ? Discuss its structure and give its laboratory as well as technical synthesis.
(*Bombay B.Sc., 1964*)

11. Describe manufacture of alizarin. Give analytical evidences in favour of its structure. Write its uses. (*Gujarat B.Sc., 1964*)

12. Discuss the preparation, properties and constitution of alizarin.
(*Madras B.Sc., 1964*)

13. (*a*) Explain with reactions which positions in anthracene are more reactive. Why is it so ?

How is anthraquinone and anthrone prepared ?
(*Banaras B.Sc. II, 1964*)

14. Discuss the constitution of alizarin. Give its method of manufacture. Starting with naphthalene, describe the manufacture of an important dye.
(*Vallabhbhai B.Sc. III, 1964*)

15. Discuss the evidence both analytical and synthetical on which the structure of Anthracene is based. (*Bombay B.Sc. II, 1967*)

49

Heterocyclic Compounds

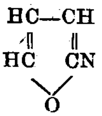
Carl T. Liebermann
(1842—1914)

He is known for his great work in connection with dyes. He synthesised alizarin and carried on work with anthracene and anthraquinone compounds.

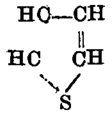
So far we have studied aromatic compounds which have rings composed of carbon atoms only (*carbocyclic*). There are a large number of compounds known in which the ring system includes atoms other than carbon (*heterc atoms*), the commonest being O, N and S. These are called **Heterocyclic compounds** (Gr. *hetero*= other ; different) The inclusion of the hetero atoms in the ring does not alter the strain relationships appreciably, since the 'valency angles' in these are about 100° which is nearly the same as in carbon. Thus the heterocyclic compounds having five and six-membered rings are most stable (*Baeyer's theory*) and will be discussed here.

Five-Membered Rings

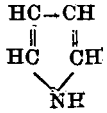
The most common heterocyclic compounds containing four carbon atoms and one hetero atom are furan, thiophene and pyrrole.



Furan

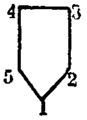


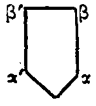
Thiophene



Pyrrole

In naming the derivatives of these compounds, the positions of substituents on the ring are indicated by numbers or by Greek letters as follows.

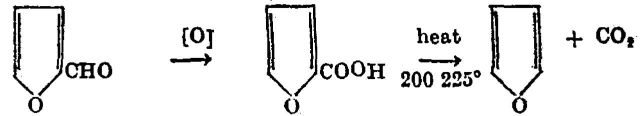




FURAN, C_4H_4O

Furan takes its name from Latin word *furfur* meaning bran, because its aldehyde furfural is obtained by distilling bran with hydrochloric acid. It is also found to be present in pine wood tar.

Preparation. Furan is best prepared by heating pyromucic acid or furoic acid which is chiefly obtained by oxidation of furfural.

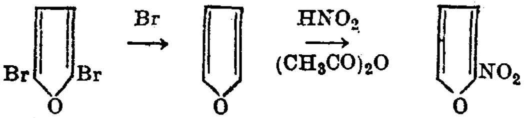


Furfural Furoic acid Furan

Properties. Furan is a colourless mobile liquid, b.p. 32° having an odour of chloroform. It is insoluble in water but is very soluble in alcohol and ether. It produces an intense green colour on pine shavings moistened with hydrochloric acid (*Test*). It is stable to alkalis, but is resinified by concentrated acids.

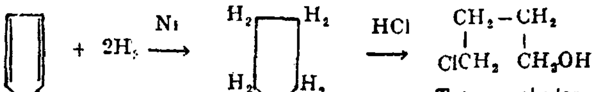
Since its molecule has alternate single and double bond structure, furan resembles benzene in behaviour and tends to open readily at the oxygen-linkages.

(1) It undergoes substitutions reactions even more readily than does benzene. Thus with bromine it forms 2, 5-dibromofuran and on nitration with nitric acid in acetic anhydride it yields 2-nitrofuran.



2, 5-Dibromofuran 3-Nitrofuran

(2) When hydrogenated in the presence of nickel at high temperature, furan forms tetrahydrofuran which on treatment with hydrogen chloride opens to give tetramethylene chlorohydrin.

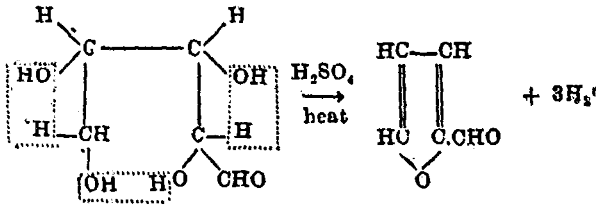


Tetrahydrofuran

Tetramethylene chlorohydrin

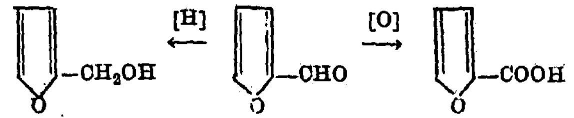
Furan is of little use but some of its derivatives (furfural) are of commercial importance.

Furfural, *furfuraldehyde*, furan-2-aldehyde, $C_4H_3O.CHO$. It is prepared industrially by distilling out husk or bran, and similar vegetable materials with dilute sulphuric acid ; the pentoses present in bran split out three water molecules and yield furfural.



Properties. Furfural is a colourless oily liquid, b.p. 162° with an odour resembling that of benzaldehyde. In chemical behaviour also it shows a marked similarity to benzaldehyde.

(1) Furfural can be reduced to furfuryl alcohol and oxidised to furoic acid by the usual methods.

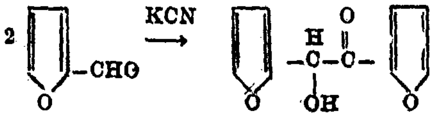


Furfuryl alcohol Furfural Furoic acid

The above products are obtained together when furfural is treated with alcoholic potash (*Cannizzaro reaction*).

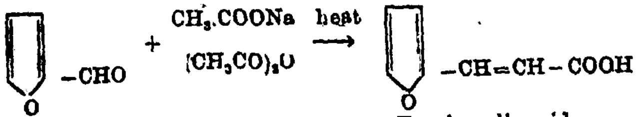
(2) It reacts with ammonia to form *hydrofurfuramide*, $(C_4H_3O.CH)_3N_2$, which is analogous in composition to hydrobenzamide.

(3) Under the influence of potassium cyanide furfural gives *furoin*, in the same way as benzaldehyde forms benzoin.



Furoin

(4) Like benzaldehyde it undergoes Perkins' reaction to form furylacrylic acid.



Furylacrylic acid

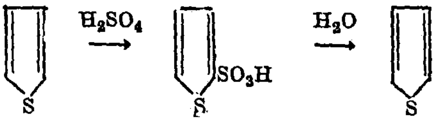
(5) Furfural produces an intense red colour with aniline and acetic acid or hydrochloric acid (*Test*).

Uses. Furfural is used : (1) as a solvent for refining lubricating oils ; (2) as a preservative for wood and leather ; and (3) in the manufacture of phenol furfural resins.

THIOPHENE, C_4H_4S

During a lecture in 1882, Victor Meyer found that pure benzene obtained by heating sodium benzoate with soda-lime did not give a blue colour when warmed with isatin and sulphuric acid (*Indophenin Test*), a test which was shown by benzene obtained from coal-tar. Pursuing the matter, Meyer proved that the coal-tar benzene contained a new sulphur compound, which he called thiophene (*Thio*-sulphur ; *phene*-benzene). Thiophene is present to the extent of 0·6% in the crude benzene obtained from coal-tar.

Preparation. (1) *From Coal-tar benzene.* Thiophene cannot be separated from benzene by fractional distillation as their boiling points are too near. It may be obtained from coal-tar benzene by shaking it with concentrated sulphuric acid which sulphonates it more readily than benzene. Thiophene sulphonic acid is then removed from the solution by the usual methods and converted into thiophene by super-heated steam.

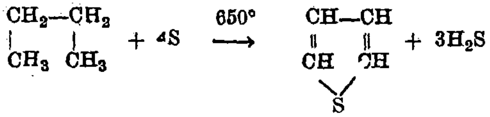


A simple method is to boil benzene-thiophene mixture with mercuric acetate. Thiophene is converted into the insoluble 1-mercuriacetate ($C_4H_3S.HgOCOCH_3$) which regenerates thiophene on boiling with concentrated hydrochloric acid.

(3) The modern method for preparing thiophene in the laboratory is by heating sodium succinate and phosphorus trisulphide.

$$\begin{array}{c} CH_2COONa \\ | \\ CH_2.COONa \\ \text{Sod. succinate} \end{array} \xrightarrow{P_2S_3} \begin{array}{c} CH{=}CH\diagdown \\ |\qquad\quad S \\ CH{=}CH\diagup \\ \text{Thiophene} \end{array}$$

(3) Thiophene is now made technically in U.S.A. by heating butane with sulphur.



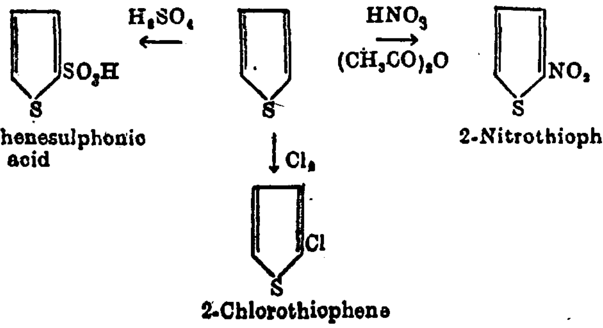
$$\begin{array}{c} CH_2-CH_2 \\ |\qquad | \\ CH_3\quad CH_3 \end{array} + 4S \xrightarrow{650^\circ} \begin{array}{c} CH-CH \\ \|\qquad \| \\ CH\quad CH \\ \diagdown\diagup \\ S \end{array} + 3H_2S$$

Properties. Thiophene is a colourless mobile liquid, b.p. 84°, having benzene-like odour. It is insoluble in water but dissolves in organic solvents. It is comparatively stable to oxidation.

Thiophene also has alternate double and single bond structure and the aromatic character in it is very pronounced as compared to furan and pyrrole.

(1) Thiophene undergoes the typical substitution reactions of benzene much more readily. Thus, it reacts with chlorine without

a catalyst and in cold, with nitric acid in acetic annydride, and with concentrated sulphuric acid in cold to yield in the first instance the 2-substitution derivatives.

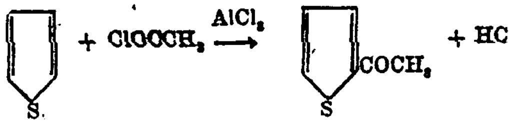


2-Thiophenesulphonic acid

2-Nitrothiophene

2-Chlorothiophene

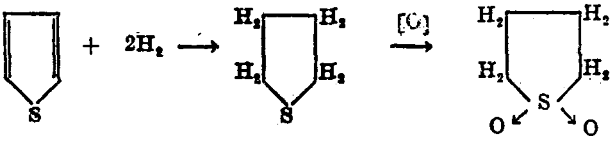
(2) It undergoes Friedel-Crafts reaction like benzene. Thus,



2-Thienyl methyl ketone

(3) Thus sulphur atom attached to the doubly bonded carbon atoms is inert and thiophene does not behave like thioethers. Thus it cannot be oxidised to a sulphoxide or to sulphone and gives no sulphonium salts with alkyl halides.

(4) Upon hydrogenation it forms a true thioether which can be oxidised to a sulphone.



(Thioether) (Sulphone)

This shows clearly that aromatic character vanishes with the disappearance of alternate double and single bond structure.

(5) When warmed with isatin and a few drops of concentrated sulphuric acid, thiophene gives a blue coloration (*Ind phenin Test*).

PYRROLE, C_3H_4NH

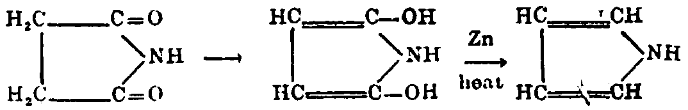
It is the most important of the five-membered heterocyclic compounds as some of the alkaloids, the bile pigments, the chlorophyll of plants, and haemin of blood have been shown to contain pyrrole units in their structure. Pyrrole received its name from the fact that its vapours produce an intense red colour when brought in contact with a pine splint moistened with hydrochloric acid (Gr. *Pyrros*-fiery red; L. *Oleum*-oil). It occurs chiefly in Dippel's oil obtained by the destructive distillation of bones.

Preparation. (1) *Isolation from Dippel's oil.* The oil obtained from de-fatted bones contains pyrrole along with hydrocarbons, pyridine bases and nitrile. It is shaken with dilute sulphuric acid to remove the pyridine base and then boiled with sodium carbonate solution to remove the nitriles. The separation of pyrrole and hydrocarbons is finally effected by fractional distillation. The fraction passing over between 100° and 150° contains pyrrole which may be removed by boiling with potassium hydroxide. Solid potassium-pyrrole, C_4H_4NK, is formed which on steam distillation gives pyrrole.

$$\underset{\text{Potassium pyrrole}}{C_4H_4NK} + H_2O \longrightarrow \underset{\text{Pyrrole}}{C_4H_4NH} + KOH$$

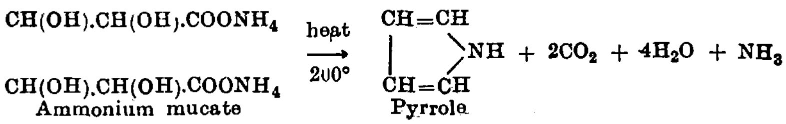
This is finally purified by distillation.

(2) Pyrrole may be obtained by the distillation of succinimide with zinc dust.



Succinimide Enol form Pyrrole

(3) It is commonly prepared in the laboratory by heating ammonium mucate with glycerol (solvent) at 200°.



Properties. Pyrrole is a colourless, highly refractive liquid, b.p. 131° ; having a pleasant chloroform like odour. It rapidly turns brown on exposure to air and finally forms a resinous mass. It is sparingly soluble in water but dissolves freely in alcohol and ether.

In pyrrole we have a conjugated system of carbon atoms, linked directly to NH grouping. The NH group activates the ring so that pyrrole undergoes the usual substitution reactions of the aromatic compounds readily. The aromatic part of the ring in turn decreases the basic character of the NH group. Thus pyridine is a weaker base than aniline and by the same token it is stronger acid than secondary aliphatic amines.

(1) When pyrrole is boiled with metallic potassium or solid potassium hydroxide, it forms potassiumpyrrole. Thus :

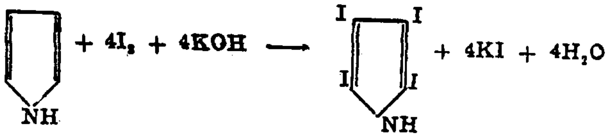
$$C_4H_4NH + K \longrightarrow C_4H_4NK + \; + \tfrac{1}{2}H_2$$
$$C_4H_4NH + KOH \longrightarrow C_4H_4NK + H_2O$$

(2) It dissolves slowly in cold dilute hydrochloric acid to form salts.

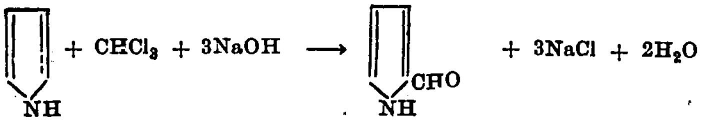
$$C_4H_4NH + HCl \longrightarrow \underset{\text{Pyrrole hydrochloride}}{C_4H_4NH.HCl}$$

With strong acids pyrrole forms resins.

(3) When treated with halogens, pyrrole substitutes readily to form tetra-substituted derivatives. Then with iodine in the presence of alkali, it yields tetraiodopyrrole which is used as a substitute of iodoform under the name of *iodole.*

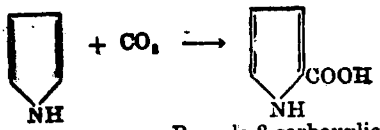


(4) Like phenols, pyrrole undergoes Reimer-Tiemann reaction.



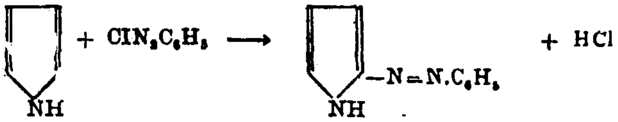
Pyrrole 2-carboxylic acid

(5) Potassiumpyrrole absorbs carbon dioxide under pressure to form 2-carboxylic acid : this is analogous to Kolbe reaction for phenols.

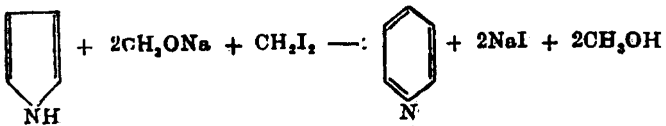


Pyrrole-2-carboxylic acid

(6) Like phenols, pyrrole couples with a diazonium salt in one or both the 2-positions.

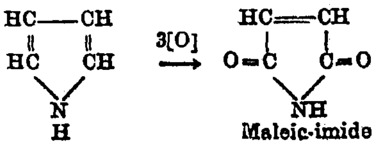


(7) When treated with sodium methoxide and methylene iodide, pyrrole undergoes ring expansion forming pyridine.

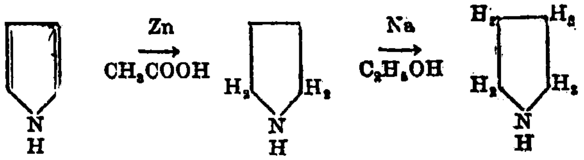


Pyridine

(8) Chromic acid oxidises pyrrole to maleic-imide.



(9) When reduced with zinc and acetic acid, pyrrole adds two atoms of hydrogen to form pyrroline which upon further reduction with sodium and alcohol yields pyrrolidine.

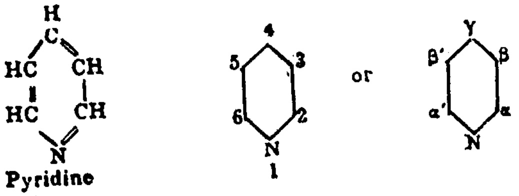


SIX-MEMBERED RINGS

The two important heterocyclic compounds of this class are pyridine and piperidine which will be discussed here.

PYRIDINE, C_5H_5N

Pyridine may be regarded as benzene in which one =CH— group has been replaced by nitrogen atom, —N=.



For the purposes of naming its derivatives the positions of the ring are designated either by numbers or by Greek letters as indicated above.

Pyridine was discovered by Anderson (1850) in bone oil. It occurs in coal-tar (0.1%) which is its sole commercial source. Pyridine is also present in tobacco smoke where it is produced by the decomposition of the alkaloid nicotine.

Isolation from Coal-tar. The light oil fraction of coal-tar which contains pyridine along with methylpyridines, quinoline and isoquinoline, is extracted with sulphuric acid. The pyridine and other bases are thus removed in the acid layer as soluble sulphates. The acid layer is then treated with sodium hydroxide when the bases are liberated as a dark brown oily liquid. Pyridine is obtained from it by fractional distillation.

Properties. (*Physical*). Pyridine is a colourless, highly refractive liquid, b.p. 115°, having an unpleasant odour. It is miscible in water in all proportions and is hygroscopic. It is also a good solvent for most organic substances, and dissolves many inorganic salts. It is about as strong a base as aniline and its aqueous solutions are only faintly alkaline to litmus.

(Chemical). Pyridine has a structure exactly analogous to that of benzene with the change that one CH group is replaced by a tertiary nitrogen atom. Thus it behaves in most respects like benzene, and also as a tertiary base. However in general it is more resistant to technical change, and is stable to oxidising agents such as chromic acid, nitric acid and alkaline potassium permanganate.

(1) FORMATION OF SALTS. Pyridine combines readily with strong acids and alkyl halides to form the respective salts. Thus :

$$C_5H_5N + HCl \longrightarrow [C_5H_5NH]^+Cl$$

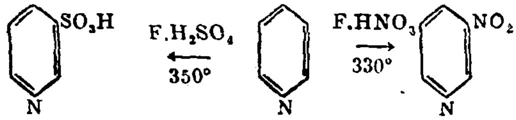
Pyridine hydrochloride

$$C_5H_5N + CH_3I \longrightarrow [C_5H_5NCH_3]^+I^-$$

N-Methylpyridinium iodide
(Quaternary salt)

Methylpyridinium iodide when treated with moist silver oxide (AgOH) yields methy pyridinium hydroxide, $[C_5H_5NCH_3]^+OH^-$ which is a strong base.

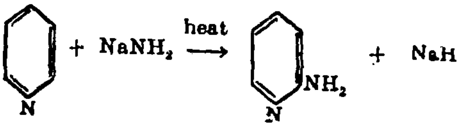
(2) SUBSTITUTION:- Substitution in pyridine is much more difficult than in benzene. Chlorine and bromine substitute slowly in 2-position. When heated with fuming nitric acid and fuming sulphuric acid above 300°, 3-substituted derivatives are obtained.



Pyridine-3-sulphonic acid

3-Nitropyridine

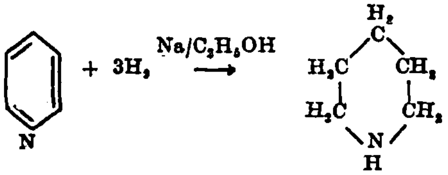
(3) ACTION WITH SODAMIDE. When heated with sodamide in toluene solution, pyridine gives 2-aminopyridine.



2-Aminopyridine

This can be diazotized in the normal way like aniline.

(4) REDUCTION. It is reduced more readily than benzene, being converted into piperidine with sodium and alcohol.

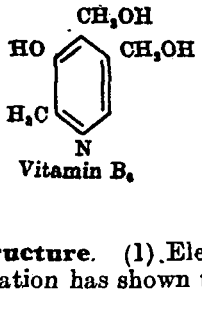


Piperidine

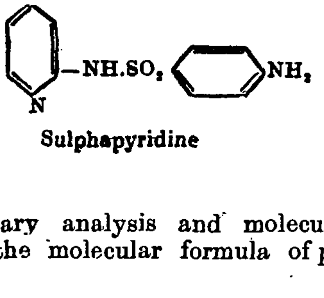
The above reduction can also be carried with hydrogen.

When pyridine is heated with hydriodic acid, reduction as well as ring-fission occurs with the production of n-pentane and ammonia.

Uses. Pyridine is used : (1) as a solvent and as acid-catching medium in organic reactions (Schotten-Baumann reaction) ; (2) to denature alcohol ; (3) for exterminating plant pests ; (4) for the preparation of derivatives such as vitamin B_6 and sulphapyridine which has achieved marvellous results in combating pneumonia, gonorrhoea, and other infectious diseases.



Vitamin B₆



Sulphapyridine

Structure. (1) Elementary analysis and molecular weight determination has shown that the molecular formula of pyridine is C_5H_5N.

(2) Pyridine exhibits marked aromatic character : (*i*) it forms substitution products ; (*ii*) its hydroxy derivatives behave like phenols ; (*iii*) its amino derivatives can be diazotized and coupled in the usual way ; (*iv*) the side-chains on the ring are oxidised to the COOH groups ; (*v*) although highly unsaturated it is stable to oxidising agents.

(3) It combines with alkyl halides to form quaternary salts.

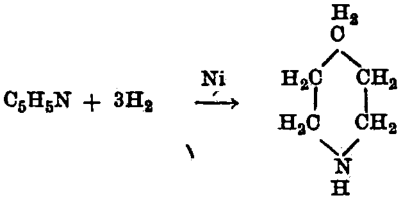
$$C_5H_5N + CH_3I \longrightarrow [C_5H_5NCH_3]^{+}I$$

N-Methylpyridinium iodide

This shows that pyridine contains a tertiary nitrogen, there is no H atom in direct union with the N atom.

(4) Pyridine on catalytic reduction adds three molecules of hydrogen to yield piperidine which shows that it contains a ring of

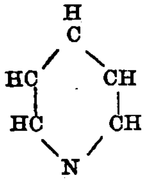
five carbon atoms and one nitrogen atom.



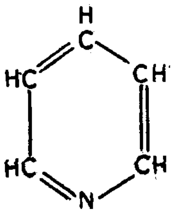
Piperidine

This reaction also indicates the presence of three double bonds in the molecule.

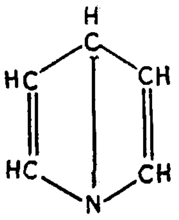
(5) Pyridine gives three monosubstitution products, which is possible only if each of the five carbon atoms of the ring is linked with one hydrogen atom. Therefore, the skeletal formula of pyridine may be written as



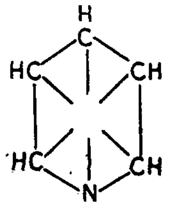
(6) Taking the above facts into consideration, three structural formulas have been proposed for pyridine.



(Korner)
I



(Riedel)
II

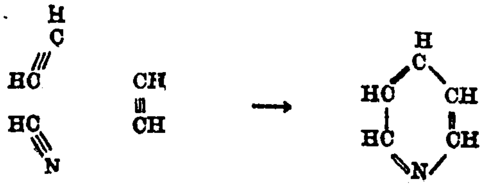


(Bamberger & von Pechmann)
III

The formulae II and III are rejected on the same ground as the similar formulae for benzene and anthracene. The Korner formula which is analogous to Kekule formula for benzene explains the largest number of facts and represents the correct structure of pyridine.

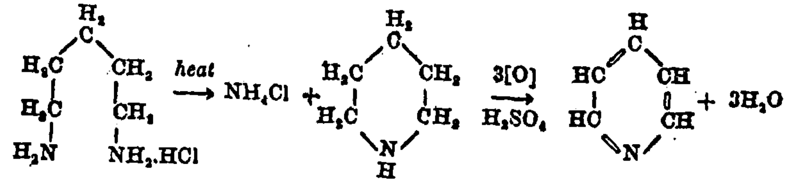
(7) The structure of pyridine is confirmed by the following **synthesis**.

(*i*) By passing a mixture of acetylene and hydrogen cyanide through a red hot tube.



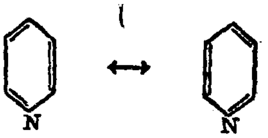
Pyridine

(*ii*) The distillation of pentamethylenediamine hydrochloride produces piperidine which on oxidation with concentrated sulphuric acid yields pyridine.



Pentamethylenediamine hydrochloride Piperidine Pyridine

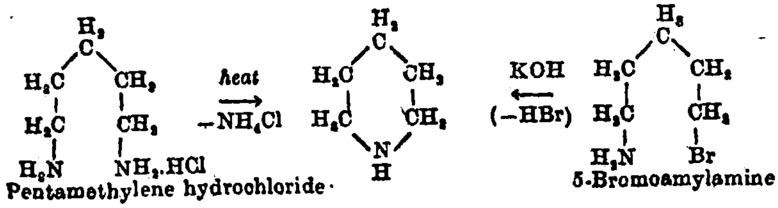
(8) Now it is believed that like benzene, pyridine is a resonance hybrid of the following two structures :



PIPERIDINE, $C_5H_{10}NH$

It is a structural unit of the alkaloid piperine and several other alkaloids.

Preparation. It is prepared conveniently by reducing pyridine with sodium and alcohol. It may be synthesised by heating pentamethylene hydrochloride, or by treating 5-bromoamylamine with alkali.



Pentamethylene hydrochloride 5-Bromoamylamine

Properties. Piperidine is a colourless liquid, b.p. 105°, having a pepper-like odour. It readily dissolves in water, alcohol and ether. It is a much stronger base than pyridine.

Piperidine gives reactions analogous to those of secondary aliphatic amines. On heating with concentrated sulphuric acid to 300°, it is oxidised to pyridine.

Piperidine is used as an accelerator in the vulcanization of rubber.

QUESTIONS

1. Explain the meaning of heterocyclic compounds. Give three examples drawn from the aliphatic series. Name three five-membered heterocyclic compounds and compare their mode of preparation and properties.

2. How is pyrrole obtained from bones ? Describe the preparation of this compound.

3. Give evidence to show that pyrrole resembles aromatic compounds and possesses properties in common with both the phenols and aromatic amines. (*Rajasthan B.Sc., 1953*)

4. Write brief notes on the preparation and properties of furan and thiophene. Bring out the points of resemblance between thiophene and benzene.

5. How is pyridine prepared from coal-tar or bone oil or synthesised from a chain compound ? What is the evidence upon which the structural formula of pyridine is based ?

6. From what sources is pyridine obtained ? Discuss its structural features and compare its chemical properties with those of benzene.

7. Outline the methods available for the synthesis of pyridine ring system. Compare the reactivity of pyridine with benzene. (*Vankateswara B.Sc. II, 1964*)

8. What is furfural ? Give its preparation and uses. Compare its properties with those of benzaldehyde. (*Nagpur B.Sc. III, 1964*)

9. Discuss the structure of pyridine. Compare its properties with those of benzene. (*Nagpur B.Sc. III, 1964*)

10. Write the structural formula of pyrrole, pyridine and thiophene. How is thiophene separated from benzene and how do you test for thiophene in benzene ? Mention the properties of thiophene. (*Gorakhpur B.Sc. III, 1967*)

11. How would you prepare pyrrole ? What are its chief uses ? (*Panjab B.Sc. III, 1968*)

12. Describe the preparation of pyridine. Compare its properties with those of benzene and state the evidence on which its structure is based. (*Ujjain B.Sc., 1968*)

13. What are "Heterocyclic compounds" ? Justify the statement that "Pyrrole behaves both as phenol and aniline". Support your answer with suitable examples. Include in your answer at least one synthetic method of preparation of pyrrole. (*Aligarh B.Sc., 1968*)

14. How is pyridine obtained ? Discuss its structure and mention its uses. (*Banaras B.Sc., 1968*)

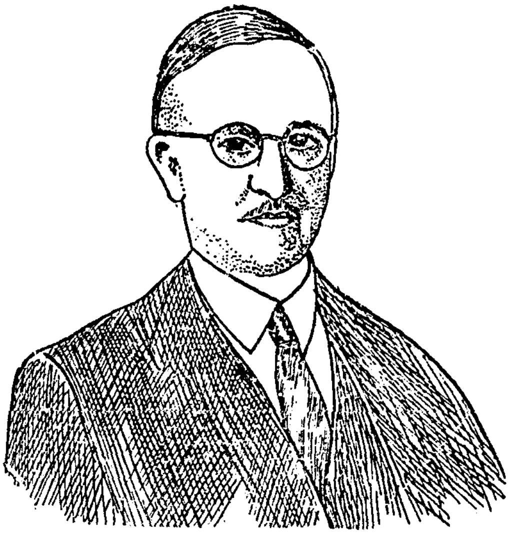
15. Discuss briefly the structures and comparative chemistry of Pyridine and Benzene. (*Ceylon B.Sc., 1968*)

16. How is pyridine prepared ? How can it be converted into (*a*) pyridine β-sulphonic acid ; (*b*) piperidine ; (*c*) 2-aminopyridine ; (*d*) pyridinium chloride. (*Udaipur B.Sc., 1969*)

17. Discuss briefly the chemistry of Furan and pyrrole. How can the compound belonging to each of these ring systems be synthesisd ? (*Panjab B.Sc., 1969*)

50

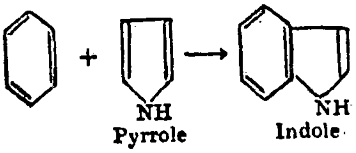
Heterocyclic Compounds (Continued)

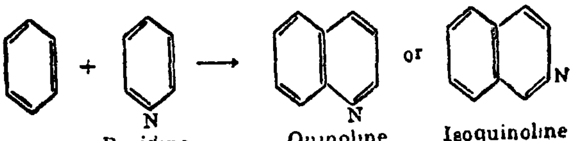


Roger Adams
(1889— , American)
Work with Chaulmoogric acid, anaesthetics, dyes, catalytic hydrogenation, alkaloids. Now head of the Chemistry Department in the university of Illinois.

Condensed Ring Systems

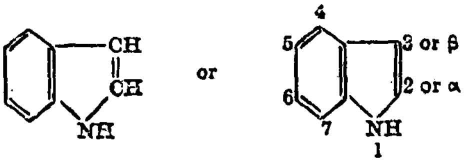
The more important heterocyclic compounds are those in which a benzene ring is condensed with a five or six-membered heterocyclic ring. Thus :





INDOLE, BENZOPYRROLE, C_8H_7N

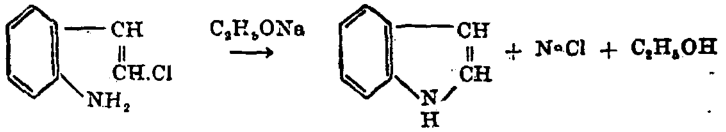
It is made of a benzene ring fused with a pyrrole ring,



Indole occurs in coal-tar, in jasmine flowers and in orange blossoms. It is the parent substance of indigo and was first obtained by Baeyer (1866) by distilling *oxindole*, a degradation product of indigo with zinc dust (hence its name).

Synthesis. Indole may be synthesised by several methods two of which are described below.

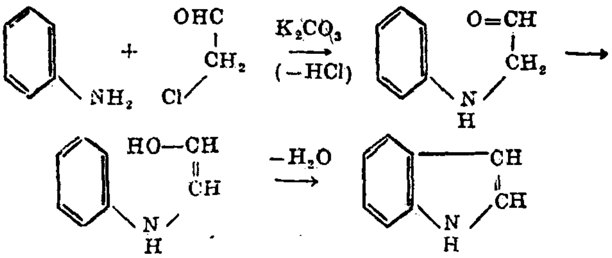
(1) By treating *o*-amino-styryl chloride with sodium alcoholate.



o-Amino-styryl chloride

Indole

(2) By heating monochloroacetaldehyde with aniline and potassium carbonate.



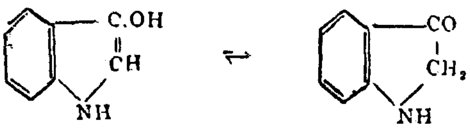
(Enolic form)

Indole

Properties. Indole forms plate-like crystals, m.p. 52°. When not quite pure, it has a strong faecal odour ; in contrast pure indole in high dilution has a flowery odour and is used in preparing jasmine and orange blossom blends in perfumery.

Indole resembles pyrrole in its chemical reactions. It forms a sodium or potassium derivative ; and gives 'pine shavings reaction' *i.e.*, pine shavings moistened with alcohol and hydrochloric acid when brought in contact with a solution of indole develop a cherry red colour. Indole is oxidised by ozone to indigotin.

Indoxyl. This is the keto form of β-hydroxyindole.



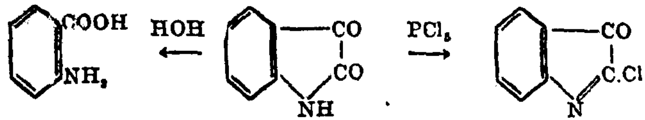
Enol form

Keto form

It occurs as a glucoside *indican* in indigo plant and may be prepared from this source (see p. 873).

Indoxyl is a yellow crystalline solid, m.p. 85°. It is readily oxidised in alkaline solution by air to indigotin.

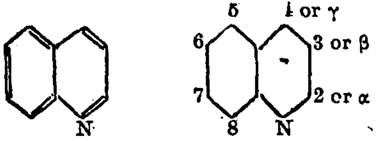
Isatin, *diketoindole*, is obtained by the oxidation of indigo with nitric acid. It is a red crystalline solid, m.p. 200°. It is slightly soluble in water but dissolves readily in alcohol. With PCl_5 it forms isatin chloride, and with warm NaOH, isatic acid.



Isatic acid Isatin Isatin chloride

QUINOLINE, α, β-BENZOPYRIDINE, C_9H_7N

It was first obtained by distilling quinine with alkali (Gerhardt, 1842), hence its name. It occurs in small quantities in coal-tar and bone oil. Structurally, the quinoline molecule is made of a benzene ring fused with a pyridine ring in α, β-positions. Thus it has the same relation to naphthalene as pyridine has to benzene.



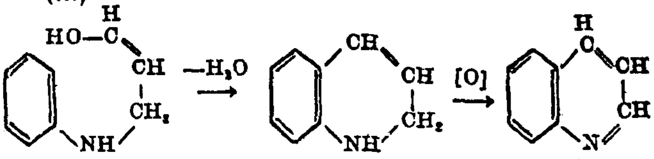
Quinoline

Preparation. Quinoline is prepared most conveniently by heating together aniline, glycerol, concentrated sulphuric acid and a mild oxidising agent (nitrobenzene or arsenic acid). Ferrous sulphate is often added to the reaction mixture in order to make the reaction less violent (**Skraup's synthesis**). The mechanism of the reaction is as follows : (*i*) Glycerol dehydrates to acrolein, (*ii*) aniline adds to acrolein at 1, 4-positions of the conjugated system of acrolein, and (*iii*) the side-chain is condensed in the ortho position to yield dihydroquinoline, and the oxidising agent converts it to quinoline by removing H atoms.

$$(i) \quad \underset{\text{Glycerol}}{CH_2OH.CHOH.CH_2OH} \xrightarrow[-2H_2O]{(H_2SO_4)} \underset{\text{Acrolein}}{CH_2{=}CH.CHO}$$

$$(ii) \quad \begin{array}{l} C_6H_5NH \text{———} H \\ CH_2{=}CH{-}CH{=}O \end{array} \longrightarrow \underset{\text{Intermediate}}{C_6H_5.NH.CH_2.CH{=}CH.OH}$$

(*iii*)



Dihydroquinolene Quinoline

If nitrobenzene is used for oxidation, it is itself reduced to aniline which is consumed in the reaction.

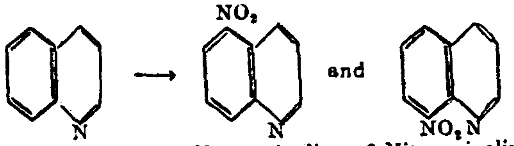
Properties. Quinoline is a colourless oily liquid, b.p. 238°, having a sharp disagreeable odour, resembling somewhat that of aniline. It is insoluble in water but dissolves readily in alcohol and ether. It is volatile in steam. It is a weak base comparable in strength to pyridine and turns blue litmus red.

Quinoline combines the behaviour of benzene and pyridine.

(1) FORMATION OF SALTS. Quinoline, like other tertiary bases, forms salts with acids, and adds alkyl halides to give quaternary alkali salts.

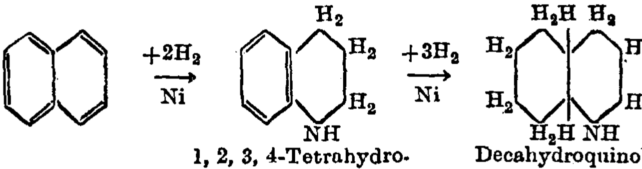
$$\underset{\text{Quinoline}}{C_9H_7N} + CH_3I \longrightarrow \underset{\text{N-Methylquinolinium iodide}}{[C_9H_7N.\overset{+}{C}H_3]I^-}$$

(2) SUBSTITUTION REACTIONS. Substituting agents attack the benzene ring of quinoline to form in the first instance 5 and 8 substituted derivatives. For example the nitration of quinoline yields 5-nitroquinoline and 8-nitroquinoline.



5 Nitroquinoline 8-Nitroquinoline

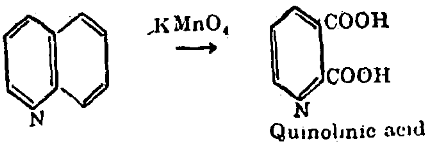
(3) REDUCTION. When quinoline is reduced with hydrogen in the presence of nickel at 160°, the pyridine ring is hydrogenated in preference to the benzene ring to form 1, 2, 3, 4-tetrahydroquinoline which is a powerful secondary base. Further reduction at high temperature and pressure saturates the benzene ring also, yielding decahydroquinoline.



1, 2, 3, 4-Tetrahydro-quinoline

Decahydroquinoline

(4) OXIDATION. Upon oxidation of quinoline, the benzene ring is broken preferentially and the product is quinolinic acid.



Quinolinic acid

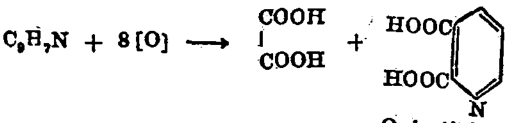
Uses. Quinoline is used : (1) as an antiseptic ; (2) for precipitation of metals in analytical work ; and (3) as a high boiling solvent for reactions when the elements of hydrogen halides are to be removed from the reactants.

Structure. (1) By analysis and molecular weight determination, quinoline has been assigned the molecular formula C_9H_7N.

(2) It undergoes nitration and sulphonation like benzene, and is stable to oxidising agents. This indicates the presence of only aromatic rings in the molecule.

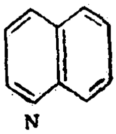
(3) It combines with alkyl halides to form quaternary salts, showing the presence of a tertiary N-atom in the molecule.

(4) On vigorous oxidation with acid potassium permanganate, it yields quinolinic acid and oxalic acid.

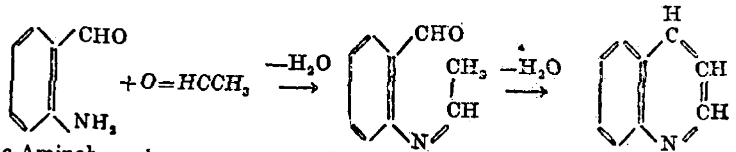


Quinolinic acid

From analogy to oxidation of naphthalene to form phthalic acid we conclude that quinoline is possibly made of a pyridine ring fused with a benzene ring which is broken in the above reaction. Thus, the structural formula of quinoline may be written as follows :



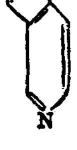
(5) The structure of quinoline is confirmed by **Friedlander's synthesis** from *o*-aminobenzaldehyde and acetaldehyde in the presence of dilute caustic alkali.



o-Aminobenzaldehyde Intermediate Quinoline

ISOQUINOLINE, C_9H_7N

It is made of a benzene ring fused with a pyridine ring in different positions than in quinoline, and may be written as :

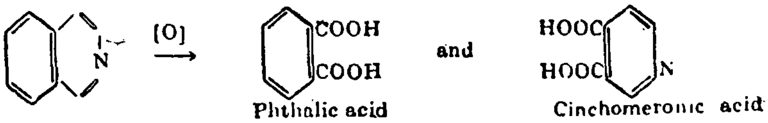


or

Isoquinoline is present in small amounts in coal-tar, along with quinoline; it may be separated from the latter by fractional crystallisation of their sulphates from alcohol in which isoquinoline sulphate is only sparingly soluble.

Properties. Isoquinoline is a colourless crystalline solid, m.p. 24°, b.p. 240°, having an odour resembling somewhat that of benzaldehyde. It is a stronger base than quinoline.

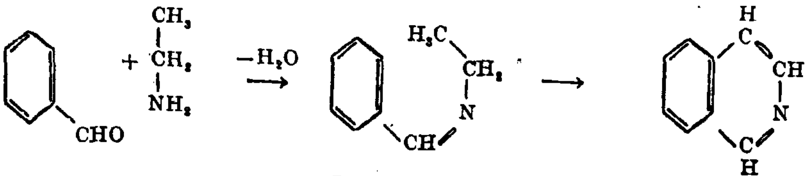
The reactions of isoquinoline are very similar to those of quinoline. It forms quaternary salts with alkyl halides. In isoquinoline, the pyridine ring is not so stable as in quinoline. Thus on oxidation with acid potassium permanganate it produces phthalic acid and cinchomeronic acid, both rings being partially broken.



Phthalic acid Cinchomeronic acid

Structure. The oxidation of isoquinoline to produce phthalic acid and cinchomeronic acid, shows that its molecule consists of one benzene ring fused with a pyridine ring at β γ-positions. In one case pyridine ring is ruptured and phthalic acid is formed and in the other it is the benzene ring which is broken to yield cinchomeronic acid.

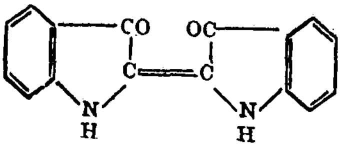
The structure of isoquinoline is confirmed by the following synthesis: (1) Benzaldehyde is condensed with ethylamine to produce benzylidene-ethylamine; (2) the vapours of the product are then passed through a red hot tube when isoquinoline results.



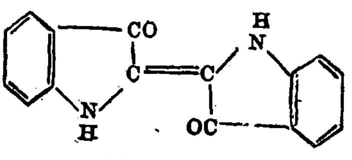
(Intermediate) Isoquinoline

INDIGO, INDIGOTIN, $C_{16}H_{10}O_2N_2$

Natural indigo is one of the earliest known blue dyes; Egyptian mummy clothes 5,000 years old, were dyed with it. It is a mixture of several dyes, the chief component being *indigotin*.



(Baeyer's formula)



(Modern formula)

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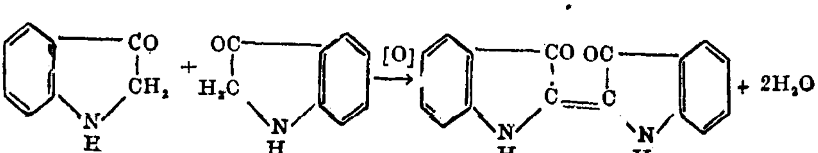
*Strictly speaking the natural dye-stuff obtained from plants is called indigo, while the term 'indigotin' is reserved for the pure synthetic product.

Indigo occurs in indigo plant (*Indigofera tinctoria*), which grows in tropical countries and in wood plant (*Istatis tinctoria*), which grows in European countries. Right from the 12th century on, indigo plant was extensively cultivated in India (hence the name of the dye ; Latin, *indicum* = Indian stuff), and the dye prepared from this source was exported to European countries in large quantities the value of exports in 1897 being Rs. 70 lakhs. The appearance of the synthetic indigotin in the market ruined the Indian industry and very little indigo is now made from indigo plants.

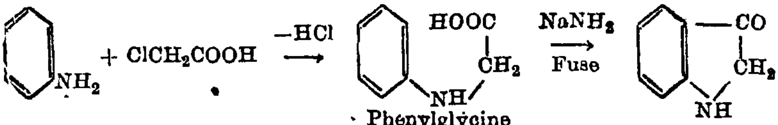
Preparation. (3) FROM INDIGO PLANTS. Indigo plants contain indigotin in the form of *indican* $C_{14}H_{17}O_6N$, which is the glucoside of indoxyl. Under the influence of an enzyme, *indimulsase* the indican is hydrolysed into glucose and indoxyl which on oxidation with air in alkaline solution, yields indigo.


Indoxyl (2 moles)

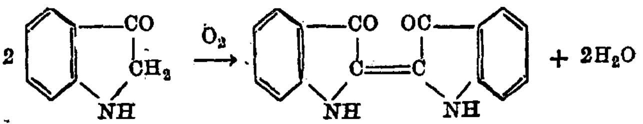
Indigotin

Shortly before flowering, the plants are cut and placed in wooden tanks containing water at 25 to 30°. The enzyme indimulsase, present in the leaves of the plants, soon brings about vigorous fermentation resulting in the hydrolysis of indican into glucose and indoxyl. The liquid extract containing indoxyl is drawn out in open vats fitted with paddle wheels. Here, it is rendered alkaline by the addition of lime and then subjected to vigorous churning with air. The indoxyl is thus oxidised to indigotin which being insoluble separates as blue flakes. The impure indigotin containing some other dyestuffs, is finally boiled with water, filtered and pressed into cakes. This is the natural dye indigo.

(2) COMMERCIAL SYNTHESES. (*a*) Indigotin is manufactured by the following synthesis due to Heumann. Aniline is first of all converted into phenylglycine which when fused with caustic soda and sodamide yields indigotin.


Phenylglycine

Indoxyl

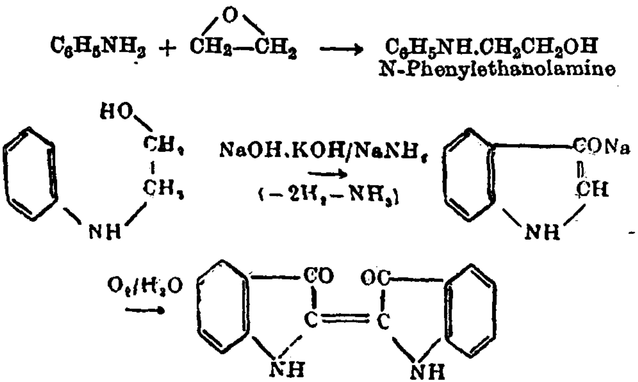

Indigotin

More recently, phenylglycine needed in the process has been prepared as follows. Formaldehyde is converted into its bisulphite compound which is then warmed with aniline, then treated with sodium cyanide, and the product hydrolysed with water.

$$C_6H_5NH_2 \xrightarrow{CH_2(OH)SO_3Na} C_6H_5NH.CH_2SO_3Na + H_2O$$

$$\xrightarrow{NaCN} C_6H_5NHCH_2CN \xrightarrow{H_2O} C_6H_5NHCH_2COOH$$

(*b*) After the World War II, Germans have disclosed another process for the manufacture of indigotin as follows. Aniline when treated with ethylene oxide, gives N-phenylethanolamine which on heating with a mixture of sodium and potassium hydroxides, and then with sodamide yields sodium salt of indoxyl which on oxidation with moist air yields indigotin.

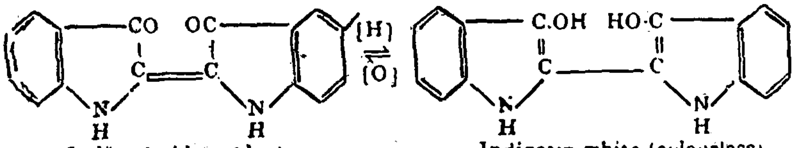


N-Phenylethanolamine

Indigotin

Properties. Indigotin is a dark blue crystalline powder, m.p. 390° to 392°. The natural product has a coppery lustre owing to the presence of other dyes in it. It is insoluble in water and most organic solvents, but fairly soluble in nitrobenzene and chloroform. It can be sublimed under reduced pressure to reddish blue vapours which on cooling yield prismatic crystals.

Indigotin is used in printing inks and very extensively for dyeing cotton by the *vat process*. Indigo paste is placed in a vat and reduced with alkaline solution of glucose or sodium hyposulphite ($Na_2S_2O_4$), when it is converted to a colourless soluble substance known as *indigotin white* or *leucoindigotin*. The fabric to be dyed is soaked in the solution of indigotin-white and then exposed to the air, whereupon indigotin white is oxidised to indigotin and the fabric develops a dark-blue colour.



Indigotin (dark blue) Indigotin-white (colourless)

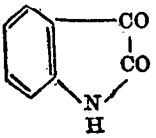
The dark-blue colour of the fabric produced as above, is extremely fast to washing and other colour destroying agents, but the shade is dull and unattractive.

Structure. (1) By analysis and vapour density measurements it has been shown to have the molecular formula $C_{16}H_{19}O_2N_2$.

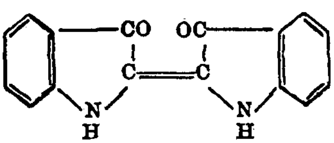
(2) Fusion of indigotin with alkali yields anthranilic acid, which shows the presence of a benzene ring further attached to one carbon atom and one nitrogen atom in the ortho positions.

(3) Strong oxidation of indigotin gives two molecules of isatin.

$$\underset{\text{Indigotin}}{C_{16}H_{10}O_2N_2} + 2[O] \longrightarrow \underset{\text{Isatin}}{2C_8H_5O_2N} \quad \text{or}$$

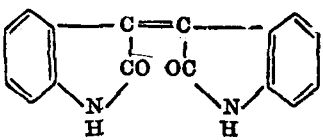


This indicates that the structural formula of indigotin can be derived by removing two O-atoms from two molecules of isatin. Hence, it can be written as



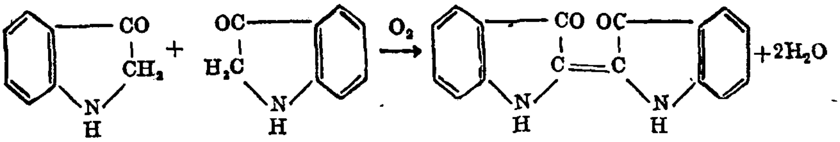
I

or



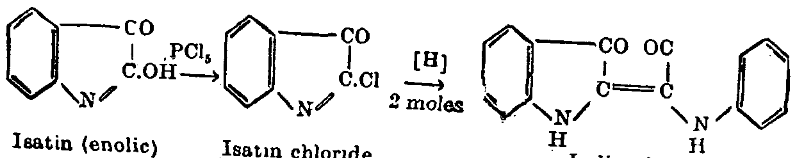
II

(4) The oxidation of indoxyl to yield indigotin can be interpreted as follows.



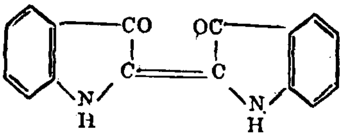
This shows formula I represents the structure of indigotin correctly.

(5) The structure of indigotin was confirmed by the following synthesis (Baeyer, 1877). Isatin is treated with phosphorus pentachloride to form isatin chloride which on reduction with zinc dust in glacial acetic acid yields indigotin.

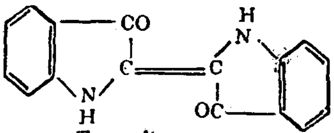


Isatin (enolic) Isatin chloride Indigotin

(6) The acceptance of the Baeyer's form of indigotin implies that it should exist in *cis* and *trans* forms.



Cis form



Trans form

All available experimental evidence and *X*-ray crystal analysis shows that ordinary indigotin is the *trans form.* Evidence of the existence of the unstable *cis form* has been obtained by Heller (1939), according to whom the aeration of a cold alkaline solution of *indigotin-white* produces *cis*-indigotin which is converted to ordinary indigotin within a few hours.

QUESTIONS

1. Write the constitutional formulae of the following :—thiophene, pyrrole, pyridine, isoquinoline and anthraquinone.

2. Give the preparation, properties and uses of indole.

3. How are quinoline and isoquinoline synthesised ? What are the products formed on oxidising them by means of $KMnO_4$?

4. How has the constitution of quinoline been established ? Enumerate the important properties of this compound.

5. What are quinolines ? Give their properties and importance. Describe Skraup's synthesis.

6. Show how the constitution of quinoline has been confirmed by synthesis.

7. How is indigo used for dyeing fabrics ? Give the theory of the process.

8. How is indigo prepared from plants ? Comment on the decline of this industry in India.

9. Describe Skraup's synthesis of quinoline. Discuss fully the constitution of quinoline.

10. Describe two methods for preparing quinoline. Describe its properties. How will you prove its constitution ? (*Gujarat B. Sc., 1964*)

11. (*a*) Give one synthesis of (*i*) pyridine ; (*ii*) quinoline ; and (*iii*) isoquinoline.

(*b*) Describe the properties of pyridine and show how they compare with those of nitrobenzene. (*Vallabhbhai B.Sc., 1964*)

12. What are heterocyclic compounds ? How are they classified ? Discuss the constitution of quinoline and isoquinoline. (*Bombay B.Sc., 1968*)

13. What is a heterocyclic compound ? Discuss the methods of preparation and structures of quinoline and isoquinoline. (*Kurukshetra B.Sc., 1968*)

14. Outline the synthesis of the following compounds :—
(*i*) Fluorescein ; and
(*ii*) Indigo. (*Banaras B.Sc., 1968*)

15. Establish the constitution of Indigo and explain how it is used as a vat-dye. (*Viswa Bharati B.Sc., 1969*)

16. How is Indigo isolated in the laboratory ? Outline the steps leading to the present accepted structure of Indigo. (*Behrampur B.Sc., 1969*)

51

Alkaloids

ALBERT LENDENBURG
(1842—1911)
German chemist. He is known for his researches in the field of alkaloids and for elucidating the structure of benzene. He proved the equivalence of the hydrogens of benzene.

The alkaloids may be defined as *the basic nitrogenous compounds of vegetable origin which have a marked physiological action when administered to animals.* Thus *coniine* is a violent poison ; *quinine* is a specific for malaria ; *cocaine* acts as a local anaesthetic ; *morphine* relieves pain ; and *atropine* dilates the pupil of the eye. The above definition of the alkaloids is by no means perfect. Piperine, the alkaloid of the pepper, is neither basic nor does it have any physiological action. And yet, there are compounds like caffeine which conform to the above definition but have been recently deleted from the list of alkaloids.

The majority of alkaloids are derivatives of the heterocyclic basic compounds *e.g.*, pyrrole, pyridine, quinoline and isoquinoline. There also exist relatively simple alkaloids having open-chain structure *e.g.*, *ephedrine.*

OCCURRENCE AND EXTRACTION

Alkaloids occur chiefly in plants of the dicotyledons families, and are localised in leaves, fruits, seeds, bark and root of these plants. They are invariably found combined with organic acids such as lactic acid, malic acid, oxalic acid, tartaric acid and citric acid, in the form of salts.

The extraction of alkaloids from plant materials and their purification offers considerable difficulty because of the several closely related compounds present with them. To this end, the vegetable material is finely powdered and digested with water acidulated with HCl or H_2SO_4. The mineral salts of the alkaloids being water-soluble, pass into solution. The aqueous extract is then filtered and basified by adding a mild alkali (Na_2CO_3, NH_4OH, CaO), when the alkaloid is liberated from the salt. The liberated alkaloid is recovered by extraction with organic solvents *e.g.*, chloroform or ether or in case of volatile alkaloids by steam distillation. Further purification of the substance is done by fractional precipitation or by fractional crystallisation depending on the nature of the other compounds present with it.

GENERAL PROPERTIES

(1) Most of the alkaloids are crystalline solids, while a few of them (coniine, nicotine) are liquids.

(2) Most of them have an intensely bitter taste and are extremely poisonous.

(3) Except the liquid alkaloids which are soluble in water, the rest are insoluble in water but dissolve readily in alcohol, ether, chloroform and benzene.

(4) They are all optically active, the majority being levorotatory.

(5) Being basic in character, they dissolve in mineral acids, forming salts.

(6) Solutio of alkaloids give precipitates with certain reagents (*alkaloidal reagents*) such as picric acid, tannic acid, phosphomolybdic acid, phosphotungstic acid, and potassium mercuric iodide. The precipitation of alkaloids with these reagents is often employed for their isolation and purification. For the same reason, tannic acid is used as an antidote for alkaloidal poisoning, the insoluble tannate being not absorbed easily from the stomach.

DETERMINATION OF STRUCTURE

Alkaloids are mostly very complex compounds and the determination of their structure needs a careful and systematic approach. The usual procedure is as follows :

(1) **Molecular formula.** The molecular formula of the alkaloid is found by analysis and by molecular weight determination by suitable methods.

(2) **Detection of groups.** The presence of various functional groups in the molecule is ascertained by applying specific tests.

(1) *Phenolic OH*, produces colour with $FeCl_3$; forms acetyl and benzoyl derivatives ; and allows coupling with diazonium salts.

(*ii*) *Alcoholic OH.* (*a*) Primary alcoholic group, CH_2OH, forms esters and on oxidation yields aldehydes ; (*b*) Secondary alcoholic group, $>CHOH$, forms esters and on oxidation gives a ketone.

(*iii*) *Carboxyl group,* COOH, forms salts and. esters, and liberates carbon dioxide with sodium bicarbonate solution.

(*iv*) *Ester group,* COOR, produces a free carboxylic acid and alcohol on hydrolysis, which may be isolated and identified.

(*v*) *Methoxy group,* OCH_3, produces methyl iodide when heated with hydriodic acid.

(*vi*) *Basic groups.* Most basic groups form salts with acids. (*a*) Aliphatic-NH_2 reacts with nitrous acid to form alcohol with the evolution of nitrogen, (*b*) Aromatic NH_2 is detected by diazo reaction, and by formation of acetyl or benzoyl derivatives, (*c*) Secondary bases, NH : react with nitrous acid to form nitrosoamines, form acetyl and benzoyl derivatives, and combine with methyl iodide to yield methiodides, (*d*) Tertiary bases, $>N.R.$, form methiodides with methyl iodide.

(*vii*) *Double linkage.* The alkene linkage $>C=C<$, can be detected by treatment with bromine water or with potassium permanganate solution.

(3) **Estimation of Groups.** Having detected the various groups present in the molecule, the alkaloid chemist proceeds to determine their number quantitatively.

(*i*) *OH group.* The number of OH groups is determined by acetylating the alkaloid and subsequent hydrolysis of the acetyl derivative with *N*-NaOH ; the excess alkali is titrated with *N*-HCl.

$$ROH \xrightarrow{CH_3COCl} RO.OCCH_3 \xrightarrow{NaOH} ROH + CH_3COOH$$

The amount of alkali used for hydrolysis gives the number of acetyl groups which correspond with the number of OH group.

(*ii*) *COOH group* is estimated by titration against *N*/10 barium hydroxide using phenolphthalein as indicator, or by the silver salt method.

(*iii*) *OR group* (methoxy or ethoxy) can be determined by heating the alkaloid with concentrated acid.

$$ROCH_3 + HI \longrightarrow ROH + CH_3I$$

The methyl iodide evolved is collected in alcoholic silver nitrate and the silver iodide formed weighed. One gram molecular weight of silver iodide will correspond to one methoxy group.

(*iv*) NH_2, $>NH$, and $-N=$ groups can be estimated : (*a*) By forming the hydrochloride and titrating its aqueous solution against N/10 KOH using phenolphthalein as indicator, and (*b*) By platinichloride method.

(4) **Degradation.** The alkaloid is decomposed by treating with suitable reagents to give simpler compounds which can be identified easily.

(*i*) *By hydrolysis.* The hydrolysis splits the molecule at the ester and the amide linkages. Thus piperine on hydrolysis yields piperic acid and piperidine

$$\underset{\text{Piperine}}{C_{11}H_9O_2CO-NC_5H_{10}} + H_2O \longrightarrow \underset{\text{Piperic acid}}{C_{11}H_9O_2COOH} + \underset{\text{Piperidine}}{C_5H_{10}NH}$$

This indicates clearly that piperine is the piperidide of piperic acid.

(*ii*) *By oxidation.* Oxidation with potassium dichromate, potassium permanganate or with hydrogen peroxide brings about several changes. Thus with potassium permanganate, the molecule may break at the double bond, or any side chain of the benzene ring may be oxidised away leaving a COOH group at the root.

(*iii*) *By distillation with zinc dust.* While distilled with zinc dust, many alkaloids yield parent compounds, or are dehydrogenated. Thus, morphine on distillation with zinc dust gives phenanthrene and hence indicates the presence of the latter as forming the basic structure in the molecule. Coniine yields conyrine by loss of the molecule of hydrogen.

(*iv*) *By exhaustive methylation.* The alkaloid is methylated and converted into the quaternary salt by treatment with methyl iodide. This is treated with moist silver oxide to form the corresponding hydroxide, which on heating decomposes to yield an open-chain unsaturated hydrocarbon and an amine.

Thus ·

$$R.CH_2.CH_2N(CH_3)_2 \xrightarrow{CH_3I} [R.CH_2.CH_2.N(CH_3)_3]I \xrightarrow{AgOH}$$

$$[R.CH_2.CH_2N(CH_3)_3]OH \longrightarrow R.CH{=}CH_2 + N(CH_3)_3 + H_2O$$

(5) **Synthesis.** A picture of the structure of the alkaloids is then constructed from a study of its qualitative and quantitative analysis as above, and from a study of its degradation products. This is then confirmed by a suitable synthesis.

INDIVIDUAL ALKALOIDS

CONIINE, $C_8H_{17}N$.

Coniine is one of the simplest alkaloids known. It occurs naturally in the seeds and other parts of the spotted hemlock (*conium maculatum*). It is of historical interest because Socrates, the Greek philosopher, was put to death by being forced to drink hemlock extract for the crime of teaching the young to think.

Isolation. The seeds of hemlock are powdered and distilled with sodium hydroxide solution. Coniine is then recovered from the distillate by extraction with ether. The ethereal extract on evaporation leaves behind the alkaloid.

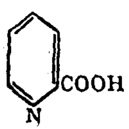
Properties. Coniine is a colourless, alkaline liquid, b.p. 167°, turning brown on exposure to air. It has an unpleasant odour recalling a mouse, and has a burning taste. It is sparingly soluble in water but readily soluble in alcohol. Both coniine and its salts are exceedingly poisonous, causing death by paralysing the nervous and the respiratory systems. The natural alkaloid is dextrorotatory $[\alpha]_d^{19°} = +15{\cdot}7$.

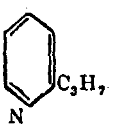
Structure. (1) The molecular formula established for coniine is $C_8H_{17}N$.

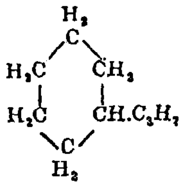
(2) When coniine is distilled over zinc dust it splits out three molecules of hydrogen and forms conyrine ($C_8H_{11}N$), which upon oxidation with potassium permanganate gives pyridine 2-carboxylic acid.

$$\underset{\text{Coniine}}{C_8H_{17}N} \xrightarrow[-3H_2]{Zn} \underset{\text{Conyrine}}{C_8H_{11}N} \xrightarrow{[O]} \underset{\text{Pyridine-2-carboxylic acid}}{C_5H_4N.COOH}$$

This shows that (*i*) conyrine is made of a pyridine ring with a side-chain in 2 position ; subtraction of C_5H_4N (pyridine radical) from $C_8H_{11}N$ (conyrine), leaves C_3H_7 for the side chain and (*ii*) coniine is the corresponding piperidine derivative of conyrine in which the three double bonds of the piperidine ring are fully saturated. Thus the formulas of conyrine and coniine may be written as follows :

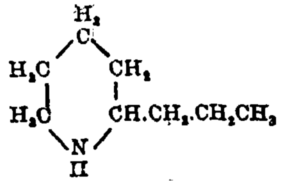

Pyridine-2-carboxylic acid


Conyrine

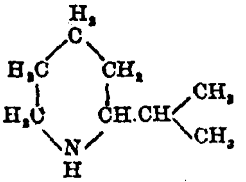

Coniine

(3) The side-chain in coniine may be normal or *iso*, so that the two possible structures of the alkaloid are :

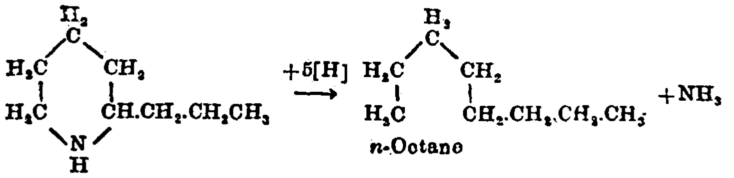
I


(2-*n*-propylpiperidine)

II

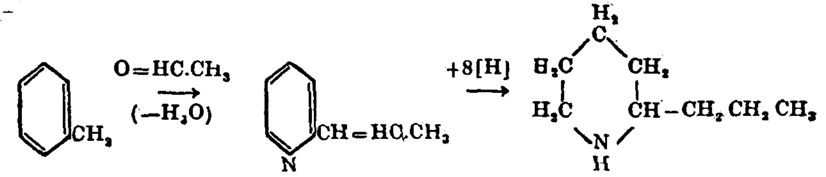

(2-isopropylpiperidine)

(4) The reduction of coniine with hydrogen iodide gives ane and ammonia. This is possible only if formula I is correct.



The formula II would have given *Iso*octane under similar conditions. Thus it is established that coniine is 2-n-propylpiperidine.

(5) The structure of coniine has been confirmed by Landenburg's synthesis (1886) as follows. The condensation of picoline (2-methylpyridine) with acetaldehyde at 250° forms 2-propenylpyridine, which on reduction with sodium and alcohol yields coniine.



From the *dl*-mixture thus obtained *d*-coniine is isolated by forming addition salts with *d*-tartaric acid ; the salt of *d*-coniine being less soluble separates first on crystallisation and yields the free alkaloid on treatment with alkali. This is found to be identical with the natural alkaloid.

PIPERINE, $N_{17}H_{19}O_3N$

Piperine is the alkaloid of black pepper (*Piper nigrum*). It is contained in the seeds of black pepper to the extent of 5 to 10 per cent and was first isolated from this source by Oerstedt in 1819.

Extraction. Black peppers are powdered and heated with milk of lime. The resulting mass is evaporated to dryness and the alkaloid recovered from the residue by extraction with ether.

Properties. Piperine forms beautiful colourless crystals, m.p. 128°. It is neutral to litmus and has the characteristic sharp flavour and taste of black pepper. It is difficultly soluble in water but its toxicity is much less than of most other alkaloids.

Piperine is used as an antipyretic and to relieve colic.

Structure. (1) By elementary analysis and molecular weight determination, piperine has been assigned the molecular formula $C_{17}H_{19}O_3N$.

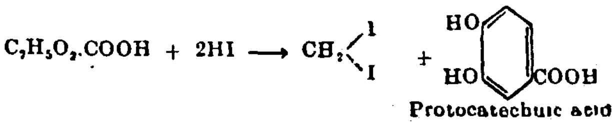
(2) When boiled with alcoholic potash, it is hydrolysed into piperidine and piperic acid.

$$C_{17}H_{19}O_3N + H_2O \longrightarrow \underset{\text{Piperidine}}{C_5H_{10}NH} + \underset{\text{Piperic acid}}{C_{11}H_9O_2.COOH}$$

Experiment shows that piperine contains a tertiary nitrogen and has no COOH group. Obviously, the alkaloid is a substituted amide of piperic acid $C_{11}H_9O_2.CON.C_5H_{10}$, which is split up by hydrolysis as shown above. We already know the structure of piperidine, and if we also know the structure of piperic acid, we can write the formula for the alkaloid.

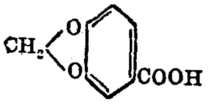
(3) *Structure of piperic acid.* (*i*) Piperic acid on oxidation gives piperonylic acid, $C_7H_5O_2.COOH$, which has C_4H_4 less than the parent acid. Therefore, C_4H_4 must have been present in the side-chain in piperic acid.

(*ii*) Piperonylic acid on boiling with conc. hydriodic acid forms methylene iodide and protocatechuic acid.

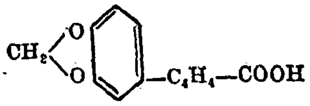


Protocatechuic acid

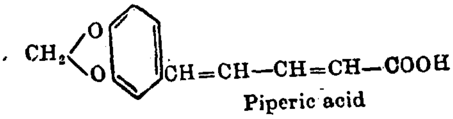
Hence, piperonylic acid is the methylene ether of protocatechuic acid and may be written as



(*iii*) As indicated by step (*i*) above, the formula of piperic acid may now be written as



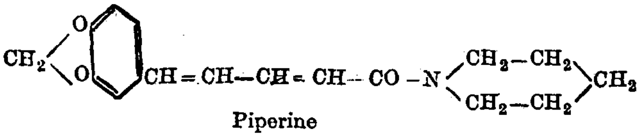
(*iv*) Piperic acid takes up four bromine atoms to form a tetrabromide showing the presence of two alkene linkages in its molecule. Therefore, it has the structural formula



Piperic acid

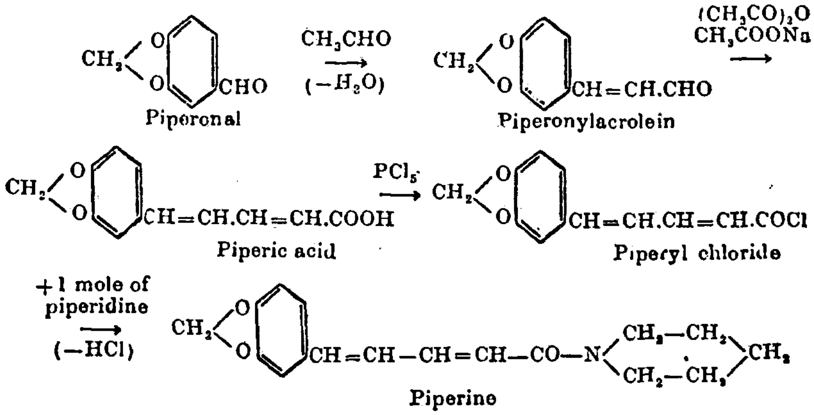
The presence of double bonds in the side-chain in alternate positions is confirmed since piperine on ozonolysis yields glyoxal and glyoxalic acid.

(4) Now structural formula of piperine can be built by uniting molecule of piperic acid with piperidine through an amide grouping as indicated in step (3).



Piperine

(5) The following synthesis of piperine due to Landenburg confirms its structure.



NICOTINE, $C_{10}H_{14}N_2$

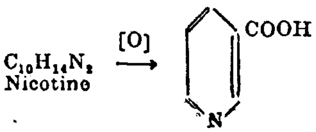
Nicotine is the principal alkaloid of tobacco (*Nicotina tabacum*) and occurs in the dry leaves to the extent of 4 to 5 per cent.

Extraction. Dry tobacco leaves are finely powdered and extracted with dilute solution of acids. To the acidic extract, is added alkali and is then steam-distilled. The crude nicotine thus obtained is purified by fractional distillation.

Properties. Nicotine is a, colourless, oily liquid, b.p. 247°, turning brown in air owing to oxidation. It has a tobacco-like smell and a burning 'alkaline' taste. It is soluble in water and also in organic solvents. The natural alkaloid is laevorotatory, $[\alpha]_D^{20} = -168.4°$. It is highly toxic to animals but in very small amounts it stimulates the nervous system for a while, which is followed by depression. The old Indian *hukka* is to be preferred to cheap cigarettes, as it washes away most of the nicotine in water. A crude tobacco extract or the foul water from *hukka*, is extensively used as an insecticide and fungicide by villagers.

Structure. (1) Analysis and molecular weight of nicotine corresponds to the formula $C_{10}H_{14}N_2$.

(2) On oxidation with chromic acid, it yields nicotinic acid (pyridine-β-carboxylic acid).

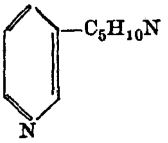


or $C_5H_4N.COOH$

Nicotinic acid

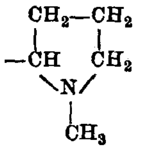
This shows that nicotine contains a pyridine nucleus having a side-chain consisting of $C_5H_{10}N(C_{10}H_{14}N_2 - C_5H_4N)$.

Thus we may write the formula of nicotine as

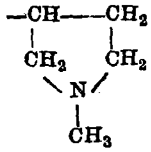


(3) When nicotine zinc chloride is distilled, the products are pyridine, pyrrole and methylamine. This suggests that the side chain $C_5H_{10}N$ is a pyrrole derivative.

(4) When nicotine is heated with concentrated hydriodic acid at 150°, methyl iodide is produced. It, therefore, seems that the side chain could be N-methylpyrrolidine.

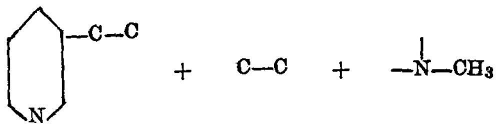


or



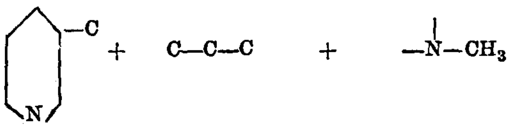
However, the point of attachment of the side-chain could be 2 or 3 as shown above.

(5) Pinner treated nicotine with bromine in acetic acid and among other products obtained the hydrobromide perbromide, $C_{10}H_{10}ON_2.Br_2.HBr.Br_2$, which upon treatment with aqueous sulphurous acid and sulphuric acid at 130—140°, gave 3-acetylpyridine, oxalic acid and methylamine. Thus the structural formula of nicotine must account for the following skeleton structural fragments :



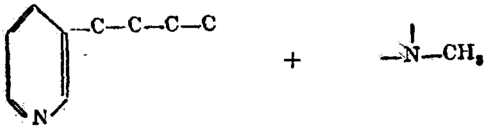
(3-acetylpyridine) (Oxalic acid) (Methylamine)

(6) Again, bromine (in the presence of hydrobromic acid) converts nicotine into dibromonicotine acid, $C_{10}H_8.O_2N_2Br$, which when heated with barium hydroxide solution at 100°, yields nicotinic acid, malonic acid and methylamine. Therefore, the structural formula of nicotine must also account for the following structural fragments :



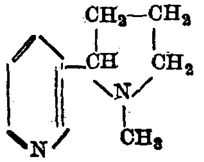
(Nicotinic acid) (Malonic acid) (Methylamine)

(7) The reactions of (6) and (7), taken together, are accounted for by postulating the following skeleton for nicotine :

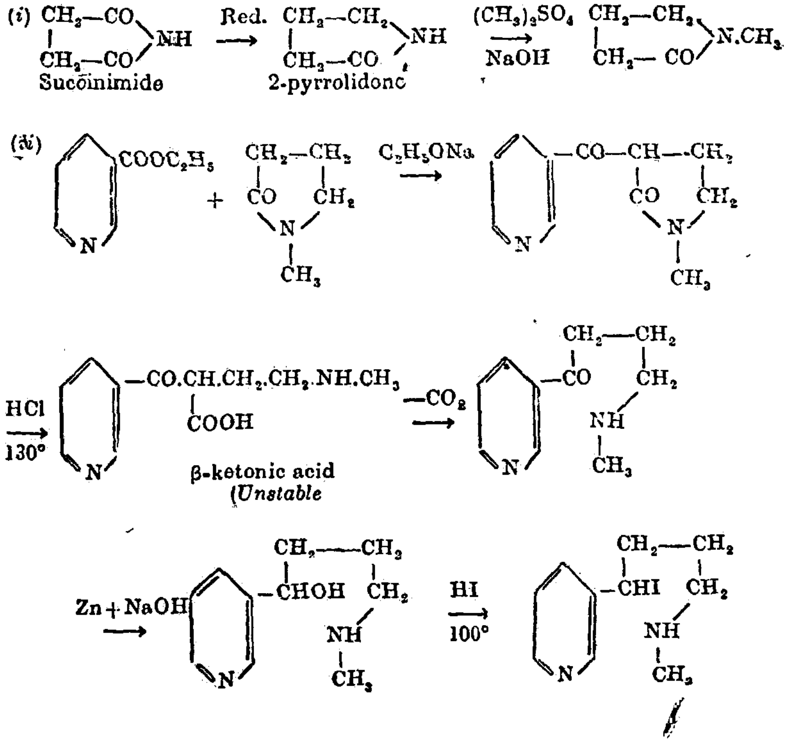


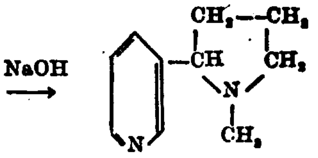
(8) Nicotine behaves as a ditertiary base and gives two addition products with methyl iodide. Thus the N-atom in the side-chain must be of the type —C—N(CH_3)—C—.

(9) Taking into consideration the above reactions, the structural formula for nicotine could be written as



(10) The structure of nicotine was confirmed by the following synthesis accomplished by Spath and Bretschneider (1928).





dl-Nicotine

The product was resolved by means of *d*-tartaric acid and the *l*-nicotine was found to be identical with the natural alkaloid.

QUININE, $C_{20}H_{24}N_2O_2$

It is the chief alkaloid present in the bark of cinchona tree (*Cinchona officinalis*), which is much cultivated in India, Ceylon and Java. The total alkaloid content of the bark is 6 per cent, of which 70 per cent is quinine.

Extraction. The finely powdered cinchona bark is treated with slaked lime and caustic soda until the material is a semi-solid mass. This is allowed to swell for 24 hours and is then extracted with hot petroleum ether. The alkaloids are removed from the solvent by treating with the dilute sulphuric acid. The sulphuric acid solution partially neutralised and concentrated if necessary. On cooling, quinine sulphate being less soluble than the sulphates of other alkaloids crystallises out. This is removed and further purified by recrystallisation from water.

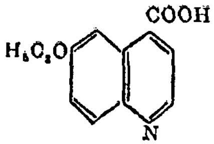
Properties. Quinine is a white solid (m.p. 177°) which crystallises with three molecules of water to form the trihydrate (m.p. 57°). It has an intensely bitter taste. The alkaloid is almost insoluble in water but dissolves more readily in organic solvents like alcohol, chloroform and petroleum ether. The natural alkaloid is laevorotatory, $[\alpha]_D^{20^\circ} = -158{\cdot}2^\circ$ (in 99% alcohol). It is weakly dibasic but forms well-defined salts with acids *e.g.*, quinine sulphate, $(C_{20}H_{24}C_2N_2)_2H_2SO_4.8H_2O$, the quinine hydrochloride. $C_{20}H_{24}O_2N_2HCl.2H_2O$. The aqueous solutions of these salts display faintly pale-blue fluorescence.

The most valuable property of quinine is that it readily kills the micro-organism causing malaria and hence the alkaloid and its salts are used as a specific for the treatment of malaria. Quinine is also an antipyretic, that is, it lowers the body temperature in high fever.

Structure. (1) Quinine has the molecular formula $C_{20}H_{24}N_2O_2$.

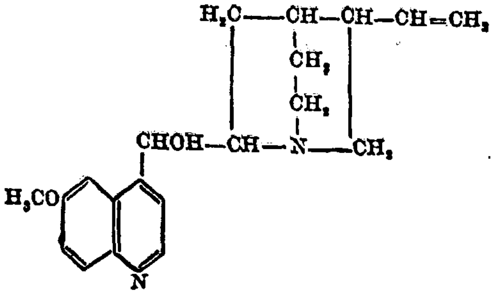
(2) On mild oxidation the alkaloid is converted into a ketone without loss of any carbon, showing the presence of a secondary alcohol grouping.

(3) On vigorous oxidation with chromic acid, quinine yields quininic acid, which indicates that it is a quinoline derivative having a side-chain in 4-position.



Quininic acid

(4) These reactions supplemented by more evidence of complex nature have shown that quinine has the structural formula.



Quinine

QUESTIONS

1. What are alkaloids? Describe their general methods of extraction and properties.

2. How do alkaloids occur in nature? Give the methods of extracting them from plants.

3. Describe the occurrence and physiological action of coniine. How is the structure of this alkaloid established?

4. What is an alkaloid, why is it so called and what is the significance of its occurrence in nature? How would you prepare the alkaloid of hemlock bark in a pure state and establish its constitution?

5. Describe the synthesis of *d*-Coniine from Pyridine.

6. What are the general methods for the extraction of alkaloids from plants? How has the constitution of piperine been established?

7. How is nicotine obtained from tobacco leaves? Suggest a method for its synthesis.

8. Discuss fully the isolation, properties and constitution of piperine. *(Madras B.Sc., 1964)*

9. Discuss analytical and synthetic evidence on the basis of which the constitution of the alkaloid piperine was arrived at. *(Bombay B.Sc., 1964)*

10. Discuss the analytical and synthetic evidences on which the structure of piperine is based. Discuss the stereo-chemistry of piperine. *(Calcutta B.Sc., 1964)*

11. Give an account of the preparation and determination of the structure of coniine. *(Banaras B.Sc. III, 1964)*

12. How is the constitution of nicotine arrived at? Give the synthesis of the compound you choose. *(Poona B.Sc. III, 1964)*

13. How is the structure of Nicotine established? *(Vankateswara B. Sc. II, 1964)*

14. (*a*) Discuss fully the structure of nicotine. Give its synthesis.

(*b*) How will you prove the presence of vinyl group in an alkaloid.
(Vallabhbhai B.Sc., 1964)

15. What are alkaloids ? How do they occur in nature ? What are their uses. How would you prepare Piperine and also establish its constitution ?
(Panjab B.Sc., 1965)

16. What are alkaloids ? Give an account of the work that established the structure of coniine. *(Banaras B.Sc. III, 1967)*

17. "Exhaustive methylation has been an important tool in the study of the structure of alkaloids." Illustrate the statement by giving examples of two alkaloids you have studied. *(Bombay B.Sc., 1967)*

How is pyridine recovered from coal-tar ? Give its important properties and show how has its constitution been established. *(J & K B.Sc., 1967)*

18. Give an account of the occurrence, extraction and properties of piperine. How has its constitution been established ? *(Panjab B.Sc. III, 1967)*

19. Describe the isolation, properties and synthesis of coniine. How has its constitution been established ? *(Panjab B.Sc. III. 1968)*

20. How would you isolate and purify an alkaloid from its natural source ? Discuss the chemistry of nicotine. *(Marathwada B.Sc., 1968)*

21. Describe the isolation and synthesis of Nicotine.
(Marathwada B.Sc., 1969)

22. Discuss the constitution of nicotine. Give its synthesis.
(Bombay B.Sc., 1969)

52

Terpenes and Related Compounds

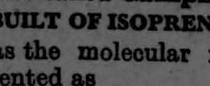
Paul Ehrlich
(1854—1915, German)
Coined the word 'Chemotherapy' for the relative action of chemicals on germs. Produced among other compounds Trypan blue for sleeping sickness and Salvarsan for syphilis. Awarded Nobel Prize in 1908.

When leaves, flowers, fruits, bark, roots, etc. of certain plants particularly pines, firs and citrus trees are steam distilled, volatile oils having characteristic fragrant odours are obtained. These oils being the essence of various plant products were named as **Essential oils**. The main constituents of the essential oils are open-chain or cyclic hydrocarbons of the general formula $(C_5H_8)_n$. These were given the name **Terpenes** since an important member of the class, terpene, was found to be present in turpentine oil (Greek : *terbinths* = turpentine oil).

In addition to terpene hydrocarbons, essential oils contain oxygen derivatives (alcohols, aldehydes and ketones) of such hydrocarbons. These are called **Camphors.**

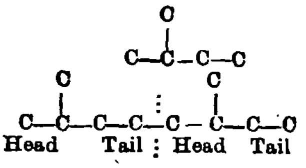
TERPENES ARE BUILT OF ISOPRENE UNITS

Isoprene has the molecular formula C_5H_8 and its structural formula is represented as



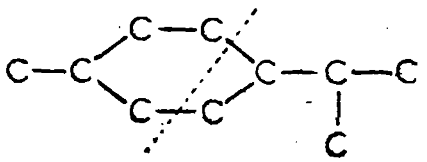
$$H_2C{=}\overset{\overset{\displaystyle CH_3}{|}}{C}{-}CH{=}CH_2$$

The general formula of terpenes is $(C_5H_8)_n$ and almost all members of this class produce isoprene on thermal decomposition. Thus we conclude that all terpenes are built of isoprene units (Wallach, 1887). From an examination of the structural formulae of terpenes, Ingold (1925) pointed out that isoprene skeletons in them are united in a regular head-to-tail fashion (the head being the branched end of isoprene). The rule that the molecules of terpenes are built of isoprene units joined head-to-tail is often referred to as the **Isoprene Rule**. Thus :



Isoprene unit or skeleton

Myrcene skeleton



Limonene Skeleton

Although a helpful guiding principle, Isoprene rule is not universal. However, its validity has been confirmed by the fact that simple terpenes can be synthesised from isoprene in the laboratory.

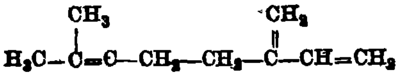
HOW ARE TERPENES CLASSIFIED ?

Terpenes are classified on the basis of isoprene units (C_5H_8) present in their molecules.

CLASS	MOL. FORMULA	CLASS	MOL. FORMULA
(*i*) *Hemiterpenes*	C_5H_8	(*iv*) *Diterpenes*	$C_{20}H_{32}$
(*ii*) Monoterpenes	$C_{10}H_{16}$	(*v*) Triterpenes	$C_{30}H_{48}$
(*iii*) Sesquiterpenes	$C_{15}H_{24}$	(*vi*) Polyterpenes	$(C_5H_8)_n$

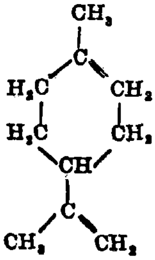
The only hemiterpene known is isoprene which does not occur free in nature although it forms the skeletal unit of almost all terpenes. The most important of the natural terpenes are monoterpenes having molecular formula $C_{10}H_{16}$. They contain 6-atoms less than the corresponding alkanes ($C_{10}H_{22}$) and are either straight chain hydrocarbons containing three double bonds or ring structures having one or two double bonds. Thus monoterpenes are subdivided into :

(*a*) *Open chain or Acyclic terpenes* containing three double bonds *e.g.*, Myrcene.

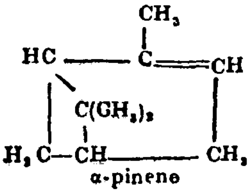


$$H_3C-\overset{CH_3}{\overset{|}{C}}=C-CH_2-CH_2-\overset{CH_2}{\overset{\|}{C}}-CH=CH_2$$

(b) *Monocyclic terpenes* containing one ring and two double bonds *e.g.*, Limonene



(c) *Bicyclic terpenes* containing two rings and one double bond, *e.g.*, Pinene



α-pinene

ISOLATION OF TERPENES

Terpenes are isolated from essential oils present in plants. The essential oil is extracted from the plant tissues by four methods : (*i*) Expression ; (*ii*) Steam distillation ; (*iii*) Digestion with solvents; (*iv*) Adsorption in purified fats. Method (*ii*) is the one most widely used. The plant tissue is macerated and then steam distilled. If a particular terpene is decomposed under these conditions, it may be removed by extraction with light petrol at 50° and the solvent distilled away under reduced pressure. Alternatively, the method of adsorption in fats may be employed. For example, the flower petals are spread over molten fat until the latter is saturated with essential oil. The fat is then digested with ethyl alcohol to remove the essential oil from it.

The essential oils obtained from plants as above usually contain a number of terpenes which are separated by fractional distillation.

GENERAL PROPERTIES

(*Physical*). Majority of terpenes are colourless liquids having a boiling point between 150° and 200°C. A few of them are solids. They are steam-volatile and dissolve in organic solvents, but usually not in water. Most of them are optically active.

(*Chemical*). Only a few terpenes have open-chain structure and they behave like olefinic hydrocarbons, while all others are unsaturated alicyclic hydrocarbons and behave likewise. Thus terpenes give addition reactions with hydrogen, halogens, halogen halides, nitrosyl chloride, etc. They undergo oxidation, polymerisation as also dehydrogenation in the ring.

USES

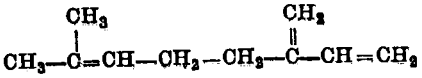
Terpenes and their derivatives are used in perfumes and medicines. They are as well used as industrial solvents in the preparation of paints and varnishes.

ACYCLIC OR OPEN-CHAIN TERPENES AND RELATED COMPOUNDS

Only a few alicyclic terpenes of the formula $C_{10}H_{16}$ are known. They are not found in abundance and are of little importance as compared with the cyclic terpenes. However, their alcohol and aldehyde derivatives are important industrially.

MYRCENE, $C_{10}H_{16}$

It is an acyclic monoterpene hydrocarbon which occurs in verbena and bay oils. It has the structural formula

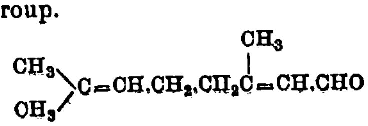


$$CH_3{-}\overset{CH_3}{\overset{|}{C}}{=}CH{-}CH_2{-}CH_2{-}\overset{CH_2}{\overset{\|}{C}}{-}CH{=}CH_2$$

Myrcene is a colourless liquid, b.p. 166-168°. It gives all reactions expected of triolefines.

CITRAL*, $C_{10}H_{16}$

It is the most important open-chain terpene derivative containing —CHO group.



$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C{=}CH.CH_2.CH_2\overset{CH_3}{\overset{|}{C}}{=}CH.CHO$$

It is also named as **Geranial**, the corresponding alcohol being Geraniol.

Citral is widely distributed and occurs to the extent 70-80% in lemon grass oil. It is also found in oil of oranges, oil of lemons (6·7%), and citronella oil.

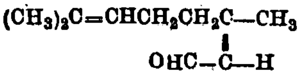
Extraction. The essential oil containing citral is treated with sodium bisulphite solution, when citral bisulphite compound is precipitated out. This is then treated with sodium carbonate to give free citral.

---

*Citral exists in two geometrical forms :

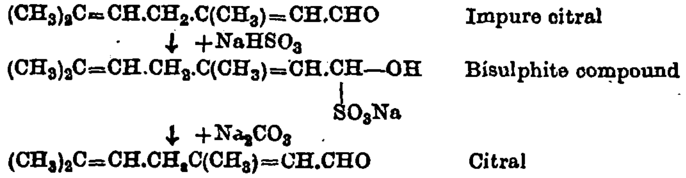
$$\begin{array}{l}(CH_3)_2C{=}CHCH_2CH_2\underset{\|}{C}{-}CH_3\\ \qquad\qquad\quad H{-}C{-}CHO\end{array}$$

Citral *a* or geranial



$$\begin{array}{l}(CH_3)_2C{=}CHCH_2CH_2\underset{\|}{C}{-}CH_3\\ \qquad\qquad\quad OHC{-}C{-}H\end{array}$$

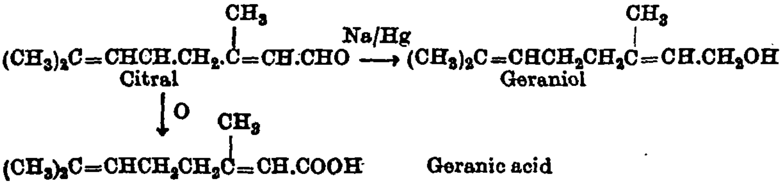
Citral *b* or neral



$$(CH_3)_2C{=}CH.CH_2.C(CH_3){=}CH.CHO \qquad \text{Impure citral}$$
$$\downarrow +NaHSO_3$$
$$(CH_3)_2C{=}CH.CH_2.C(CH_3){=}CH.\underset{SO_3Na}{\underset{|}{CH}}{-}OH \qquad \text{Bisulphite compound}$$
$$\downarrow +Na_2CO_3$$
$$(CH_3)_2C{=}CH.CH_2C(CH_3){=}CH.CHO \qquad \text{Citral}$$

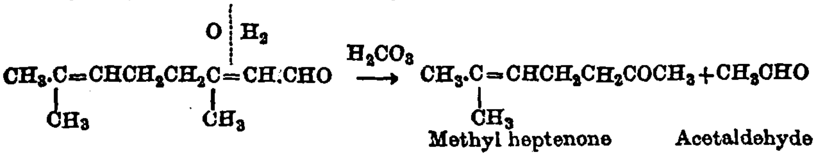
Properties. Citral is a colourless oily liquid with a strong lemon-like odour, b.p. 220°. Chemically it behaves as a diolefine and an aldehyde. Some important reactions of citral are :

(1) When reduced with sodium amalgam it gives an alcohol, geraniol, and upon oxidation with silver oxide it forms geranic acid.



$$\underset{\text{Citral}}{(CH_3)_2C{=}CHCH.CH_2.\overset{CH_3}{\overset{|}{C}}{=}CH.CHO} \xrightarrow{Na/Hg} \underset{\text{Geraniol}}{(CH_3)_2C{=}CHCH_2CH_2\overset{CH_3}{\overset{|}{C}}{=}CH.CH_2OH}$$
$$\downarrow O$$
$$(CH_3)_2C{=}CHCH_2CH_2\overset{CH_3}{\overset{|}{C}}{=}CH.COOH \qquad \text{Geranic acid}$$

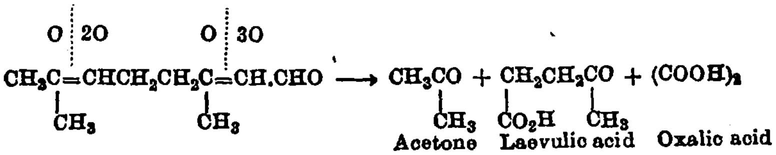
(2) Upon hydrolysis with potassium carbonate, citral yields methyl heptenone and acetaldehyde.



$$CH_3.\underset{CH_3}{\underset{|}{C}}{=}CHCH_2CH_2\underset{CH_3}{\underset{|}{C}}{=}\overset{O \,\vdots\, H_2}{CH.CHO} \xrightarrow{H_2CO_3} \underset{\text{Methyl heptenone}}{CH_3.\underset{CH_3}{\underset{|}{C}}{=}CHCH_2CH_2COCH_3} + \underset{\text{Acetaldehyde}}{CH_3CHO}$$

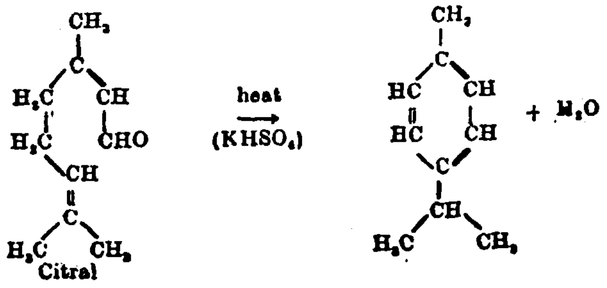
This reaction throws light on the structure of citral.

(3) Oxidation of citral with alkaline permanganate and then with chromic acid, gives acetone, oxalic and laevulic acids. This reaction gives an idea of the location of double bonds in the molecule.

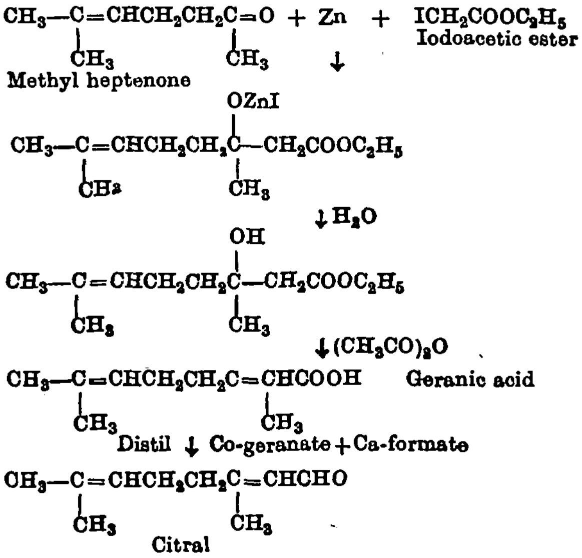


$$\overset{O \,\vdots\, 2O}{CH_3\underset{CH_3}{\underset{|}{C}}{=}}CHCH_2CH_2\overset{O \,\vdots\, 3O}{\underset{CH_3}{\underset{|}{C}}{=}}CH.CHO \longrightarrow \underset{\text{Acetone}}{CH_3\underset{CH_3}{\underset{|}{CO}}} + \underset{\text{Laevulic acid}}{\underset{CO_2H}{\underset{|}{CH_2}}CH_2\underset{CH_3}{\underset{|}{CO}}} + \underset{\text{Oxalic acid}}{(COOH)_2}$$

(4) When heated with potassium hydrogen sulphate, citral is converted to *p*-Cymene.



Synthesis. Citral may be synthesised by the following steps starting from methyl heptenone.



$$\underset{\text{Methyl heptenone}}{CH_3-\underset{CH_3}{C}=CHCH_2CH_2\underset{CH_3}{C}=O} + Zn + \underset{\text{Iodoacetic ester}}{ICH_2COOC_2H_5}$$

$$\downarrow$$

$$CH_3-\underset{CH_3}{C}=CHCH_2CH_2\overset{OZnI}{\underset{CH_3}{C}}-CH_2COOC_2H_5$$

$$\downarrow H_2O$$

$$CH_3-\underset{CH_3}{C}=CHCH_2CH_2\overset{OH}{\underset{CH_3}{C}}-CH_2COOC_2H_5$$

$$\downarrow (CH_3CO)_2O$$

$$CH_3-\underset{CH_3}{C}=CHCH_2CH_2\underset{CH_3}{C}=CHCOOH \quad \text{Geranic acid}$$

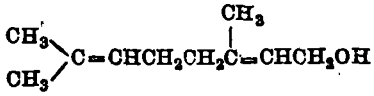
$$\text{Distil} \downarrow \text{Ca-geranate} + \text{Ca-formate}$$

$$\underset{\text{Citral}}{CH_3-\underset{CH_3}{C}=CHCH_2CH_2\underset{CH_3}{C}=CHCHO}$$

Uses. Citral is used for scenting cosmetics, perfumes, soaps and in lemon flavours. Its chief industrial use is in the manufacture of geraniol.

GERANIOL, $C_{10}H_{18}O$

It is the parent alcohol of citral and has the structural formula



$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C=CHCH_2CH_2\overset{CH_3}{C}=CHCH_2OH$$

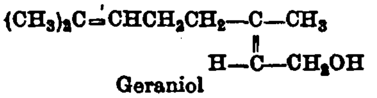
Geraniol is found in the oils of roses, geranium and eucalyptus.

Extraction. Geraniol is obtained from the cheap oil of palmrosa. The oil is treated with anhydrous calcium chloride with which geraniol forms crystalline addition product. This is separated and decomposed with water to liberate geraniol.

Geraniol is also obtained by reduction of citral with Al-amalgam.

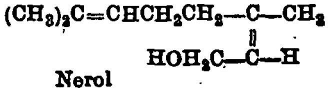
Properties. Geraniol is a colourless oil having pleasant odour. It boils at 229-230°C. It is a diolefinic primary alcohol and gives the reactions of diolefines and primary alcohols.

Geraniol exhibits geometrical isomerism. Thus :



$$(CH_3)_2C=CHCH_2CH_2-\underset{\underset{H-C-CH_2OH}{\|}}{C}-CH_3$$

Geraniol



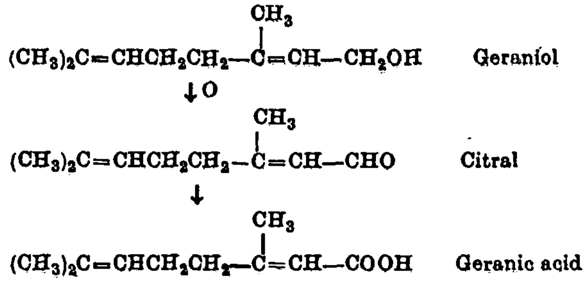
$$(CH_3)_2C=CHCH_2CH_2-\underset{\underset{HOH_2C-C-H}{\|}}{C}-CH_3$$

Nerol

Nerol also occurs naturally in various essential oils (oil of neroli, bergamot) and its boiling point is 225-226°.

Some reactions of geraniol are mentioned below.

(1) Upon oxidation, geraniol is first converted to citral and then to geranic acid.



$$(CH_3)_2C{=}CHCH_2CH_2{-}\overset{CH_3}{\overset{|}{C}}{=}CH{-}CH_2OH \qquad \text{Geraniol}$$

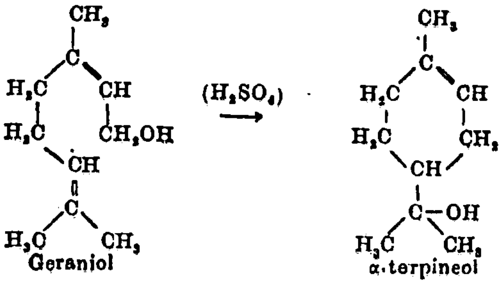
$$\big\downarrow O$$

$$(CH_3)_2C{=}CHCH_2CH_2{-}\overset{CH_3}{\overset{|}{C}}{=}CH{-}CHO \qquad \text{Citral}$$

$$\big\downarrow$$

$$(CH_3)_2C{=}CHCH_2CH_2{-}\overset{CH_3}{\overset{|}{C}}{=}CH{-}COOH \qquad \text{Geranic acid}$$

(2) When treated with sulphuric acid, geraniol gives α-terpineol. In the first step a water molecule is eliminated to form a ring which is followed by hydration in the side-chain to give α-terpineol.

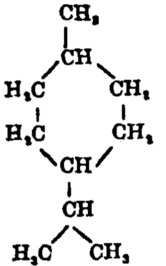


Geraniol α-terpineol

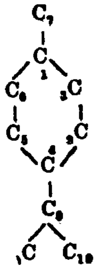
Uses. Geraniol is used for preparing artificial rose scents and as an agent for luring insects into traps.

MONO-CYCLIC TERPENES AND RELATED COMPOUNDS

All the monocyclic terpenes with the side-chains in the para position are regarded as derived from a hydrocarbon *p*-menthane, the carbon atoms of which are numbered for reference as follows :

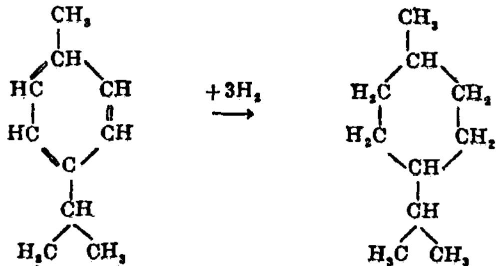


p-Menthane



***p*-Menthane**, 4-isopropyl-2-methyl cyclohexane, $C_{10}H_{20}$.

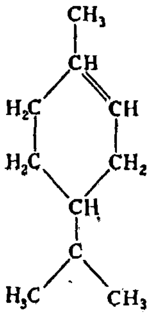
It is obtained by the hydrogenation of *p*-Cymene or limonene.



p-Cymene *p*-Menthane

p-Menthane is a liquid having fenne-like odour, b.p. 169° to 170° C.

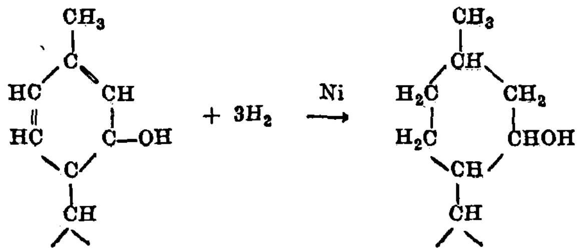
Menthol, 3-*p*-menthanol,



Menthol is the chief constituent of oil of peppermint.

Preparation. It is obtained from peppermint oil by cooling in air till menthol crystallises out.

Menthol is also produced by catalytic hydrogenation of thymol.

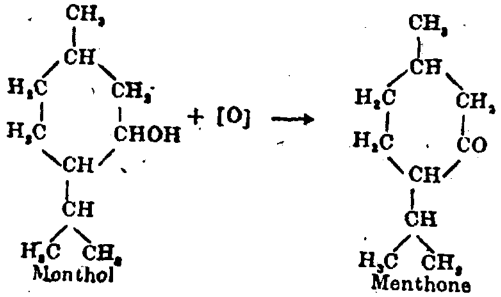


Thymol Menthol

Properties. Menthol obtained from peppermint oil forms white crystals, m.p. 42° to 43° and b.p. 216°. It is levo-rotatory. It has the smell and taste of peppermint.

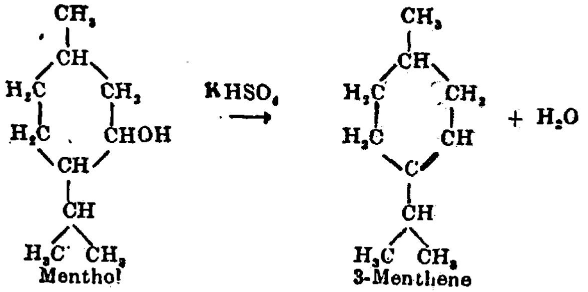
Chemically it behaves as a cyclic secondary alcohol.

(1) Upon oxidation with chromic acid-sulphuric acid mixture, it gives the corresponding ketone, menthone.



Menthol Menthone

(2) When heated with potassium hydrogen sulphate, menthol is dehydrated to form 3-menthene by removal of OH from carbon atom 3 and H atom from carbon atom 4.

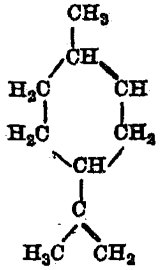


Menthol 3-Menthene

(3) When reduced with hydrogen iodide, menthol gives *p*-menthane.

Uses. Menthol is used medicinally as anaesthetic and antiseptic, and also for relieving toothache and congestion of nasal passages. It is used in face creams, shaving creams, tooth pastes, and ointments because of the cooling sensation that it imparts to the skin.

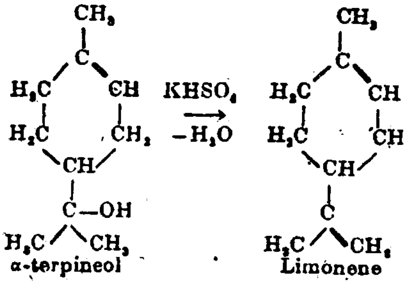
LIMONENE, 1, 8 (9)-Methandiene, $C_{10}H_{16}$



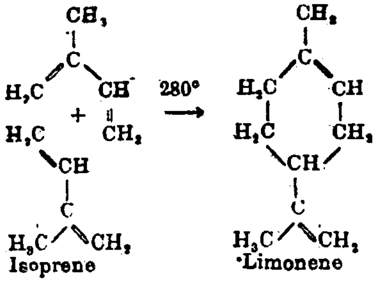
It is the most important monocyclic terpene. It is optically active. *d*-limonene occurs in lemon and orange oils, *l*-limonene in peppermint oil, and *dl*-limonene also known as **dipentene**, in turpentine oil. Dipentene is also produced by racemisation of the *d*- and *l*-forms at about 250°.

Preparation. (1) Limonene can be obtained from the essential oils by the formation of nitrosyl chloride addition product as mentioned earlier.

(2) It is prepared by the dehydration of α-terpineol with potassium hydrogen sulphate.



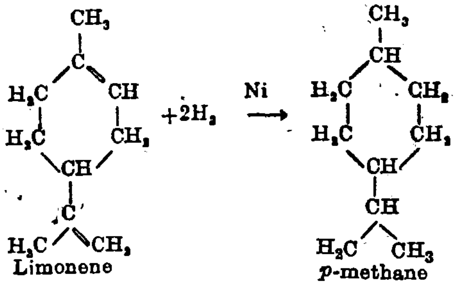
(3) It can also be obtained by heating isoperene to 280°C, which is simply a Diels-Alder 1, 4 addition reaction.



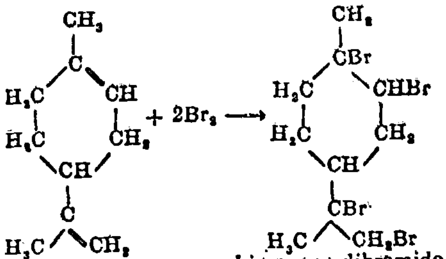
Properties. Limonene is a liquid having an odour like that of lemons. The dextro and levo forms boil at 177°. It is insoluble in water.

Chemically, it behaves as a diolefine. Thus :

(1) On catalytic hydrogenation it gives *p*-menthane.

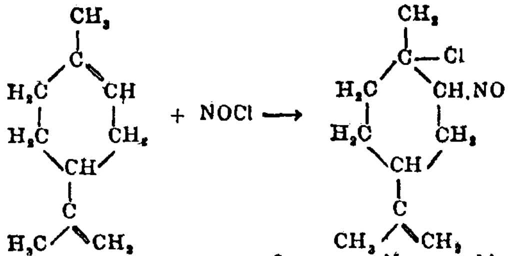


(2) It readily takes up bromine, giving a crystalline tetrabromide.



Limonene Limonene dibromide

(3) With nitrosyl chloride it forms nitroso-chloride derivative.

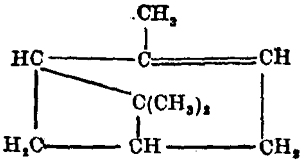


Limonene Limonene Nitroso-chloride

BICYCLIC TERPENES AND CAMPHOR

The bicyclic terpenes are hydrocarbons containing two ring systems and one double bond, while the camphors are alcohols and ketones related to them.

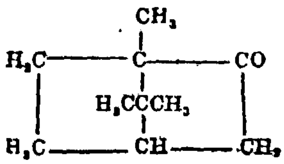
α-PINENE, $C_{10}H_{16}$



It is the most widely distributed of all natural terpenes. It occurs in both the *d*- and *l*-forms in all turpentine oils. Pinenes are also found in oil of eucalyptus. Pure pinene boils at 154-156°. Chemically, pinene gives the reactions of olefines.

Turpentine oil which is largely pinene is used as a solvent for resins, as a thinner for paints and varnishes, and also in the technical synthesis of camphor.

CAMPHOR, $C_{10}H_{16}O$



It exhibits optical isomerism. The *d*-form occurs naturally in the oil of camphor. Oil of camphor is obtained by steam-distilling the wood, leaves or bark of the camphor tree which grows in Formosa and Japan. It was also prepared technically by a synthetic process but it was abandoned on account of the high cost of production.

Properties. Camphor is a colourless, crystalline substance melting at 179° and boiling at 207°. It has a very strong characteristic odour.

Camphor is a ketone and shows the properties typical of carbonyl group. Thus it forms oxime with hydroxylamine, and yields a secondary alcohol on reduction with sodium and alcohol.

Uses. Camphor is used : (*a*) as a plasticiser in making celluloid, photographic films, and smokeless powder ; (*ii*) as medicine on account of its analgesic, expectorant, and antiseptic effects ; (*iii*) as a moth repellant, and (*iv*) as a preservative in cosmetics.

QUESTIONS

1. What are essential oils ? How are they isolated from natural sources ?

2. "Isoprene skeleton is the chief building block of framework of terpenes." Amplify this statement.

3. What are terpenes and camphors ? How are terpenes classified ?

4. Give the methods of extraction of terpenes from essential oils and describe their general properties.

5. Describe the occurrence, extraction, synthesis, reactions and uses of Citral.

6. How is geraniol extracted from oil of roses ? Give its physical and chemical properties, and commercial uses.

7. Give in detail the method of preparation, properties and uses of Menthol.

8. How is limonene obtained ? Give its structural formula and chief chemical reactions.

9. Write names of two important bicyclic terpenes or camphors. Write their structural formulas and enumerate their industrial uses.

10. What are the important sources of geraniol ? Discuss the structure. (*Banaras B.Sc. III, 1962*)

11. Give the analytical and synthetic evidence on the basis of which the constitution of citral was arrived at. (*Bombay B.Sc., 1964*)

12. What are the important sources of geraniol ? Discuss its constitution. (*Banaras B.Sc. III, 1967*)

13. Discuss the oxidative degradation of camphor. Indicate the products by their structural formulae. Give the synthesis of (*i*) Camphoronic acid and (*ii*) Camphor from camphoric acid. Show how you would convert pinene into camphor. (*Poona B.Sc., 1968*)

14. What are the important sources of geraniol ? Discuss its chemistry. (*Banaras B.Sc., 1968*)

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