ORGANIC CHEMISTRY

for

UNIZIK STUDENTS

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Chapter 1

INTRODUCTION

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1.1. WHAT IS ORGANIC CHEMISTRY

Organic Chemistry is the chemistry of carbon compounds with the exception of the oxides of carbon, carbonates, carbides and carbon disulphide. This classification is mainly one of convenience because of the very large number of carbon compounds. Organic chemistry is a field of importance to technology. It is the chemistry of drugs, dyes, rubber, food. clothes etc. It is fundamental to biology, medicine and related courses.

Why Carbon Forms Many Compounds

Carbon forms many compounds because carbon atoms can attach themselves to one another to form chains of thousands of atoms long (a property known as *catenation*) and rings of all sizes. To the chains and rings are attached other atoms mainly hydrogen, oxygen, the halogens, nitrogen, sulphur, phosphorus etc. Each different arrangement of atoms correspond to a different compound, with its own characteristic set of chemical and physical properties.

Characteristics of Organic Compounds

1. *They do not ionize and do not conduct electricity.*
2. *They are mostly insoluble in water but soluble in non-polar solvents such as benzene and diethyl ether.*
3. *Their melting points and boiling points are generally low.*
4. *They burn in plentiful supply of air to give CO_2 and H_2O and when the supply of air is limited CO and H_2O are formed.*

Homologous Series

To make the study of organic chemistry easy, the compounds are studied in groups or families called ***homologous series***. A homologous series is a family of organic compounds with the following characteristics.

- The members have the same general molecular formular.
- All members are prepared by chemically similar methods.
- A member varies from a successive member by a CH_2 (methylene) group or a molecular mass of 14.
- Members show similar chemical properties although they vary in reactivity along the series.
- The physical properties of members change gradually in the same direction along the series. For example, the melting and boiling points and density of members increase as the number of carbon atoms increases. The solubility of members decreases as the number of carbon atoms increases.

Functional Group

A functional group is an atom or group of atoms which is common to a family of homologous series and determines the behaviour of that family. Bonds such as C-C in alkanes, C=C in alkenes, C≡C in alkynes can also be regarded as functional groups since they determine the behaviour of these groups of compounds. Other examples of functional groups are the hydroxyl group, -OH, in alkanols, the alkanoic acid group, -COOH, in alkanoic acids, the amino group, $-NH_2$, in amines, the carbonyl group,  $\mathrm{H-C=O}$ in alkanals and  $\mathrm{R-C=O}$ in alkanones etc.

1.2. BONDING IN ORGANIC COMPOUNDS

1.2.1. The Carbon Atom

Organic chemistry, being the chemistry of carbon compounds, carbon therefore, occupies a central position in the subject. Let us look at the way carbon forms bonds with itself and with other atoms. The atomic number of carbon is 6. The electronic configuration of carbon in it's **ground state** is $1s^2 2s^2 2p_x^1 2p_y^1$. There are only two unpaired electrons. This suggests that carbon is divalent. But carbon is known to be quadrivalent. This may be accounted for by carbon having an excited configuration in which one 2s electron is promoted into $2p_z$ orbital.

This new arrangement has four unpaired electrons which can form four bonds.

$$1s^2 2s^2 2p_x^1 2p_y^1 \longrightarrow 1s^2 2s^1 2p_x^1 2p_y^1 2p_z^1$$

1.2.2. Hybridization

If carbon forms four bonds with the unpaired electrons of the excited sta configuration, the bonds will not be equivalent. There would be one non-dire bond (with the 2s spherical orbital) and three directed bonds mutually at right an (with three 2p orbitals). But in methane, for example, the four C-H bonds are kn to be identical and symmetrically disposed at an angle of 109°28' to each other. This observation is accounted for by ***hybridisation***. "Hybridization is the combinin or mixing of two or more pure atomic orbitals belonging to the same quantum lev to give a new set of orbitals, which are exactly equivalent and can, overlap maxim ally The new orbitals are known as ***hybrid orbitals***." It is possible to hybridize these atomic orbitals (A.O's) of carbon in a number of ways to give four valencies. The important methods of hybridization are sp^3, sp^2, and sp hybridizations.

1. Sp^3 (Tetrahedral) Hybridization

This is the mixing or hybridization of one 2s and three 2p orbitals form four equivalent Sp^3 hybrid orbitals arranged tetrahedrally i.e. p ting towards the four corners of a regular tetrahedron at 109°28' each other.

Structure of a hybrid orbital

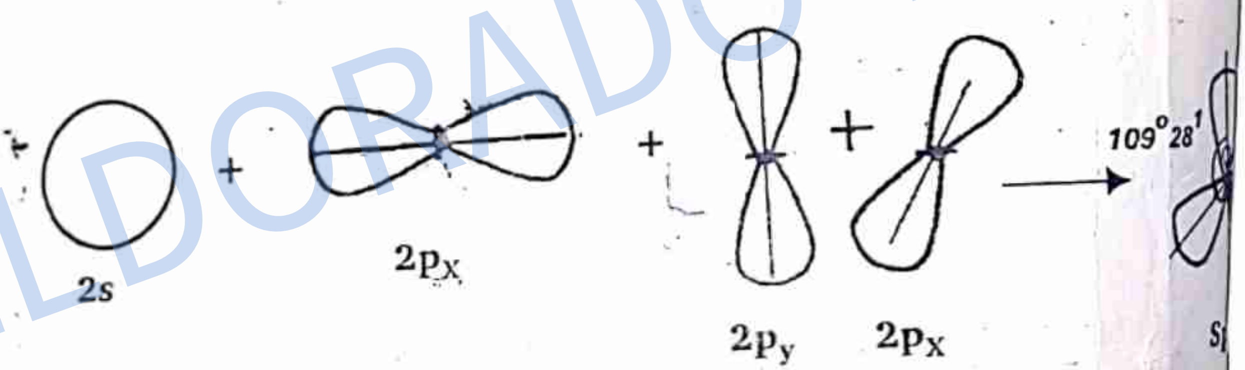


Fig. 1.1. Formation of four tetrahedral sp^3 hybrid orbitals

Four Sp^3 orbitals are involved in bonding when carbon forms four single in Methane, CH_4. The four hybrid orbitals overlap with a 1s orbital of four atoms to form four sigma (σ) bonds arranged tetrahedrally. All H-C-H b ngles are 109°28'.

The combination of two carbon atoms in ethane, for example, res the axial overlap of two sp^3 atomic orbitals one from each carbon ato form strong bond between them.

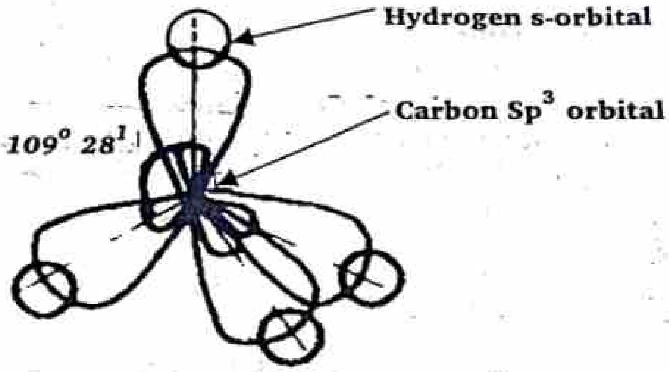


Fig. 1.2. Tetrahedral Structure of Methane

2. Sp^2 (Trigonal) Hybridization

This is the mixing or hybridization of one 2s and two 2p atomic orbitals to give three equivalent sp^2 hybrid orbitals, which are equilateral and directed at angles of 120° to each other. The 2p orbital which is unhybridized is directed at right angles to the plane of the three orbitals.

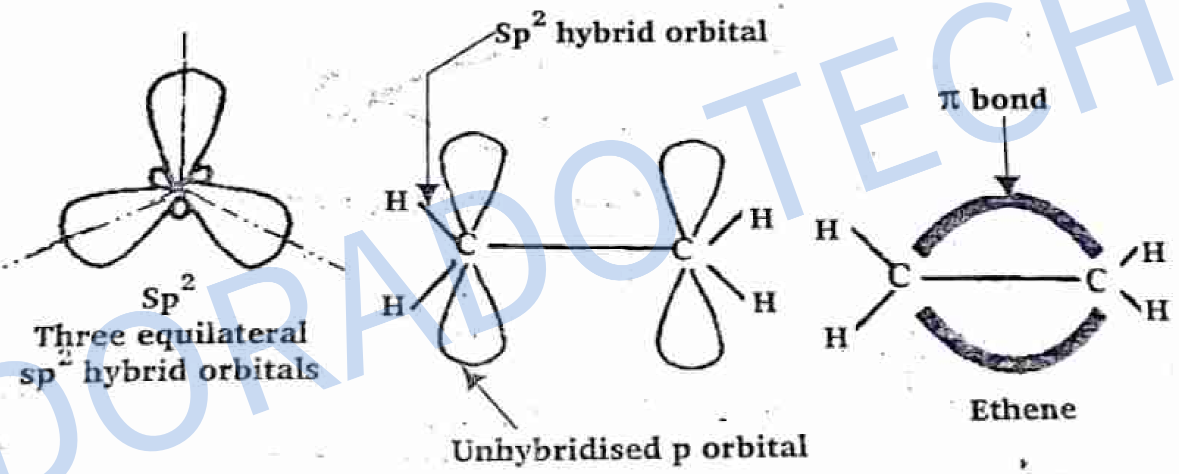


Fig. 1.3. Sp^2 Hybrid Orbitals and Bonding in Ethene

Ethene, C_2H_4, is an example of a compound in which the carbon atoms are in this state of hybridization. To form the ethene molecule, two of the sp^2 orbitals of each carbon atom overlap with 1s orbitals of two hydrogen atoms to form the strong C-H bonds, while the third Sp^2 orbital of each carbon atom overlap to form a strong C-C bond. The unhybridised p-orbitals of the two carbon atoms **overlap laterally** to form a *pi* (π) bond. This bond is spread out in two lobes above and below the plane containing the two carbon atoms and four hydrogen atoms. The additional π bond that is formed has the effect of drawing the carbon atoms closer and the C=C distance in ethene is 0.134nm, compare this with C-C distance in ethane 0.153nm. The distribution of the electrons in the two lobes above and below the plane of the molecule means that a region of negative charge isavallable for attack by *electrophilic (electron seeking) reagents*. This explains why the characteristic reactions of C=C are with such reagents.

3. Sp (Diagonal) Hybridisation

This is the hybridization of one 2s and one 2p orbitals to form two equivalent collinear Sp hybrid orbitals directed at 180° to each other. Two 2p orbitals, i.e. $2p_y$ and $2p_z$, remain unhybridised and are at right angles to each other and to the plane of the sp orbitals.

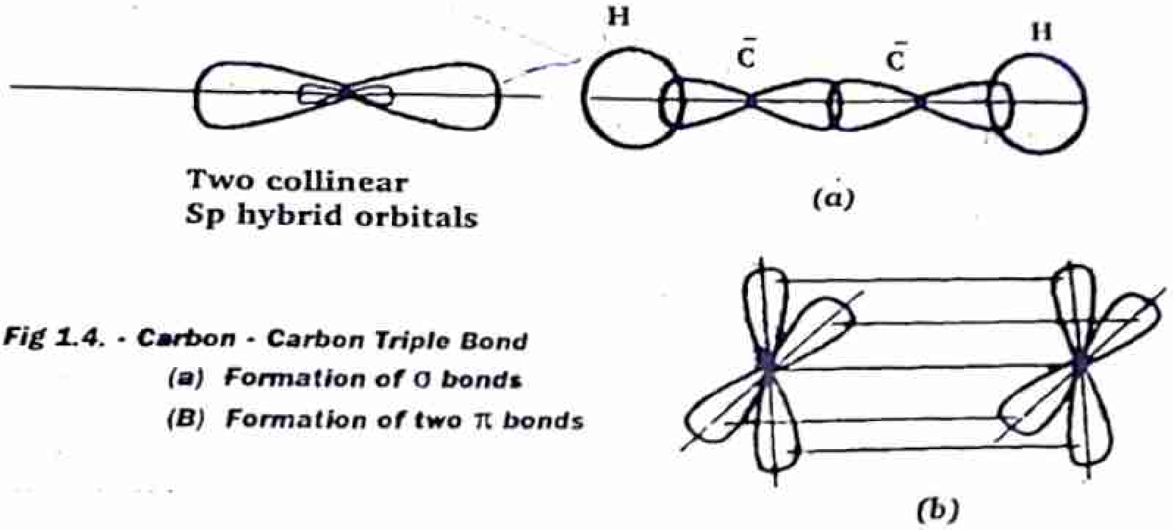


Fig 1.4. - Carbon - Carbon Triple Bond
(a) Formation of σ bonds
(B) Formation of two π bonds

Ethyne, C_2H_2, is an example of a compound in which the carbon atoms are in sp hybridization. To form the *ethyne* molecule (**H-C≡C-H**), one sp hybrid orbital of each carbon atom forms a σ bond with one hydrogen atom. The remaining sp hybrid orbitals overlap with one another to form a **C-C** bond. The two unhybridised P_y orbitals of each carbon atom overlap to form a π bond perpendicular to a second π bond formed by the overlap of two unhybridised P_z orbitals from each carbon atom. The ethyne molecule is thus effectively sheathed in a cylinder of negative charge and is very susceptible to electrophilic attack. The carbon atoms are drawn closer making the **C≡C** bond distance 0.121nm. the **C-H** bond length is 0.110nm.

1.3. CLASSIFICATION OF ORGANIC COMPOUNDS

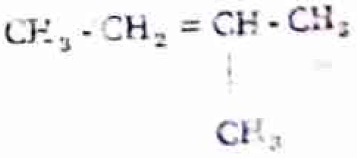
Organic compounds can be classified according to their molecular structure into ***aliphatic, alicyclic, aromatic, heterocyclic*** and ***polycyclic or polynuclear compounds.***

1. Aliphatic Compounds

These are organic compounds in which the carbon atoms are joined together in chains. A given carbon chain may be straight or branched. Examples of aliphatic compounds are:

$CH_2 - CH_2 - CH_2 - CH_2 - CH_3$

Pentane

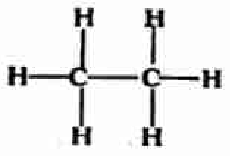


$$\begin{array}{c} CH_3 - CH_2 = \underset{\displaystyle CH_3}{\underset{|}{CH}} - CH_3 \end{array}$$

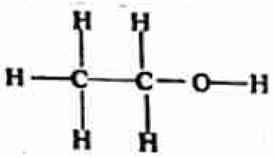
2 - methylbutane

Introduction

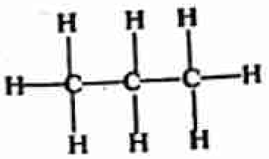
Aliphatic compounds may be ***saturated*** or ***unsaturated***. They are saturated when all the bonds between the atoms are single. The single bond may be between carbon and another atom. Examples are:



Ethane

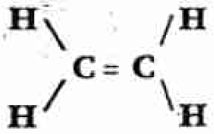


Ethanol



Propane

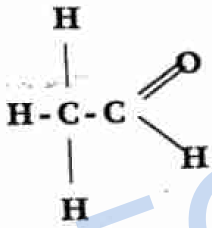
They are unsaturated when carbon atoms are joined together by double or triple bonds or when the bond between carbon and another element is double or triple. Examples include:



Ethene

$H-C\equiv C-H$

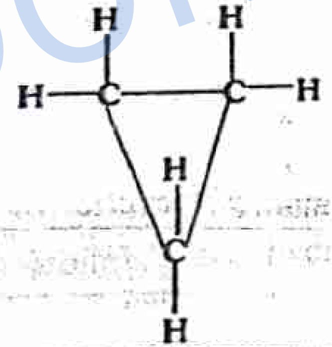
Ethyne



Ethanol

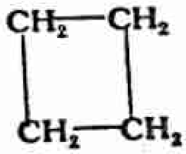
2. Alicyclic Compounds

They are compounds in which the carbon atoms join together to form a ring. Examples are:



Cyclopropane

and

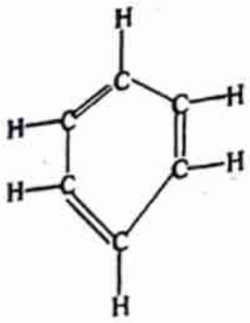


Cyclobutane

3. Aromatic Compounds

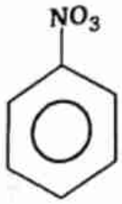
These are special types of alicyclic compounds, which contain rings based on benzene, C_6H_6, a 6-carbon ring compound.

Example

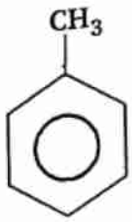


OR

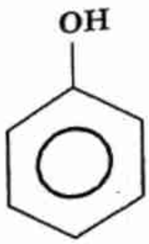
Benzene



Nitrobenzene



Toluene

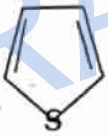


Phenol

4. Heterocyclic Compounds

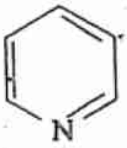
These are cyclic compounds containing elements other than carbon in the rin
These elements called **heteroatoms** could be sulphur, nitrogen, oxygen, e.g.

Furan



Thiophene

Pyrrole

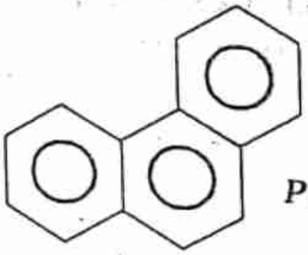


Pyridine

5. Polycyclic or Polynuclear Compounds

These compounds contain two or more rings linked together e.g.

Naphthalene



Phenanthrene

1.4. ISOLATION AND PURIFICATION OR ORGANIC COMPOUNDS

Organic compounds are normally obtained by extraction from plant
animal sources or by synthesis in the laboratory. They are rarely ever obtained p

from these sources. To purify them, they are separated from the impurities and two substances can be separated if some differences in their physical properties are known. Differences that are often used are solubility and boiling point. The greater the difference between the two substances, the easier it is to separate them.

1. Distillation

(a) Simple Distillation

This technique is used to separate and purify a mixture of miscible liquids, one of the compounds must be volatile and the other non-volatile. It can also be used for effective separation if there is a considerable difference in boiling points between the components. The mixture is gently heated in a distillation flask. At the boiling point of the more volatile component, it goes into vapour. The vapour passes into the condenser where it condenses and the pure liquid (distillate) is collected. The less volatile liquid remains in the flask.

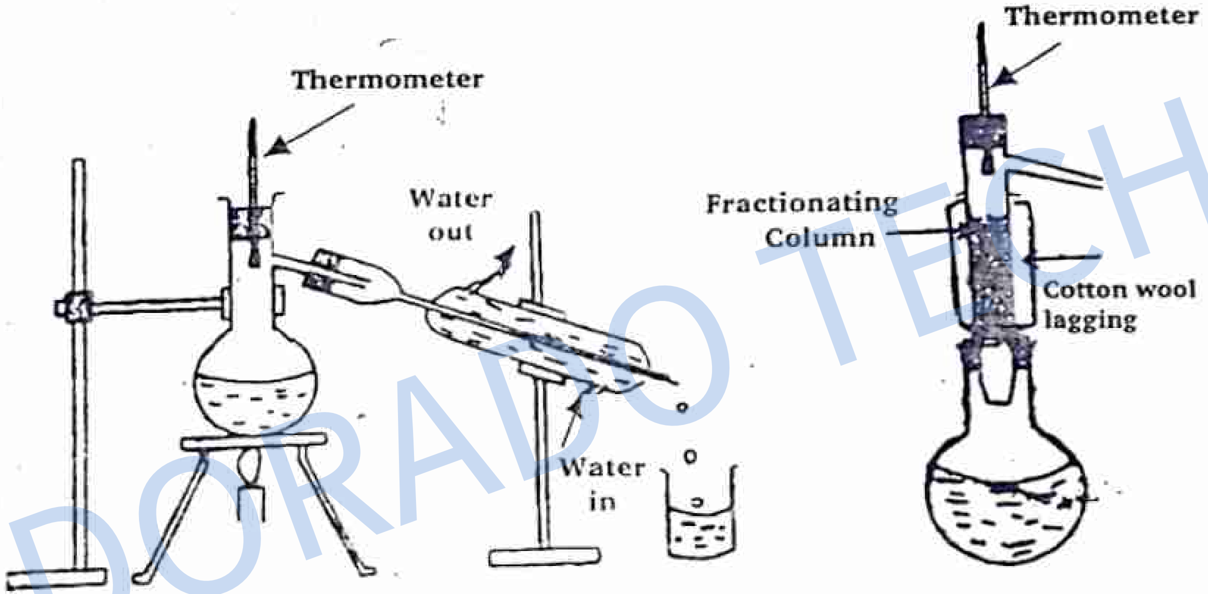


Fig. 1.7. (a) Simple Distillation *(b) Fractional Distillation*

(b) Fractional Distillation

If the simple distillation is used to separate a mixture of non-volatile or volatile liquids, only a very partial separation of the liquid components of the mixture is usually obtained. To obtain a sharper and more complete separation, fractional distillation is used.

In fractional distillation, the fractionating column is inserted vertically between the flask containing the boiling liquid and the condenser. The fractionating column consists of a vertical column packed with inert materials (such as pieces of glass or porcelain) or having some other devices (such as icentations) to increase the surface on which the rising vapour may condense. If the mixture is heated gently in the flask, the vapour rises up the fractionating column, and condenses. It trickles down. The condensed liquid meets more vapour going up. When this happens, the heat from the vapour vapourises the more volatile component in the descending liquid. The ascending column of the vapour becomes steadily richer in the lower-boiling component, and the descending column of the condensate becomes steadily richer in the higher-boiling component. The vapour of the lower boiling component passes first into the condenser where it is condensed to liquid and is collected. The vapour of the higher boiling component passes into the condenser after the lower boiling component has been collected.

(c) Steam Distillation

This is used to purify compounds both liquid and solid that are insoluble in water and are steam volatile. The impurities must be non-volatile.

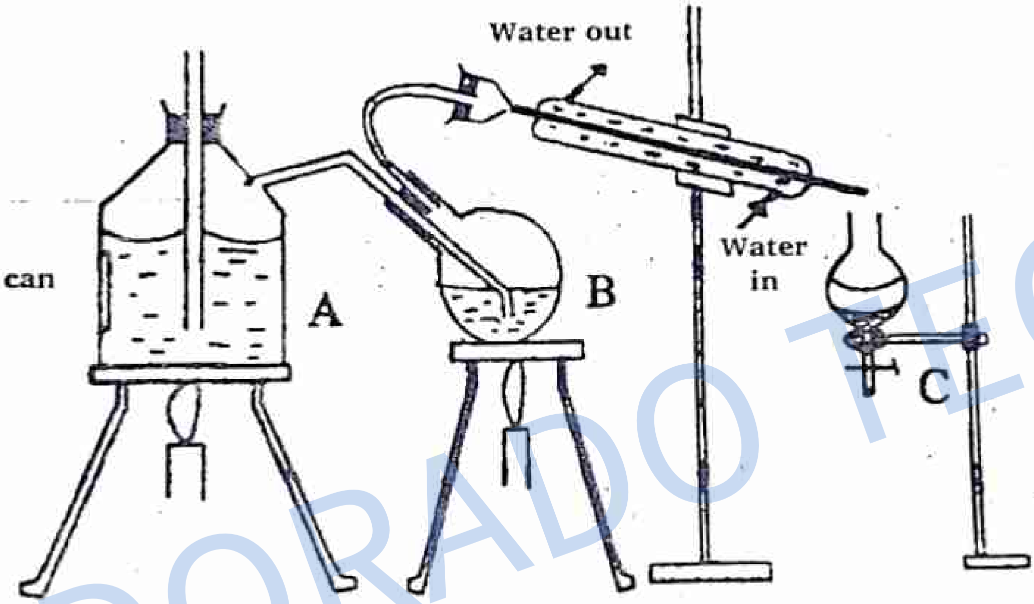


Fig. 1.8. - Steam Distillation.

The impure mixture is put in the ***flask B***. Steam generated in the ***steam can** A* is passed into the ***flask B*** and the volatile compound vapourises. It 's vapour mixed with steam passes into the condenser where it is condensed to liquid and collected at C. Since the compound is water-insoluble, two layers are formed at C. These layers are separated using a separating flask. The flask *B* can also be heated to prevent excessive accumulation of water in it.

2. Recrystallisation

This is a purification technique for solids. Solid organic compounds when isolated from organic reactions are seldom pure. They are usually contaminated with small amounts of other compounds (impurities) which are produced along with the desired products. The purification of pure crystalline compounds is usually carried out by recrystallisation. The technique is based upon differences in the solubilities of solids in a given solvent or mixture of solvents.

A solvent is found by trial in which the compound is more soluble when hot than when cold. The impure compound is dissolved in a minimum amount of the solvent at or near the boiling point of the solvent. The hot solution is rapidly filtered and the hot filterate is allowed to cool. The crystals, which appear are collected by filteration. They are dried. The melting point is determined. A pure solid should have a sharp melting point i.e. the difference between the temperature when the solid starts to melt and when it has completely melted should not be more than 1°C A larger range shows that the compound is impure. If this happens the process is repeated.

3. Chromatography

Chromatography is a technique used to separate and purify substances. The technique depends on the differential distribution of the components of the mixture between mobile and stationary phases. The stationary phase could be in the form of a column packed with alumina or silica gel (**column chromatography**) through which a mobile phase is allowed to flow. It can also be in the form of a thin layer adhering to a suitable form of backing materials (**thin-layer chromatography, TLC**) over which the mobile phase is allowed to ascend by capillary action.

Classification

Chromatography is essentially of two classes namely, ***adsorption*** and ***partition***.

(a) Adsorption Chromatography

In this class, the mobile phase is usually a liquid and the stationary phase is alumina or silica gel (**liquid – solid chromatography**). Separation depends on the selective adsorption of the components of a mixture on the surface of the solid. Example of adsorption chromatography is **column chromatography**. In column chromatography, the components of a mixture are separated by washing them down the column using a solvent. This is known as ***elution*** and the solvent used is the **eluent.**

(b) Partition Chromatography

In partition chromatography, the stationary phase is a thin liquid film e.g. Water absorbed evenly on the surface of an essentially inert support such as a glass plate. The mobile phase may be either a liquid (**liquid – liquid chromatography**) or a gas (**gas-liquid chromatography, GLC**). Separation depends on the partition between the mobile phase and the thin liquid film. The mobile liquid phase rises up the plate by capillary action. Examples are **paper chromatography** and **thin layer chromatography**.

In thin layer chromatography and paper chromatography the **R_f value** is use to establish the identity of an known substance. R_f value is the **retardation factor**. It is also known as **rate of flow.**

$$R_f = \frac{\textbf{Distance moved by substance}}{\textbf{Distance moved by solvent front}}$$

Two substances can be compared if their R_f values are measured under the same conditions.

In chromatography the separation of coloured solutes is achieved visually. If colourless substances are involved, ultraviolet illumination or chemical treatment is used to distinguish one solute from another. In TLC, iodine vapour is usually used to produce coloured spots.

4. Extraction

In synthesis, a desired product may be mixed with by-products, excess reactants, impurities and other substances at the end of a reaction. Similarly, substances in nature are always mixed with other substances. Extraction is the most common technique used to separate a desired organic product from a reaction mixture or to isolate an organic substance from its natural source.

Extraction usually involves adding a solvent (in which a desired product is more soluble) to a solution or mixture containing the product and shaking. The solvent added must be immiscible with the solution of the compound. The solvents form two layers on standing. Most of the product goes into the added solvent because it is more soluble in it. The layers are separated. It is usually necessary to repeat the extraction several times to effect complete separation. The extracts are mixed and the product recovered by distillation.

A good extraction solvent should dissolve the substance to be extracted with ease. It should not react with the substance and should be immiscible with the solvent from which the desired substance is to be extracted. Examples of common organic solvents which satisfy these requirements include benzene, petroleum ether, trichloromethane, tetrachloromethane, and ethoxyethane.

Chemical reactions could be used for certain extractions. For example, acids and phenols can be extracted from neutral water-insoluble substances using dilute sodium hydroxide solution. The sodium salts will dissolve in the water layer while the neutral substance remains in the organic layer.

$$\mathrm{RCOOH + NaOH \longrightarrow RCOONa + H_2O}$$

$$\mathrm{ArOH + NaOH \longrightarrow ArONa + H_2O}$$

After the layers have been separated the sodium salt is converted back into the acid or phenol by acidifying the aqueous layer with strong acids

$$\mathrm{RCOONa + HCl \longrightarrow RCOOH + NaCl}$$

$$\mathrm{ArOH + NaOH \longrightarrow ArOH + NaCl}$$

1.5. ELEMENTAL OR QUALITATIVE ANALYSIS

Elemental analysis is carried out to determine the elements present in a compound. Carbon, hydrogen, oxygen, nitrogen, sulphur and the halogens are usually expected. Tests are carried out to determine the presence of any of the elements. However, no satisfactory test is carried out for the determination of the presence of oxygen.

1. Test for Carbon and Hydrogen

An organic compound is assumed to contain carbon and hydrogen. Their presence can be determined by heating a mixture of dry compound and eight times dry powdered copper (II) oxide in a hard test-tube. If carbon is present, it is oxidized to carbon (IV) oxide, which turns lime water milky. If hydrogen is present, droplets of water (which turn white anhydrous copper (II) tetraoxosulphate (VI) blue) is observed at the upper part of the test tube.

2. Test for Nitrogen, Sulphur, and the Halogens

The Sodium Fusion or Lassaignes Test

A small piece of sodium is added to a small amount of the substance in a dry ignition tube and the mixture is heated gently initially and then strongly until the tube is dull red hot. It is dropped into a mortar containing about 20cm^3 of distilled water. It ruptures and any excess sodium reacts with water. The contents are ground and filtered. The filtrate is used for the test for nitrogen, sulphur and the halogens.

$$\text{Na + organic compound} \xrightarrow{\Delta} \text{NaCN, } Na_2S\text{, NaX}$$

(X = halogen)

The ions expected are **CN^-, S^{2-} X^-.** The filtrate is alkaline because of the presence of sodium hydroxide.

(a) Test for Nitrogen, present as NaCN

Pour 2-3 cm^3 of the filtrate into a test-tube containing 0.1 — 0.2g of powered iron (II) tetraoxosulphate (VI) crystals. Heat the mixture gently with shaking until it boils, then without cooling add just enough dilute tetraoxosulphate (VI) acid to dissolve the hydroxide and to acidify the filtrate. A Prussian blue precipitate or colouration appears and shows the presence of nitrogen. The Prussian blue precipitate could be made purer by the addition of 1cm^3 of 5% potassium fluoride solution. If no Prussian blue appears immediately, leave to stand for 15 minutes, then filter through a small filter paper and wash the paper with water to remove all traces of coloured solution. Any Prussian blue present will be seen at the cone of the filter paper.

$$Fe^{2+}(aq) + 2OH(aq) \longrightarrow Fe(OH)_2(s)$$

$$Fe(OH)_2(s) + 6CN^-(aq) \longrightarrow Fe(CN)_6^{4-}(aq) + 2OH^-(aq)$$

$$3Fe(CN)_6^{4-}(aq) + 4Fe^{3+} \longrightarrow Fe_4\left[Fe(CN)_6\right]_3(s)$$

*(Iron (III) hexacyano ferrate (II)
prussian blue)*

(b) Test for Sulphur, present as Na_2S

(i) *To about 2cm^3 of the filtrate add a crystal of disodium pentacyanonitrosylferrate (sodium nitroprusside), $Na_2[Fe(CN)_5NO]$. A purple colouration indicates sulphur. The colouration slowly fades on standing.*

(ii) *Acidify 2cm^3 of the filtrate with dilute ethanoic acid and add a few drops of lead ethanoate solution. A black precipitate of lead sulphide indicates the presence of sulphur.*

(c) Test for the halogens, present as NaCl or NaBr or NaI

If nitrogen or sulphur or both are absent, acidify 2cm^3 of the filtrate with dilute trioxonitrate (V) acid and add a few drops of silver trioxonitrate (V) solution. A precipitate indicates the presence of a halogen. Decant the mother liquor and treat the precipitate with dilute aqueous ammonia. **White** readily **soluble** precipitate indicates the **presence of chlorine. Pale yellow (or cream) slightly soluble** precipitate indicates **bromine. Yellow insoluble** precipitate indicates **iodine.** If nitrogen or sulphur or both are present then add dilute trioxonitrate (V) acid to filtrate and boil to expel hydrogen cyanide and/or hydrogen sulphide. Cool under tap. Add silver trioxonitrate (V) solution to the mixture and observe the colour of the precipitate and its solubility in aqueous ammonia. Sodium cyanide or sodium sulphide gives precipitate with silver trioxnitrate (V) solution.

The presence of a halogen may be confirmed by acidifying the filtrate with dilute tetraoxosulphate (VI) acid, adding benzene and chlorine water and shaking. A yellowish brown colour in the benzene layer indicates bromine, and a violet colour indicates iodine. If the layer is colourless then chlorine is present.

1.6. QUANTITATIVE ANALYSIS

This is the determination of the composition by mass of an organic compound. The methods used are based on simple principles.

1. Estimation of Carbon and Hydrogen

A known mass of the dry substance is heated at about 700°C in a stream of oxygen in the presence of copper (II) oxide. Carbon in the compound is converted to carbon (IV) oxide and hydrogen is converted to steam or water. The masses of carbon (IV) oxide ad water are estimated by their absorption in weighed tubes containing soda- lime and anhydrous magnesium (II) tetraoxochlorate (VII) respectively. From the masses of carbon (IV) oxide and water formed the masses of carbon and hydrogen in the compound are calculated.

2. Estimation of Nitrogen

(a) Duma's Method

When a known mass of the compound is heated in a stream of oxygen in the presence of copper (II) oxide, the carbon present is converted into carbon (IV) oxide, and sulphur into sulphur (IV) oxide. Nitrogen and the hydrogen into water or steam

$$= \frac{12}{44} \times 0.2681 = 0.07312g$$

Mass of hydrogen in the compound

$$= \frac{\text{Relative atomic mass of hydrogen} \times 2 \times 0.1090}{\text{Relative molecular mass of water}}$$

$$= \frac{2}{18} \times 0.1090 = 0.0121g$$

$$\%C = \frac{0.07312 \times 100}{0.1824} = 40.1$$

$$\%H = \frac{0.0121 \times 100}{0.1824} = 6.6$$

$$\%O = 100 - (40.1 + 6.6) = 53.3$$

	C	H	C
% composition	40.1	6.6	53.3
relative atomic proportion	$\frac{40.1}{12} = 3.36$	$\frac{6.6}{1} = 6.6$	$\frac{53.3}{16} = 3.33$
Divide by the smallest (to get whole number)	$\frac{3.36}{3.33} = 1.01$	$\frac{6.6}{3.33} = 1.98$	$\frac{3.33}{3.33} = 1$
	1	2	1

Empirical Formula = CH_2O

Suppose that after dividing by the smallest, the numbers got were as follows:

C: 1.52 **H: 2.97** **O: 1**

It would be incorrect to round off to the nearest whole number i.e. for the empiric formula to be C_2H_3O because 1.52 is not nearly a whole number. The numbers ar multiplied by a small number until a ratio of nearly whole numbers is got. In thi case, multiplying by two gives

C: 3.04 **H: 5.94** **O: 2**

Empirical formula $C_3H_6O_2$.

1.8. MOLECULAR FORMULA

The molecular formula gives the actual number of atoms of each kind in th molecule. It is obtained from the empirical formula if the relative molecular mass i known. The relative molecular mass of compounds is determined by methods halogens are evolved in their free state. The volume of nitrogen is measured using a nitrometer and converted into volume at s.t.p. From the result the amount of nitrogen is calculated.

(b) *Kjeldahl's Method*

The method is limited only to a few nitrogen containing compounds, especially foodstuffs. In the method, a known mass of the organic compound is heated with concentrated tetraoxosulphate (VI) acid. The nitrogen present is converted into ammonium tetraoxosulphate (VI). The solution is made alkaline by adding excess sodium hydroxide solution. On heating, ammonia is liberated. The ammonia is estimated by titrating it with standard acid. The mass of nitrogen is calculated from the mass of ammonia.

3. Estimation of halogens: *Carius method*

A known mass of the organic compound is heated at about 200°C with a mixture of fuming trioxonitrate (V) acid and silver trioxonitrate (V) in a sealed tube for about five hours. The halogen present in the organic compound is converted into silver halide. The silver halide is washed out of the tube dried and weighed. The mass of the halide in the silver halide is calculated and this mass is the mass of the halide present in the organic compound.

4. Estimation of Sulphur

The **Carius method** is also used to estimate sulphur. Sulphur in the organic compound is converted into tetraoxosulphate (VI) acid when the compound is heated with fuming trioxonitrate (V) acid. The acid is washed out of the tube and converted into barium tetraoxosulphate (VI) by adding excess barium chloride solution. The barium tetraoxosulphate (VI) is filtered off, washed, dried and weighed. The amount of sulphur present in the barium tetraoxosulphate (VI) is calculated.

5. Estimating Oxygen

The amount of oxygen present in an organic compound is difficult to estimate. It is generally estimated by difference.

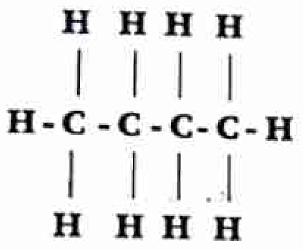
1.7. EMPIRICAL FORMULA

The empirical formula shows the relative numbers of each kind of atom in a molecule. It is calculated from the percentage composition of the compound. The following example will illustrate the procedure:

0.1824g of a compound containing carbon, hydrogen and oxygen gave on complete combustion 0.2681g of carbon (IV) oxide and 0.1090g of water. What is the empirical formula of the compound?

Mass of carbon in the compound

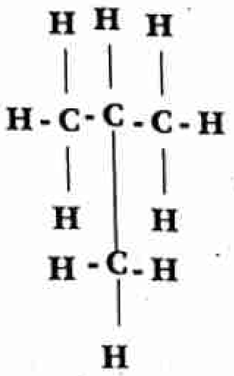
$$= \frac{\textbf{Relative atomic mass of carbon} \times 0.2681}{\textbf{Relative molecular mass of carbon (IV) oxide}}$$



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

Butane

and



2 - methylpropane (isobutane)

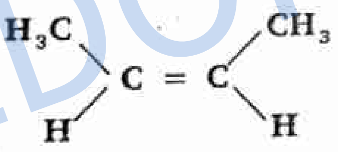
1.11. STEREOISOMERISM

This is another type of isomerism in which although, the structures of two compounds are the same, the orientations of some atoms in space in the structures are different. Two types of steroisomerism are ***geometrical isomerism and optical siomerism.***

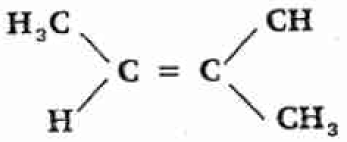
1. Geometrical (or *cis - trans*) Isomerism

This is the existence of two compounds with the same structures but different orientations in space. The different orientations are caused by the presence of carbon – carbon double bond link or a ring of atoms in a molecule. These "lock" the molecule in position by preventing free rotation.

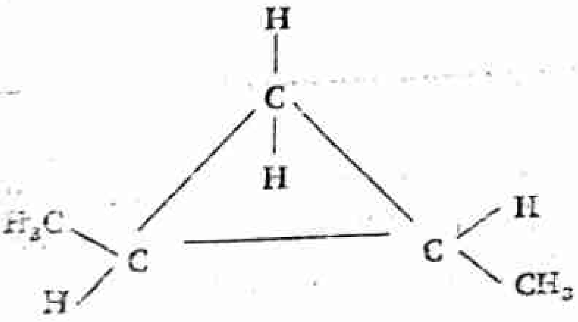
Examples:



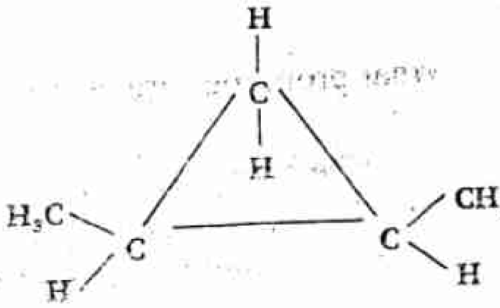
Cis but - 2- ene



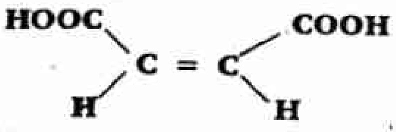
Trans but - 2 - ene



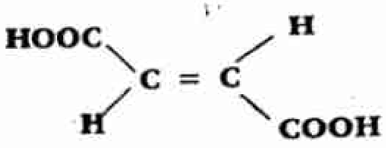
Trans 1, 2-dimethylcyclopropane



Cis 1, 2-dimethylcyclopropane



Cis butenedioic acid



Trans butenedioic acid

The isomers have different configurations.

The chemical properties of *cis* – trans isomers are the same but their physical properties differ. The melting point and stability of the trans-isomers are higher than those of the cis-isomers. This is due to steric effects. In the *cis*-isomers, the groups are on the same side. They are closer together than in the trans-isomer and experience greater steric repulsion. Consequently, the *cis* form is under greater strain than the trans and the molecule is destabilized. Therefore, the melting points, and stability of the *cis* isomers are lower, while the boiling point, density, refractive index, solubility, dipole moment, heat of combustion, and dissociation constant (if an acid) of the *cis* are greater than those of the trans isomer.

2. Optical Isomerism

Optical isomers have identical chemical and physical properties. They however, rotate the plane of polarization of plane polarized light to the same extent but in opposite directions. One rotates to the right and is dextro – rotatory while the other rotates to the left and is laevo-rotatory for example dextro and laevo lactic acids.

REVIEW QUESTIONS

1. What properties are desirable in a recrystallization solvent?

2. Describe how you would separate a mixture of 4-methylaniline (a base with mp. 45°C), 2-naphthol (a weak acid with mp. 123°C), and 1, 4-dichlorobenzene (a neutral substance with mp. 133°C).

3. With a suitable example illustrate sp^2 hybridisation. Give two reactions that are characteristics of this type of hybridization.

4. A sample of organic compound containing C, H and O weighing 1.50g ga on complete combustion 1.738g of CO_2 and 0.711g of H_2O. If its relati molecular mass was 76, calculate its molecular formula, write a structure fo the compound and give its IUPAC name. (H = 1, C = 12, O = 16).

5. An organic compound containing carbon, hydrogen and chlorine has a vapo density of 59.5 1g of the compound gives 3.602g of silver chloride whe treated by the Carius method. If the compound contains 10.05% of carbo what is its structural formula?

6. Name three methods used for the purification of organic compounds. Expla the principles involved in the methods you have named.

7. How would you attempt to find out whether a given organic solid was pu or not? If impure, describe how you will purify it.

8. How can the presence of nitrogen sulphur and bromine in an orga compound be determined?

Chapter 2

THE IUPAC NOMENCLATURE OF ORGANIC COMPOUNDS

IUPAC means ***International Union of Pure and Applied Chemistry.*** IUPAC nomenclature is a systematic method of naming chemical compounds developed by the Union.

2.1. ALKANE

Rules:

- *Names end in – ane*
- *Choose the longest continuous carbon chain.*

The names of the alkanes are as follows:

One carbon atom - *Methane*
Two carbon atoms - *Ethane*
Three carbon atoms - *Propane*
Four carbon atoms - *Butane*
Five carbon atoms - *Pentane*
Six carbon atoms - *Hexane*
Seven carbon atoms - *Heptane*
Eight carbon atoms - *Octane*
Nine carbon atoms - *Nonane*
Ten carbon atoms - *Decane, etc.*

(1) The carbon atoms of the longest continuous chain so chosen are numbered. there is a branch (or substituent), the carbon atom bearing the branches substituents is given the lowest number. If there are more than one branch substituent, the numbering is done in such a way as to give the lowest sum to

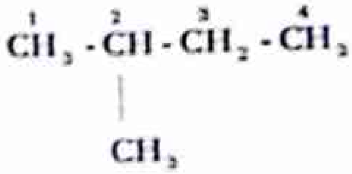
sum of the numbers of the carbon atoms bearing the branches or substituents. Examples of substituents are the halogens **-Cl** *(chloro)*, **-Br** *(bromo)* and **-I** *(iodo)*. Another common substituent is the alkyl group. An **Alkyl group** is an alkane that has lost one hydrogen atom e.g. if **methane, CH_4** loses a hydrogen atom it becomes **$-CH_3$ (methyl group).** Other examples are:- **$-C_2H_5$ ethyl**, **$-C_3H_7$ propyl, $-C_4H_9$ butyl**.

(2) Identify the substituents and name the compounds using numbers to show the carbon atoms which have the substituents. If there are more than one substituents they are arranged in alphabetical order.

Example:

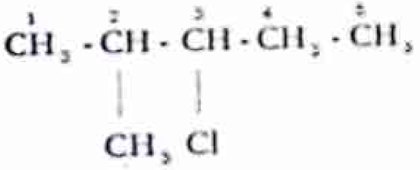
$CH_3-CH_2-CH_2-CH_3$

Butane



$\overset{1}{C}H_3-\underset{\displaystyle CH_3}{\overset{2}{C}H}-\overset{3}{C}H_2-\overset{4}{C}H_3$

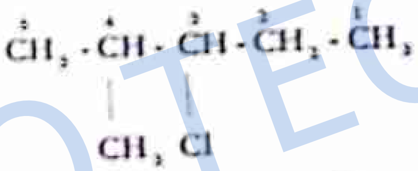
2 - Methylbutane



$\overset{1}{C}H_3-\underset{\displaystyle CH_3}{\overset{2}{C}H}-\underset{\displaystyle Cl}{\overset{3}{C}H}-\overset{4}{C}H_2-\overset{5}{C}H_3$

2 + 3 = 5

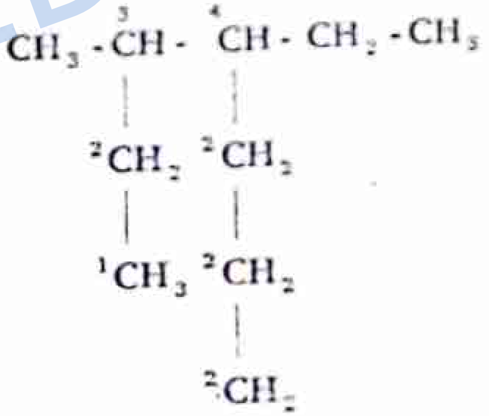
or



$\overset{5}{C}H_3-\underset{\displaystyle CH_3}{\overset{4}{C}H}-\underset{\displaystyle Cl}{\overset{3}{C}H}-\overset{2}{C}H_2-\overset{1}{C}H_3$

3 + 4 = 7

The numbering which gives a sum of 5 is used. There is a methyl group at **C - 2** and a *chloro* group at C-3. The name of the compound is **3 - chloro - 2 - methylpentane**



$\underset{\displaystyle \overset{1}{C}H_3}{\underset{|}{\overset{2}{C}H_2}}\!-\!\overset{3}{C}H-\overset{4}{C}H-CH_2-CH_3$ with $^2CH_2-{}^2CH_2-{}^2CH_3$ on C-4

Substituents

Methyl at C - 3

Ethyl at C - 4

e before m

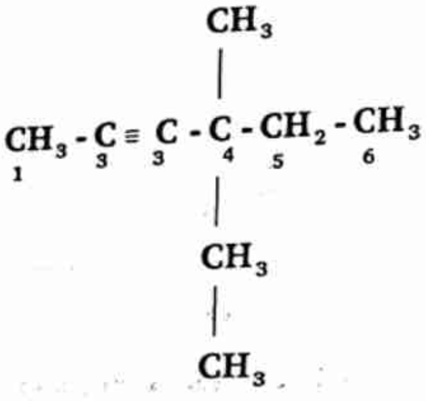
Name of compound is **4 - ethyl - 3 - methylheptane**

(3) If there are two identical substituents at the same carbon atom, the number is repeated and ***di, tri*** or ***tetra*** etc is used as prefix if there are 2, 3, or 4 etc Substituents respectively e.g.

Alkynes

1. Names end in *–yne*.
2. The longest continuous chain chosen should contain the triple bond.
3. Numbers are used to show the positions of the substituents and the triple bo

The first carbon of the triple bond is given the lowest number.



$$\underset{1}{CH_3}-\underset{3}{C}\equiv\underset{3}{C}-\underset{4}{C}(CH_3)(CH_2CH_3)-\underset{5}{CH_2}-\underset{6}{CH_3}$$

4-ethyl-4-methylhex-2-yne

$\underset{4}{CH_2}=\underset{3}{CH}-\underset{2}{C}\equiv\underset{1}{CH}$

But-3-ene-1-yne

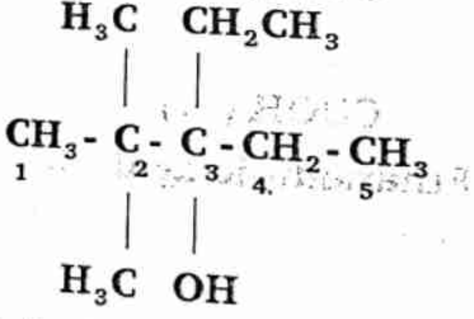
Alkanols

1. Names end in *–ol*
2. The longest continuous chain chosen should contain the –OH group.
3. The numbering is done in such a way as to give the carbon atom bearing the –OH group the lowest number.

Example:

$\underset{5}{CH_3}-\underset{4}{CH_2}-\underset{3}{CH_2}-\underset{2}{CH_2}-\underset{1}{CH_2}-OH$

Pentan-1-ol

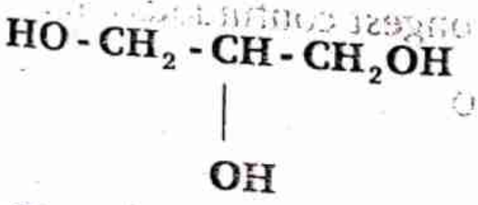


$$\underset{1}{CH_3}-\underset{2}{C}(CH_3)_2-\underset{3}{C}(OH)(CH_2CH_3)-\underset{4}{CH_2}-\underset{5}{CH_3}$$

3-ethyl-2, 2-dimethylpentan-3-ol

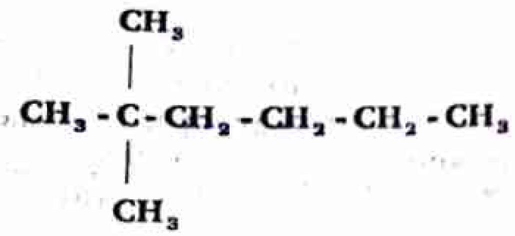
$HO-CH_2-CH_2-OH$

Ethane-1,2-diol

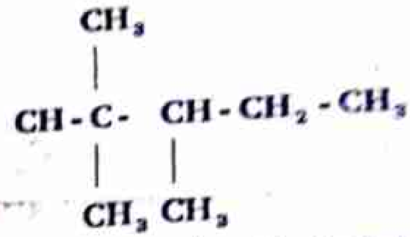


$$HO-CH_2-CH(OH)-CH_2OH$$

Propan-1, 2, 3-triol

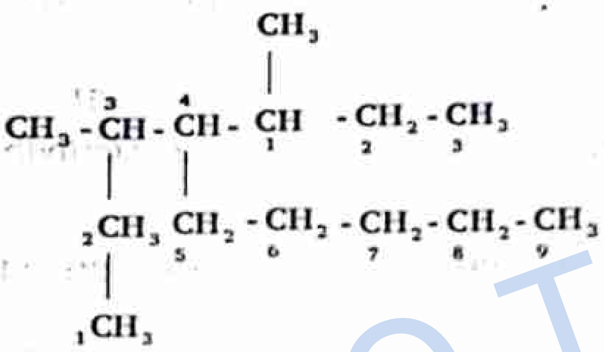

$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-CH_2-CH_2-CH_3$

2, 2 - Dimethylpentane


$CH-\overset{CH_3}{\underset{CH_3}{C}}-\underset{CH_3}{CH}-CH_2-CH_3$

2, 2, 4 - Trimethylpentane

(4) If the parent carbon chain (longest continuous chain) contains a branch chain with a substituent, the branch chain is numbered beginning with the carbon directly joined to the parent chain and the name of this side chain is put in parenthesis e.g.

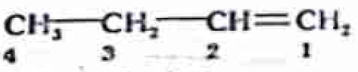


3 - methyl - 4 - (1 - methylpropyl) nonane

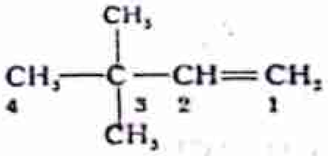
Alkenes

1. Names end in *–ene*
2. The longest continuous chain chosen should contain the double bond.
3. Numbers are used to indicate the positions of the substituents and the double bond. The first carbon of the double bond is given the lowest number.

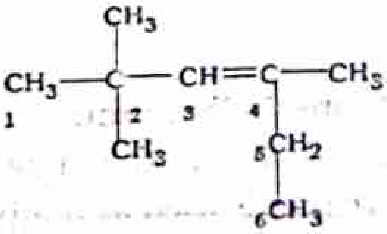
Examples


$\underset{4}{CH_3}-\underset{3}{CH_2}-\underset{2}{CH}=\underset{1}{CH_2}$

But - 1 - ene

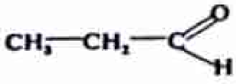

$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH=CH_2$

3, 3 - dimethylbut - 1 - ene

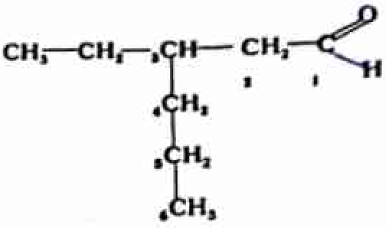

$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH=\underset{CH_2-CH_3}{C}-CH_3$

2, 2, 4 - trimethylhex - 3 - ene

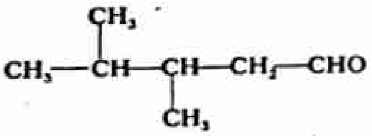
Examples:



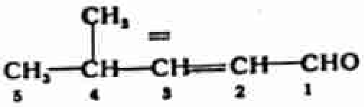
Propanal



3 - ethylhexanal



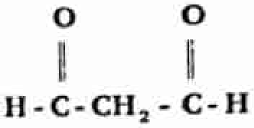
3, 4 - dimethylpentanal



4 - methylpent - 2 - enal

$$CHO-CHO$$

Ethanedial



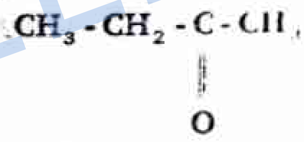
$$H-\underset{}{\overset{O}{\overset{\|}{C}}}-CH_2-\overset{O}{\overset{\|}{C}}-H$$

Propanedial

Alkanones

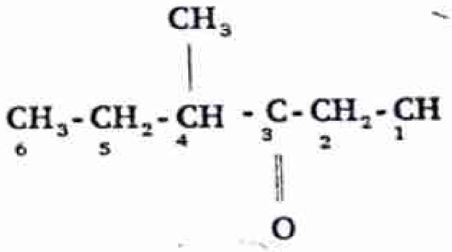
1. Names end in *–one*
2. The longest continuous chain chosen should contain the carbonyl group $>C=O$
3. Numbering gives the carbonyl carbon the lowest number.

Examples:



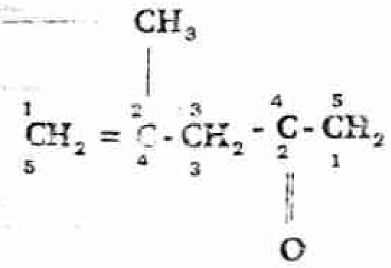
$$CH_3-CH_2-\underset{\underset{O}{\|}}{C}-CH_3$$

Butanone



$$\underset{6}{CH_3}-\underset{5}{CH_2}-\underset{4}{\overset{\overset{CH_3}{|}}{CH}}-\underset{\underset{O}{\|}}{\underset{3}{C}}-\underset{2}{CH_2}-\underset{1}{CH_3}$$

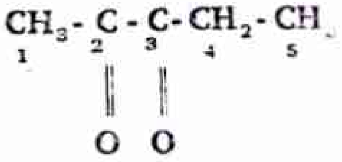
4 - Methylhexan - 3 - one



$$\overset{1}{\underset{5}{CH_2}}=\overset{2}{\underset{4}{\overset{\overset{CH_3}{|}}{C}}}-\overset{3}{\underset{3}{CH_2}}-\overset{4}{\underset{\underset{O}{\|}}{\underset{2}{C}}}-\overset{5}{\underset{1}{CH_3}}$$

4 - Methylpent - 4 - ene - 2 - one (C = O lower number)

or 2 - Methyl - 4 - oxopent - 1 - ene (C = C lower number)



$$\underset{1}{CH_3}-\underset{\underset{O}{\|}}{\underset{2}{C}}-\underset{\underset{O}{\|}}{\underset{3}{C}}-\underset{4}{CH_2}-\underset{5}{CH_3}$$

Propan - 2, 3 - dione

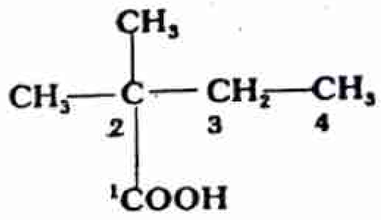
Alkanoic Acids

1. Names end in *–oic* acids
2. The longest continuous chain chosen should contain -COOH group
3. When there are substituents numbering starts with the carbon atom of the -COOH.

Examples

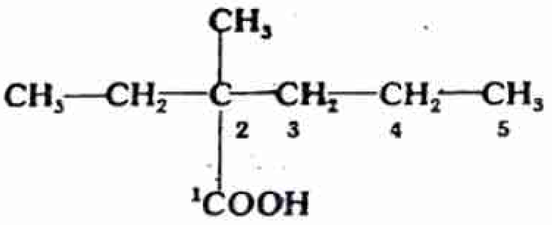
$\underset{4}{CH_3}-\underset{3}{CH_2}-\underset{2}{CH_2}-\underset{1}{COOH}$

Butanoic acid



$CH_3-C(CH_3)(COOH)-CH_2-CH_3$

2, 2-dimethylbutanoic acid



$CH_3-CH_2-C(CH_3)(COOH)-CH_2-CH_2-CH_3$

2 - ethyl - 2 - methylpentanoic acid

$\underset{4}{CH_3}-\underset{3}{CH}=\underset{2}{CH}-\underset{1}{COOH}$

But - 2 - enoic acid

$COOH-COOH$

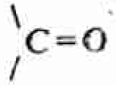
Ethanedioic acid

$HOOC-CH_2-CH_2-COOH$

Butanedioic acid

Alkanals

1. Names end in *- al*
2. The longest continuous chain chosen should contain the carbonyl group,



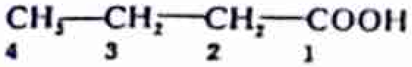
$>C=O$

3. Numbers are used to show the position of substituents or branches and the number starts from the carbonyl carbon.

Alkanoic Acids

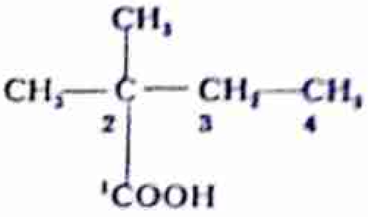
1. Names end in *–oic* acids
2. The longest continuous chain chosen should contain -COOH group
3. When there are substituents numbering starts with the carbon atom of the -COOH.

Examples



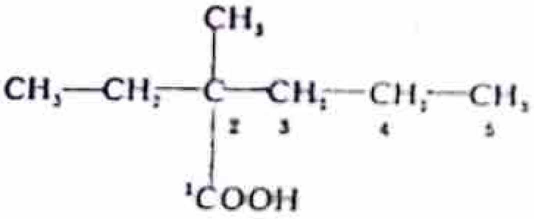
$\underset{4}{CH_3}-\underset{3}{CH_2}-\underset{2}{CH_2}-\underset{1}{COOH}$

Butanoic acid



$CH_3-\overset{CH_3}{\underset{^1COOH}{\underset{2}{C}}}-\underset{3}{CH_2}-\underset{4}{CH_3}$

2, 2-dimethylbutanoic acid



$CH_3-CH_2-\overset{CH_3}{\underset{^1COOH}{\underset{2}{C}}}-\underset{3}{CH_2}-\underset{4}{CH_2}-\underset{5}{CH_3}$

2 - ethyl - 2 - methylpentanoic acid

$\underset{4}{CH_3}-\underset{3}{CH}=\underset{2}{CH}-\underset{1}{COOH}$

But - 2 - enoic acid

$\begin{array}{c} COOH \\ | \\ COOH \end{array}$

Ethanedioic acid

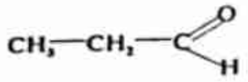
$HOOC-CH_2-CH_2-COOH$

Butanedioic acid

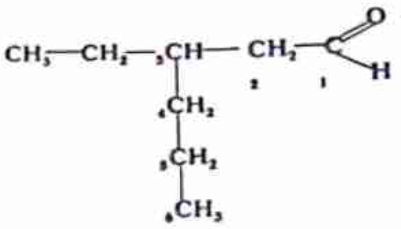
Alkanals

1. Names end in ***- al***
2. The longest continuous chain chosen should contain the carbonyl group, $>C=O$
3. Numbers are used to show the position of substituents or branches and the number starts from the carbonyl carbon.

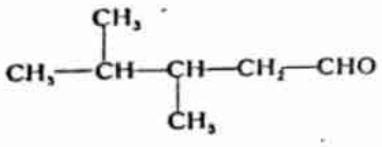
Examples:



Propanal

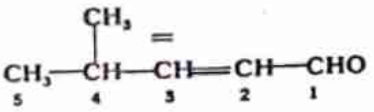


3 - ethylhexanal



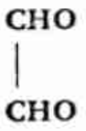
$CH_3-\overset{CH_3}{\overset{|}{CH}}-\underset{CH_3}{\underset{|}{CH}}-CH_2-CHO$

3, 4 - dimethylpentanal



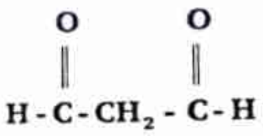
$\underset{5}{CH_3}-\underset{4}{\overset{CH_3}{\overset{|}{CH}}}-\underset{3}{CH}=\underset{2}{CH}-\underset{1}{CHO}$

4 - methylpent - 2 - enal



$\begin{array}{c}CHO\\|\\CHO\end{array}$

Ethanedial



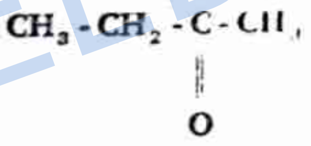
$H-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-H$

Propanedial

Alkanones

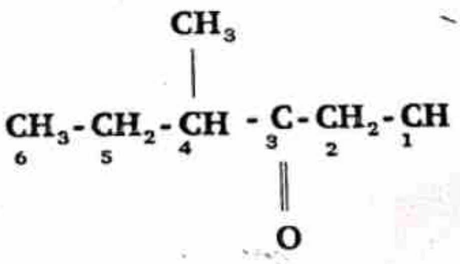
1. Names end in ***–one***
2. The longest continuous chain chosen should contain the carbonyl group $>C=O$
3. Numbering gives the carbonyl carbon the lowest number.

Examples:



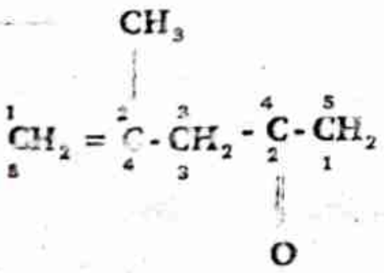
$CH_3-CH_2-\underset{O}{\underset{\|}{C}}-CH_3$

Butanone



$\underset{6}{CH_3}-\underset{5}{CH_2}-\underset{4}{\overset{CH_3}{\overset{|}{CH}}}-\underset{\underset{O}{\|}}{\underset{3}{C}}-\underset{2}{CH_2}-\underset{1}{CH}$

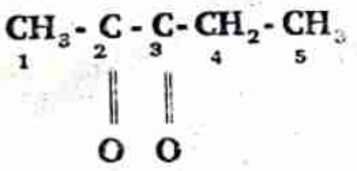
4 - Methylhexan - 3 - one



$\underset{5}{\overset{1}{CH_2}}=\underset{4}{\overset{\overset{CH_3}{|}}{\overset{2}{C}}}-\underset{3}{\overset{3}{CH_2}}-\underset{\underset{\underset{O}{\|}}{2}}{\overset{4}{C}}-\underset{1}{\overset{5}{CH_2}}$

4 - Methylpent - 4 - ene - 2 - one (C = O lower number)

or 2 - Methyl - 4 - oxopent - 1 - ene (C = C lower number)



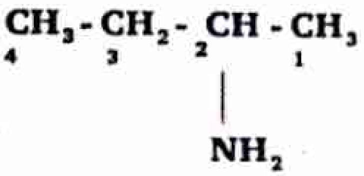
$\underset{1}{CH_3}-\underset{\underset{\underset{O}{\|}}{2}}{C}-\underset{\underset{\underset{O}{\|}}{3}}{C}-\underset{4}{CH_2}-\underset{5}{CH_3}$

Propan - 2, 3 - dione

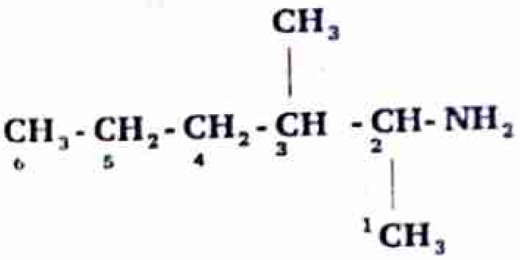
Amines

1. Simple structured amines are still named as derivatives of alkanes e.g $CH_3–NH_2$, methylamine, CH_3-CH_2-CH_2NH_2 propylamine, $C_6H_5NH_2$ phenylamine
2. The complicated amines are named by the IUPAC system. The longest continuous chain chosen must contain the amino group $–NH_2$.
3. Number is used to show the position of the $–NH_2$ group ie. the amino group is treated as a substituent. In the presence of another substituent, the numbering that gives the lowest sum is used.

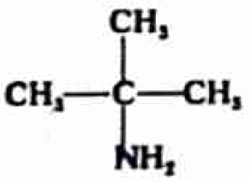
Examples:



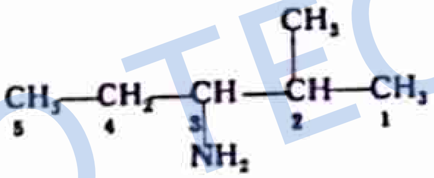
2 - Aminobutane



2 - Amino - 3 - methylhexane



2-Amino - 2 - methylpropane

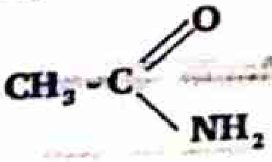


3-Amino - 2 - methylpentane

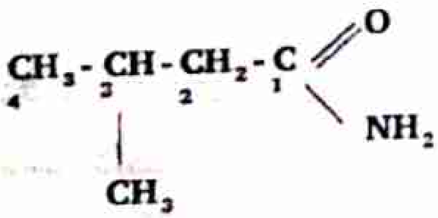
Amides

Amides contain the functional group -$CONH_2$. They are named as derivatives of the parent alkanoic acid with the names ending in – ***amide***.

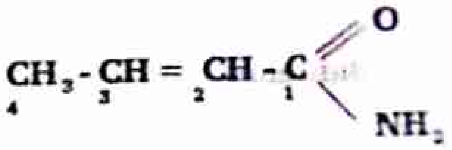
Example



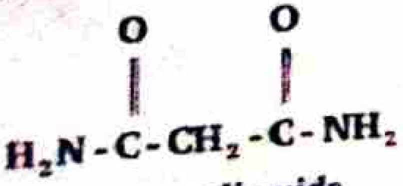
Ethanamide



3 - Methylbutanamide



But - 2 - enamide



Propanediamide

Alkanoates

Alkanoates are derived from alkanoic acids and alkanols. They have the gene molecular formula RCOOR^1 where R is the alkyl group of the alkanoic acid and R^1 is t alkyl group of the alkanol. In naming the alkanoates, the alkyl group of the alkano named first followed by the alkanoic acid with **–*noic*** replaced by **–*noate***.

Example

$CH_3-CH_2-COOCH_3$

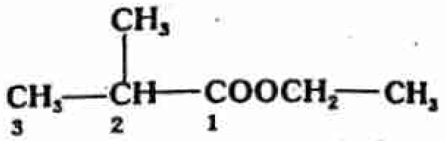
Methyl propanoate

$HCOOCH_3$

Methyl methanoate

$CH_3-CH_2-COOCH_2-CH_3$

Ethyl propanoate



$\underset{3}{CH_3}-\underset{2}{\overset{\overset{CH_3}{|}}{C}H}-\underset{1}{COOCH_2}-CH_3$

Ethyl - 2 - methyl propanoate

ACID CHLORIDES AND ACID ANHYDRIDES

Acid chlorides and acid anhydrides are named from their parent alkanoic aci For acid chlorides **-*noyl*** chloride replaces **-*noic*** acid. For acid anhydride, the wo anhydride is added after the acid.

Examples

CH_3-COCl

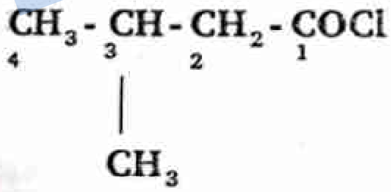
ethanoyl chloride

CH_3-CH_2-COCl

Propanoyl chloride

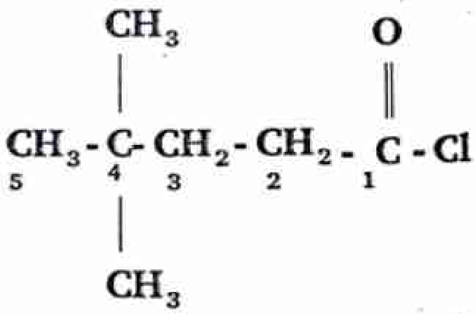
C_6H_5COCl

Benzoyl chloride



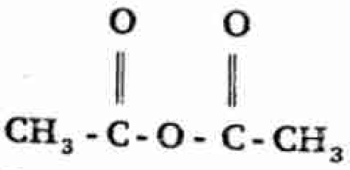
$\underset{4}{CH_3}-\underset{\underset{CH_3}{|}}{\underset{3}{CH}}-\underset{2}{CH_2}-\underset{1}{COCl}$

3 - Methylbutanoyl chloride



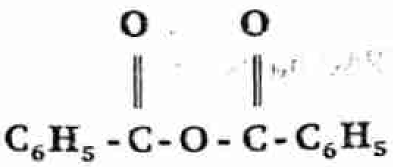
$\underset{5}{CH_3}-\underset{\underset{CH_3}{|}}{\underset{4}{\overset{\overset{CH_3}{|}}{C}}}-\underset{3}{CH_2}-\underset{2}{CH_2}-\underset{1}{\overset{\overset{O}{\|}}{C}}-Cl$

4, 4 - Dimethylpentanoyl chloride



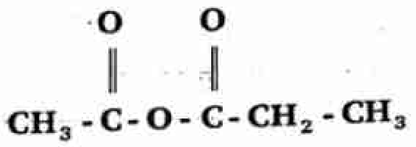
$CH_3-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-CH_3$

Ethanoic anhydride



$C_6H_5-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-C_6H_5$

Benzoic anhydride.



$$CH_3-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-CH_2-CH_3$$

Ethanoic propanoic anhydride

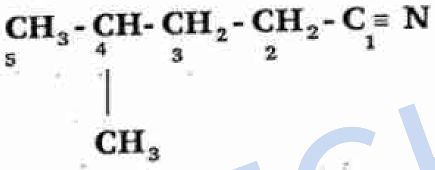
(mixed anhydride).

NITRILES

Nitriles are named as **nitriles** of the acids, which are produced on hydrolysis with the suffix ***-oic*** replaced by ***-onitrile.***

CH_3CN — *Ethanonitrile*

$CH_3-CH_2-C\equiv N$ — *Propanonitrile*



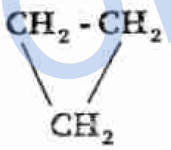
$$\underset{5}{CH_3}-\underset{4}{\underset{|}{\overset{}{CH}}}-\underset{3}{CH_2}-\underset{2}{CH_2}-\underset{1}{C}\equiv N \quad (CH_3 \text{ on C-4})$$

4 - Methylpentanonitrile

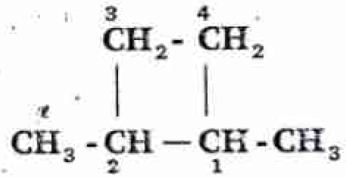
Cycloalkanes

1. These are named as alkanes but cyclo-is used to indicate the cyclic nature.
2. When there are more than one substituents, the number system used is the one that gives the carbon atoms bearing the substituents the lowest sum.

Example



Cyclopropane

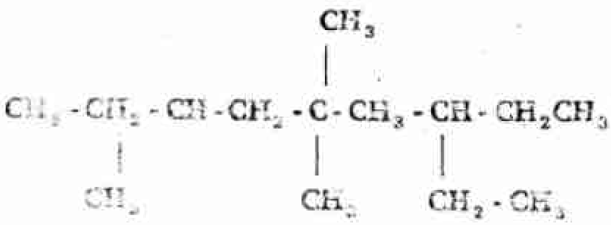


1, 2 - Dimethylcyclobutane

REVIEW QUESTIONS

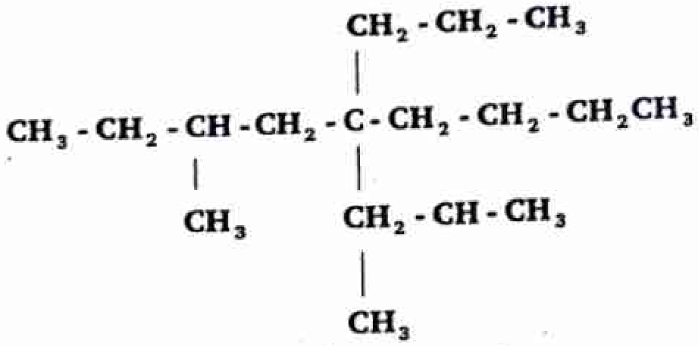
1. Give the IUPAC names of each of the following

(a)



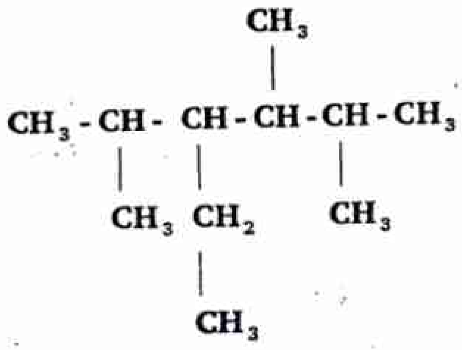
$$CH_3-CH_2-\underset{\underset{CH_3}{|}}{CH}-CH_2-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3-\underset{\underset{CH_2-CH_3}{|}}{CH}-CH_2CH_3$$

(b)



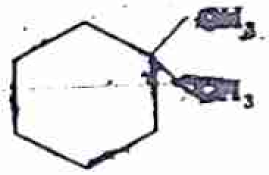
$CH_3-CH_2-\underset{CH_3}{CH}-CH_2-\overset{CH_2-CH_2-CH_3}{\underset{\underset{CH_3}{CH_2}-CH-CH_3}{C}}-CH_2-CH_2-CH_2CH_3$

(c)



$CH_3-\underset{CH_3}{CH}-\underset{\underset{CH_3}{CH_2}}{CH}-\overset{CH_3}{CH}-\underset{CH_3}{CH}-CH_3$

(d)



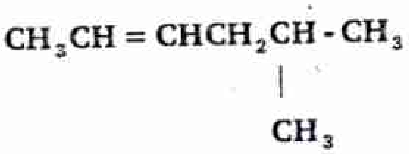
2. Write the structure of each of the following

a. *5-ethyl-2, 3-dimethyloctane.*
b. *3, 4, 9-trimethyldecane*
c. *2, 3, 5-trimethyl-4-propylheptane.*

3. a. Give the IUPAC names of the following:

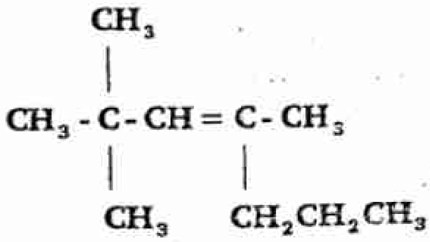
(i) $CH_3CH=C(CH_3)-CH_2CH_3$

(ii)



$CH_3CH=CHCH_2\underset{CH_3}{CH}-CH_3$

(iii)



$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH=\underset{CH_2CH_2CH_3}{C}-CH_3$

b. Write the structural formula of each of the following

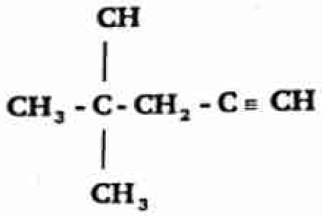
i. *1-methylcyclobutene*
ii. *2,3-dimethylpent-2-ene*
iii. *trans-Hex-3-ene*
iv. *2-ethylpent-3-ene*

4. Give the IUPAC name of each of the following:

(a)

$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2CH_2-C\equiv CH$

(b)



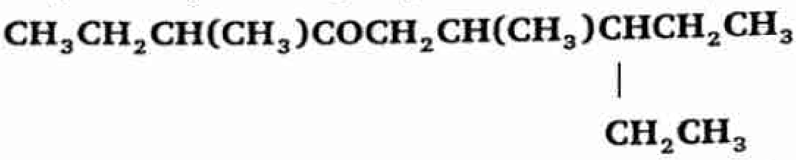
$CH_3-\overset{\displaystyle CH}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-CH_2-C\equiv CH$

(c) $CH_3-CH_2C\equiv C-CH_2CH_3$

5. a. Write the IUPAC names of the following

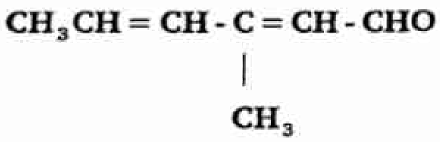
i. $CH_3CH(CH_3)CH(CH_3)CH_2\text{-}CHO$

ii.



$CH_3CH_2CH(CH_3)COCH_2CH(CH_3)\underset{\displaystyle CH_2CH_3}{\underset{|}{CH}}CH_2CH_3$

iii.



$CH_3CH=CH-\underset{\displaystyle CH_3}{\underset{|}{C}}=CH-CHO$

b. Give the structural formulae of the following compounds.

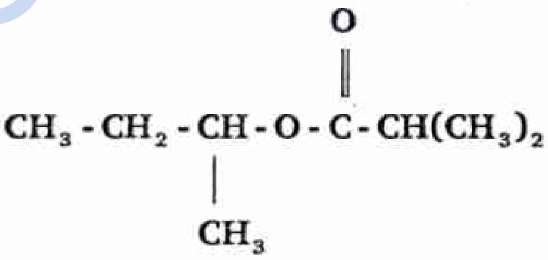
(i) *2,2,5 - trimethylheptan - 4 - one*

(ii) *2, 6 - dimethyloct - 4 - ene - 3 - one*

(iii) *2 - ethylhex - 2 - enal*

6. Give the IUPAC names of the following compounds:

(a)



$CH_3-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-O-\overset{\displaystyle O}{\overset{\|}{C}}-CH(CH_3)_2$

(b) $CH_3C(CH_3)_2CH_2COOC(CH_3)_2CH_3$

(c) $CH_3CH_2C(C_2H_5)CONH_2$

(d) $CH_3CH(CH_3)CONHCH_3$

(e) $CH_3CH_2COOCOCH_2(CH_2)CH_3$

(f) $CH_3(CH_2)_4COCl$

Chapter 3

ALKANES

3.1. INTRODUCTION

A compound composed only of carbon and hydrogen is known hydrocarbon. The hydrocarbons are classified into ***aliphatic, cyclic*** and ***arom*** **hydrocarbon**. The aliphatic hydrocarbons are made up of alkanes, alkenes ***hydrocarbons***. The aliphatic hydrocarbons are made up of alkanes, alkenes alkynes. Alkanes are saturated hydrocarbons and contain only single covalent bo Early organic chemists called them **paraffin** (a term derived from Latin mea ***"having little affinity")*** because they are unreactive. They do however, burn undergo some substitution reactions.

3.2. SOURCES OF ALKANES

1. *Natural gas: main source of Methane;*
2. *Petroleum: primary source of alkanes;*
3. *Methane is present in coal mines and can accumulate in mine sufficient quantities to form an explosive mixture with air.*
4. *Methane is the main component of "marshgas" produced by bacterial decomposition of organic matter in the absence of ai*

3.3. METHODS OF PREPARATION

1. From Halogenoalkanes

(a) When halogenoalkanes are reduced, alkanes with the same numbe carbon atoms per molecule are obtained. Iodoalkanes are the m easily reduced. The reducing agents used include magnes amalgam and ethanol, $Mg-Hg/C_2H_5OH$, lithi tetrahydridoaluminate (III), $LiAlH_4$ and zinc in hydrochloric a Zn/HCl.

Example

$$CH_3-CH_2-CH_2-CH_2-I + 2(H) \rightarrow CH_3-CH_2-CH_2-CH_3 + HI$$

The bromo and chloroalkanes can be converted to alkanes via the ***Grignard reagent***. Grignard reagent is an organometallic compound with the general formula RMgX or ArMgX (R = alkyl group, Ar = phenyl group, X = halogen) usually formed by the reaction of halogenoalkane and magnesium in sodium dry ether. When Grignard reagent is treated with dilute mineral acids, alkanes are formed.

Example:

$$CH_3CH_2Br + Mg \xrightarrow{ether} CH_3CH_2MgBr$$

$$CH_3CH_2MgBr + H^+ \xrightarrow[acid]{dilute} CH_3CH_3 + Mg^{2+} + Br^-$$

(b) Wurtz Reaction

Symmetrical alkanes are produced by the reaction of ethereal solution of halogenoalkanes and sodium.

$$2R-I + 2Na \xrightarrow{ether} R-R + 2NaI$$

$$\text{e.g. } 2C_5H_{11}I + 2Na \xrightarrow{ether} C_{10}H_{22} + 2NaI$$

2. From Alkenes

Alkanes are produced from alkenes by the catalytic hydrogenation of the alkenes. The catalysts used include Raney nickel, platinum or palladium. Temperatures of 25°C to 100°C and pressure of 1 atm to 10 atm are used e.g.

$$\underset{\textit{But-1-ene}}{CH_3-CH_2-CH=CH_2} + H_2 \xrightarrow[\substack{25^\circ C \\ 10\ atm}]{Ni} \underset{\textit{Butane}}{CH_3-CH_2-CH_2-CH_3}$$

3. Decarboxylation

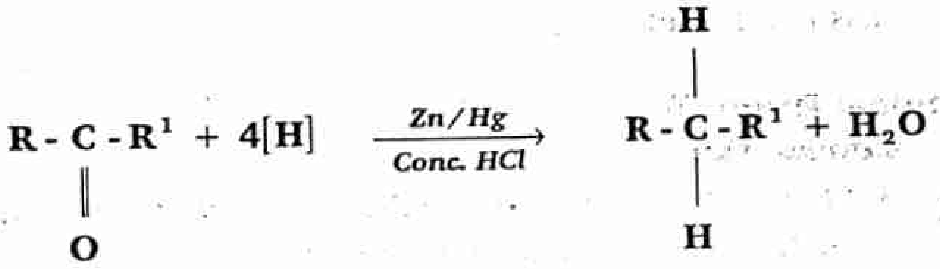
When the sodium salt of an alkanoic acid is heated with sodalime ($Ca(OH)_2$ + NaOH) an alkane with one carbon atom less than the alkanoic acid is formed e.g.

$$\underset{\textit{Sodium propanoate.}}{C_2H_5COONa} + \underset{\textit{Sodalime}}{NaOH} \rightarrow \underset{\textit{Ethane}}{C_6H_6} + Na_2CO_3$$

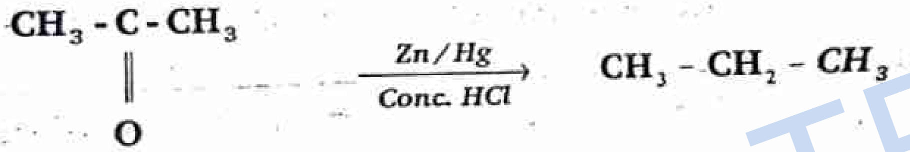
$$\underset{\text{Sodium ethanoate}}{CH_3COONa} + NaOH \rightarrow \underset{\text{Methane}}{CH_4} + Na_2CO_3$$

4. From Carbonyl Compounds ***(Clemensen reduction)***

The carbonyl group in alkanals and alkanones can be converted to methylene group by reduction using amalgamated zinc and concentrated hydrochloric acid. This is known as clemmensen reduction.



$$R-\overset{\displaystyle O}{\overset{\|}{C}}-R^1 + 4[H] \xrightarrow[\text{Conc. HCl}]{\text{Zn/Hg}} R-\overset{H}{\underset{H}{C}}-R^1 + H_2O$$



$$CH_3-\overset{\displaystyle O}{\overset{\|}{C}}-CH_3 \xrightarrow[\text{Conc. HCl}]{\text{Zn/Hg}} CH_3-CH_2-CH_3$$

Propanone *Propane*

3.4. PROPERTIES OF ALKANES

3.4.1. Physical Properties

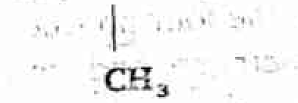
1. Methane to butane are colourless gases at room temperature. Pentane to heptadecane ($C_{17}H_{36}$) are colourless liquids at room temperature. Octadecane and higher members are colourless waxy solids at room temperature.

2. The boiling points and melting points of the alkanes increase as the number of carbon atom increases. Branched isomers have lower boiling points and melting points than straight chain isomers. The more the branching, the lower the boiling point and melting point.

$CH_3-CH_2-CH_2-CH_2-CH_3$

Pentane

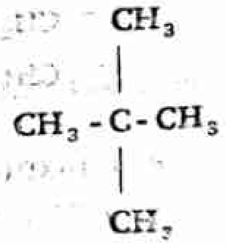
bp = 36.2°C



$$CH_3-\underset{CH_3}{CH}CH_2CH_3$$

2-methylbutane

bp = 28°C



$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_3$$

2, 2-dimethylpropane

bp = 9.7°C

The decrease in the boiling points and melting points of branched isomers is because branching reduces the surface area and the molecule tends to be spherical. The intermolecular forces are reduced and less energy is required to break the forces during boiling or melting. Therefore, boiling point or melting point is reduced. The effect of branching on boiling point is observed in all families of organic compounds.

3. The alkanes are non-polar. They are soluble in non-polar solvents such as benzene, trichloromethane and ethoxyethane (ether) and are insoluble in water and other highly polar solvents. When used as solvents, liquid alkanes dissolve compounds of low polarity and do not dissolve those of high polarity.

3.4.2. Chemical Properties

1. Combustion

Alkanes like other hydrocarbons burn in adequate supply of oxygen to form carbon (IV) oxide and steam e.g.

$$CH_2(g) + 2O_2\,(g) \rightarrow CO_2\,(g) + 2H_2O(g)$$

generally

$$C_xH_y + (x + y/4)\,O_2 \rightarrow xCO_2 + (y/2)\,H_2O.$$

Heat is also produced in this reaction. The reaction is of practical importance in the internal combustion engines where the heat energy generated is made use of.

2. Halogenation

Akanes react with halogens at temperature of 275°C – 400°C or in the presence of ultraviolet light or strong daylight to form various halogenoalkanes. This is a substitution reaction in which one or more of the hydrogen atoms in the alkane is replaced by the halogen with the elimination of hydrogen halide. In the chlorination of methane, for example, the products formed are chloromethane, dichloromethane, trichloromethane and tetrachloromethane.

$$CH_2(g) + Cl_2(g) \rightarrow CH_3Cl(g) + HCl(g)$$

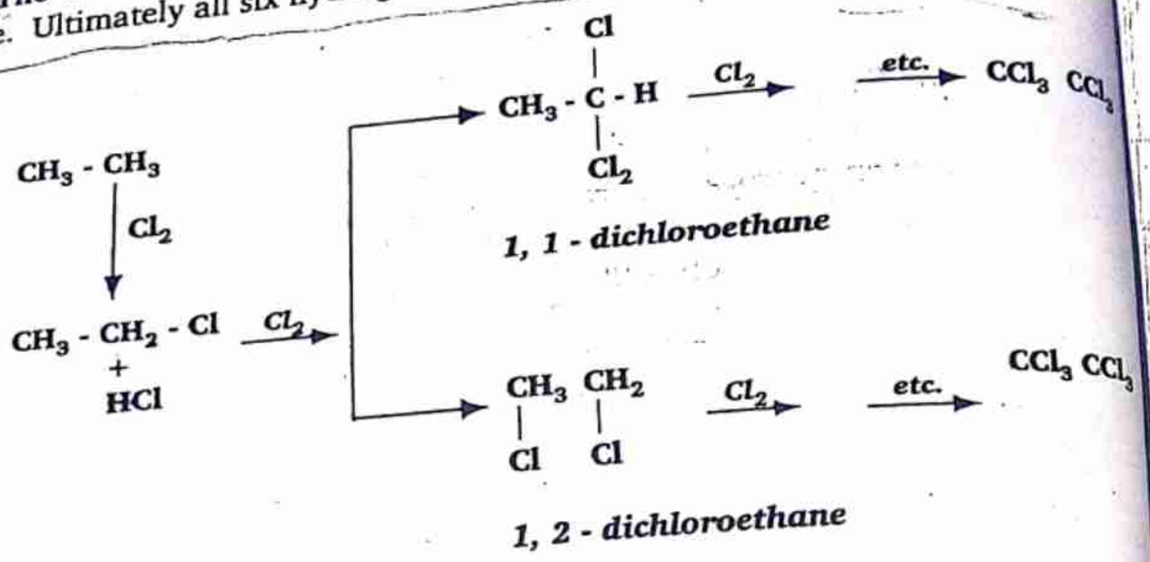
$$CH_3Cl(g) + Cl(g) \rightarrow CH_2Cl_2(g) + HCl(g)$$

$$CH_2Cl_2(g) + Cl_2(g) \rightarrow CHCl_3(l) + HCl(g)$$

$$CHCl_3(l) + Cl_2(g) \rightarrow CCl_4(l) + HCl(g)$$

In practice, a mixture of the four products is obtained. It's composition depends on the initial proportion of methane and chlorine. The mono substituted alkane predominates if excess of the alkane is used and the fully substituted product predominates with an excess of chlorine. The reaction is exothermic. But the reaction with iodine is endothermic, slow and reversible. Fluorination is vigorous and explosive.

The reaction between ethane and chlorine is similar to the chlorinatio methane. Ultimately all six hydrogen atoms of ethane may be replaced.



echanism of Chlorination of Methane

A detailed step-by-step description of a chemical reaction is calle **mechanism**. Two important experimental observations are made abo reaction of methane and chlorine.

i. *The reaction is promoted by heat or light. Methane and chlorine d react in the dark or at room temperature. Reaction takes place re in the dark at temperature of over 250°C or at room temperature mixture is irradiated by ultraviolet light.*

ii. *The light-promoted reaction is highly efficient. A small amount of forms relatively large amount of chlorinated product.*

iii. *The presence of a small amount of oxygen slows down the reaction* ***free radical chain*** *reaction mechanism is most consistent with observations and it occurs in three major steps, namely,* ***initiat*** ***propagation*** *and* ***termination.***

Initiation Step

The action of heat or light fragments the chlorine molecule into chl dicals.

$$Cl_2 \xrightarrow[\text{or light or uv light}]{\text{heat}} 2Cl\cdot$$

In this step, energy is absorbed and a reactive particle with unpaired electron is generated. An atom or group of atoms possessing an unpaired electron is called a ***free radical***.

b. Propagation Step

i. *The chlorine radical (atom) abstracts a hydrogen atom from the methane to form hydrogen chloride and methyl radical.*

$$\mathrm{Cl\cdot + CH_4 \rightarrow HCl + \underset{\textit{Methyl radical}}{\cdot CH_3}}$$

ii. *The methyl radical abstracts a chlorine atom from chlorine molecule to form chloromethane and chlorine radical.*

$$\mathrm{\cdot CH_3 + Cl_2 \rightarrow CH_3Cl + Cl\cdot}$$

These two steps are the chain propagation steps because in each a reaction particle is consumed and another generated. These steps are repeated until all the methane and chlorine molecules have reacted.

c. Termination

In this step reactive, particles are consumed but not generated. This is achieved by any of the following.

i. $\mathrm{Cl\cdot + Cl\cdot \rightarrow Cl_2}$
ii. $\mathrm{\cdot CH_3 + \cdot CH_3 \rightarrow CH_3 - CH_3}$
iii $\mathrm{\cdot CH_3 + Cl\cdot \rightarrow CH_3Cl}$

Inhibitors

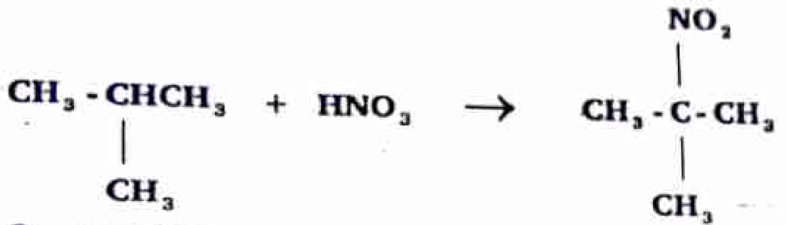
Addition of a small amount of oxygen slows down the reaction. Oxygen reacts with a methyl radical to form a new radical, which is not as reactive as the methyl radical and therefore, cannot continue the chain.

$$\mathrm{\cdot CH_3 + O_2 \rightarrow CH_3 - O - O\cdot}$$

A molecule of oxygen can prevent the formation of thousands of molecules of chloromethane. The reaction proceeds normally only when all the oxygen has been exhausted. A substance that slows down or stops a reaction even though it is present in small amounts is called an inhibitor.

3. Nitration

Alkanes react with concentrated trioxonitrate (V) acid when a mixture of the alkane and the acid vapour is heated at 450°C. Nitroalkanes are formed. The reaction can also take place when the alkane and the acid are heated together at 140°C under pressure. (liquid phase nitration) e.g.



$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_3 + HNO_3 \rightarrow CH_3-\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle NO_2}{\overset{|}{C}}}}-CH_3$$

2 - methylpropane *2-nitro-2-methylpropane*

4. Sulphonation

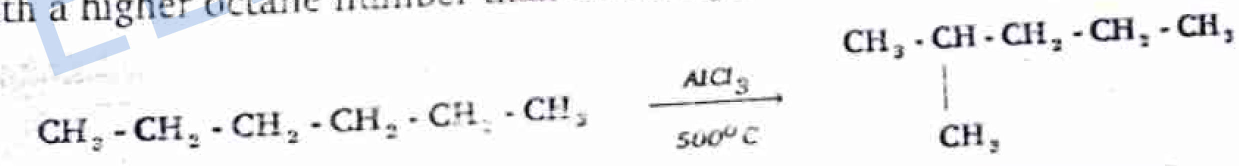
Sulphonation is the replacement of **H** atom by the sulphonic acid group, **$-SO_3H$**. Direct sulphonation using concentrated tetraoxosulphate (VI) acid is hard to achieve, especially in lower alkanes. Alkanes react with a mixture of chlorine and sulphur (IV) oxide or sulphonyl chloride, SO_2Cl_2 at 50°C in the presence of light to give alkane sulphonyl chlorides. These are converted to sulphonic acid by hydrolysis.

$$R-H + SO_2Cl_2 \rightarrow R-SO_2Cl + HCl$$
$$R-SO_2Cl + H_2O \rightarrow R\text{-}SO_2OH + HCl$$

Hexane and higher alkanes are sulphonated directly using fuming tetraoxosulphate (VI) acid, (oleum).

5. Isomerisation

This is the conversion of straight chain alkanes to branched isomers by rearrangement. This reaction is catalysed by aluminium chloride and is important in the petroleum industry where hexane at 500°C gives 2-methylpentane, a compound with a higher octane number than the straight chain isomer.



$$CH_3-CH_2-CH_2-CH_2-CH_2-CH_3 \xrightarrow[500^oC]{AlCl_3} CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-CH_2-CH_3$$

Hexane *2-methylpentane*

3.4.3. Uses of Alkanes

They are used as fuel for heating at home and industries. Higher alkanes are contained in kerosene and are used as fuel for jet engines. Alkanes are also used as solvents for paints and varnishes. At higher temperatures methane burns and produces carbon black, which is used for making printer's ink, paints and motor tyres.

REVIEW QUESTIONS

1. Arrange the following in order of increasing boiling points (highest boiling at the top, lowest at the bottom) and explain the order: 3, 3-dimethylpentane, heptane, 2-methylheptane, pentane, 2-methylhexane.

2. Use chemical equations only to show the preparation of a named alkane from:
   - *a. an alkene*
   - *b. an alkanol*
   - *c. alkanoic acid*
   - *d. halogenoalkane.*

3. Complete the following equations.

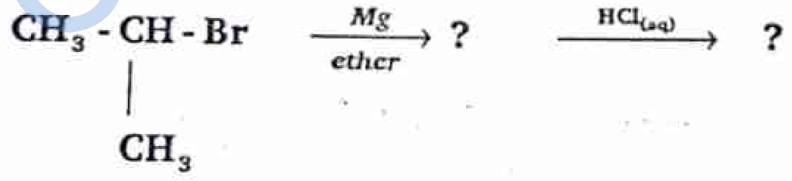
a. $C_3H_7I + 2Na \xrightarrow[\Delta]{Ether}$

b. $CH_3-CH_2-CH=CH_2+H_2 \xrightarrow[\substack{25^{o}C \\ 10\ atm.}]{Ni}$

c. $CH_3-CH_3 + Cl_2 \xrightarrow[Dark]{\Delta}$

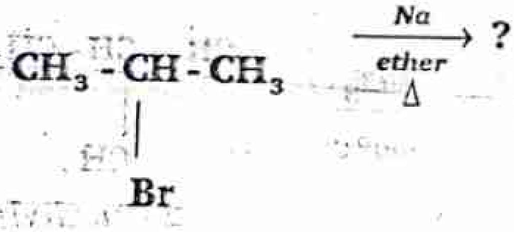
d. $CH_3-CH_2-CH_2Cl \xrightarrow{LiAlH_4}$

e.



$$\underset{\displaystyle CH_3}{CH_3-\underset{|}{CH}-Br} \xrightarrow[ether]{Mg} \ ? \xrightarrow{HCl_{(aq)}} \ ?$$

f.



$$\underset{\displaystyle Br}{CH_3-\underset{|}{CH}-CH_3} \xrightarrow[\substack{ether \\ \Delta}]{Na} \ ?$$

Chapter 4

ALKENES

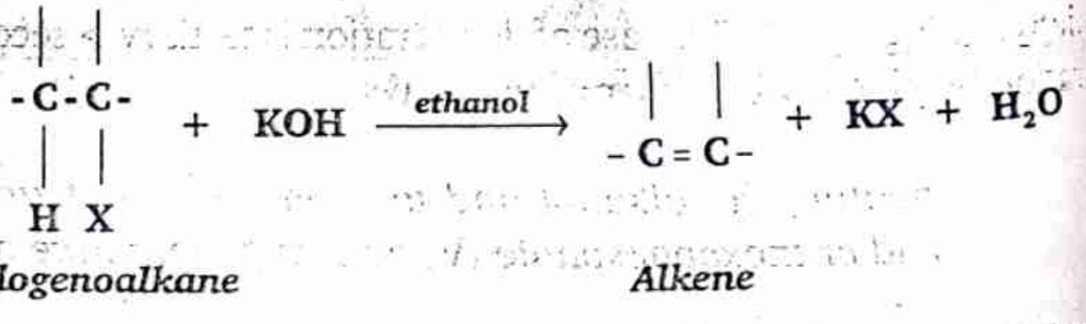
4.1. INTRODUCTION

The alkenes are unsaturated hydrocarbons with carbon carbon double per molecule. The double bond is the functional group of the alkenes a determines their chemical properties. The lower alkenes are produced durin cracking of diesel and lubricating oil fractions of petroleum. The simplest me ethene is used to promote the ripening of fruits, to manufacture polyethene, eth polychloroethene (PVC), polyphenylethene, ethane –1, 2-diol etc. Propene is for the manufacture of propanone, perspex, artificial rubbers, bakelite type r polypropene etc.

4.2. METHODS OF PREPARATION

1. *Dehydrohalogenation of Halogenoalkanes*

This is the removal of a molecule of hydrogen halide using a hot ethanolic sol of potassium or sodium hydroxide. The hydrogen atom is removed fro carbon atom adjacent to the one bearing the halogen.



$$\underset{\substack{|\quad|\\ H\quad X}}{\overset{|\quad|}{-C-C-}} + KOH \xrightarrow{ethanol} \overset{|\quad|}{-C=C-} + KX + H_2O$$

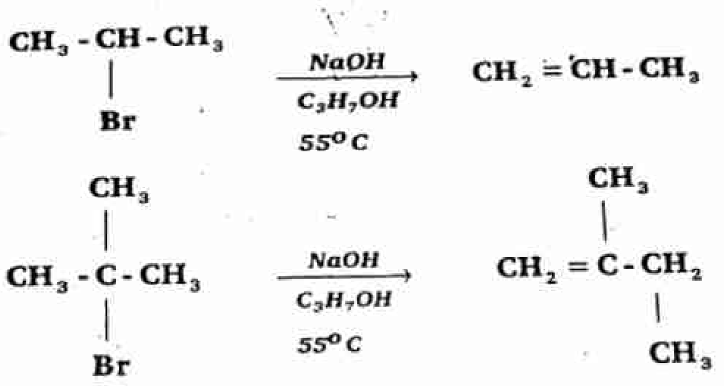
Halogenoalkane *Alkene*

A solution of KOH or NaOH in ethanol generates the ethoxide ion $C_2H_5O^-$ whic very strong base. This reagent is used because an acid is eliminated.

$$\overline{O}H + C_2H_5OH \rightarrow H_2O + C_3H_5\overline{O}$$

Side reactions such as the substitution of halogen by $\bar{O}H$ to form alkanol are possible. To minimize these side reactions and increase yield, secondary and tertiary halogenoalkanes are used. If we must begin with a primary halogenoalkane then a bulky base is used.

Example



$$CH_3-\underset{\underset{Br}{|}}{CH}-CH_3 \xrightarrow[C_3H_7OH\ 55^oC]{NaOH} CH_2=CH-CH_3$$

$$CH_3-\underset{\underset{Br}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3 \xrightarrow[C_3H_7OH\ 55^oC]{NaOH} CH_2=\overset{\overset{CH_3}{|}}{C}-\underset{\underset{CH_3}{|}}{CH_2}$$

In certain cases a mixture of isomeric alkenes are formed, e.g.

$CH_3-CH_2-CHBrCH_3 \xrightarrow[Ethanol]{KOH} CH_3-CH=CHCH_3 + CH_3-CH_2-CH=CH_2$

But-2-ene **But - 1 - ene**

$CH_3-CH_2-CH_2CHBrCH_3 \xrightarrow[Ethanol]{KOH} CH_3-CH_2-CH=CH-CH_3 + CH_3-CH_2-CH_2CH=CH_2$

Pent - 2 - ene **Pent - 1 - ene**

The product that predominates is the one which has the more highly substitute double bond. Thus *but-2-ene* and *pent-2-ene* predominate. One can also say that th alkene which is formed by elimination of hydrogen from the carbon with low number of hydrogen atoms predominates.

2. *Dehydration of Alkanols*

The general reaction is the removal of a molecule of water from the alka by the dehydrating agent. The ease of dehydration is tertiary > secondary > prima Dehydration is achieved by either of two ways.

i. *heating the alkanol and the concentrated tetraoxosulphate acid or trioxophosphate (V) acid at temperature of about 170°C*

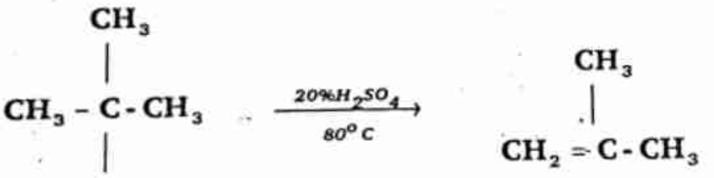
ii. *passing the alkanol vapour over aluminium oxide at 360°C e*

$CH_3-CH_2-OH \xrightarrow[170^\circ C]{96\%\ H_2SO_4} CH_2=CH_2 + H_2O$

Ethene

$CH_3-CH_2-CHOH-CH_3 \xrightarrow[100^\circ C]{60\%\ H_2SO_4} CH_3-CH=CH-CH_3 + H_2O$

Butan-2-ol　　But-2-ene

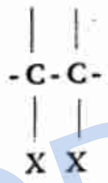


$$CH_3-\overset{\overset{\Large CH_3}{|}}{\underset{\underset{\Large OH}{|}}{C}}-CH_3 \xrightarrow[80^\circ C]{20\% H_2SO_4} CH_2=\overset{\overset{\Large CH_3}{|}}{C}-CH_3$$

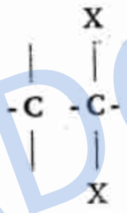
2-methylpropan-2-ol　　2-methylpropene

3. By Debromination of Vicinal Dibromides

Vicinal or vic dihalides are dihalo compounds with the halogens on adjacent carbon atoms. Germinal or gem dihalides have the halogen atoms on the same carbon atom.

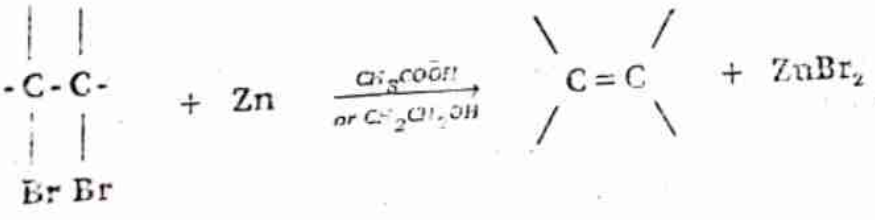


Vic dihalide



Gem dihalide

When vic dibromides are treated with a solution of sodium iodide in propanone or a mixture of zinc dust in ethanoic acid (or ethanol) they lose a molecule of bromine and alkenes are formed.



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4.3. PROPERTIES OF ALKENES

4.3.1. Physical Properties

Their physical properties are similar to those of the alkanes. The lower members are gases; C_5 to C_{15} are volatile liquids; above C_{15} are solids. The presence of the double bond makes the alkene slightly more compact than the corresponding alkane. This reduces the attractive forces. They have slightly lower boiling points than the corresponding alkanes e.g.

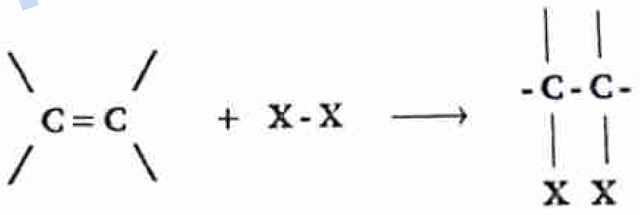
		Boiling point (°C)
CH_3-CH_3	Ethane	-89
CH_2=CH_2	Ethene	-104
CH_3-CH_2-CH_3	Propane	-42
CH_2=CH-CH_3	Propene	-48
CH_2=CH_5-CH_2-CH_2-CH_3	Pentane	36
CH_2=CH-CH_2-CH_2-CH_3	Pent – 1– ene	29
$CH_3(CH_2)_6CH_3$	Octane	126
CH_2=CH$(CH_2)_5CH_3$	Oct – 1 – ene	121
CH_3CH=CH$(CH_2)_4CH_3$	Oct – 2 – ene	125

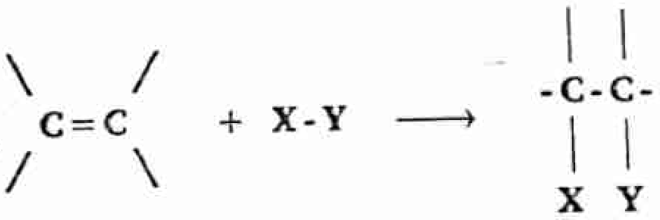
4.3.2. Chemical Reactions

1 ***Addition Reactions***

The chemical reactions of alkenes are due to the presence of the double bond. Th double bond in alkene consists of a strong σ bond and a weak π bond. Therefore the chemical reactions of alkenes involve the breaking of this weak π bond and th formation of two strong σ bonds.

The most common reaction for compounds containing carbon-carbon double bon is addition.





The double bond in an alkene is made up of a σ bond. The π electrons are loos held and are available to reagents seeking electrons. Therefore compounds that react w alkenes are those that are seeking electrons. They are acidic and electron deficient are called ***electrophilic reagents***.

Free radicals also react with alkenes because each seeks an electron.

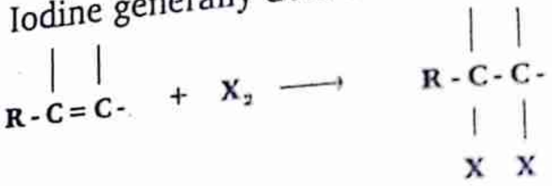
a. **Addition of Hydrogen (Catalytic Hydrogenation)**

Alkenes react with hydrogen in the presence of finely divided ni palladium or platinum to form alkanes. One atom of hydrogen adds to carbon of the double bond e.g.

$$CH_2=CH_3 + H_2 \xrightarrow[\text{or pt. }25^o]{Ni.Pd} CH_3-CH_3$$

b. **Addition of Halogen**

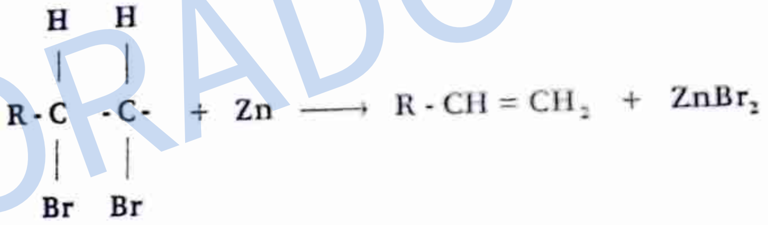
Alkenes react rapidly with chlorine or bromine at room temperature absence of light. Iodine generally does not react. The general reactio



$$R-\overset{|}{C}=\overset{|}{C}- + X_2 \longrightarrow R-\underset{X}{\overset{|}{\underset{|}{C}}}-\underset{X}{\overset{|}{\underset{|}{C}}}-$$

$(X_2 = Cl_2 \text{ or } Br_2)$

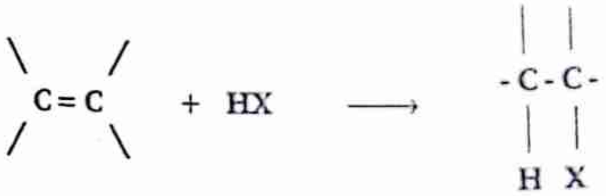
The reaction is carried out simply by mixing the alkene and the halo tetrachloromethane. The reaction with bromine can be used to disti alkene from alkane. The reddish brown colour of bromine is discharge alkene can be regenerated from the dibromoalkane by reacting it wi dust.



$$R-\underset{Br}{\overset{H}{C}}-\underset{Br}{\overset{H}{C}}- + Zn \longrightarrow R-CH=CH_2 + ZnBr_2$$

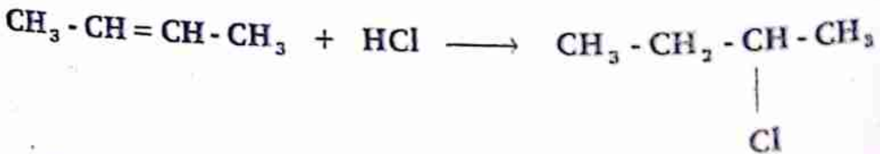
c. **Addition of Hydrogen Halides**

The hydrogen halides (HF, HCl, HBr, and HI) add readily to the double of alkenes to form the corresponding halogenoalkanes.



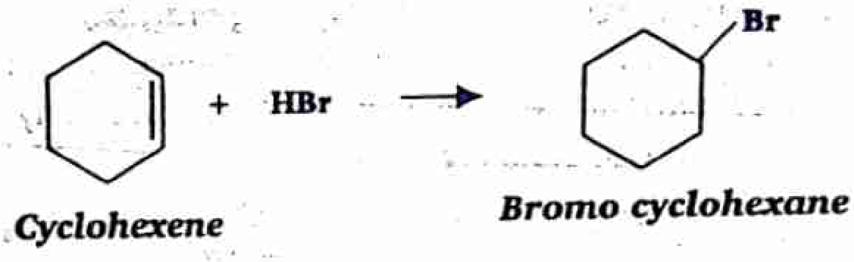
$$>C=C< + HX \longrightarrow -\underset{H}{\overset{|}{C}}-\underset{X}{\overset{|}{C}}-$$

(X = F, Cl, Br, I)



$$CH_3-CH=CH-CH_3 + HCl \longrightarrow CH_3-CH_2-\underset{Cl}{CH}-CH_3$$

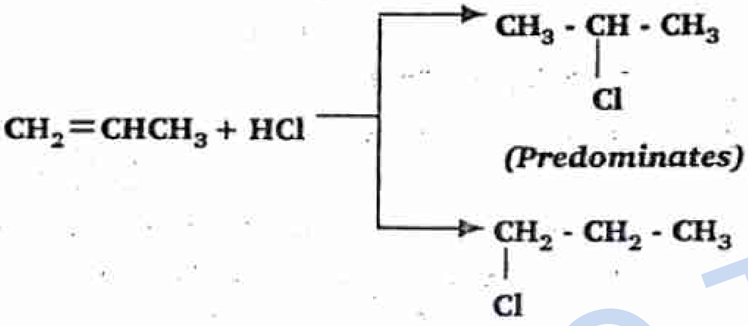
But-2-ene 2-chlorobutane



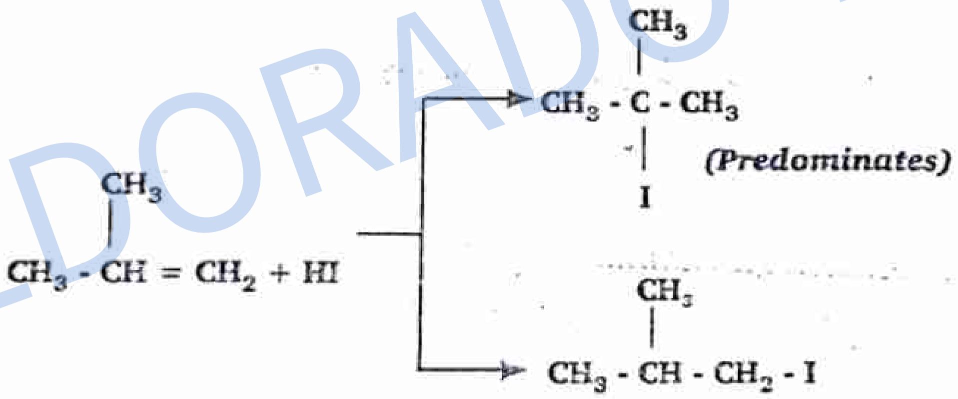
The reaction is usually carried out by passing the dry gaseous hydrogen halide directly into the alkene or by adding a solution of the hydrogen halide to the alkene.

MARKOVNIKOV'S RULE

The addition of hydrogen halide to an unsymmetrical alkene theoretically leads to two products. One product however, predominates in practice.



$$CH_2{=}CHCH_3 + HCl \rightarrow CH_3-\underset{\displaystyle Cl}{\underset{|}{CH}}-CH_3 \text{ (Predominates)} + \underset{\displaystyle Cl}{\underset{|}{CH_2}}-CH_2-CH_3$$

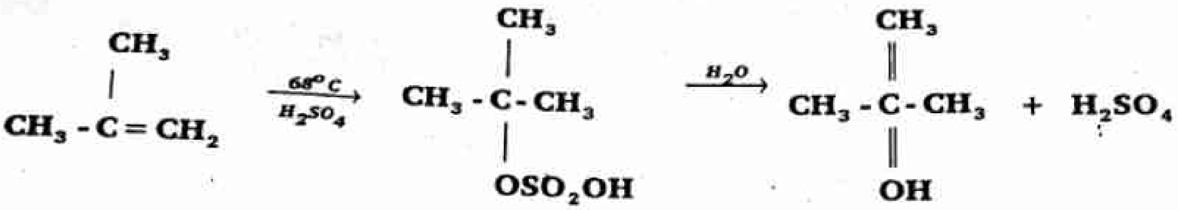


$$CH_3-\overset{\displaystyle CH_3}{\overset{|}{CH}}=CH_2 + HI \rightarrow CH_3-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle I}{\underset{|}{C}}}}-CH_3 \text{ (Predominates)} + CH_3-\overset{\displaystyle CH_3}{\overset{|}{CH}}-CH_2-I$$

Markovnikov's rule is used to explain many examples like these. The rule states that in the addition of compounds of the form HX across a double bond, the hydrogen adds to the carbon of the double bond with the greater number of hydrogen atoms.

Addition of hydrogen bromide

Addition of HCl and HI to unsymmetrical alkenes follows Markovnikov's rule. But in the presence of peroxides the addition of HBr to unsymmetrical alkenes give products, which are contrary to the predictions of Markovnikov's rule. This reversal of orientation caused by the presence of peroxides is called *peroxide effect.*

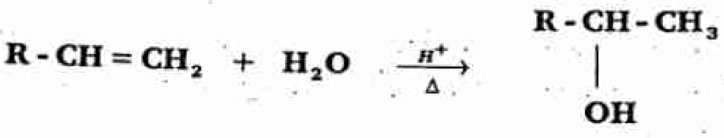


$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{C}=CH_2 \xrightarrow[H_2SO_4]{68^{\circ}C} CH_3-\underset{\underset{\displaystyle OSO_2OH}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-CH_3 \xrightarrow{H_2O} CH_3-\underset{\underset{\displaystyle OH}{\|}}{\overset{\overset{\displaystyle CH_3}{\|}}{C}}-CH_3 + H_2SO_4$$

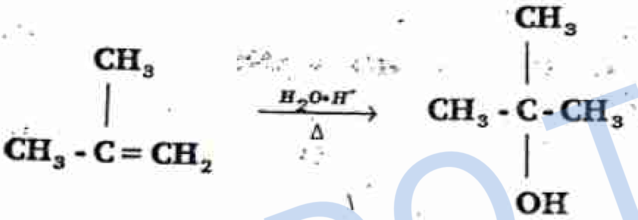
b. **Addition of Water: Hydration**

Water adds to the more reactive alkenes in the presence of acids to give alkanols. This is a convenient method for the preparation of secondary and tertiary alkanols. The acids most commonly used are tetraoxosulphate (VI) acid and trioxophosphate (V) acid. The addition to unsymmetrical alkenes follows Markovnikov's rule.

Example



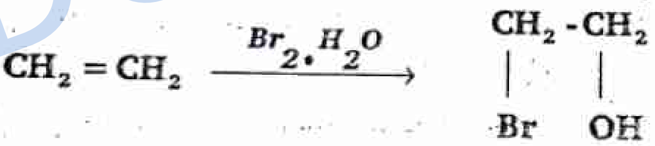
$$R-CH=CH_2 + H_2O \xrightarrow[\Delta]{H^+} R-\underset{\underset{\displaystyle OH}{|}}{CH}-CH_3$$



$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{C}=CH_2 \xrightarrow[\Delta]{H_2O \cdot H^+} CH_3-\underset{\underset{\displaystyle OH}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-CH_3$$

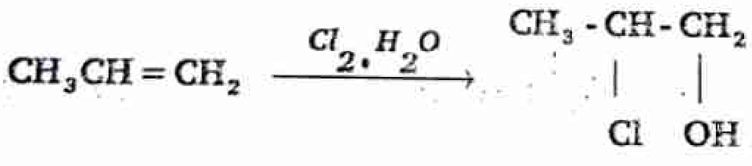
c. **Halohydrin Formation**

Addition of chlorine or bromine in the presence of water gives compounds containing the halogen and hydroxyl groups on adjacent carbon atoms. These compounds are called ***halohydrins*** e.g.



$$CH_2=CH_2 \xrightarrow{Br_2, H_2O} \underset{\underset{\displaystyle Br}{|}}{CH_2}-\underset{\underset{\displaystyle OH}{|}}{CH_2}$$

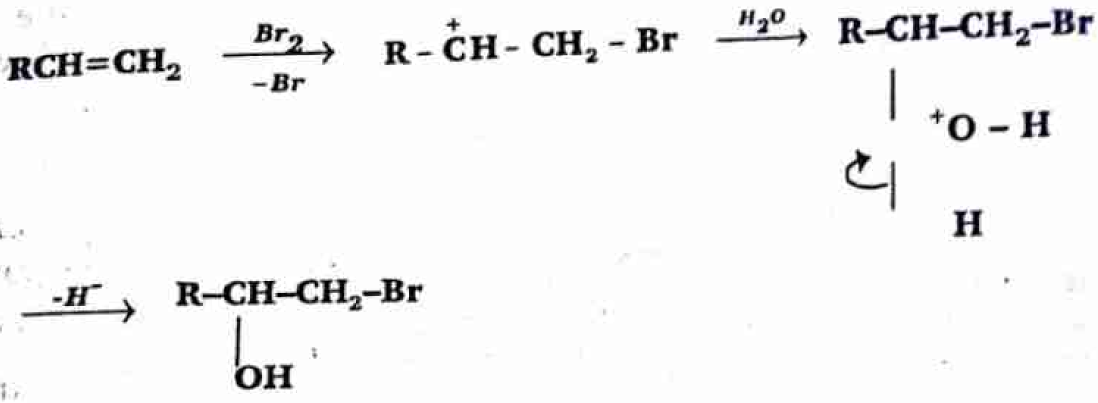
2-Bromoethanol



$$CH_3CH=CH_2 \xrightarrow{Cl_2, H_2O} CH_3-\underset{\underset{\displaystyle Cl}{|}}{CH}-\underset{\underset{\displaystyle OH}{|}}{CH_2}$$

2-Chloropropan-1-ol

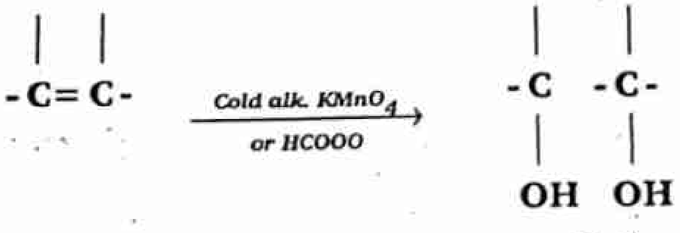
These compounds are formed by the addition of pre-formed oxoacid, HOX. However, the products show the addition of the elements of the oxo acid (HO^- and –X).



$$RCH{=}CH_2 \xrightarrow[-Br]{Br_2} R-\overset{+}{C}H-CH_2-Br \xrightarrow{H_2O} R-\underset{\overset{+}{O}-H\ \ H}{CH}-CH_2-Br \xrightarrow{-H^+} R-\underset{OH}{CH}-CH_2-Br$$

d. **Hydroxylation**

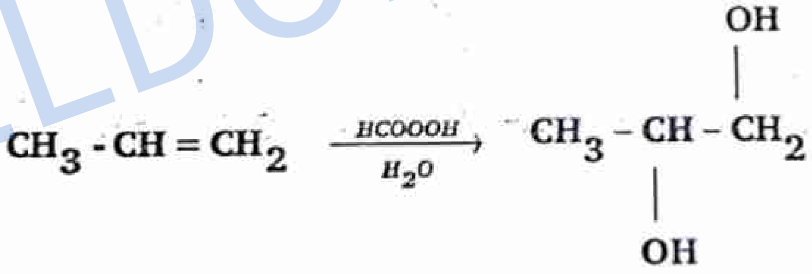
Some oxidizing agents such as cold alkaline $KMnO_4$ or peroxymethanoic aci H–COOOH convert alkenes to diols. This reaction is known as hydroxylatio



$$-\overset{|}{C}=\overset{|}{C}- \xrightarrow[\text{or HCOOO}]{\text{Cold alk. } KMnO_4} -\underset{OH}{\overset{|}{C}}\ \ -\underset{OH}{\overset{|}{C}}-$$

diol

$$3CH_2=CH_2 + 2KMnO_4 + 4H_2O \longrightarrow 3\underset{OH}{CH_2}-\underset{OH}{CH_2} + 2MnO_2 + 2KOH$$

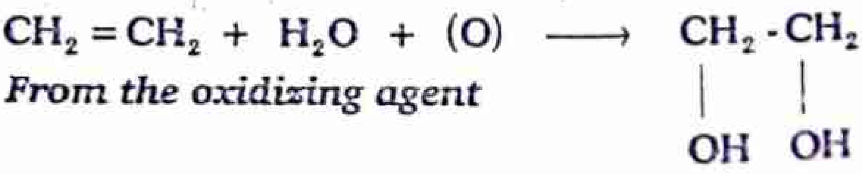


$$CH_3-CH=CH_2 \xrightarrow[H_2O]{HCOOOH} CH_3-\underset{OH}{CH}-\overset{OH}{CH_2}$$

With alkaline $KMnO_4$ the product is cis-diol while with HCOOH the product is a trans–diol.

e. **Oxidation**

Alkenes are oxidized to diols (compounds with two hydroxyl groups attache These are formed by the addition of the hydroxyl groups across a double bond.

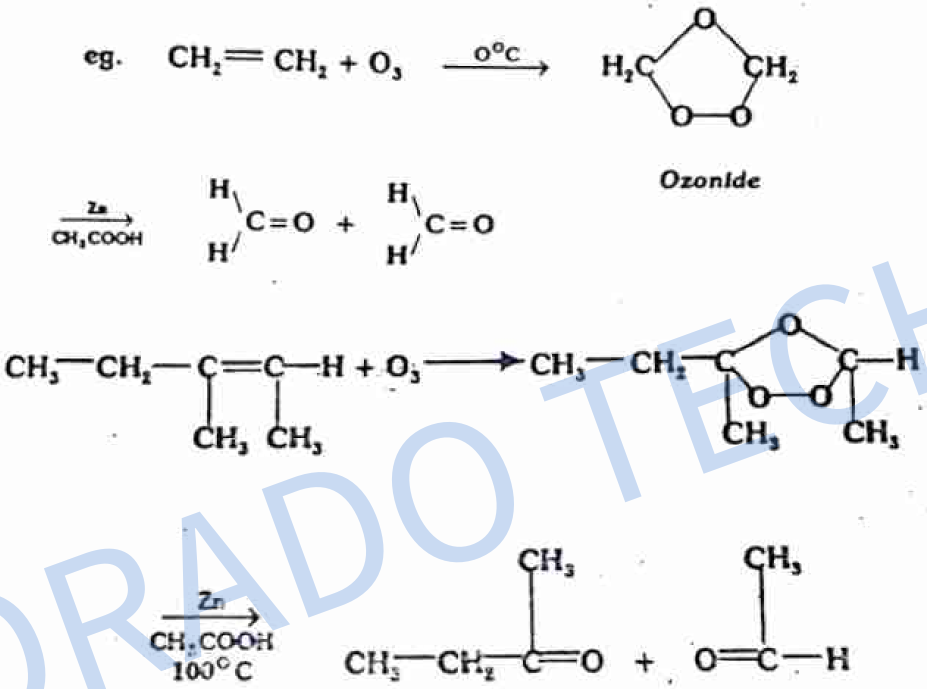


$$CH_2=CH_2 + H_2O + \underset{\text{From the oxidizing agent}}{(O)} \longrightarrow \underset{OH}{CH_2}-\underset{OH}{CH_2}$$

The oxidizing agents used are cold acidified potassium tetraoxomanganate (VII), $KMnO_4$, or acidified potassium heptaoxochromate (VI), $K_2Cr_2O_7$. The purple colour of $KMnO_4$ is discharged while the $K_2Cr_2O_7$ is changed from yellow to green.

f. Ozonolysis

Ozonolysis is the addition of trioxygen (ozone) to an alkene and the hydrolysis of the ozonide formed to yield the cleavage products which contain the carbonyl group, $\rangle C=O$, at the site of the double bond in the original compound. Ozonolysis provides valuable information about the position of the double bond in the structure of the alkene. The hydrolysis of the ozonide is carried out by treatment with zinc dust and ethanoic acid.



Test for Unsaturation

1. Pass ethene (alkene) through reddish brown bromine water. It decolourized.

2. Pass ethene through bromine in tetrachloromethane, CCl_4, decolourized.

3. Pass ethene through purple acidified $KMnO_4$. It is decolouri Ethane (alkane) does not undergo these reactions because i saturated.

REVIEW QUESTIONS

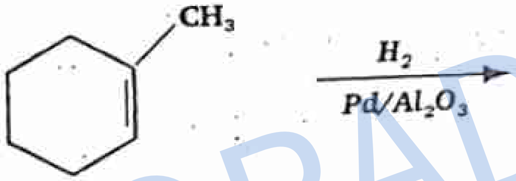
1. Give the reactions of **$CH_3-CH=C(CH_3)CH_2-CH$** with the following reagents.
   i. H_2SO_4 ii $KMnO_4$ iii Br_2 iv. Hbr, peroxides.

2. Use chemical equations only to show the preparation of a named alkene from

   a. *Alkanol* b. *Halogenaalkane*
   c. *alkane* d. *vicinal dibromide*

3. Complete the following reactions:

   a. $CH_2=CH_2 + H_2 \longrightarrow$

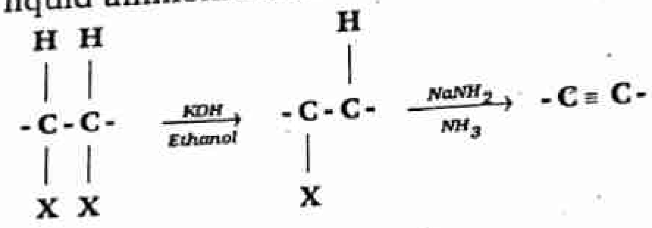


   b. $CH_3CH=CH_2 + HCl \longrightarrow$

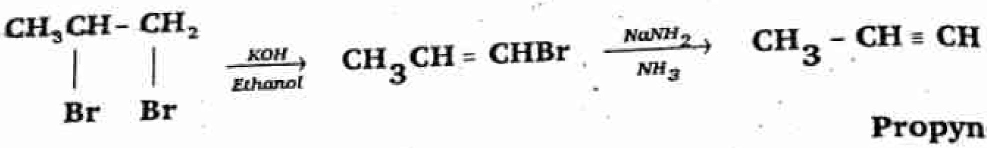
   c. $CH_3CH_2CH=CH_2 + HBr \longrightarrow$

   d. $CH_3CH_2CH=CH_2 \xrightarrow[CHCl_3\ 0^\circ C]{O_3} ? \xrightarrow{Zn/CH_3\ COOH} ? + ?$

3. **Dehydrohalogenation of dihalogenoalkanes**
Dehydrogenation of dihalogenoalkanes using alcoholic KOH gives halogenoalk with the halogen atom attached directly to the doubly-bonded carb (vinylhalide). This is unreactive and the reaction steps. A stronger ba sodamide in liquid ammonia is therefore, used to form the alkyne.


$$-\underset{X}{\overset{H}{C}}-\underset{X}{\overset{H}{C}}- \xrightarrow[Ethanol]{KOH} -\underset{X}{C}-\overset{H}{C}- \xrightarrow[NH_3]{NaNH_2} -C\equiv C-$$

e.g.


$$CH_3\underset{Br}{CH}-\underset{Br}{CH_2} \xrightarrow[Ethanol]{KOH} CH_3CH=CHBr \xrightarrow[NH_3]{NaNH_2} CH_3-CH\equiv CH$$

Propyne

4. **Reaction of Sodium Alkynide With Halogenoalkanes**
This method is used to convert smaller alkynes with hydrogen at one carbon larger ones Primary halogenoalkanes are used. The required sodium alkynid prepared by treating an alkyne with hydrogen atom attached to one carbon at with a solution of sodamide in ammonia.

$$R-C\equiv C-H + NaNH_2 \rightarrow R-C\equiv C-Na + NH_3$$

Sodium alkynide

This sodium alkynide is reacted with the primary halogenoalkane to give alkyne.

$$R-C\equiv C-Na + R'I \rightarrow R-C\equiv C-R' + NaI$$

5.3. PROPERTIES OF ALKYNES

5.3.1. Physical Properties

1. The terminal alkynes are slightly more soluble in water than alkanes and alke This is because $-C\equiv C-H$ bond makes terminal alkynes sufficiently polar to dissolved by water.

The alkynes haves higher boiling points than alkanes or alkenes with the sa carbon skeleton. For example.

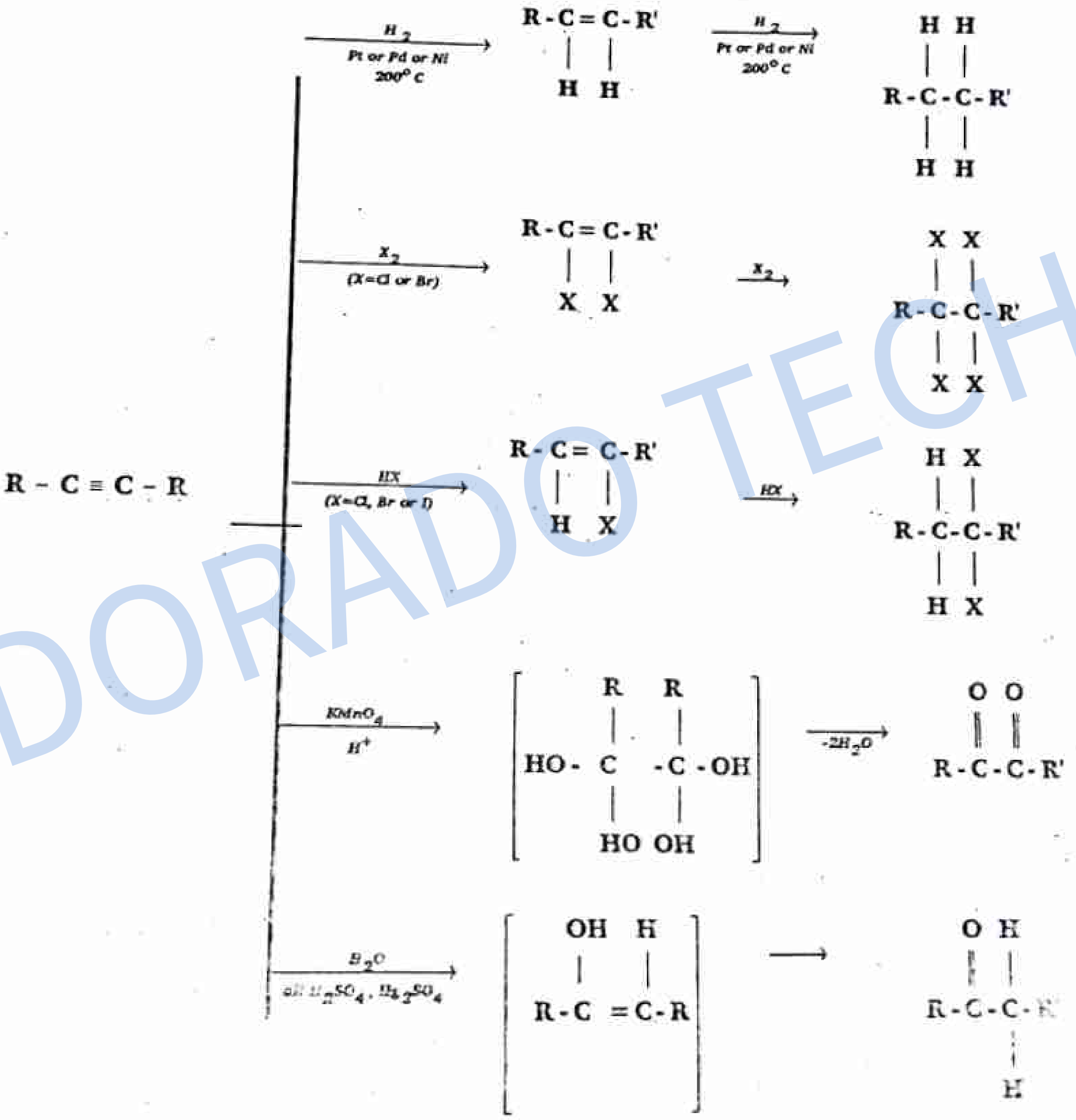
	b.p (°C)
but-l-ene	-65
cis but-2-ene	-3.7
but-l-yne	8.6
but-2-yne	27.2
butane	- 0.5

This is because the C–H bond in –C≡C–H is sufficiently polar. This makes i possible for intermolecular attraction to exist. This attraction overcomes th compactness of the alkyne molecule.

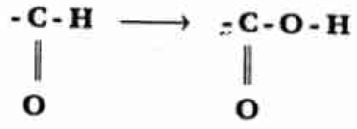
5.3.2. Chemical Properties

1. *Addition reactions*

Like alkenes, alkynes undergo electrophilic addition because of availability o loosely held electrons. The reactions take place in two stages i.e. requires tw moles of the reagent; C≡C bond is first converted to C=C, and then to C–C bond.



In the oxidation of alkyne using acidified KMnO$_4$, if an alkanal group formed, the group is further oxidized to alkanoic acid.



$$-\underset{\underset{O}{\|}}{C}-H \longrightarrow -\underset{\underset{O}{\|}}{C}-O-H$$

$$-CHO \rightarrow -COOH$$

2. ***Combustion***

Alkynes burn in air to give a very luminous and smoky flame because of the carbon content. Ethyne burns in pure and excess oxygen to give a non-luminous and very hot flame (~3000°C) used in oxy-ethyne torch for welding and cutting metals.

$$2C_2H_{2(g)} + 5O_{2(g)} \rightarrow 4CO_{2(g)} + 2H_2O_{(g)}$$

3. ***Formation of Metallic Derivatives***

Terminal alkynes form covalent metal derivatives with silver and copper (I) ions. If a terminal alkyne such as ethyne is passed into ammonical solution of silver trioxonitrate (V) or copper (I) chloride, a precipitate of silver alkynide (yellowish white) or copper (I) alkynide (reddish brown) is formed respectively.

$$R-C\equiv C-H + Ag(NH_3)_2^+ + \overline{O}H \xrightarrow{H_2O} R-C\equiv C-Ag + H_2O + 2NH_3$$

Silver alkynide

$$R-C\equiv C-H + Cu(NH_3)_2^+ + \overline{O}H \xrightarrow{H_2O} R-C\equiv C-Cu + H_2O + 2NH_3$$

Copper (I) alkynide

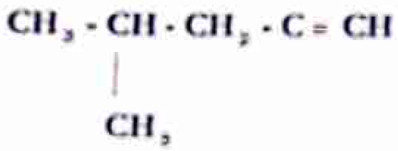
The formation of these alkynides serves as a distinguishing test for ethyne and other terminal alkynes from ethane and other alkenes. Alkenes and alkynes decolourise acidified $KMnO_4$, bromine and bromine water. Alkenes do not react with ammoniacal $AgNO_3$ and ammoniacal CuCl. The formation of these alkynides can also be used for separating terminal alkynes from alkynes that have an internal triple bond. Once separation has been achieved the terminal alkyne can be regenerated by treating the alkynide with a strong acid or sodium cyanide.

$$R-C\equiv C-R + Ag(NH_3)_2^+ + OH \longrightarrow \text{No precipitate}$$

$$R-C\equiv C-H + Ag(NH_3)_2^+ OH \longrightarrow R-C\equiv C-C-Ag_{(s)} \xrightarrow[H_2O]{\overline{C}N} R-C\equiv C-H$$

REVIEW QUESTIONS

1. Give the structure of the product of



$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-C\equiv CH$$

with two moles of:

a. *Br_2*
b. *HCl*
c. *HBr and peroxides*
d. *ammoniacal silver trioxonitrate (V), $Ag(NH_3)_2OH$*
e. *Acidified $KMnO_4$*

2. Show how you can prepare a butyne from 1, 2-dibromobutane

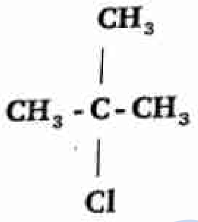
3. A compound A of molecular formular $C_5H_{12}O$, reacts with concentrat tetraoxosulphate (VI) acid at 170°C to yield an alkene B, which on ozonoly gives C and D. Bromination of B with bromine yields dibromide E, which transformed to compound F with KOH/C_2H_5OH. F gives a white precipita with ammoniacal $AgNO_3$ solution. What is the structure of A? Write chemi equations to show the reactions that have taken place in each of the ab transformation. Deduce the structures of B, C, D, E and F.

Chapter 6

HALOGENOALKANES

6.1. INTRODUCTION

In this chapter we shall deal with aliphatic and aromatic compounds in one or more hydrogen atoms in alkanes or benzenes have been replaced by ha atoms. Example includes:

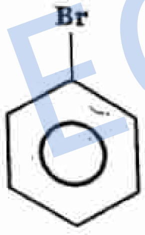


$$CH_3-\overset{\overset{\large CH_3}{|}}{\underset{\underset{\large Cl}{|}}{C}}-CH_3$$

2 – chloro – 2 – methylpropane

CH_3CH_2I

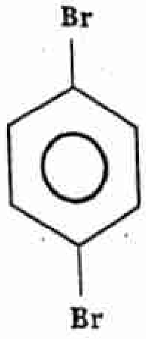
Iodoethane



Bromobenzene

$Cl-CH_2CH_2-Cl$

1, 2 - dichloroethane



1, 4 - dibromobenzene

The halogenoalkanes are very useful intermediates in organic chem because the halogen atom especially bromine and chlorine, can be easily replace other groups. The chemical and physical properties of halogenoalkanes a halogenobenzenes are different. Most halogenobenzenes are extremely unreac when compared to halogenoalkanes.

6.2. METHODS OF PREPARATION

6.2.1. Preparation of Halogenoalkanes

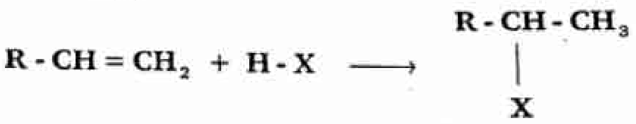
1. ***Direct Halogenation of Alkanes***

   This method has already been discussed in *section 3.2.2.* It is used effectively for the preparation of chloro- and bromoalkanes. In order to ensure good yields of the mono-substituted compound rather than the polyhalogeno derivatives, a large excess of the alkane is used.

$$C_3H_8 + Cl_2 \longrightarrow C_3H_7Cl + HCl$$

2. ***Addition of Hydrogen Halide to an Alkene***

   When a hydrogen halide reacts with an alkene, halogenoalkane is obtained *(section 4.3.2.)*.



$$R-CH=CH_2 + H-X \longrightarrow \begin{array}{c} R-CH-CH_3 \\ | \\ X \end{array}$$

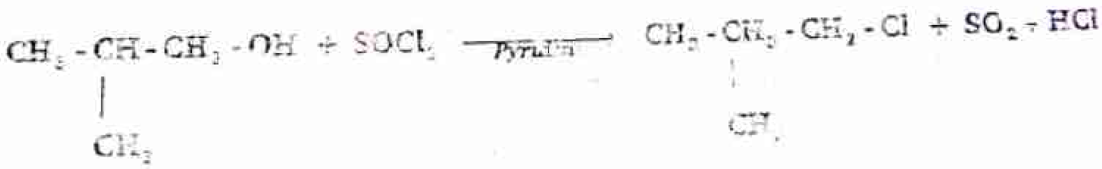
3. ***From Alkanols***

   Alkanols react readily with hydrogen halides to form halogenoalkanes. In this reaction, the –OH group of the alkanol is replaced by a halogen.

The order of reactivity of the hydrogen halides is HI> HBr> HCl (HF is generally unreactive). The order of reactivity of the alkanols is tertiary > secondary > primary. The reaction requires the presence of a strong acid, which may be the hydrogen halide itself (for tertiary alkanols) or concentrated H_2SO_4 (secondary and primary alkanols). Secondary and primary alkanols are converted to the halogenoalkanes by reacting them with a mixture of sodium halide and concentrated tetraoxosulphate (VI) acid. The acid acts as both catalyst and generator of the hydrogen halide.

$$ROH + NaX + H_2SO_4 \longrightarrow R-X + NaHSO_4 + H_2O$$

The hydrogen chloride reacts with primary alkanols only in the presence of zinc chloride because the chloride ion is a weak nucleophile. Replacement of the –OH group in primary or secondary alkanols to form halogenoalkanes can also be carried out using sulphur dichloride oxide, (thionyl chloride) $SOCl_2$, or phosphorous tribromide. Examples of the use of these reagents are shown below:

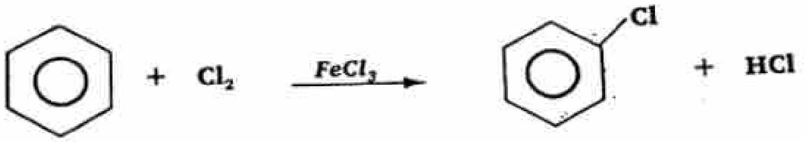


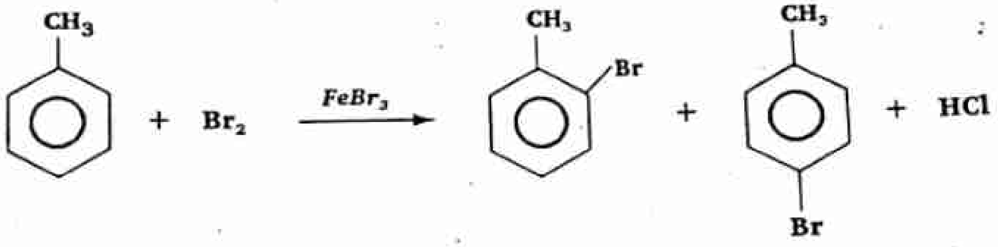
$$\begin{array}{c} CH_3-CH-CH_2-OH \\ | \\ CH_3 \end{array} + SOCl_2 \xrightarrow{Pyridine} \begin{array}{c} CH_3-CH_2-CH_2-Cl \\ | \\ CH_3 \end{array} + SO_2 + HCl$$

6.2.2. Preparation of Halogenobenzene and their Derivatives

1. From Aromatic Hydrocarbons

Chloro- and bromo-derivatives may be prepared by the halogenation of aromatic hydrocarbons in the presence of a Lewis acid catalyst.

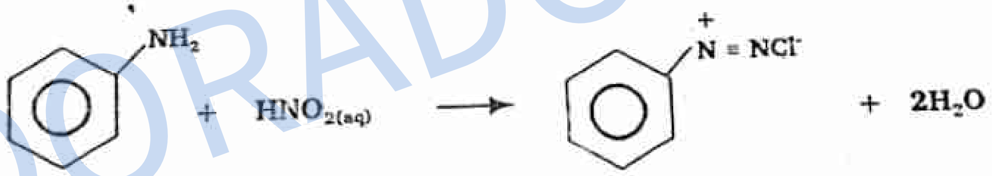




2. From Diazonium Salts

The reaction of aromatic primary amines with a mixture of sodium dioxonitrate (II) and dilute acids at 0-5°C give diazonium salts. Benzene diazonium chloride for example is prepared by using dilute hydrochloric acid.

$$NaNO_{2(aq)} + HCl_{(aq)} \longrightarrow HNO_{2(aq)} + NaCl_{(aq)}$$



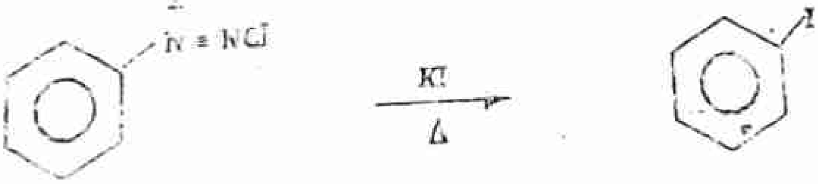
or

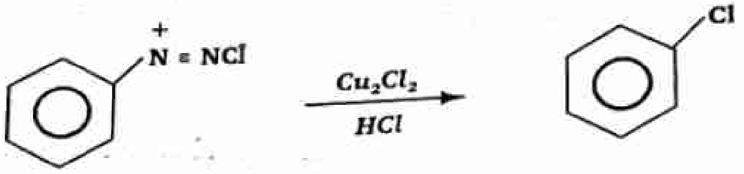
$$C_6H_5NH_2 + HNO_2 \xrightarrow{HCl} C_6H_5N_2Cl + 2H_2O$$

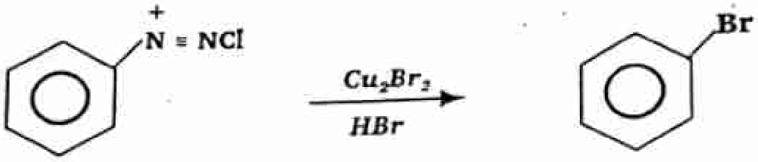
Benzenediazonium chloride

The $-N_2Cl$ group of the benzene diazonium chloride can be replaced by –Cl, –Br or –I group to form halogenobenzene.

Examples:







6.3. PHYSICAL PROPERTIES

The boiling points of the halogenoalkanes are higher than those of alkanes with the same number of carbon atoms. The boiling point of a given halogenoalkane increases as the atomic mass of the halogen increases, thus fluorides have the lowest boiling points while the iodides have the highest boiling points. They are insoluble in water, but soluble in organic solvents.

The physical properties of unsubstituted halogenobenzenes are very much like the corresponding halogenoalkanes. For example, the boiling points of chlorobenzene and bromobenzene are nearly the same as those of chlorohexane, and bromohexane respectively. Halogenobenzenes are also insoluble in water but soluble in organic solvents.

6.4. CHEMICAL PROPERTIES

6.4.1. Halogenoalkanes

1. Nucelophilic Substitution

The typical reactions of halogenoalkanes are nucleophilic substitution reactions, whereby the halogen atom is replaced by nucleophiles. The nucleophiles are either negative ions or neutral bases (these have lone pairs of electrons). Examples include:

$$\overline{\text{O}}\text{H},\ \overline{\text{C}}\text{N},\ \overline{\text{O}}\text{R},\ \text{NH}_3,\ \text{H}_2\text{O},\ \text{R-OH}\ \ \text{etc.}$$

Often the R–X bond is converted into R–O, R–C and R–N bonds. This conversion makes the halogenoalkanes very useful in organic synthesis.

The nucleophilic substitution reaction can be represented as

$$\text{R-X} + \overline{\text{Y}} \rightarrow \text{R-Y} + \overline{\text{X}} \quad \text{or}$$
$$\text{R-X} + \text{H-Y:} \rightarrow \text{R-Y} + \text{H-X}$$

a. *with aqueous alkali*

$$C_2H_5Br + \bar{O}H \rightarrow C_2H_5OH + \bar{Br}$$

b. *with sodium alkoxide in ethanol*

$$C_2H_5Br + CH_3CH_2\bar{O} \rightarrow C_2H_2OC_2H_5 + \bar{Br}$$

c. *with hot alkali metal cyanide in ethanol*

$$C_2H_5Br + \bar{C}N \rightarrow C_2H_5CN + \bar{Br}$$

d. *with ammonia in ethanol*

$$C_2H_5Br + NH_3 \rightarrow C_2H_5NH_2 + HBr$$

e. *with hot water*

$$C_2H_5Br + H_2O \rightarrow C_2H_5OH + HBr$$

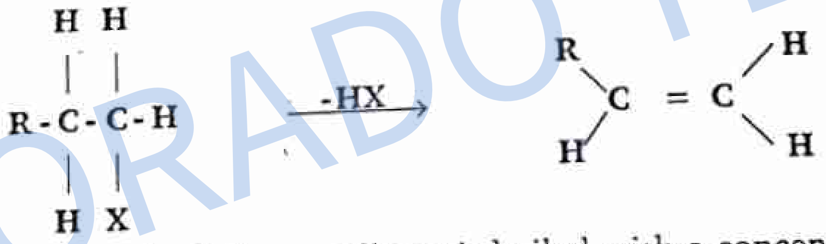
f. *with Na or Ag ethanoate*

$$C_2H_5Br + CH_3CO\bar{O} \rightarrow C_2H_5OOCCH_3$$

Generally, the rate of reaction is iodides> bromides> chlorides> flu
This is because the rate of reaction is determined by the ability of the hali
which are replaced to be relatively stable. They are stable if they are weak base
order of basic strength of the halides is $F^- > Cl^- > Br^- > I^-$.

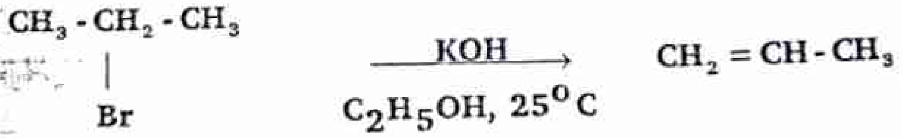
2. **Elimination Reaction**

Halogenoalkanes undergo elimination reaction. A molecule of hy
halide is eliminated, an alkene is formed, for example

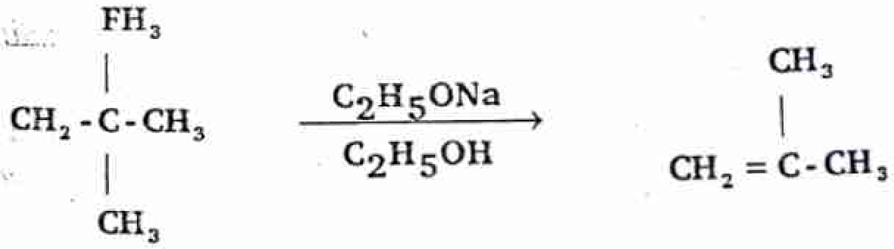


This reaction occurs when the halogenoalkane is boiled with a concentrated solu
a strong base in ethanol. The bases used include **KOH, NaOH, C_2H_5ONa** and pot
2-methylpropoxide (potassium ter-butoxide).

Examples



$$CH_3-\underset{\displaystyle Br}{\underset{|}{CH_2}}-CH_3 \xrightarrow[C_2H_5OH,\ 25^\circ C]{KOH} CH_2=CH-CH_3$$



$$CH_2-\overset{\displaystyle FH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-CH_3 \xrightarrow[C_2H_5OH]{C_2H_5ONa} CH_2=\overset{\displaystyle CH_3}{\overset{|}{C}}-CH_3$$

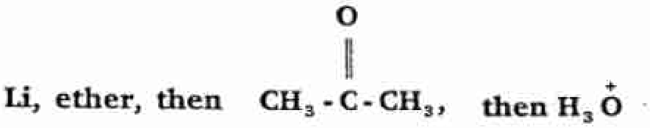
REVIEW QUESTIONS

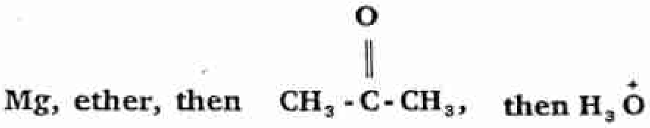
1. With the aid of chemical equations, show how the following can be prepared from any organic halogen compound.

a. *Butan - 2 - ol*
b. *Ethylbenzene*
c. *2 - methylpropene*
d. *2 - methylethoxypropane*
e. *But - 1 - ene*
f. *Propyne*

2. What product would be formed from the reaction of 1-bromo-2-methylpropane with each of the following reagents?

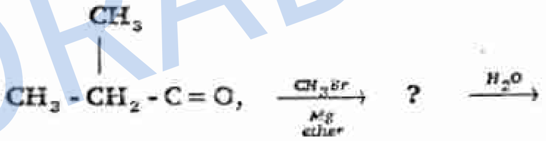
a. $\bar{O}H,\ H_2O$
b. $\bar{C}N$, *alkanol*
c. $(CH_3)_3C\bar{O},\ (CH_3)_3COH$
d. $CH_3\bar{O},\ CH_3OH$

e.

$$\text{Li, ether, then}\ CH_3-\overset{\overset{\Large O}{\|}}{C}-CH_3,\ \text{then}\ H_3\overset{+}{O}$$

f.

$$\text{Mg, ether, then}\ CH_3-\overset{\overset{\Large O}{\|}}{C}-CH_3,\ \text{then}\ H_3\overset{+}{O}$$

3. Write the product for each of the following reactions:

a. $C_6H_5CHICH_3 + NaOH \longrightarrow$
b. $C_6H_5CH_2I + NaOH \longrightarrow$
c. $CH_3CH_2CH_2I + KCN \xrightarrow{\text{ethanol}}$
d. $CH_3CHICH_2CH_3 + CH_3ONa \xrightarrow{CH_3OH}$

e.

$$CH_3-\underset{\displaystyle CH_2}{\overset{\displaystyle CH_3\ \ }{}}\!\!-C=O,\ \xrightarrow[\text{Mg ether}]{CH_3Br}\ ?\ \xrightarrow{H_2O}$$

4. Identify compounds A, B and C with molecular formular C_4H_9Br using the information provided below:

a. *'A' was hydrolysed with dilute sodium hydroxide solution to $C_4H_{10}O$ which when oxidized gave a compound C_4H_8O. On warming C_4H_8O with iodine and aqueous alkali, a yellow precipitate was obtained.*

b. *Hydrolysis of 'B' gave a compound which was stable in alkaline $KMnO_4$.*

c. *Elimination of HBr from 'C' by concentrated KOH solution in ethanol gave a hydrocarbon C_4H_8 which was oxidized to a compound with formular $C_3H_6O_2$.*

Chapter 7

ALKANOLS

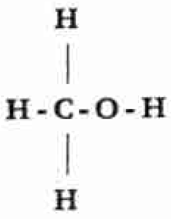
7.1. INTRODUCTION

The alkanols are the organic compounds with the hydroxyl (—OH) functional group.

7.1. TYPES

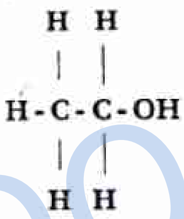
1. Monohydric Alkanols

Monohydric alkanols have one hydroxyl group, for example,



$$\mathrm{H-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-O-H}$$

Methanol

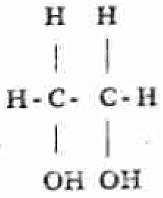


$$\mathrm{H-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-OH}$$

Ethanol

2. Dihydric alkanols (Diols)

Dihydric alkanols have two hydroxyl groups, for example

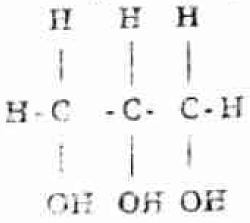


$$\mathrm{H-\overset{\displaystyle H}{\underset{\displaystyle OH}{C}}-\overset{\displaystyle H}{\underset{\displaystyle OH}{C}}-H}$$

Ethane - 1 - 2 - diol

3. Trihydric alkanols

Trihydric alkanols have three hydroxyl groups, for example



$$\mathrm{H-\overset{\displaystyle H}{\underset{\displaystyle OH}{C}}-\overset{\displaystyle H}{\underset{\displaystyle OH}{C}}-\overset{\displaystyle H}{\underset{\displaystyle OH}{C}}-H}$$

Propan - 1, 2, 3 - triol

4. **Polyhydrc compounds**

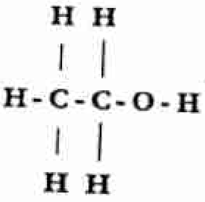
Polyhydric compounds have more than three hydroxyl groups, for example, $CH_2OH(CHOH)_4CHO$, glucose.

7.2. MONOHYDRIC ALKANOLS

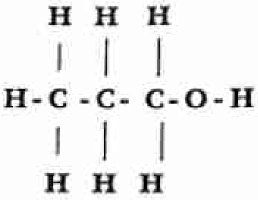
7.2.1. Classification

1 **Primary Alkanols**

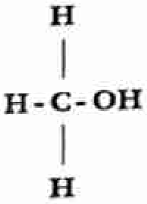
In the primary alkanols, the carbon atom, which has the hydroxyl group, is attached to one alkyl group, or to two hydrogen atoms, for example.



Ethanol



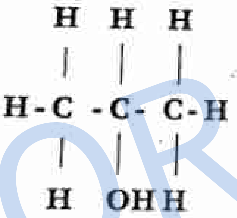
Propan-1-ol



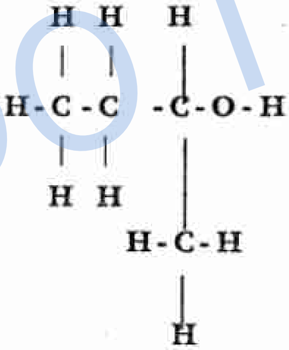
Methanol

2. **Secondary Alkanols**

In the secondary alkanols, the carbon atom which has the hydroxyl group is attached to two alkyl groups, or to one hydrogen atom, for example.



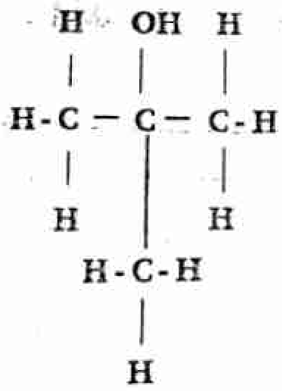
Propan-2-ol



Butan-2-ol

3. **Tertiary Alkanols**

In the tertiary alkanols, the carbon atom, which has the hydroxyl group, is attached to three alkyl groups or to no hydrogen atom for example,



2-methylpropan-2-ol

7.2.2. Preparation

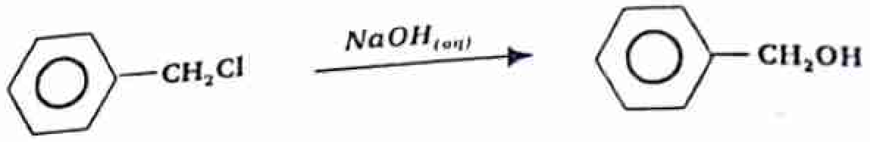
1. **By Hydrolysis of Halogenoalkanes**

This is achieved using any alkali or silver oxide, Ag_2O mixed with water

$$R-X \xrightarrow{OH^-} R-OH + X$$

Examples

$$CH_3CH_2CH_2Br + OH \rightarrow CH_3CH_2CH_2OH + \bar{Br}$$



Phenylmethychloride (benzyl chloride)

Phenylmethanol (benzyl alcohol)

2. **Hydrolysis of an alkanoate with an alkali**

$$RCOOR^1 + \bar{O}H \rightarrow RCOO^- + R^1OH$$

Alkanoate		Salt of acid	Parent alkanol

xample

$$CH_3COOC_2H_5 + NaOH \rightarrow CH_3COONa + C_2H_5OH$$

By Reduction of Carbonyl Compounds

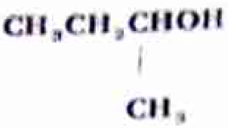
Alkanals are reduced to primary alkanols. Alkanones are reduced secondary alkanols. Alkanoates are reduced to a mixture of two alka Any of the following reducing agents can be used: ***sodium in ethanol, m in acid, for example Zn/HCl, Lithium tetrahydridoaluminate (III), Li and catalytic hydrogenation.***

$$CH_3-CHO + 2[H] \xrightarrow{Zn/HCl} CH_3CH_2OH$$

Ethanal **Ethanol**

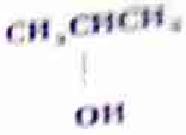
$$CH_3-CO-CH_3 + 2[H] \xrightarrow[ether]{LiAlH} CH_3-CH(OH)-CH_3$$

Propanone **Propan-2-ol**



$$\underset{CH_3}{CH_3CH_2CHOH}$$

108°C



$$\underset{OH}{CH_3CHCH_3}$$

Therefore, if isomeric alkanols are compared, the order of boiling points primary > secondary > tertiary. for example:

Hexan-1-ol	156°C
Hexan-3-ol	135°C
2-methypentan-2-ol	121°C

Polyhydric alkanols provide more than one site for hydrogen-bonding i molecule and as such have higher boiling points. For example, ethane- 1, 2-diol b at 198°C and is completely miscible with water while ethanol boils at 78°C. Etha 1, 2-diol owes its usefulness as antifreeze to its high boiling point, low freezing p and high solubility in water.

7.3.2. Chemical Properties

1. Acid - Base Properties

Alkanols can be regarded as alkyl substituted water. Like water they amphoteric.

Acid character: $R-OH + \bar{B} \rightleftharpoons \overset{+}{B}H + R\bar{O}$

Basic character:

$$R-OH + HA \rightleftharpoons \underset{H}{R-\overset{+}{O}-H} + \bar{A}$$

Alkyl groups are electron releasing. Therefore alkanols are less acidic water. They are very weak acids and react as acids only with very strong b for example,

$$C_2H_5OH + \underset{\textit{Sodamide}}{NaNH_2} \longrightarrow C_2H_5ONa + NH_3$$

$$C_2H_5OH + \underset{\textit{Sodium hydride}}{NaH} \longrightarrow C_2H_5ONa + H_2$$

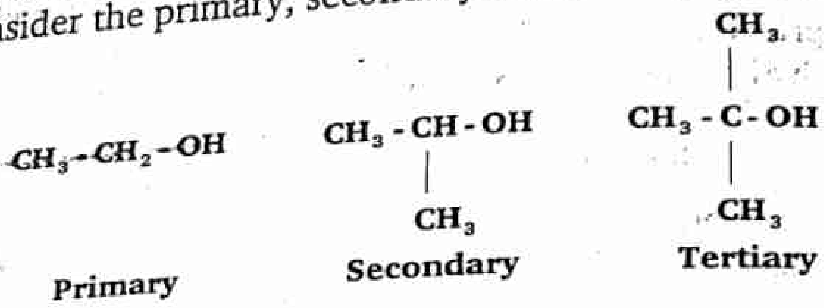
The acidic nature of alkanols is illustrated by their reactions with active (Na, K, Zn) to liberate hydrogen, for example,

$$2C_2H_5OH + 2Na \longrightarrow \underset{\text{Sodium ethoxide}}{2C_2H_5ONa} + H_2$$

This reaction can sometimes be used to produce hydrogen for reduction purpo

Order of Acidity

Consider the primary, secondary and tertiary alkanols below:



CH_3-CH_2-OH Primary

$CH_3-CH(CH_3)-OH$ Secondary

$CH_3-C(CH_3)_2-OH$ Tertiary

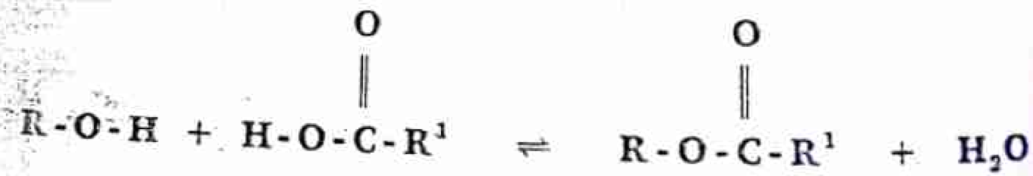
Methyl group has +1 effect and therefore pushes electrons to oxygen atom. oxygen atom of the tertiary alkanol has the highest density of negative charge is followed by that of the secondary alkanol. Therefore, the hydrogen atom i tertiary alkanol is most strongly held and is the least acidic. The order of acidi primary > secondary>tertiary. The oxygen atom in the tertiary alkanol ha strongest attraction for a proton. Therefore, the order of basic strength is tertiary > secondary > primary.

2. Esterification

Alkanols react with alkanoic acids to form alkanoates. The reactio catalysed by strong acids such as concentrated tetraoxosulphate (VI) acid, example,

$$C_2H_5OH + CH_3COOH \underset{}{\overset{Conc.\ H_2SO_4}{\rightleftharpoons}} \underset{\text{Ethyl ethanoate}}{CH_3COOC_2H_5} + H_2O$$

The reaction involves loss of a hydrogen atom, not a hydroxyl group from t alkanol.



$$R-O-H + H-O-\overset{\overset{\displaystyle O}{\|}}{C}-R^1 \rightleftharpoons R-O-\overset{\overset{\displaystyle O}{\|}}{C}-R^1 + H_2O$$

Alkanols also react with acid chlorides and anhydrides to form alkanoates. Th esterification process is faster than the reaction of alkanol and alkanoic ac for example,

$$C_2H_5OH + CH_3COCl \longrightarrow CH_3COOC_2H_5 + HCl$$

$$C_2H_5OH + (CH_3CO)_2O \longrightarrow CH_3COOC_2H_5 + CH_3COOH$$

3. Reaction with Hydrogen Halide

Alkanols react with hydrogen halide to form halogenoalkanes and water. The reaction is carried out either by passing the dry hydrogen halide gas into the alkanol or by heating the alkanol with the concentrated aqueous acid. Hydrogen chloride is the least reactive and requires the presence of zinc chloride for primary and secondary alkanols. Tertiary alkanols react with concentrated hydrochloric acid at room temperature.

$$R - OH + HX \longrightarrow R - X + H_2O$$

Inorganic halides of non-metals such as PCl_5, PCl_3 and $SOCl_2$ also react with alkanols to form halogenoalkanes.

Examples

$$CH_3CH_2CH_2OH + PCl_5 \qquad CH_3CH_2CH_2Cl + POCl_3 + HCl$$

$$\underset{CH_3}{CH_3CHCH_2OH} + SOCl_2 \qquad \underset{CH_3}{CH_3-CHCH_2Cl} + SO_2 + HCl$$

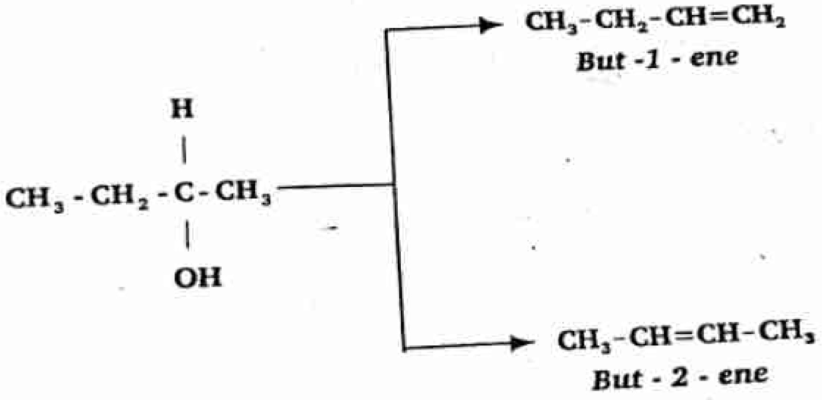
4. Dehydration

Alkanols are dehydrated to alkenes by excess concentrated tetraoxosulphate (VI) acid at 170°C or by alumina, Al_2O_3 at 350°C (vapour phase dehydration) to alkenes.

$$R-\underset{R\ R}{\overset{H\ OH}{C-C}}-R \longrightarrow R-\underset{R\ \ R}{C=C}-R + H_2O$$

Mechanism

Since the stabilities of the carbocations formed are in the order tertiary > secondary > primary, the relative rates of dehydration are in the same order. When there are two carbon atoms adjacent to the carbon atom with the hydroxyl group, then two dehydration products are possible, for example;



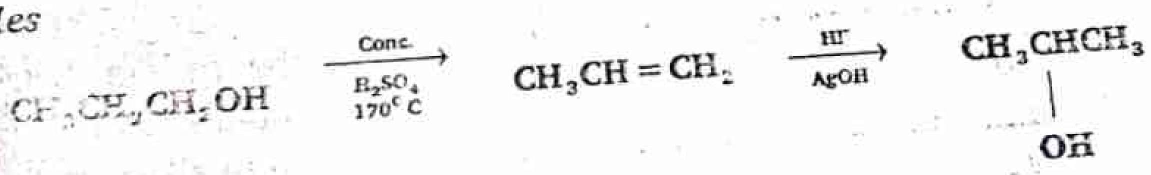
Which predominates? We apply **Saytzeff''s rule** to find the answer. Saytzeff's rule states that ***the carbon with the least number of hydrogen atoms will lose the proton (this applies also to the elimination of hydrogen halide from halogenoalkanes).*** Thus the dehydration of butan-2-ol produces but-2-ene rather than but-1-ene.

At 140°C and in the presence of excess alkanol, the alkanol is converted to alkoxyalkane e.g.

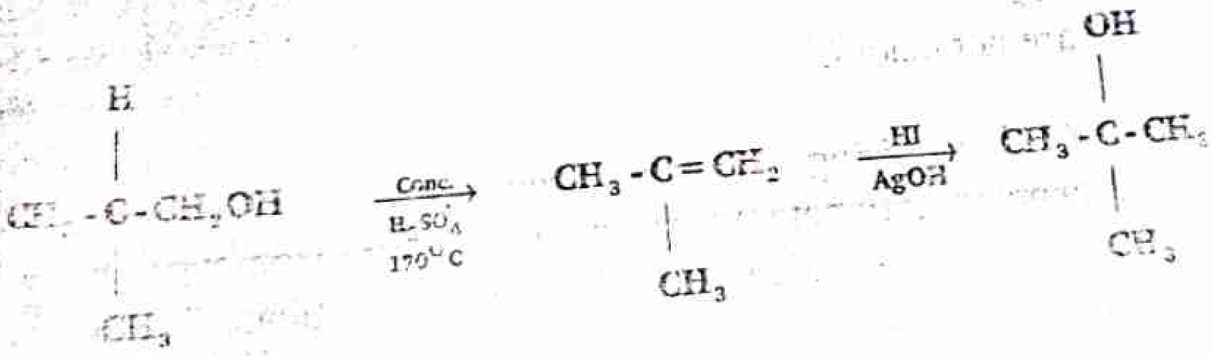
$$2C_2H_5OH \xrightarrow{Conc.\ H_2SO_4} C_2H_5OC_2H_5 + H_2O$$

Dehydration of alkanols can be used to transform primary alkanols to secondary or tertiary alkanols and secondary to tertiary.

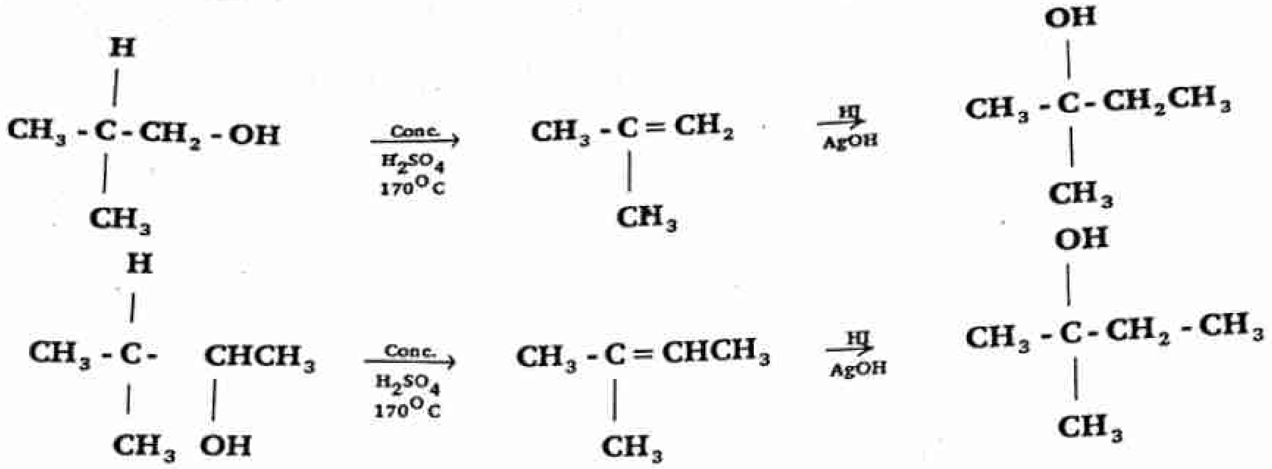
Examples



$$CH_3CH_2CH_2OH \xrightarrow[H_2SO_4,\ 170^\circ C]{Conc.} CH_3CH=CH_2 \xrightarrow[AgOH]{HI} CH_3\underset{\underset{OH}{|}}{C}HCH_3$$



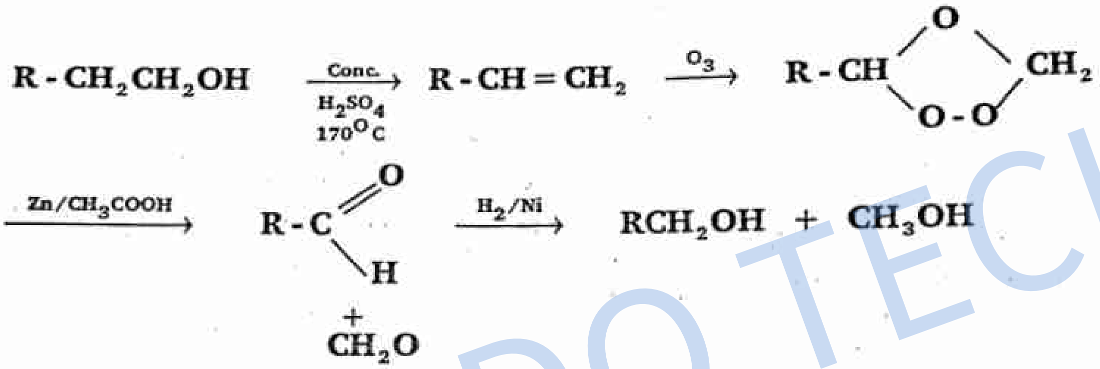
$$CH_3-\overset{\overset{H}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2OH \xrightarrow[H_2SO_4,\ 170^\circ C]{Conc.} CH_3-\underset{\underset{CH_3}{|}}{C}=CH_2 \xrightarrow[AgOH]{HI} CH_3-\overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3$$



$$CH_3-\overset{H}{\underset{CH_3}{C}}-CH_2-OH \xrightarrow[170^{o}C]{Conc.\ H_2SO_4} CH_3-\underset{CH_3}{C}=CH_2 \xrightarrow[AgOH]{HI} CH_3-\overset{OH}{\underset{CH_3}{C}}-CH_2CH_3$$

$$CH_3-\overset{H}{\underset{CH_3}{C}}-\underset{OH}{CHCH_3} \xrightarrow[170^{o}C]{Conc.\ H_2SO_4} CH_3-\underset{CH_3}{C}=CHCH_3 \xrightarrow[AgOH]{HI} CH_3-\overset{OH}{\underset{CH_3}{C}}-CH_2-CH_3$$

It can also be used to step down an alkanol i.e. to produce an alkanol containing lower number of carbon atoms, for example,



$$R-CH_2CH_2OH \xrightarrow[170^{o}C]{Conc.\ H_2SO_4} R-CH=CH_2 \xrightarrow{O_3} R-CH\langle O,\ O-O\rangle CH_2 \xrightarrow{Zn/CH_3COOH} R-C\overset{O}{\underset{H}{}} + CH_2O \xrightarrow{H_2/Ni} RCH_2OH + CH_3OH$$

5. Oxidation

a. Alkanols burn in air to form carbon (IV) oxide and water, for example,

$$C_2H_5OH(l) + 3O_{2(g)} \longrightarrow 2CO_{2(g)} + 3H_2O_{(ag)}$$

b. Primary and secondary alkanols are also oxidized by loss of hydrogen to alkanals and alkanones respectively. The hydrogen atom of the hydroxyl group together with that from the carbon bearing the hydroxyl groups are lost. When primary alkanols are oxidized, the initial alkanal formed may be further oxidized to alkanoic acid. This happens particularly when the oxidizing agent is in excess. Alkanones are not oxidised.

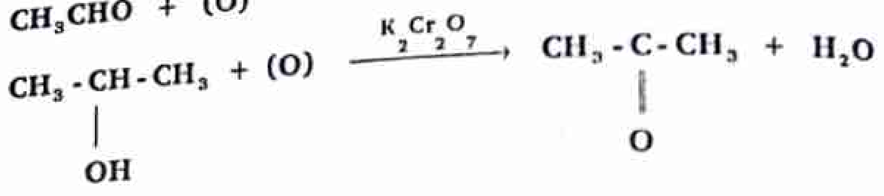
The oxidizing agents used include acidified potassium heptaoxochromate (VI) and potassium tetraoxomanganate (VII). They are usually acidified with dilute tetraoxosulphate (VI) acid.

Tertiary alkanols have no hydrogen atom on the carbon a bearing the hydroxyl group and are not readily oxidized wit oxidizing agents mentioned above. Oxidation of tertiary alka under forcing conditions fragments the carbon skeleton. T reaction is of little synthetic utility.

Example

$CH_3CH_2OH + (O) \xrightarrow{KMnO_4} CH_3CHO + H_2O$

$CH_3CHO + (O) \xrightarrow{KMnO_4} CH_3COOH$



$CH_3-\underset{\underset{OH}{|}}{CH}-CH_3 + (O) \xrightarrow{K_2Cr_2O_7} CH_3-\underset{\underset{O}{\|}}{C}-CH_3 + H_2O$

7.4. DISTINCTION BETWEEN PRIMARY, SECONDARY AND TERTIARY ALKANOLS

The Lucas Test

The Lucas reagent is a cold solution of 13.6g anhydrous $ZnCl_2$ in 10 concentrated hydrochloric acid. The test depends upon the different rate formation of the chloroalkanes upon treatment with Lucas reagent ($HCl - ZnCl_2$).

To 1cm^3 of the alkanol in a small test tube add quickly about 6cm^3 of t Lucas reagent. Close the tube with a cork. Shake and allow to stand. Obser the mixture for five minutes. The following results may be obtained.

i. *If the solution remains clear, it shows the alkanol is primary*

ii. *If the solution becomes cloudy in five minutes, the alkanol is second*

iii. *If an immediate white precipitate is observed, the alkanol is tertiary*

REVIEW QUESTIONS

1. A compound analysed for **C** 64.89% and **H** 13.59%. If the molecular mass of the compound is 74.
   a. *What is the molecular formula of the compound?*
   b. *Write down the structural formulae of all the isomers with the molecul formula.*

c. *How would you distinguish between the isomers?*

d. *Use chemical equations to show how you would convert the isomers were possible to named alkanes.*

2. a. Give the structure and name of

i. *a primary alkanol:*
ii. *a secondary alkanol*
iii. *a tertiary alkanol.*

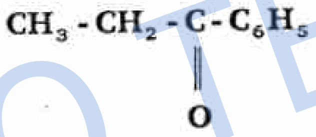
b. Give one method of preparation of the alkanol named in (a) above.

3. Complete the following reaction schemes.

(a) $C_2H_3\text{-}COOH \xrightarrow{?} C_2H_5CH_2OH$

(b) $CH_3CH=CHCHO \xrightarrow{H_2/Ni}$?

(c) ? $\xrightarrow[H_2SO_4]{KMnO_4}$



$CH_3\text{-}CH_2\text{-}C(=O)\text{-}C_6H_5$

(d) $CH_3CH(CH_3)CH(OH)CH_3 \xrightarrow[\Delta]{Al_2O_3}$?

(e) $CH_3COOH + CH_3CH_2CH_2OH \xrightarrow{H^+}$?

(f) $CH_3CH(OH)CH_2CH_3 + K_2Cr_2O_7 \xrightarrow{H_2SO_4}$?

4. Arrange the following in order of increasing boiling points and explain the order. Butan-2-ol, pentane, butan-1-ol and 2-methylbutane.

Chapter 8

ALKANALS AND ALKANONES

8.1. INTRODUCTION

Alkanals and alkanones have the carbonyl functional group $>C=O$. In alkanals, the functional group is terminal while it is within the structure of alkanones. The general formula of alkanals is RCHO, 

$$R-\overset{O}{\overset{\|}{C}}-H$$

, where R is an alkyl or phenyl group. The simplest alkanal is methanal, HCHO (R=H). Alkanones have the general formula $RCOR^1$, 

$$R-\overset{O}{\overset{\|}{C}}-R'$$

, where $R=R^1$, $R \neq R^1$, R or R^1 = alkyl or phenyl group and never hydrogen. The simplest alkanone is propanone CH_3-CO-CH_3 ($R=R^1=CH_3$). Since both alkanals and alkanones contain the carbonyl group, they are called carbonyl compounds. This functional group determines to a great extent the chemistry of alkanals and alkanones. Therefore, they have similar chemical properties. Differences in reactivity exist because the carbonyl carbon is attached to two hydrogen atoms in methanal, one alkyl group in other alkanals and two alkyl groups in alkanones.

8.2. METHODS OF PREPARATION

8.2.1. Alkanals

1. *Oxidation of Primary Alkanols*

i. Primary alkanols are easily oxidized to alkanals *(see also section 7.3.2.)*. The common oxidizing agent used is potassium tetraoxomanganate (VII) or sodium heptaoxochromate (VI) acidified with tetraoxosulphate (VI) acid. Because the alkanal formed is easily oxidized to alkanoic acid, it is necessary to remove it as it is formed. This is achieved by dropping the alkanol on the heated oxidizing agent. The alkanal vapour formed is distilled off.

$$R\text{-}CH_2OH + (O) \longrightarrow RCHO + H_2O$$

b. At 300° – 350°C, primary alkanols may be dehydrogenated usin a copper catalyst to alkanals.

$$R\text{-}CH_2OH \xrightarrow[300^\circ - 350^\circ C]{Cu} RCHO + H_2$$

The hydrogen molecule is the hydrogen atom of *–OH* group an the hydrogen atom attached to the carbon atom bearing the *–OH* group.

2. **Reduction of acid Chlorides (Rosenmund reaction)**

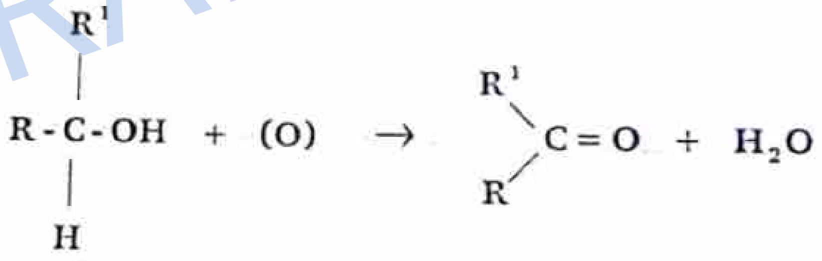
Alkanals can also be prepared by the reduction of acid chlorides. Th acid chloride is hydrogenated in presence of palladium catalyst, whic is poisoned by barium tetraoxosulphate (VI). The catalyst is poisone to prevent further reduction of the alkanal to primary alkanol.

$$R\text{-}COCl + H_2 \xrightarrow{Pd/BaSO_4} RCHO + HCl$$

8.2.2. Alkanones

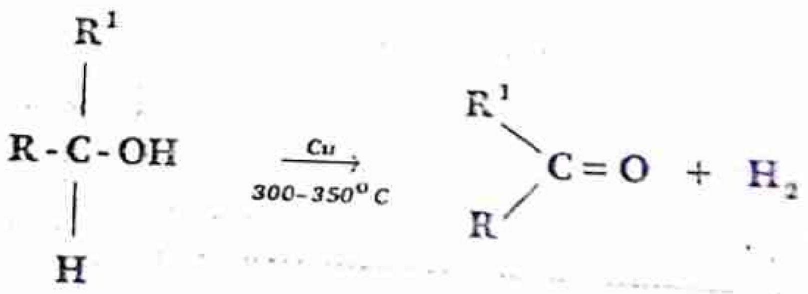
1. **Oxidation of Secondary Alkanols**

Secondary alkanols are also easily oxidized, and alkanones ar obtained.



$$R\text{-}\underset{H}{\overset{R^1}{C}}\text{-}OH + (O) \rightarrow R^1R\,C=O + H_2O$$

At 300 – 350°C secondary alkanols can also be dehydrogenated in t presence of copper to alkanones.



$$R\text{-}\underset{H}{\overset{R^1}{C}}\text{-}OH \xrightarrow[300-350^\circ C]{Cu} R^1R\,C=O + H_2$$

8.4. GENERAL PROPERTIES OF ALKANALS AND ALKANONES

8.4.1. Physical Properties

They have lower boiling points than comparable alkanols because the form intermolecular hydrogen bonds formed by alkanols. They can not do this the hydrogen is bonded only to carbon (alkanals). For example, butanal has a point of 76°C and butanone boils at 80°C whereas butan-l-ol boils at 118°C.

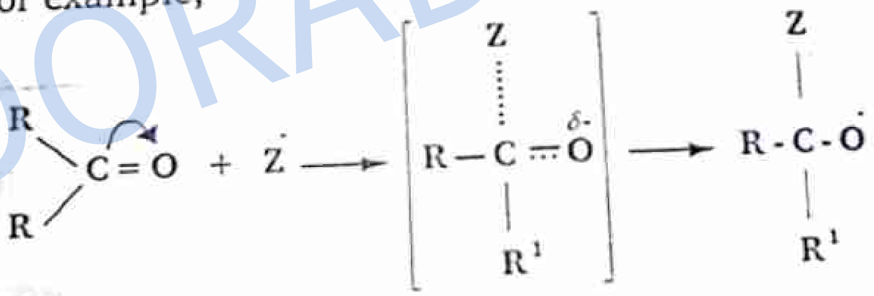
They have higher boiling points than alkanes of comparable mo weight because the presence of the polar carbonyl group makes the compounds. Polar compounds have higher boiling points than no compounds. For example, the boiling points of pentane, butanal and butan the same molecular mass) are 36°C, 76°C and 80°C respectively.

The lower members are completely miscible with water, but the decreases from the five-carbon members.

8.4.2. Chemical Properties

1. Nucleophilic Attack on C=O Bond

The chemistry of alkanals and alkanones is determined by the carbo The carbonyl group governs the chemistry of alkanals and alkanones by pro for nucleophilic addition and by increasing the acidity of the alpha carb These effects are due to the electronegativity of the oxygen atom, which ma to accommodate a negative charge. The nucleophile attacks the electron carbon atom, for example,

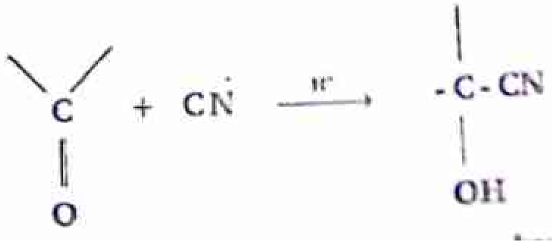


Transition state

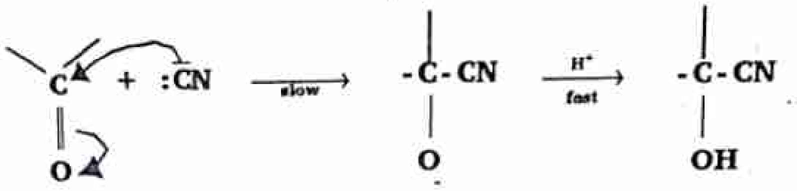
Alkanals generally undergo nucleophilic addition more than alkanones. We sh look at the examples of nucleophilic addition of alkanals and alkanones.

(a) Addition of Cyanide

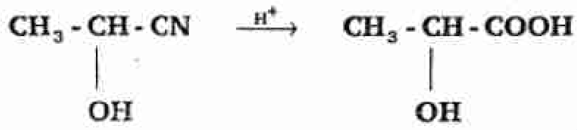
Hydrogen cyanide adds to the carbonyl group of alkanals and alk to form cyanohydrins.



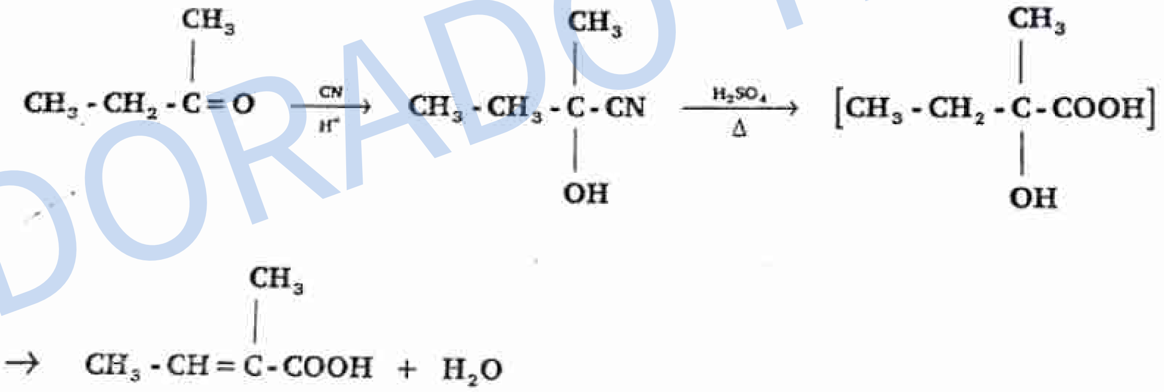
The reaction is often carried out by adding a mineral acid to a mixture of the carbonyl compound and aqueous sodium cyanide. The mechanism involves the nucleophilic attack of the carbonyl carbon by the basic ion followed by the rapid addition of the proton.



Cyanohydrins when hydrolysed give α -hydroxy acids or unsaturated acids. For example:



$$CH_3-\underset{\underset{\textstyle OH}{|}}{CH}-CN \xrightarrow{H^+} CH_3-\underset{\underset{\textstyle OH}{|}}{CH}-COOH$$

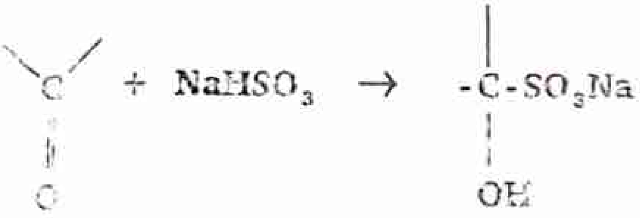


$$CH_3-CH_2-\overset{\overset{\textstyle CH_3}{|}}{C}=O \xrightarrow[H^+]{CN^-} CH_3-CH_3-\overset{\overset{\textstyle CH_3}{|}}{\underset{\underset{\textstyle OH}{|}}{C}}-CN \xrightarrow[\Delta]{H_2SO_4} [CH_3-CH_2-\overset{\overset{\textstyle CH_3}{|}}{\underset{\underset{\textstyle OH}{|}}{C}}-COOH]$$

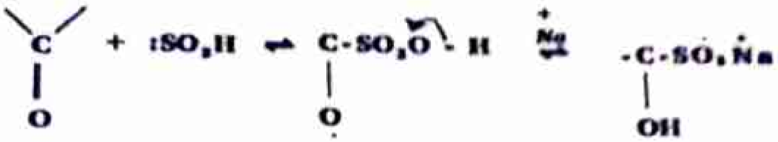
$$\rightarrow CH_3-CH=\overset{\overset{\textstyle CH_3}{|}}{C}-COOH + H_2O$$

5. Addition of Sodium Hydrogentrioxosulphate (IV), $NaHSO_3$.

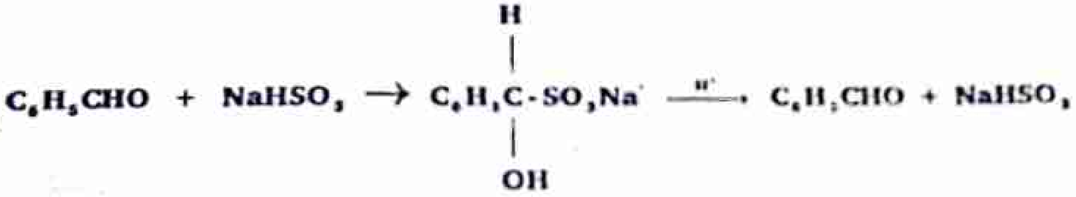
Alkanals and alkanones form addition compounds with $NaHSO_3$. Th reaction is carried out by mixing concentrated solution of $NaHSO_3$ with th alkanal or alkanone. The reaction involves the attack of the carbonyl carbon b the nucleophilic reagent, SO_3H, followed by the addition of hydrogen ion to th carbonyl oxygen.



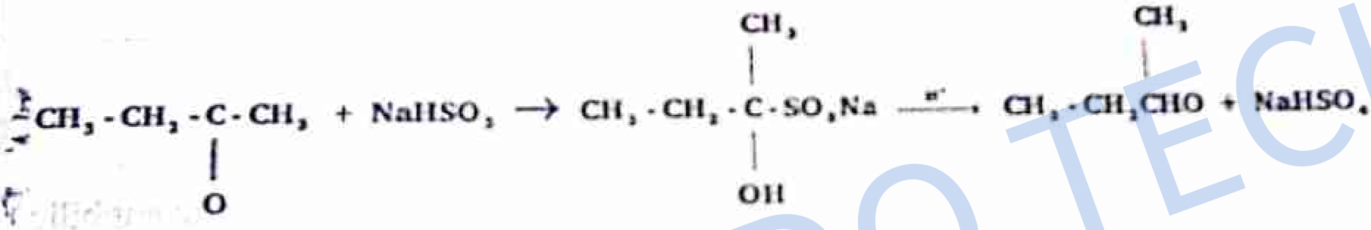
$$\underset{\underset{\textstyle O}{\|}}{C} + NaHSO_3 \rightarrow -\overset{|}{\underset{\underset{\textstyle OH}{|}}{C}}-SO_3Na$$



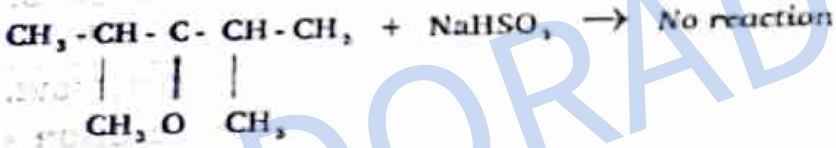
The addition product separates as a crystalline solid. Alkanones containing bulky groups do not react with $NaHSO_3$ because of steric hindrance. The hydrogen trioxosulphate (IV) addition products are generally prepared to separate a carbonyl compound from a non-carbonyl compound. The crystalline addition compound separated from the non-carbonyl compound when acidified regenerates the carbonyl compound. For example,



$$C_6H_5CHO + NaHSO_3 \rightarrow C_6H_5\overset{\displaystyle H}{\underset{\displaystyle OH}{C}}-SO_3Na \xrightarrow{H^+} C_6H_5CHO + NaHSO_3$$



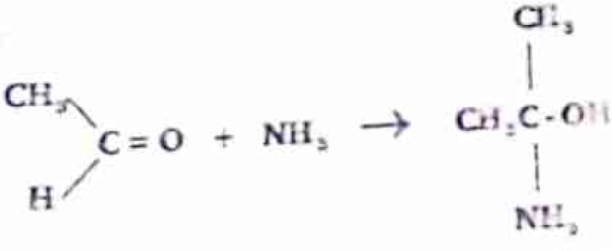
$$CH_3-CH_2-\underset{\displaystyle O}{C}-CH_3 + NaHSO_3 \rightarrow CH_3-CH_2-\overset{\displaystyle CH_3}{\underset{\displaystyle OH}{C}}-SO_3Na \xrightarrow{H^+} CH_3-\overset{\displaystyle CH_3}{CH_2}CHO + NaHSO_3$$



$$CH_3-\underset{\displaystyle CH_3}{CH}-\underset{\displaystyle O}{C}-\underset{\displaystyle CH_3}{CH}-CH_3 + NaHSO_3 \rightarrow \textit{No reaction}$$

c. Addition of Ammonia

Alkanals and alkanones react with ammonia to form hydroxyamines but the reaction of ammonia and methanal yields hexamine.



2-amino-2-hydroxypropane

$$6HCHO + 4NH_3 \rightarrow (CH_2)_6N_4 + 6H_2O$$

Hexamine

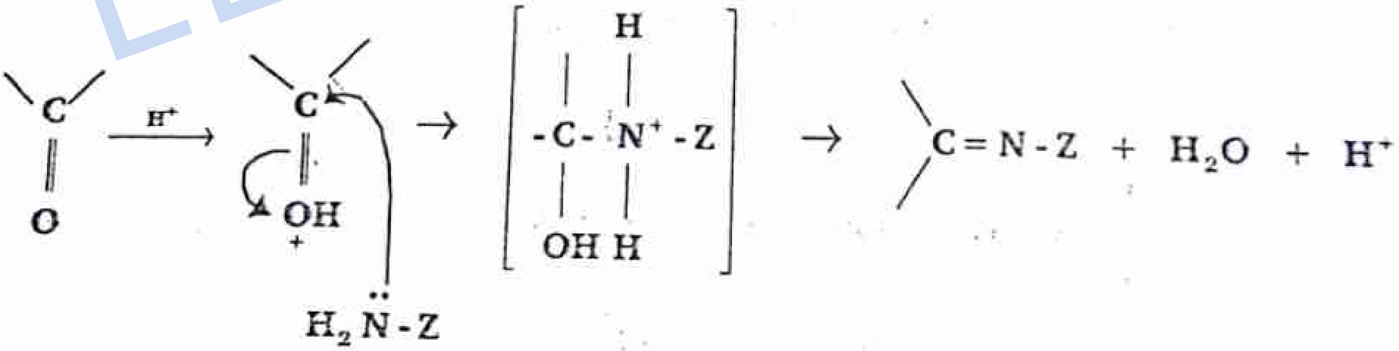
d. Addition of Ammonia Derivatives

The derivatives of ammonia are compounds of the form NH_2-Z. H_2N-Z compounds used and products formed are:

H_2N-OH →	$>C=NOH$
Hydroxylamine	*Oxime*
H_2N-NH_2 →	$>C=N-NH_2$
Hydrazine	*Hydrazone*
$H_2N-NHC_6H_5$ →	$>C=N-NH-C_6H_5$
Phenylhydrazine	*Phenylhydrazone*
$H_2N-NHCOC_6H_5$ →	$>C=N-NHCOC_6H_5$
Semicarbazide	*Semicarbazone.*

The reaction medium is usually made acidic. This addition involves nucleophilic ttack by the basic nitrogen compound on the carbonyl carbon after protonation of he carbonyl oxygen, which makes the carbonyl carbon more susceptible to ucleophilic attack. Low acidity favours the protonation of the nitrogen compound. hus the right acidity depends on the reagent. These reactions are ***addition - ondensation reactions.***

echanism



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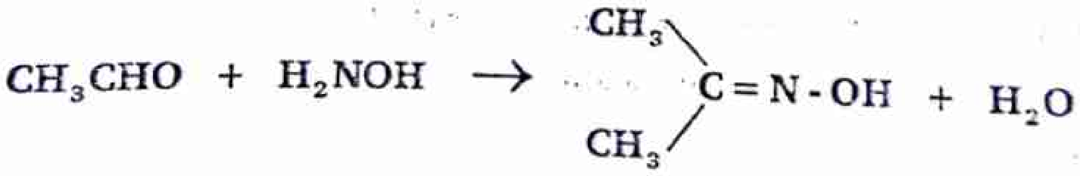
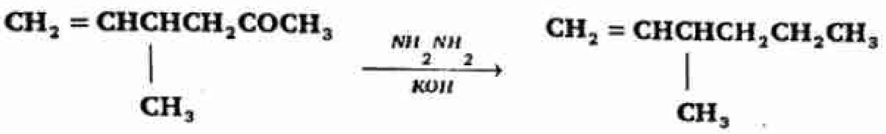


$$CH_3CHO + H_2NOH \rightarrow (CH_3)_2C=N-OH + H_2O$$

(b)



$$CH_2=CH\underset{\underset{CH_3}{|}}{C}HCH_2COCH_3 \xrightarrow[KOH]{NH_2NH_2} CH_2=CH\underset{\underset{CH_3}{|}}{C}HCH_2CH_2CH_3$$

The double bond is sensitive to acid. If the compound is reduced by amalgamated zinc and conc. HCl, the double bond is attacked and saturated by HCl.

3. "The Haloform" Reaction

Alkanals and alkanones containing CH_3CO- group (or alkanols which can be oxidized to it) when warmed with iodine dissolved in KI solution followed by addition of NaOH solution give a pale yellow precipitate with antiseptic smell. The compound formed is triodomethane (iodoform). The reaction is known as iodoform test. For example,

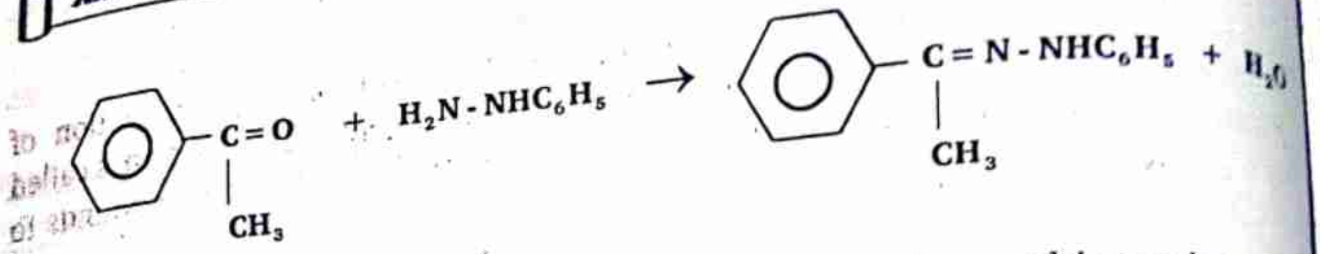
$$CH_3COR \xrightarrow[KI]{I_2} CI_3COR \xrightarrow{NaOH} CHI_3 + RCOONa$$

4. Oxidation of Alkanals and Alkanones

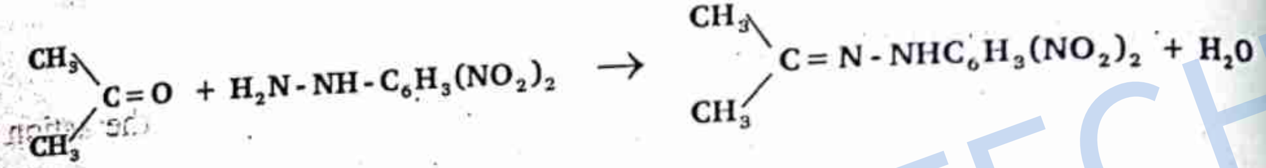
Alkanals are easily oxidized to alkanoic acids but alkanones are not. Oxidation is the main difference between alkanals and alkanones. This difference arises because of the difference in their structures. In oxidation, a proton or hydrogen atom is abstracted from the carbonyl carbon. Alkanals have a hydrogen atom attached to the carbonyl carbon whereas alkanones do not. **The oxidizing agents used in the oxidation of alkanals are the very mild reagents such as Tollens'' reagent (ammoniacal $AgNO_3$), cold dilute neutral $KMnO_4$ or $K_2Cr_2O_7$and fehlings solution.** In each of these tests, apart from the formation of alkanoic acids, distinctive colour changes are observed. Tollens reagent gives a deposit of silver (silver mirror) on the inside walls of the test-tube.

$$CH_3CHO + \underset{\textit{Tollen's reagent}}{Ag(NH_3)_2^+} + H_2O \longrightarrow Ag + CH_3COOH + 2N\overset{+}{H_4}$$

The purple colour of $KMnO_4$ is discharged. The orange colour of $K_2Cr_2O_7$ changes to green. A brick red precipitate is formed with fehlings solution.

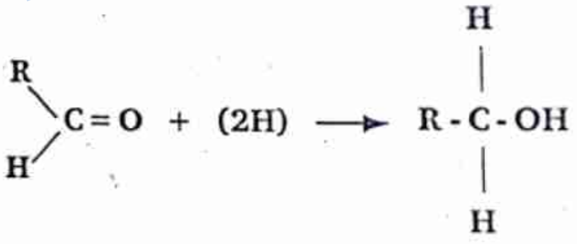


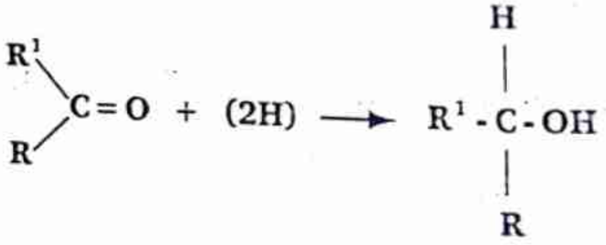
The compounds formed are crystalline solids with convenient melting points. Th are used for the identification of alkanals and alkanones when prepared as the derivatives. The reaction of alkanals or alkanones with 2, 4-dinitrophenylhydrazin gives 2, 4-dinitrophenylhydrazones, which are generally formed rapidly as orange o red crystalline precipitates. This reaction provides a convenient method o identification of carbonyl group.



2. Reduction of Alkanals and Alkanones

a. Alkanals and alkanones undergo reduction to primary and secondary alkanols respectively. The reduction may be catalytic using H_2/Pt. or H_2/Pd or H_2/Ni It can also be achieved by using other reducing agents such as $LiAlH_4$ or $NaBH_4$ or $LiBH_4$. The overall effect is the addition of hydrogen to the C=O bond.





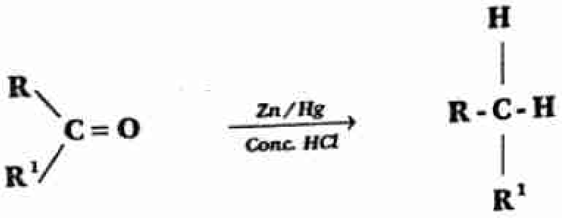
Examples

$$CH_3CH=CHCHO + 2(H) \xrightarrow{LiAlH_4} CH_3CH=CHCH_2OH$$

$$C_6H_5COCH_3 + 2(H) \xrightarrow{NaBH_4} C_6H_5CHOHCH_3$$

b. **Clemmensen Reduction**

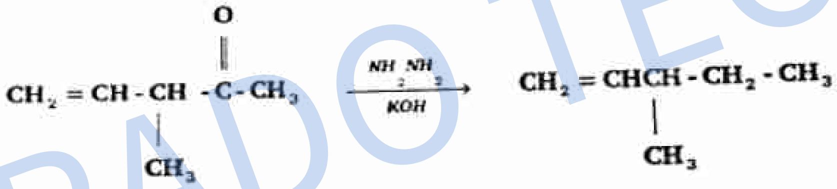
Alkanals and alkanones are reduced to hydrocarbons by the action of amalgamated zinc and concentrated hydrochloric acid. This reaction is called ***Clemmensen*** reduction and it is used to convert the carbonyl compounds to alkanes.



$$C_6H_5COCH_2CH_2CH_3 \xrightarrow[Conc.\ HCl]{Zn/Hg} C_6H_5CH_2CH_2CH_2CH_3$$

c. **Wolff – Kishner Reduction**

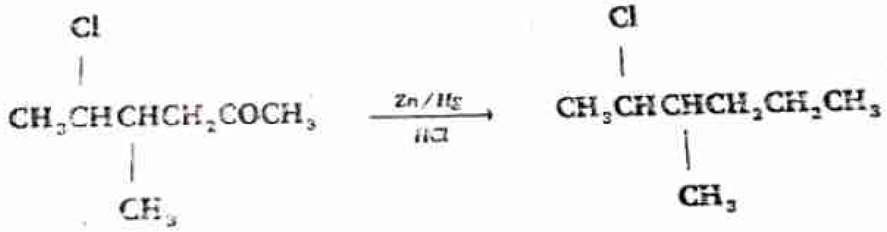
This is the reduction of alkanals and alkanones to alkanes by the action of hydrazine and a strong base such as potassium hydroxide.



$$CH_2=CH-\underset{\displaystyle CH_3}{\underset{|}{CH}}-\overset{\displaystyle O}{\overset{\|}{C}}-CH_3 \xrightarrow[KOH]{NH_2NH_2} CH_2=CH\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-CH_3$$

Clemmensen reduction and Wolff-Kishner reduction complement each other in that Clemmensen reduction is carried out in acidic medium while Wolff-Kishner reduction is carried out in basic medium. Thus compounds that are sensitive to acids are reduced by Wolff-Kishner procedure while compounds sensitive to bases are reduced by the Clemmensen method, for example,

(a)



$$CH_3\overset{\displaystyle Cl}{\overset{|}{C}H}\underset{\displaystyle CH_3}{\underset{|}{CH}}CH_2COCH_3 \xrightarrow[HCl]{Zn/Hg} CH_3\overset{\displaystyle Cl}{\overset{|}{C}H}\underset{\displaystyle CH_3}{\underset{|}{CH}}CH_2CH_2CH_3$$

The chlorine atom is sensitive to base if the compound above is reduced NH_2NH_2/KOH, the chlorine atom will be replaced by OH group in addition to reduction of the carbonyl group.

REVIEW QUESTIONS

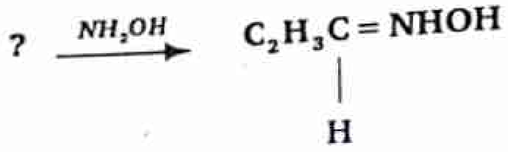
1. a. Give two methods for the preparation of alkanals.

b. How will you differentiate between alkanals and alkanones, structurally and chemically?

2. Copy and complete the following reaction schemes:

a. $? \xrightarrow[BaSO_4]{H_2/Pd} CH_3CHO$

b.



$? \xrightarrow{NH_2OH} \underset{\displaystyle H}{\underset{|}{C_2H_3C}}=NHOH$

c. $? \xrightarrow[Conc.\ HCl]{Zn/Hg} C_6H_5CH_2CH_2CH_3$

d. $CH_3COCH_2CH_2CH_3 \xrightarrow{NaBH_4} ?$

e. $CH_3CH(OH)CH_2CH_3 + K_2Cr_2O_7 \xrightarrow{H_2SO_4} ?$

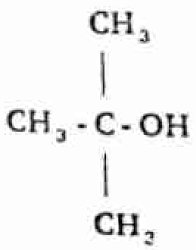
3. Use chemical equation to show how the following compounds would be synthesiz from propanal.

(a) *Propene*
(b) *Propyne*
(c) *2 - hydroxybutanoic acid*
(d) *Methyl propanoate*
(e) *Butanoic acid.*

4. What simple chemical test would you perform to distinguish between the follow pairs of isomeric compounds?

a. $CH_3CH_2COCH_2CH_3$ and $CH_3COCH_2CH_2CH_3$

b. $CH_3CH_2OCH_2CH_3$ and



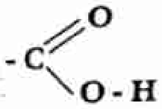
$CH_3-\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}-OH$

c. CH_3CH_2CHO and CH_3COCH_3

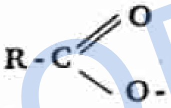
Chapter 9

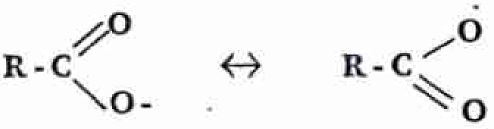
ALKANOIC ACIDS

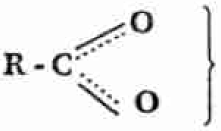
9.1. STRUCTURE

The alkanoic acids are organic compounds, which contain the carboxyl group - **COOH or**  . The group is attached to hydrogen atom, (HC alkyl group (RCOOH) or an aryl group (Ar COOH). For example,

HCOOH	CH_3COOH	C_6H_5COOH
Methanoic acid	***Ethanoic acid***	***Benzoic acid***

The carboxylate ion  is symmetrical and the distance of the two atoms from the carbon atom is 0.13nm. This is intermediate between C-O (0.1 and C=O (0.128nm). Thus the carboxylate ion is a resonance hybrid of two



The structure can be represented as  .

9.2. METHODS OF PREPARATION

1. Oxidation of Primary Alkanols and Alkanals

They are prepared by the oxidation of primary alkanols and alka In the laboratory the oxidising agents used are $K_2Cr_2O_7$, $Na_2Cr_2O_7$ or KM acidified with H_2SO_4 chromium (VI) oxide, CrO_3 in anhydrous ethanoic can also be used.

In the

For E

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Benzo
KMnC

2. Al

give

Acid

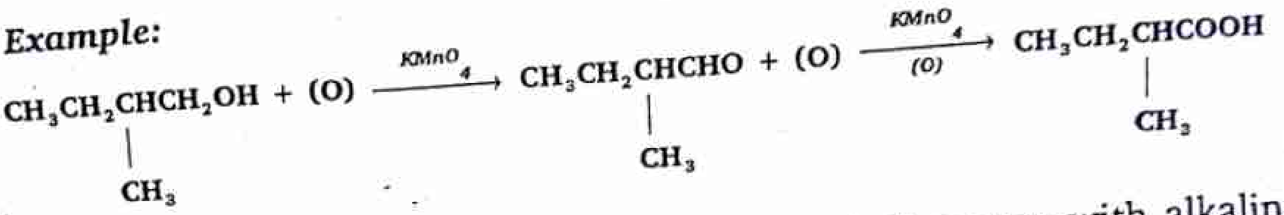
Al

In the oxidation of primary alkanols, alkanals are formed as intermediate.

$$RCH_2OH + (O) \xrightarrow[H_2SO_4]{K_2Cr_2O_7} RCHO + H_2O$$

$$RCHO + (O) \xrightarrow[H_2SO_4]{K_2Cr_2O_7} RCOOH$$

For Example:



$$\underset{\substack{|\\CH_3}}{CH_3CH_2CHCH_2OH} + (O) \xrightarrow{KMnO_4} \underset{\substack{|\\CH_3}}{CH_3CH_2CHCHO} + (O) \xrightarrow[(O)]{KMnO_4} \underset{\substack{|\\CH_3}}{CH_3CH_2CHCOOH}$$

Benzoic acid is also prepared by oxidation of methylbenzene with alkaline $KMnO_4$.

2. Alkaline or Acid Hydrolysis of Nitriles

The alkaline hydrolysis gives the salt of the acid which when acidified gives the acid.

Acid hydrolsis:

$$R{-}C{\equiv}N + H^+ + H_2O \rightarrow R{-}COOH + \overset{+}{N}H_4$$

Alkaline hydrolysis:

$$R{-}C{\equiv}N + \bar{O}H + H_2O \rightarrow R{-}CO\bar{O} + NH_3$$

$$RCO\bar{O} + H^+ \rightarrow RCOOH.$$

Examples

$$C_6H_5CN \xrightarrow{20\%\ H_2SO_4} C_6H_5COOH$$

$$C_6H_5CN \xrightarrow[H_2O]{\bar{O}H} C_6H_5CO\bar{O} \xrightarrow{H^+} C_6H_5COOH$$

3. Using Grignard Reagent

When carbon (IV) is passed into a solution of Grignard reagent and t product is hydrolysed, an alkanoic acid is obtained. Hydrolysis can be achieved wi dilute mineral acid or water.

$$RX \xrightarrow[ether]{Mg} RMgX \xrightarrow{CO_2} RCOOMgX \xrightarrow{H^+} RCOOH$$

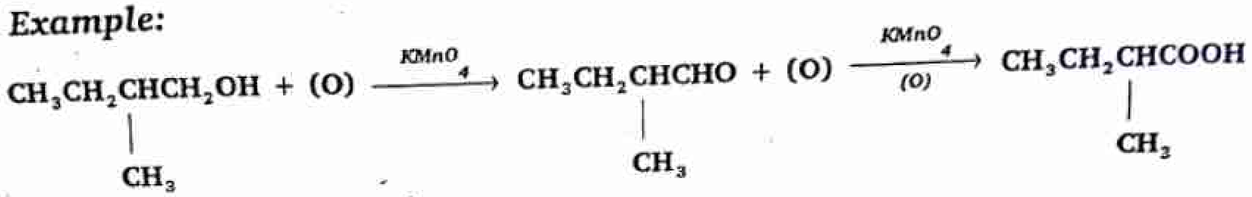
$$ArX \xrightarrow[ether]{Mg} ArMgX \xrightarrow{CO_2} ArCOOMgX \xrightarrow{H^+} ArCOOH$$

In the oxidation of primary alkanols, alkanals are formed as intermediate.

$$RCH_2OH + (O) \xrightarrow[H_2SO_4]{K_2Cr_2O_7} RCHO + H_2O$$

$$RCHO + (O) \xrightarrow[H_2SO_4]{K_2Cr_2O_7} RCOOH$$

For Example:



$$CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2OH + (O) \xrightarrow{KMnO_4} CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HCHO + (O) \xrightarrow[(O)]{KMnO_4} CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HCOOH$$

Benzoic acid is also prepared by oxidation of methylbenzene with alkaline $KMnO_4$.

2. Alkaline or Acid Hydrolysis of Nitriles

The alkaline hydrolysis gives the salt of the acid which when acidified gives the acid.

Acid hydrolsis:

$$R\text{-}C\equiv N + H^+ + H_2O \rightarrow R\text{-}COOH + \overset{+}{N}H_4.$$

Alkaline hydrolysis:

$$R\text{-}C\equiv N + \overset{-}{O}H + H_2O \rightarrow R\text{-}CO\overset{-}{O} + NH_3$$

$$RCO\overset{-}{O} + H^+ \rightarrow RCOOH.$$

Examples

$$C_6H_5CN \xrightarrow{20\%\ H_2SO_4} C_6H_5COOH$$

$$C_6H_5CN \xrightarrow[H_2O]{\bar{O}H} C_6H_5CO\overset{-}{O} \xrightarrow{H^+} C_6H_5COOH$$

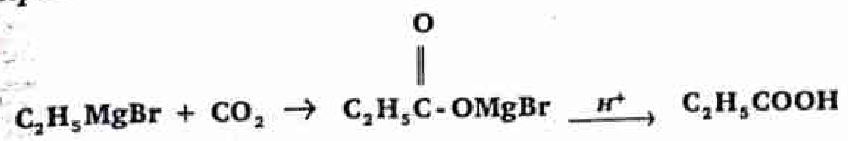
3. Using Grignard Reagent

When carbon (IV) is passed into a solution of Grignard reagent and th product is hydrolysed, an alkanoic acid is obtained. Hydrolysis can be achieved wi dilute mineral acid or water.

$$RX \xrightarrow[ether]{Mg} RMgX \xrightarrow{CO_2} RCOOMgX \xrightarrow{H^+} RCOOH$$

$$ArX \xrightarrow[ether]{Mg} ArMgX \xrightarrow{CO_2} ArCOOMgX \xrightarrow{H^+} ArCOOH$$

Example



$$C_2H_5MgBr + CO_2 \rightarrow C_2H_5\overset{\overset{O}{\|}}{C}\text{-}OMgBr \xrightarrow{H^+} C_2H_5COOH$$

$$(CH_3)_3CCl \xrightarrow[ether]{Mg} (CH_3)_3CMgCl \xrightarrow{CO_2} (CH_3)_3CCOOMgCl \xrightarrow{H_2O} (CH_3)_3CCOOH$$

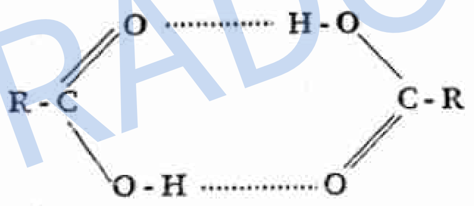
9.3. PROPERTIES

9.3.1. Physical Properties

1. Solubility

Alkanoic acids can form hydrogen bonds with each other and with water. They are polar. The first four members are liquids very miscible with water. Straight chain acids with five to nine carbon atoms are also liquids but they are partially soluble in water. Higher members are solids and are insoluble in water, because the effect of water-insoluble hydrocarbon chain predominates that of the water-soluble carboxylic group.

The lower members are also soluble in less polar solvents like ether, alkanol, benzene etc., because in such solvents they are present as dimers formed by H-bonding between a pair of carboxylic groups.



2. Boiling Points

The boiling points of alkanoic acids are higher than those of the alkanoates and alkanols of comparable masses. For example ethanoic acid with relative molecular mass of 60 has boiling point of 118°C whereas the boiling points of methyl methanoate, propan-1-ol and propan-2-ol with the same mass are 32°C, 97°C and 83°C respectively. **The reason for this is that whereas there is no hydrogen bonding in alkanoates, the hydrogen bond in alkanols is weaker than that in alkanoic acids.** A pair of the acids is held together by two hydrogen bonds instead of one as in a pair of alkanols.

9.3.2. Chemical Properties

1. Acidity of Alkanoic Acids

Alkanoic acids are weaker than mineral acids but they are stronger than alkanols. In water, an acid or an alkanol exists in equilibrium with the carboxylate anion or an alkoxide ion respectively and hydronium ion.

$$RCOOH + H_2O \rightleftharpoons RCO\bar{O} + H_3O^+$$

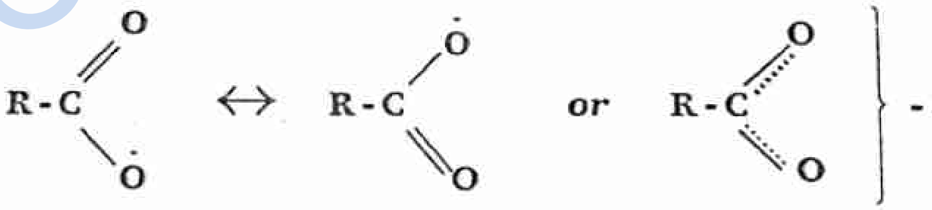
$$ROH + H_2O \rightleftharpoons R\bar{O} + H_3O^+$$

The strength of the acid depends on the equilibrium position. The stronger the acid, the further to the right the equilibrium position. Therefore, the readiness with which the O–H group splits to release its proton determines the strength of the acid. The O-H bond in alkanoic acid splits more readily than the O-H bond in alkanols for the following reasons:

i. *The carbonyl group in the alkanoic acids withdraws electrons by electromeric shift. This facilitates the split of O-H bond. No such effect is found in alkanols because of the absence of the carbonyl group.*

$R-\overset{O}{\overset{\|}{C}}-O-H \qquad R-O-H$

ii. *The strength of alkanoic acid is also due to the powerful resonance stabilization of its carboxylate anion which is made possible by the carbonyl group.*



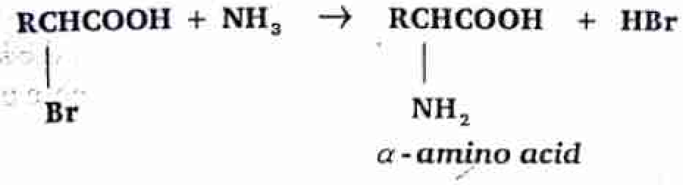
Resonance does not exist in the alkoxide ion R–Ō of alkanol.

Effect of substituents on the strength of the acid

How does a change in the structure of a group attached to –COOH affect th strength of the acid? Acidity is measured by the ability of the proton of the acid combine with water to give the hydronium ion and the carboxylate anion, RCOŌ. A factor that stabilizes the anion more than it does the acid increases acidity. Convers any factor that makes the anion less stable decreases acidity.

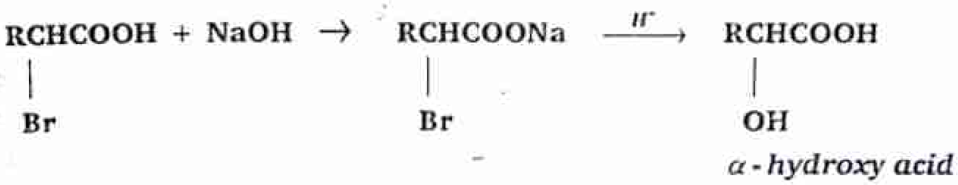
Electron-withdrawing substituents (-I) reduce negative charge, stabilize the anion a increase acidity i.e. reduce the readiness of the anion to react with hydronium ion to give h

Methanoic acid cannot be halogenated because it has no α-hydrogen atom. The importance of this reaction is that the halogen atoms of the halogenated acids can easily be replaced by $-NH_2$ group or by -OH group to give amino acids or hydroxy acids respectively.



$$\underset{\displaystyle Br}{RCHCOOH} + NH_3 \rightarrow \underset{\displaystyle NH_2}{RCHCOOH} + HBr$$

α-amino acid



$$\underset{\displaystyle Br}{RCHCOOH} + NaOH \rightarrow \underset{\displaystyle Br}{RCHCOONa} \xrightarrow{H^+} \underset{\displaystyle OH}{RCHCOOH}$$

α-hydroxy acid

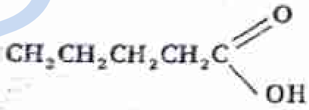
The halogenated acid can also undergo elimination reaction to form α, β-unsaturated acid.

$$\underset{\displaystyle Br}{RCH_2CHCOOH} \xrightarrow[ethanol]{KOH} RCH=CHCOOH \xrightarrow{H^+} RCH=CHCOOH$$

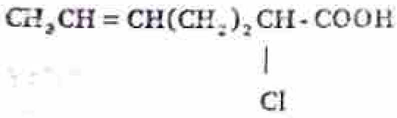
α, β-unsaturated acid

REVIEW QUESTIONS

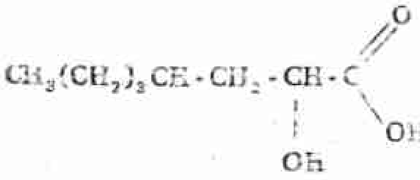
1. Write the IUPAC names of the following:

i. 

$CH_3CH_2CH_2CH_2C(=O)OH$

ii. 

$CH_3CH=CH(CH_2)_2\underset{\displaystyle Cl}{CH}-COOH$

iii. 

$CH_3(CH_2)_3CH-CH_2-\underset{\displaystyle OH}{CH}-C(=O)OH$

the acid. While electron-releasing-groups (+1) increase the negative charge, destabilize the anion and decrease acidity i.e. increase the readiness of the anion to react with hydronium ion to give back the acid.

Halogens are electron-withdrawing and therefore increase acidity if present in the group attached to -COOH group of alkanoic acids. A look at the acidity constants, Ka illustrate this:

	Ka
HCOOH	17.7×10^{-5}
CH_3COOH	1.75×10^{-5}
$CH_2ClCOOH$	136×10^{-5}
$CHCl_2COOH$	553×10^{-5}
CCl_3CCOOH	23200×10^{-5}

Inductive effect decreases with distance therefore as Cl atom is moved away from -COOH, the acid strength diminishes.

	Ka
$CH_3CHClCH_2COOH$	8.9×10^{-5}
$ClCH_2CH_2CH_2COOH$	2.96×10^{-5}

The order of electron withdrawing effect (-1) of the halogens is I < Br < Cl < F. Therefore, iodosubstituted acid is the weakest while fluoro substituted acid is the strongest.

	Ka
FCH_2COOH	260×10^{-5}
$BrCH_2COOH$	125×10^{-5}
ICH_2COOH	67×10^{-5}

Action as Acids

Aqueous solution of the acids show the typical behaviour of the acids. or example, they affect indicators; react with active metals such as magnesium nd zinc to liberate hydrogen, form salts with bases and liberate carbon (IV) ide from trioxocarbonates.

3. Reduction

The acid group is reduced to primary alkanol by only lithiu tetrahydridoaluminate (III), $LiAlH_4$.

$$R\text{-}COOH + 4(H) \xrightarrow{LiAlH_4} R\text{-}CH_2OH + H_2O$$

Example

$$(CH_3)_3CCOOH \xrightarrow[Ether]{LiAlH_4} (CH_3)_3CCH_2OH$$

$$HOOC(CH_2)_8COOH \xrightarrow{LiAlH_4} HOCH_2(CH_2)_8CH_2OH$$

$$C_6H_5COOH \xrightarrow[Ether]{LiAlH_4} C_6H_5CH_2OH$$

4. Formation of Acid Chlorides

Acids can be converted to the acid chlorides by heating with thionyl chlorid or phosphorous pentachloride or phosphorous trichloride.

$$RCOOH + SOCl_2 \rightarrow RCOCl + HCl + SO_2$$

$$RCOOH + PCl_5 \rightarrow RCOCl + HCl + POCl_3$$

$$3RCOOH + PCl_3 \rightarrow 3RCOCl + H_3PO_3$$

Example

$$CH_3(CH_2)_2COOH + SOCl_2 \rightarrow CH_3(CH_2)_2COCl + SO_2 + HCl$$

$$C_6H_5COOH + PCl_5 \rightarrow C_6H_5COCl + POCl_3 + HCl$$

$$3CH_3CH_2COOH + PCl_3 \rightarrow 3CH_3CH_2COCl + H_3PO_3$$

5. Formation of Alkanoates: Esterification

This reaction has been discussed in 7.3.2.

6. Halogenation

Chlorination of ethanoic acid by gaseous chlorine in presence of phosphorous successively yields *mono*-, *di*- and trichloroethanoic acid. Better yi are obtained if the reaction is carried out in bright sunlight.

$$CH_3COOH \xrightarrow[P]{Cl_2} CH_2ClCOOH \xrightarrow[P]{Cl_2} CHCl_2COOH \xrightarrow[P]{Cl_2} CCl_3COOH$$

Chlorination of other aliphatic acids gives a mixture of several monochlori products. This reaction is not of synthetic value. Bromination, however, yields the α-bromoacid because it is selective.

$$CH_3CH_2COOH \xrightarrow[P]{Br_2} CH_3CHBrCOOH \xrightarrow[P]{Br_2} CH_3CBr_2COOH \xrightarrow[P]{Br_2}$$

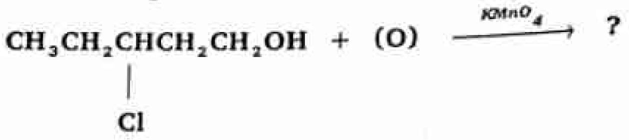
No further substitution

b. Give the structural formulae of the following compounds:

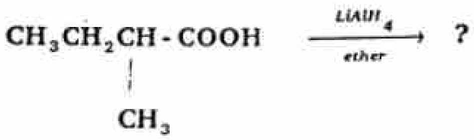
i. *Hex - 3 - enoic acid*
ii. *Cis - butenedioic acid*
iii. *3 - phenylpropanoic acid.*

2. a. Give two methods for the preparation of alkanoic acids.
b. How would you show the presence of a simple alkanoic acid in the laboratory?
c. Explain why the boiling point of alkanoic acid is higher than those of alkanoate and alkanols of comparable molecular masses.

3. Complete the following reactions:

i.

$$CH_3CH_2\underset{\displaystyle Cl}{\underset{|}{C}}HCH_2CH_2OH + (O) \xrightarrow{KMnO_4} ?$$

ii. $$CH_3CH_2Br \xrightarrow[ether]{Mg} ? \xrightarrow{CO_2} ? \xrightarrow{H^+} ?$$

iii.

$$CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}H-COOH \xrightarrow[ether]{LiAlH_4} ?$$

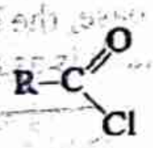
iv. $$(CH_3)_3C-CH_2CO_2H \xrightarrow{SOCl_2} ?$$

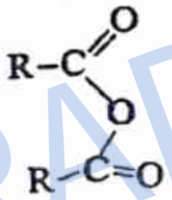
Chapter 10

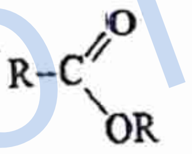
DERIVATIVES OF ALKANOIC ACIDS

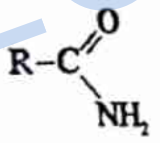
10.1. INTRODUCTION

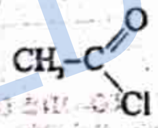
The derivatives of alkanoic acids are a group of compounds obtained by replacement of the hydroxyl group of alkanoic acids by an atom or group of atoms. They include acyl or aeid chlorides obtained by the replacement of hydroxyl group by a chlorine atom. Acyl or acid anhydride obtained by the replacement of the hydroxyl group by -OOCR group. Alkanoates obtained by the replacement of the hydroxyl group by the alkoxy group, -OR and amides obtained by the replacement of the hydroxyl group by the amino group, $-NH_2$.

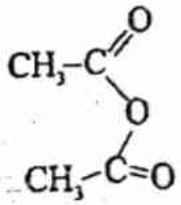

Acid chloride

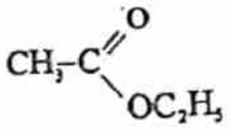

Acid anhydride

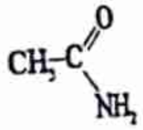

Alkanoate


Amide


Ethanoyl chloride

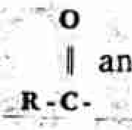

Ethanoic anhydride

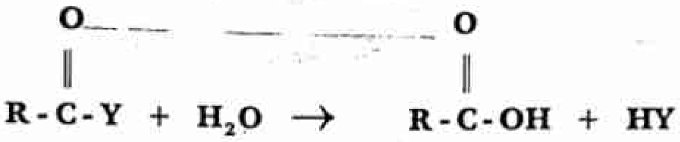

Ethyl ethanoate


Ethanamide

10.2. General Properties

1. The presence of the carbonyl group in the compounds makes them polar. The group is not changed in most of their reactions and it determines the chemical behaviour of the compounds as in alkanals and alkanones. It does this by providing a site for nucleophilic attack. It also increases the acidity of alpha hydrogen atoms.

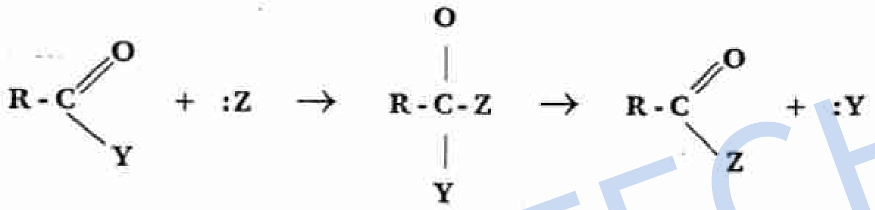
2. They all contain the acyl group,  $\overset{O}{\overset{\|}{R-C-}}$ and are all hydrolysed to the parent acid



$$R-\overset{O}{\overset{\|}{C}}-Y + H_2O \rightarrow R-\overset{O}{\overset{\|}{C}}-OH + HY$$

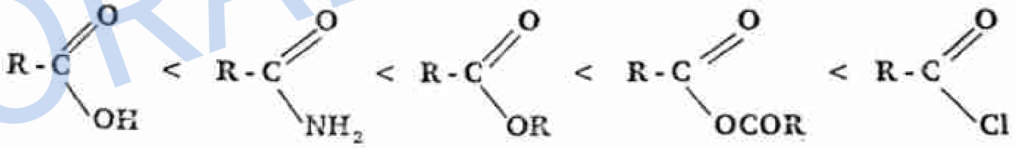
$(Y = Cl, OR, NH_2, OOCR)$.

3. The typical reaction of the compounds with the acyl group, alkanoic acids and their derivatives, is nucleophilic substitution in which -OH, -Cl, -OOCR, -NH$_2$ or -OR^1 is replaced by a basic group.



$(-Y = -OH, Cl, -OOCR, -NH_2, -OR^1)$

The ease of the loss of Y depends on its basicity. The weaker the base, the better th leaving group. The general order of reactivity to nucleophilic attack is as follows:



In general it is easier to convert a compound from the right to one to the le than vice versa.

Alkanals and alkanones are less susceptible to nucleophilic substitution tha acyl compounds because in alkanal or alkones the leaving group is the hydride io $(:H^-)$ or alkide ion $(:R^-)$. The hydride and alkide ions are the strongest base Therefore nucleophilic addition rather than substitution takes place in alkanals an alkanones.

10.3. ACID CHLORIDES

10.3.1. Preparation

The preparation of acid chlorides has been discussed in section 9.3.

10.3.2. Physical Properties

The acid chlorides have sharp and irritating odours. They fume in moist air. The sharp, irritating odour and the fuming properties are due to the ready hydrolysis of the acid chlorides to HCl and alkanoic acids.

10.3.3. Chemical Properties

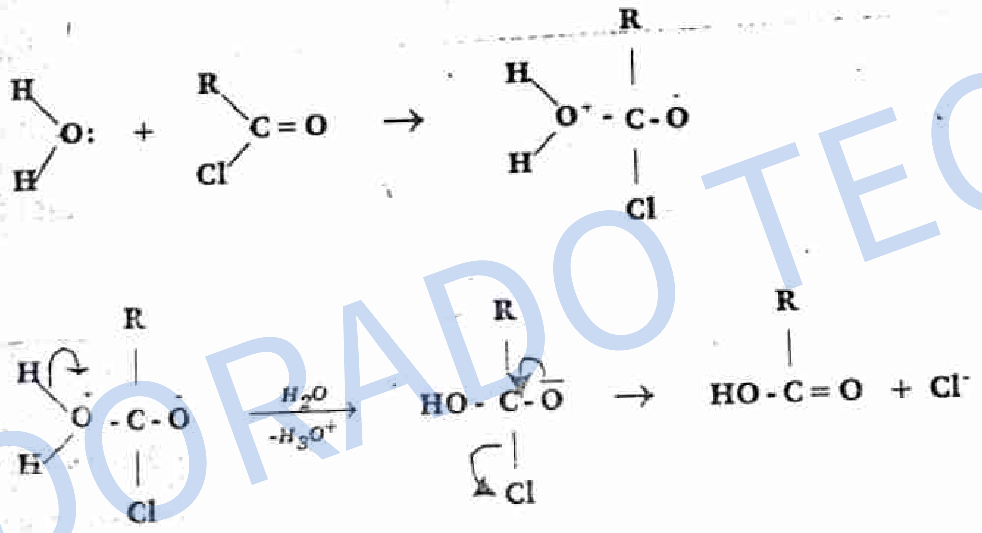
1. Hydrolysis

The aliphatic acid chlorides readily react with water to give the corresponding alkanoic acid and hydrogen chloride.

$$RCOCl + H_2O \longrightarrow RCOOH + HCl$$

$$CH_3COCl + H_2O \longrightarrow CH_3COOH + HCl$$

The mechanism of hydrolysis involves the nucleophilic addition of water, which is followed by loss of a proton and a chloride ion.



2. Reaction with Alkanols and Phenols

They react with alkanols and phenols to form alkanoates. For example:

$$CH_3COCl + CH_3CH_2OH \longrightarrow CH_3COOCH_2CH_3 + HCl$$

$$CH_3COCl + C_6H_5OH \longrightarrow CH_3COOC_6H_5 + HCl$$

3. Reaction with Ammonia

They react with ammonia to form the corresponding acid amide.

$$CH_3COCl + NH_3 \longrightarrow CH_3CONH_2 + HCl$$

4. **Reaction with Primary and Secondary Amines**

Primary and Secondary amines react with acid chlorides to form N-substituted and N, N-substituted amides respectively.

$$CH_3COCl + CH_3NH_2 \longrightarrow CH_3CONHCH_3 + HCl$$

$$CH_3COCl + (CH_3)_2NH \longrightarrow CH_3CON(CH_3)_2 + HCl$$

5. **Friedel - Crafts Reaction**

Benzene reacts with ethanoyl chloride in the presence of aluminium chloride to form phenylethanone.

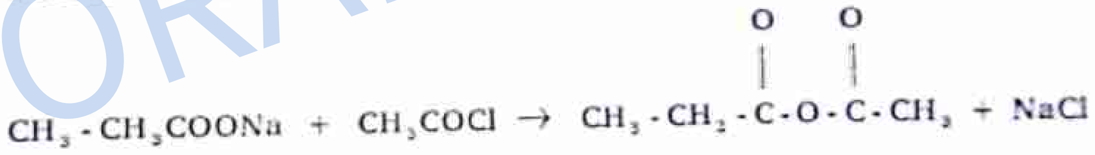
$$C_6H_6 + CH_3COCl \xrightarrow{AlCl_3} C_6H_5COCH_3 + HCl$$

In the reactions we have discussed above, a hydrogen atom has been replaced by a acyl group. Reactions in which the acyl group replaces hydrogen, especially thos with phenol, alkanols and amines, are known as ***acylation***. If the group is CH_3CO- it is known as ***ethanoylation*** (acetylation) and if the group is C_6H_5CO-, it i ***benzoylation.***

6. **Formation of Anhydrides**

An acid chloride when heated with the anhydrous sodium salt of an alkano acid forms and acid anhydride.

$$RCOCl + R^1COONa \rightarrow RCOOCOR^1 + NaCl$$



$$CH_3\text{-}CH_2COONa + CH_3COCl \rightarrow CH_3\text{-}CH_2\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}O\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}CH_3 + NaCl$$

7. **Reduction**

Acid chlorides are reduced by hydrogen and other reducing agents, suc as Lithium tetrahydridoaluminate (III), to the corresponding prima alkanol.

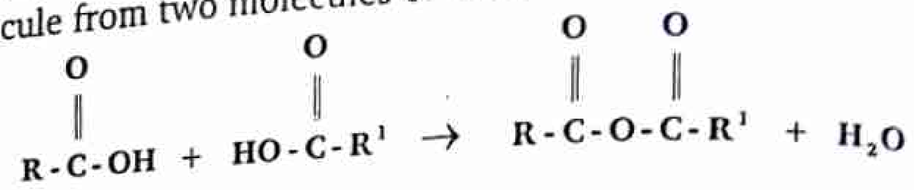
$$RCOCl \xrightarrow[\text{or } LiAlH_4]{H_2/Pd} RCHO \xrightarrow[\text{or } LiAlH_4]{H_2/Pd} RCH_2OH$$

But if in the reduction with hydrogen, the palladium catalyst is poisoned w BaSO$_4$ the reduction stops at the first step and an alkanal is produced. This known as ***Rosenmund reduction.***

$$RCOCl \xrightarrow[Pd/BaSO_4]{H_2} RCHO$$

10.4. ACID ANHYDRIDES

Alkanoic acids except methanoic acid form acid anhydrides by the elimination of a water molecule from two molecules of acid.



$$R-\overset{\overset{O}{\|}}{C}-OH + HO-\overset{\overset{O}{\|}}{C}-R^1 \rightarrow R-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-R^1 + H_2O$$

When $R=R^1$, a simple anhydride is formed. But when $R \neq R^1$ a mixed anhydride is formed.

10.4.1. Preparation

Acid anhydrides are prepared by the reaction between an acid chloride and anhydrous sodium salt of an alkanoic acid *(Section 10.3.3.)*.

$$RCOONa + R^1COCl \longrightarrow RCOOCOR^1 + NaCl$$

2. Ethanoic anhydride, which is most widely used, is prepared on an industrial scale by passing ethenone (ketene) into ethanoic acid. Ethenone is prepared by the cracking of propanone in the presence of Ni/Cr alloy.

$$CH_3COCH_3 \xrightarrow[750^oC]{Ni/Cr\ alloy} \underset{\text{Ethenone}}{CH_2=C=O} + CH_4$$

$$CH_2=C=O + CH_3COOH \rightarrow CH_3CO-O-COCH_3$$

10.4.2. Physical Properties

Acid anhydrides have strong irritating odours. They are slightly soluble in water and are slowly hydrolysed to the corresponding alkanoic acids

10.4.3. Chemical Properties

The acid anhydrides have similar chemical properties with acid chlorides. They are also used as ethanoylating agents although they are less reactive. The lower reactivity of acid anhydride is due to the presence of CH-CO-O- group, which has a lower electron withdrawing power than the chlorine atom in acid chlorides.

With the exception of the Rosenmund reduction and the reaction with sodium salts of alkanoic acids, they undergo all the other reactions of acid chlorides treated in *section 10.3.3.*

Ethanoic anhydride is used in making cellulose ethanoate and ethenyl (vinyl) ethanoate, which are monomers for making acrilic fibres and rayons respectively

10.5. ALKANOATES

The alkanoates are formed by the esterification reaction, the reaction between alkanoic acid and alkanol to form alkanoates and water. The reaction is reversible and slow and is usually catalysed by hydrogen ion from concentrated H_2SO_4 or dry HCl.

$$\text{acid} + \text{alkanol} \rightleftharpoons \text{Alkanoate} + \text{water}$$

The simple alkanoates have pleasant fragrant odours. Many natural scents and flavours of many fruits are due to traces of alkanoates. They are used as artificial flavours and essences. For example banana flavouring is made from 3-methylbutyl ethanoate and pineapple flavouring from methyl butanoate. They are used as solvent for gums, resins, oils, varnishes and paints.

10.5.1. Preparation

1. From acid chloride and anhydride.

$$ROH + R^1COCl \longrightarrow RCOOR + HCl$$

$$ROH + R^1COOCOR \longrightarrow R^1COOR + R^1COOH$$

2. From sodium or silver salt of alkanoic acids.

$$RCOONa + R^1\text{-}X \longrightarrow RCOOR^1 + NaX$$

$$RCOOAg + R^1\text{-}X \longrightarrow RCOOR^1 + AgX$$

10.5.2. Physical Properties

Alkanoates with about ten carbon atoms per molecule are liquids. The lower members are very volatile. **They have boiling points that are much lower than those of the parent acids because hydrogen bonding is not possible in alkanoates.**

10.5.3. Chemical Properties

1. Hydrolysis

Alkanoates are hydrolysed very slowly to alkanoic acid and alkanol when boiled with water.

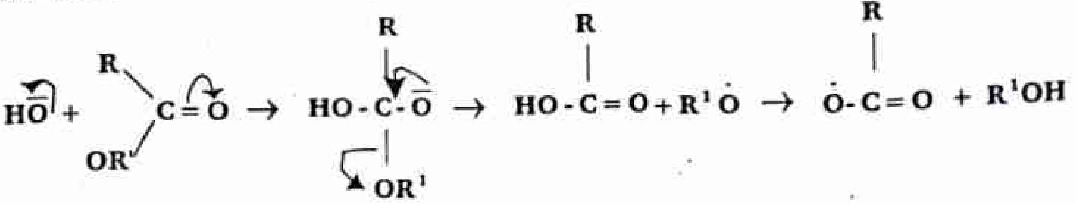
$$R\text{-}COOR^1 + H_2O \longrightarrow RCOOH + R^1OH$$

This reaction can be catalysed by both acids and bases. When acid-catalysed the reverse of esterification occurs. Being reversible a good yield of the alkanoate is obtained when excess of the acid solution is used.

In the base-catalysed process, the carboxylate ion is formed. This process is not reversible.

$$RCOOR^1 + \bar{O}H \longrightarrow R\text{-}CO\bar{O} + R^1\text{-}OH$$

Mechanism



2. Ammonolysis

Alkanoates react with concentrated ammonia to form the alkanol and the amide or the alkanoic acid. This reaction is known as ammonolysis.

$$RCOOR^1 + NH_3 \longrightarrow RCONH_2 + R^1OH$$

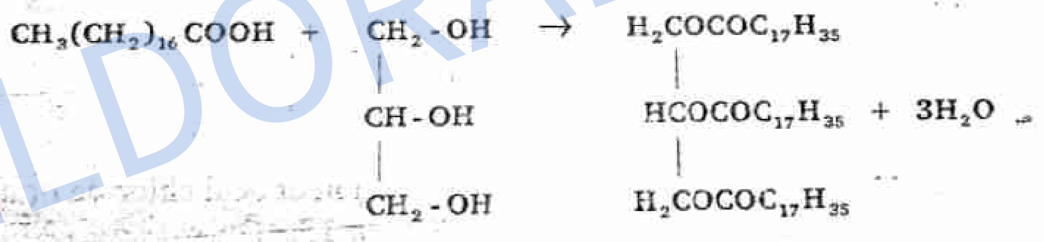
3. Reduction

Alkanoates are reduced to a pair of alkanols by the action of Na/C_2H_5OH or $LiAlH_4$.

$$RCOOR^1 + 4(H) \longrightarrow RCH_2OH + R^1OH$$

10.5.4. Fats and Oils

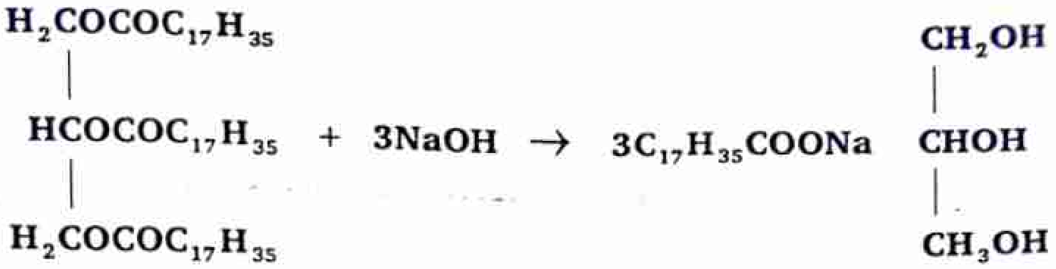
Fats and oils are naturally occurring alkanoates formed by the esterification of long chain natural acids, such as hexadecanoic acid (palmitic acid), octadecanoic acid (stearic acid) or octadeca-9-enoic acid (oleic acid) with propan 1, 2, 3-triol (glycerol).



$$CH_3(CH_2)_{16}COOH + \begin{array}{l}CH_2\text{-}OH\\ \quad| \\ CH\text{-}OH\\ \quad| \\ CH_2\text{-}OH\end{array} \rightarrow \begin{array}{l}H_2COCOC_{17}H_{35}\\ \quad| \\ HCOCOC_{17}H_{35}\\ \quad| \\ H_2COCOC_{17}H_{35}\end{array} + 3H_2O$$

The oils differ from the fats in that a greater proportion of their constituent alkanoic acids are unsaturated. This makes the oils liquids at room temperature since unsaturated acids have lower melting points than the saturated acids.

The alkaline hydrolysis of naturally occurring alkanoates (fats and oils) to form soaps and propan-1, 2, 3-triol is known as *saponification*. Thus soap is the sodium or potassium salt of long chain naturally occuring acids.



$$\begin{array}{l} H_2COCOC_{17}H_{35} \\ | \\ HCOCOC_{17}H_{35} \\ | \\ H_2COCOC_{17}H_{35} \end{array} + 3NaOH \rightarrow 3C_{17}H_{35}COONa \begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_3OH \end{array}$$

Apart from hydrolysis, another reaction which oils can undergo i **hydrogenation**. This reaction is carried out by treating the oil with hydrogen in the presence of finely divided nickel. The oils are saturated by the hydrogen. The product is harder and resembles a natural fat. The oil is said to be ***hardened.*** Thi process is made use of in the manufacture of margarine. Margarine is made b mixing the hydrogenated oils with milk. Vitamins and artificial colouring are als added to make the margarine as good as butter, which it is substituting.

10.6. ACID AMIDES

14.6.1. Preparation

1. By Heating the Ammonium Salt of Alkanoic Acid

$$R\text{-}COONH_4 \xrightarrow{\Delta} R\text{-}CONH_2 + H_2O$$

$$RCOOH + (NH_4)_2CO_3 \xrightarrow{\Delta} 2RCONH_2 + CO_2 + 3H_2O$$

2. Ammonolysis of other Acid Derivatives

$$RCOCl + NH_3 \rightarrow RCONH_2 + HCl$$

$$RCOOCOR + NH_3 \rightarrow RCONH_2 + RCOOH$$

$$RCOOR^1 + NH_3 \rightarrow RCONH_2 + R^1OH$$

3. N-substituted amides are prepared by the reaction of acid chloride or anhydride with primary amines or secondary amines. *(Section 10.3.3).*

$$RCOCl + R^1NH_2 \rightarrow RCONHR^1 + HCl$$

$$RCOCl + R_2^1NH \rightarrow RCONR_2^1 + HCl$$

$$(RCO)_2O + R^1NH_2 \rightarrow RCONHR^1 + RCOOH$$

For example

$$C_6H_5NH_2 + CH_3CO\cdot O\cdot COCH_3 \rightarrow CH_3CONHC_6H_5 + CH_3COOH$$

Chapter 11

NITRILES, AND AMINES

11.1. NITRILES

The nitriles have the general formula R-CN. An example is ethanonitrile, CH_3CN.

11.1.2. Preparation

1. **Displacement of Halogen in Halogenoalkanes by Cyanide ion**

The reaction involves heating the halogenoalkane (usually the chloride or bromide) with sodium cyanide in methanolic or ethanolic solution.

$$\mathrm{R-Br} + \mathrm{C}\overline{\mathrm{N}} \rightarrow \mathrm{RC\equiv N} + \mathrm{B}\overline{\mathrm{r}}$$

In this reaction, a carbon atom is added to the chain. Aprotic solvents such as dimethyl sulphoxide (DMSO) and dimethyl formamide (DMF) can also be used.

$$CH_3(CH_2)CH_2Br + NaCN \xrightarrow{CH_3OH} CH_2(CH_2)_4CH_2CN + NaBr$$

$$CH_3(CH_2)_2CH_2Cl + NaCN \xrightarrow{DMSO} CH_3(CH_2)_2CH_2CN + NaBr$$

2. **Dehydration of Amides**

Nitriles are prepared by dehydration of amides with phosphorous (V) oxides or sulphur dichloride oxide, (thionyl chloride) $SOCl_2$.

$$RCONH_2 \xrightarrow[SOCl_2]{P_2O_5 \text{ or}} RCN + H_2O$$

Example

$$(CH_3)_2CHCONH_2 \xrightarrow{P_2O_5} (CH_3)_2CHCN + H_2O$$

$$CH_3(CH_2)_4CONH_2 + SOCl_2 \rightarrow CH_3(CH_2)_4CN + SO_2 + 2HCl$$

11.1.3. Physical Properties

The lower members are water soluble pleasant-smelling colourless liquids. Their boiling points are rather high. For example butane and propanonitrile with relative molecular masses that are close boil at -0.5 and 97°C respectively. The high boiling points of nitriles are due to the high polarity of $C^{\delta+} \equiv N^{\delta-}$ bond.

11.1.4. CHEMICAL PROPERTIES

1. **Hydrolysis**
   Nitriles are hydrolysed by acids or alkalis to the corresponding acid via the intermediate formation of the amide.

$$RC\equiv N + H_2O \rightarrow R\text{-}CONH_2 \xrightarrow{H_2O} R\text{-}COOH + NH_3$$

2. **Reduction**
   Nitriles are reduced to primary amines by catalytic reduction or sodium in ethanol or $LiAlH_4$.

$$R\text{-}C\equiv N + 4(H) \rightarrow R\text{-}CH_2NH_2$$

11.2. AMINES

Amines are compounds derived by replacing one or more hydrogen atoms of ammonia by alkyl and/or aryl groups.

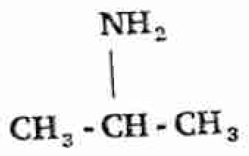
11.2.1. Types

1. **Primary (1°) Amines**
   The primary amines are formed by the replacement of one hydrogen atom of ammonia by alkyl or aryl group.

Examples

CH_3NH_2
Methylamine

$C_6H_5NH_2$
Phenylamine



$$CH_3\text{-}\underset{}{\overset{NH_2}{\overset{|}{CH}}}\text{-}CH_3$$

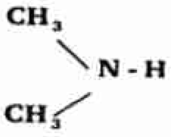
2-aminopropane

Primary amines have the general formula $R\text{-}NH_2$. **R** represents alkyl, or aryl group. They contain the $-NH_2$, amino group.

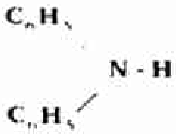
2. **Secondary (2°) Amines**

Secondary amines are formed by replacement of two hydrogen atoms of ammonia by alkyl groups. They contain the -NH group. The general formula is R_2NH.

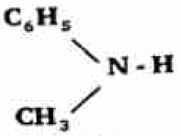
Examples:



Dimethylamine



Diphenylamine

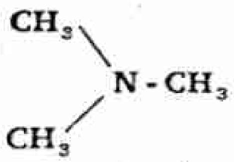


N - methylphenylamine

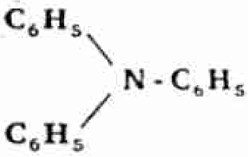
3. **Tertiary (3°) Amines**

Tertiary amines are formed by the replacement of all the hydrogen atoms of ammonia by alkyl and/or aryl groups.

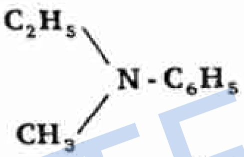
Examples:



Trimethylamine



Triphenylamine



N, N - ethylmethylphenylamine.

11.2.1. Physical Properties

1. The lower aliphatic amines are gases or very volatile liquids with fish-like ammoniacal odour. They dissolve in water to form basic solutions. Phenylamine is a colourless oily liquid when freshly distilled. Due to atmospheric oxidation it usually turns yellowish or brownish with age. It is slightly soluble in water and has a characteristic pleasant odour.

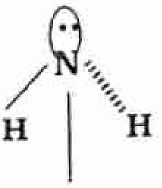
2. **Primary and secondary amines have higher boiling points than tertiar amines of comparable molar masses. This is due to the formation of hydroge bonds.** Primary amines with two hydrogen atoms form more hydrogen bonds tha the secondary amines with only one hydrogen atom. Tertiary amines have hydrogen atom on nitrogen and do not form hydrogen bonds. Alkanols of comparal molar masses with amines have higher boiling points because oxygen is m electronegative than nitrogen and form stronger hydrogen bonds.

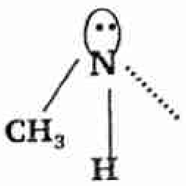
11.2.2. Chemical Properties

The principal feature of the chemistry of amines is the presence of the lone pair of electrons on nitrogen. They act as nucleophiles and combine with carbon atoms, which carry partial positive charges. Their reactivity is influenced by the nature of the groups attached to the nitrogen atom. Electron-releasing groups increase their reactivity while electron-withdrawing groups reduce their reactivity. Therefore, aliphatic amines are more reactive than aromatic amines.

1. ***Basic Character***

Amines and ammonia have structural similarity. Each has a lone pair of electrons occupying one of the hybridised orbitals of the tetrahedral nitrogen atom.





Both are bases because of the presence of the lone pair of electrons on nitrogen available for protonation. Both are weak bases in water because they dissociate partially in water.

$$NH_3 + H_2O \rightleftharpoons \overset{+}{N}H_4 + \overline{O}H$$

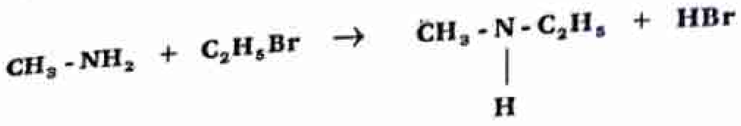
$$R_3N + H_2O \rightleftharpoons R_3\overset{+}{N}H + \overline{O}H$$

The electron-releasing effect of the alkyl group makes aliphatic amines stronger bases than ammonia. They increase the charge on nitrogen. Aromatic amines are weaker bases than ammonia because the negative charge on nitrogen is reduced by the electron-withdrawing phenyl group. The order of basic strength of aliphatic amine, ammonia and aromatic amine is as follows:

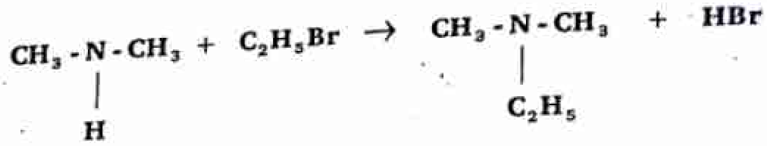
aliphatic amines > ammonia > aromatic amine

The order of basic strength in aliphatic amines is expected to be tertiary amine > secondary amine > primary amine. It is observed that tertiary amines are weaker than primary amines. For example the pK_b values for methylamine, dimethylamine and trimethylamine are 3.36, 3.23 and 4.20 respectively.

The strength of an amine in water is determined not only by the electron availability on the nitrogen atom, but also the extent to which the cation formed



$$CH_3-NH_2 + C_2H_5Br \rightarrow CH_3-\underset{\displaystyle H}{\underset{|}{N}}-C_2H_5 + HBr$$



$$CH_3-\underset{\displaystyle H}{\underset{|}{N}}-CH_3 + C_2H_5Br \rightarrow CH_3-\underset{\displaystyle C_2H_5}{\underset{|}{N}}-CH_3 + HBr$$

Tertiary amines react with halogenoalkanes to form quaternary ammonium salts. Quaternary ammonium salts are derivatives of ammonium salts or ammonium hydroxide formed by replacing all four hydrogen atoms of ammonium ion by alkyl and/or aryl groups.

$$(C_2H_5)_3N + C_2H_5I \rightarrow (C_2H_5)_4\overset{+}{N}\overset{-}{I}$$

Tetraethyl ammonium iodide.

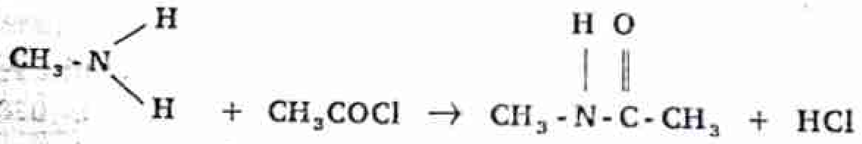
Quartenary ammonium salts when treated with silver hydroxide or moist silver oxide form quartenary ammonium bases, which when heated decompose to alkenes and tertiary amines.

$$2(C_2H_5)_4\overset{+}{N}\overset{-}{I} + Ag_2O + H_2O \rightarrow 2(C_2H_5)_4\overset{+}{N}\overset{-}{O}H + 2AgI$$

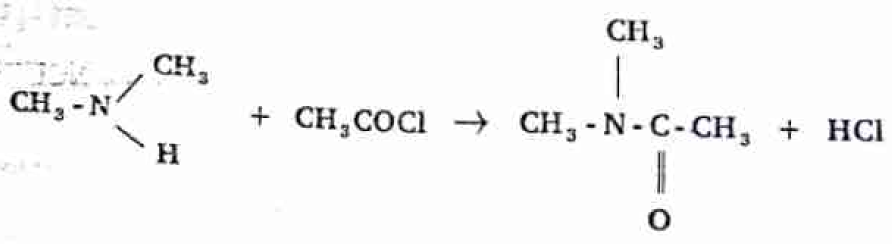
$$(C_2H_5)_4\overset{+}{N}\overset{-}{O}H \rightarrow CH_2=CH_2 + (C_2H_5)_3N + H_2O.$$

4. Ethanoylation and Benzoylation

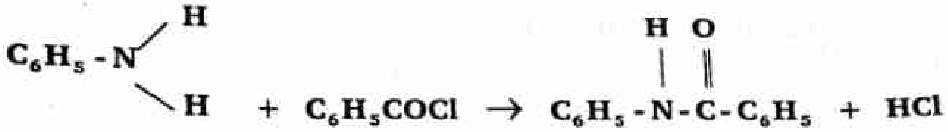
Primary and secondary amines can be ethanoylated or benzoylated with ethanoyl chloride or anhydride and benzoyl chloride respectively. In the reaction, hydrogen atom attached to nitrogen is replaced by CH_3CO^- or $C_6H_5CO^-$ groups.



$$CH_3-N\begin{matrix}H\\H\end{matrix} + CH_3COCl \rightarrow CH_3-\overset{\displaystyle H}{\overset{|}{N}}-\overset{\displaystyle O}{\overset{\|}{C}}-CH_3 + HCl$$



$$CH_3-N\begin{matrix}CH_3\\H\end{matrix} + CH_3COCl \rightarrow CH_3-\overset{\displaystyle CH_3}{\overset{|}{N}}-\underset{\displaystyle O}{\underset{\|}{C}}-CH_3 + HCl$$



$$C_6H_5-NH_2 + C_6H_5COCl \rightarrow C_6H_5-\underset{}{\overset{H}{N}}-\overset{O}{\overset{\|}{C}}-C_6H_5 + HCl$$

The electron-withdrawing effect of the phenyl group makes benzoylation slower than ethanoylation. Benzoylation is best carried out in presence of sodium hydroxide.

The reaction cannot be carried out with tertiary amines because they do not contain hydrogen atom attached to nitrogen.

5. **Formation of Diazonium Salts**

Primary amines react with dioxonitrate (III) acid, HNO_2, generated in situ by the action of dilute hydrochloric acid on sodium dioxonitrate (III), $NaNO_2$ to form diazonium salts.

$$R-NH_2 + HNO_2 + HCl \rightarrow R-N\equiv\overset{+}{N}Cl^- + 2H_2O.$$

Alkyl diazonium salts are unstable and decompose immediately to form nitrogen and a carbocation.

$$R-N\equiv\overset{+}{N}Cl^- \rightarrow R^+ + N_2 + Cl^-$$

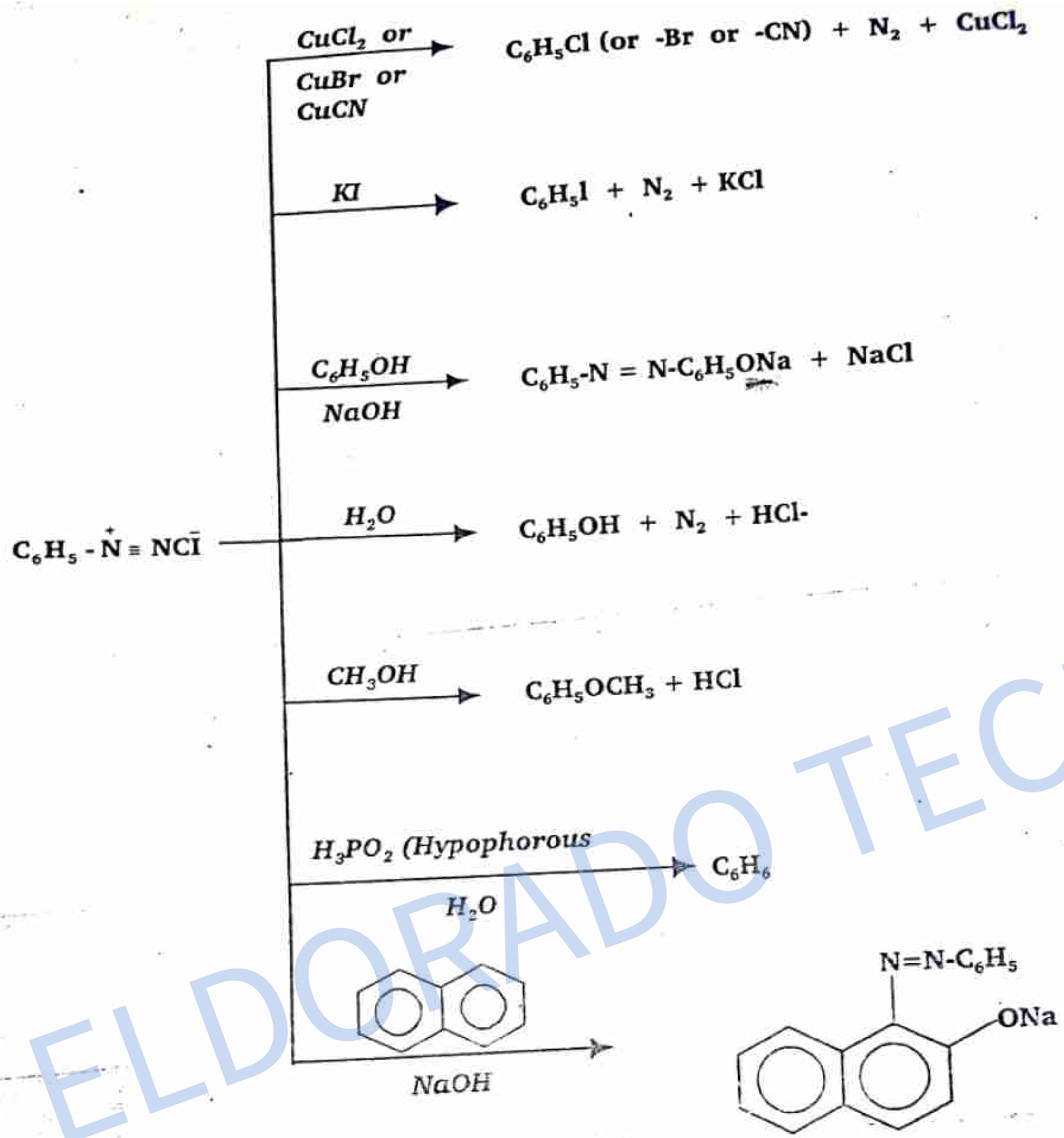
The carbocation can be used as an intermediate for the production of various products. For example it can react with water to form an alkanol or rearrange to form an alkene.

$$R^+ + H_2O \rightarrow ROH + H^+$$

$$\therefore \quad CH_3-CH_2-\overset{+}{C}H_2 \rightarrow CH_3CH=CH_2 + H^+$$

Aromatic diazonium salts are more stable and can be isolated at very low temperatures such as 0-5°C. Thy can be used as synthetic intermediates for many very important compounds.

$$C_6H_5-NH_2 + HNO_2 + HCl \xrightarrow{0-5^\circ C} C_6H_5-\overset{+}{N}\equiv NCl^- + 2H_2O$$



6. The "Carbylamine" Reaction

Primary aliphatic amines when warmed with an alcoholic solution of potassium hydroxide and trichloromethane react to form isonitriles.

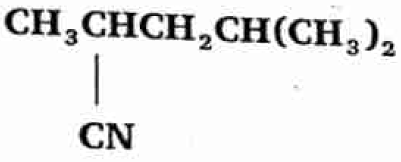
$$CH_3-NH_2 + CHCl_3 + 3KOH \rightarrow CH_3-\overset{+}{N}\equiv\overset{-}{C} + 3KCl + 3H_2O$$

Isocyanomethane
(Carbylamine)

This reaction is used to distinguish primary aliphatic amines from secondary and tertiary amines, which do not form isonitriles.

REVIEW QUESTIONS

1. Give the IUPAC names of the following compounds

a.

$CH_3CH(CN)CH_2CH(CH_3)_2$

b. $CH_3CH_2C(C_2H_5)_2CH_2NH_2$

2. Write down the structural formulae of the following

a. *3-methyl-5-ethyloctanonitrile*
b. *N, N-dimethylethlamine*
c. *N-methyl-4-nitrophenylamine.*

3. Complete the following reactions:

a. $CH_3CH_2Br + KCN? \xrightarrow{DMF} ?$

b. $CH_3CONH_2 \xrightarrow{P_2O_5} ?$

c. $CH_3CH(CH_3)CN \xrightarrow{H_2O} ?$

d. $CH_3(CH_2)_4CN \xrightarrow{LiAlH_4} ?$

4. Write balanced equations to illustrate the reduction of the following:

(a) *Propanonitrile* (b) *Propanamide.*

Multiple Choice Questions

1. Carbon forms many compounds because: I. Carbon atoms can form a long chain. II. Carbon can form multiple bonds. III. Carbon atoms can form rings.
   A. I Only ***B. II Only*** ***C. III Only*** ***D. I, II and III.***

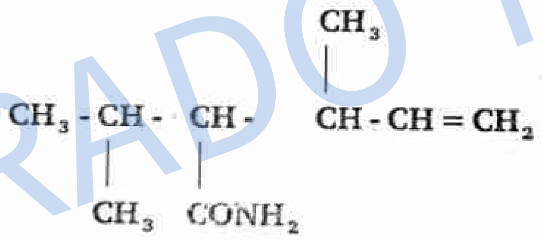
2. Carbon forms single and multiple bonds because it can
   A. Polymerise ***B. Catenate*** ***C. Hybridise*** ***D. All of the above.***

3. The number of sigma bonds in the propyne molecule is ***A. 8*** ***B. 7*** ***C.6*** ***D. 5***

4. A heterocyclic compound is: ***A. A cyclic compound***
   B. A cyclic compound that is heterocyclic in nature
   C. An alicyclic hetero compound
   D. An alicyclic compound with an atom other than carbon in the ring.

5. A functional group I. Identifies the family of organic compounds
   II. Determines the chemical properties of a family of organic compounds.
   III. Determines the physical properties of the family of organic compounds.
   A. I only ***B. II only*** ***C. I and II only*** ***D. I, II and III***

6. The IUPAC name of



$CH_3-CH(CH_3)-CH(CONH_2)-CH(CH_3)-CH=CH_2$

   A. 3 - methyl - 2 - (1 - methylethyl) pent-4-enamide
   B. 3 - methyl - 2 - (1 - methylpropyl) pent-4-enamide
   C. 3 - methyl - 2 - propylpent- 4 - enamide
   D. 3, 5 dimethyl - 4 - carbonylhex - l - ene.

7. The number of structural isomers with molecular formular $C_4H_{10}O$ is
   A. 6 ***B. 5*** ***C. 4*** ***D. 3***

8. Which of these is functional group of nitrile
   A. -NH₂ ***B. -CN*** ***C. -COCl*** ***D. -CONH₂***

9. The general molecular formular of the Cycloalkanes is
   A. C_nH_n ***B.*** C_nH_{2n} ***C.*** C_nH_{2n+2} ***D.*** C_nH_{2n-2}

10. Two compounds have the same molecular formular, the same structure but different orientations of some atoms or groups. The compounds are
    A. Structural isomers ***B. geometrical isomers***
    C. Optical isomers ***D. Enantiomers.***

11. The reduction of alkylnitriles with $LiAlH_4$ in ether gives
A. Arylhalide **B. Acylhalide** **C. Alkylhalide** **D. Alkylamine**

12. The order of reactivity of hydrogen halides is **A. $HF>HCl>HBr>HI$**
B. $HF<HCl<HBr<HI$ **C. $HF<HBr<HCl>HI$** **D. $HF>HI>HBr>HCl$.**

13. Primary amines react with acid halides to form:
A. Primary alkanol **B. Secondary alkanol** **C. Tertiary alkanol** **D. Amide.**

14. Grignard reagent decomposes in the presence of water to give
A. Alkylhalide **B. Acylhalide** **C. Alkene** **D. alkane.**

15. The reaction that is used to prepare symmetrical alkanes is
A. Esterification **B. Gabriel's synthesis** **C. Wurtz reaction** **D. Clemmensen reaction.**

16. Ozonolysis of 3-methylhex-3-ene in the presence of ozone and zinc in ethanoic acid gives
A. Propanone and butanal **B. Propanone and butan-2- one.**
C. Propanal and butanal **D. Propanal and butan-2-ol.**

17. Sodium alkynides react with halogenoalkanes to form
A. Alkanes **B. Alkenes** **C. Alkynes** **D. Alkylhalides.**

18. The method for converting of carbonyl group to a methylene group is
A. Hydrohalogenation **B. Hydroxylation**
C. Hydrogenation **D. None of the above.**

19. $CH_2-CH_2-CH_2-Br \xrightarrow[C_2H_5OH]{KOH} X \xrightarrow{HBr} Y$. X and Y are respectively
A. $CH_3-CH=CH_2$ and $CH_3-CH_2-CH_2Br$ B. $CH_3-CHBrCH_2Br$ and $CH_3-CHBr-CH_3$
C. $CH_3-CH=CH_2$ and $CH_3-CHBrCH_3$ D. $CH_3-CH_2-CH_3$ and $CH_3-CH_2-CH_2Br$

20. $CH_3-CH_2-CH_2CH=CH_2 \xrightarrow[H_2O]{Br_2} X$ X is
A. $CH_3-CH_2-CH_2-CHBrCH_2-OH$ B. $CH_3-CH_2-CH_2-CHOHCH_3$
C. $CH_3-CH_2-CH_2-CHOHCH_2-Br$ D. $CH_3-CH_2-CH_2-CHOHCH_3$

21. Analysis of an organic compound containing carbon hydrogen and oxygen only showed it to contain 48.7[illegible] C and 8.07% H. The empirical formular of the compound is (C = 12, H = 1, O = 16)
A. C_2H_6O B. C_2H_5O C. $C_3H_6O_2$ D. None of the above.

22. An organic compound was analysed using sodium fusion test. If the fusion filtrate turned purple on the addition of sodium nitroprusside, it shows of
A. Sulphur B. Nitrogen C. Chlorine D. Bromine

23. In a [illegible] chromatography, the stationary and mobile phases respectively are
A. liquid and gas B. liquid and solid C. gas and liquid D. solid and gas

24. The [illegible] boiling point of the [illegible] [illegible] solvent extraction D. Crystallisation
A distillation [illegible]

25. Recrystallisation can be improved by one of the following:
A. Adding a crystal of the compound of interest
B. Increasing the temperature of the solution
C. Reducing the saturation of the solution
D. All of the above.

26. In chromatography Rf value refers to:
A. Ratio of solvent to that of solute
B. Ratio of solute distance to that of the solvent front.
C. Ratio of solvent to eluent
D. Ratio of eluent to solvent.

27. One of the following is untrue of steam distillation
A. It is used to isolate steam-volatile compounds
B. Is used to isolate compounds that are insoluble in water
C. The water must dissolve impurities.
D. Two layers are usually formed at the end.

28. One of these alkanols reacts readily with Lucas reagent:
A CH_3CH_2OH
B. $(CH_3)_3COH$
C. $CH_3CHOHCH_3$
D. $CH_3(CH)_2CH_2OH$

29. An alkanol in which the carbon atom that has the hydroxyl group is attached to two alkyl groups is
A. Primary alkanol
B. Secondary alkanol
C. Tertiary alkanol
D. Polyhydric alkanol.

30. Alkanols can undergo the following reactions except:
A. Esterification
B. Oxidation
C. Dehydration
D. Reduction

31. Acid hydrolysis of nitrile gives:
A. Amine
B. Alkanol
C. Alkanoic acid
D. Salt of the acid

32. One of these is not correct about alkanoic acid
A. Alkanoic acids are stronger than mineral acids
B. The readiness with which OH group splits to release its proton determines the strength of the acid
C. The C=O in acid withdraws electron and this facilitates the split of OH bond
D. The OH group in acid splits more readily than that of alkanol

33. Alkanoic acids undergo the following reaction except:
A. $CH_3COOH + SOCl_2 \rightarrow CH_3COCl + HCl + SO_2$
B. $CH_3COOH + CH_3OH \leftrightarrow CH_3COOCH_3 + H_2O$
C. $CH_3COOH\ 4[H] \rightarrow CH_3CH_2OH + H_2O$
D. $CH_3COOH + [O] \rightarrow CH_3CH_2OH + H_2O$

34. The following equations can be used to prepare acid chloride except:
A. $CH_3COOH + SOCl_2 \rightarrow CH_3COCl + HCl + SO_2$
B. $CH_3CH_2COOH\ PCl_5 \rightarrow CH_3CH_2COCl + H_3PO_3$
C. $CH_3CH_2COOH + Cl_2 \rightarrow CH_3CH_2COCl + HCl$
D. $C_6H_5COOH + PCl_5 \rightarrow C_6H_5COCl + POCl_3 + HCl$

35. Hydrolysis of acid anhydride gives:
A. Alkanols
B. Acids
C. Acid chloride
D. None of the above

36. The reaction of acid chloride with ammonia produces
A. Amine
B. Acid amide
C. Acetic anhydride
D Nitrile

37. The reduction of acid chlorides with hydrogen in the presence of palladium poisoned by barium tetraoxosulphate (IV) is called:
A. **Clemensen reduction** B. **Rosenmund reduction**
C. **Hofmann reduction** D. **Roseman reduction**

38. One of these is a mixed anhydride A. $CH_3COOCOCH_3$ B. $CH_3COOCOC_2H_5$
C. $C_2H_5COOCOC_2H_5$ D. $C_3H_7COOCOC_3H_7$

39. Acid anhydride reacts with water to yield
A. **Alkanols** B. **Alkanoates** C. **Alkanals** D. **Alkanioc acids**

40. All of the following are naturally occurring alkanoates except:
A. **Waxes** B. **Oils** C. **Fats** D. **Margarine.**

41. All of the following statements about nitriles are correct except:
A. **The simplest organic nitrile is propanonitrile,**
B. **Small nitriles are liquid at room temperature,**
C. **Nitriles react with $LiAlH_4$ in ether to give primary amines,**
D. **Small nitriles have high boiling points due to polarity of $-C^{\delta+} \equiv N^{\delta-}$ bond.**

42. Ammonolysis of alkanoate leads to the production of
A. **Hydrochloric acid** B. **Alkanoic acid** C. **Amide** D. **Amine.**

43. The reaction of propanone and hydrogen cyanide generates
A. **Hydroxy propanonitrile,** B. **2 - hydroxy - 2 - methylpropanonitrile,**
C. **Propanonitrile** D. **2 - hydroxy propanonitrile**

44. Oils melt below room temperature because they are
A. **Saturated** B. **Unsaturated** C. **Alkanoates** D. **Liquids**

45 Fats and waxes are collectively referred to as:
A. **Liquids** B. **Fats** C. **Lipids** D. **Glycerol.**

46. Alkaline hydrolysis of fats and oils to form soap is known as:
A. **Saponification** B. **Esterification** C. **Alkanolysis** D. **Soaponification.**

47. The reduction of alkanals and alkanones in the presence of hydrazine and KOH is known as:
A. **Clemmensen reduction** B. **Haloform reaction**
C. **Aldol condensation reaction** D. **Wolff Kishner reaction**

48. When nitriles are heated with dil HCl:
A. **Alkanol is produced,** B. **Alkanone is generated,**
C. **Ammonia gas is produced** D. **Alkanoic acid is formed**

49. The dehydration of amides to nitriles is achieved by the addition of
A. P_4O_{10} B. Conc. H_2SO_4 C. H_3PO_4 D. **None of the above**

50. What is the formula for the compound produced from the reduction of propanone with $LiAlH_4$
A. C_3H_8O B. C_3H_7O C. C_3H_6O D. C_3H_8OH

51. The following are solutions used in differentiating alkanals from alkanones except:
A. **Fehling's Solution** B. **Tollen's reagent**
C. **Acidified $KMnO_4$ Solution** D. **Sodium in ethanol**

3. Complete the following reaction schemes.

a. $CH_3COCl + ? \rightarrow CH_3COOCH_2CH_3 + HCl$

b. $CH_3COCl + CH_3NH_2 \rightarrow ?$

c. $C_6H_6 + CH_3COCl \xrightarrow{AlCl_3} ?$

d. $? \xrightarrow[Pd/BaSO_4]{H_2} CH_3CH_2CHO$

e. $CH_3CH_2COOCH_3 + NH_3 \rightarrow ?$

f. $CH_3CH_2COOCH_3 \xrightarrow{LiAlH_4} ?$

g. $? \xrightarrow{LiAlH_4} CH_3CH_2CH_2NH_2$?

h. $CH_3CONH_2 + ? \rightarrow CH_3COOH + N_2 + H_2O$

i. $CH_3CH_2CONH_2 \xrightarrow{?} CH_3CH_2C \equiv N$

j. $CH_3CH_2CONH_2 \xrightarrow{?} CH_3CH_2NH_2$.

3. **Reaction with dioxonitrate (III) acid, HNO_2**

Amides react with HNO_2, generated in situ from sodium dioxonitrate (III) and dilute acid, to form the corresponding acid and nitrogen.

$$R-CONH_2 + HNO_2 \rightarrow RCOOH + N_2 + H_2O$$

4. **Dehydration**

Amides are dehydrated to nitriles when heated with phosphorous (V) oxide.

$$R-CONH_2 \xrightarrow[\Delta]{P_2O_5} R-C\equiv N + H_2O$$

5. **Hofmann's degradation of Amide**

This is the reaction of amides with bromine (or chlorine) and alkali. The reaction converts $-CONH_2$ group to $-NH_2$ group i.e. an amine with one carbon atom less is formed

$$R-CONH_2 + Br_2 + 4KOH \rightarrow R-NH_2 + 2KBr + K_2CO_3 + 2H_2O$$

$$R-CONH_2 \xrightarrow[KOH]{Br_2} R-NH_2$$

REVIEW QUESTIONS

1. Starting from ethanoic acid show how you can obtain the following: *ethanoyl chloride, ethyl ethanoate and ethanamide.*

2. It is proposed to convert ethanoic acid, CH_3COOH to ethylamine, $CH_3CH_2NH_2$ by the following steps:

i. $CH_3COOH \rightarrow CH_3COOCH_3$

ii. $CH_3COOH_2 \rightarrow CH_3CONH_2$

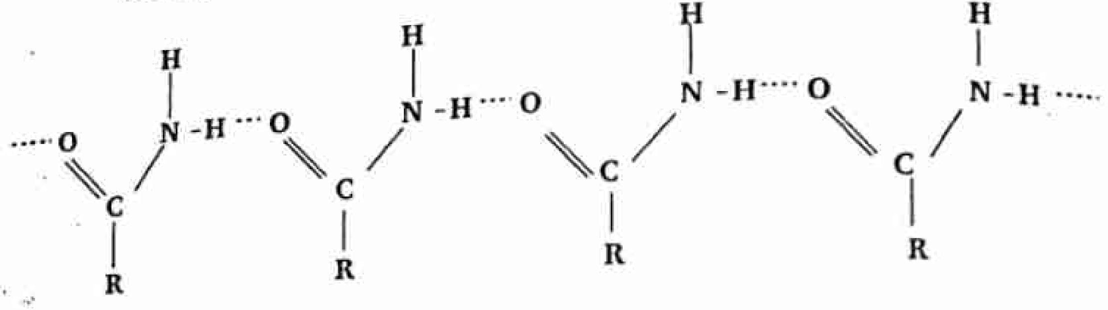
iii. $CH_3CONH_2 \rightarrow CH_3CH_2NH_2$

State the reagents and the conditions required for these steps.

10.6.2. Physical Properties

1. Ethanamide is a liquid at room temperature. The other members of the family are colourless crystalline solids.

2. They have quite high boiling points and melting points when compared with other acid derivatives because they are capable of strong intermolecular hydrogen bonding.



10.6.3. Chemical Properties

Amides are generally less basic than their corresponding amines. They are protonated under strongly acid conditions. **The lower basic character of amides is due to the presence of the electron withdrawing carbonyl group, which decreases the electron density of the lone pair on nitrogen.**

1. **Hydrolysis**

Amides are hydrolysed slowly by water and more readily by acids and alkalis. The alkaline hydrolysis is relatively faster. Acid hydrolysis gives the free acid, while alkaline hydrolysis gives the salt of the acid and ammonia.

$$R\text{-}CONH_2 + H_2O + H^+ \rightarrow R\text{-}COOH + NH_4^+$$

$$R\text{-}CONH_2 + \bar{O}H \rightarrow RCO\bar{O} + NH_3$$

The mechanisms of the reactions are similar to those for the hydrolysis of alkanoates but amides are hydrolysed more slowly.

2. **Reduction**

Primary amides are readily reduced to primary amines by reducing agents such as Na/C_2H_5OH and $LiAlH_4$

$$R\text{-}CONH_2 + 4(H) \rightarrow RCH_2NH_2 + H_2O$$

c. *How would you distinguish between the isomers?*

d. *Use chemical equations to show how you would convert the isomers were possible to named alkanes.*

2. a. Give the structure and name of

i. *a primary alkanol:*

ii. *a secondary alkanol*

iii. *a tertiary alkanol.*

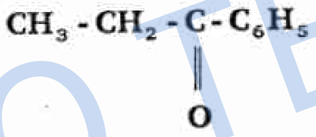
b. Give one method of preparation of the alkanol named in (a) above.

3. Complete the following reaction schemes.

(a) $C_2H_3\text{-}COOH \xrightarrow{?} C_2H_5CH_2OH$

(b) $CH_3CH=CHCHO \xrightarrow{H_2/Ni} ?$

(c) $? \xrightarrow[H_2SO_4]{KMnO_4}$



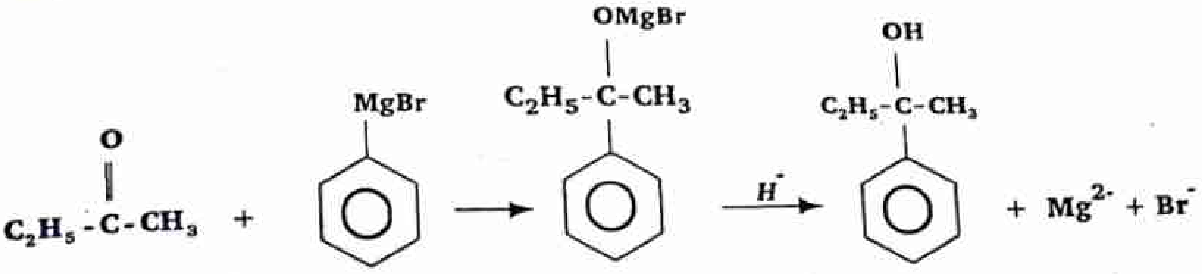
$CH_3\text{-}CH_2\text{-}\underset{\underset{O}{\|}}{C}\text{-}C_6H_5$

(d) $CH_3CH(CH_3)CH(OH)CH_3 \xrightarrow[\Delta]{Al_2O_3} ?$

(e) $CH_3COOH + CH_3CH_2CH_2OH \xrightarrow{H^+} ?$

(f) $CH_3CH(OH)CH_2CH_3 + K_2Cr_2O_7 \xrightarrow{H_2SO_4} ?$

4. Arrange the following in order of increasing boiling points and explain the order. Butan-2-ol, pentane, butan-1-ol and 2-methylbutane.



2-phenylbutan-2-ol

This method is very convenient for preparing tertiary alkanols.

7.3. PROPERTIES

7.3.1. Physical Properties

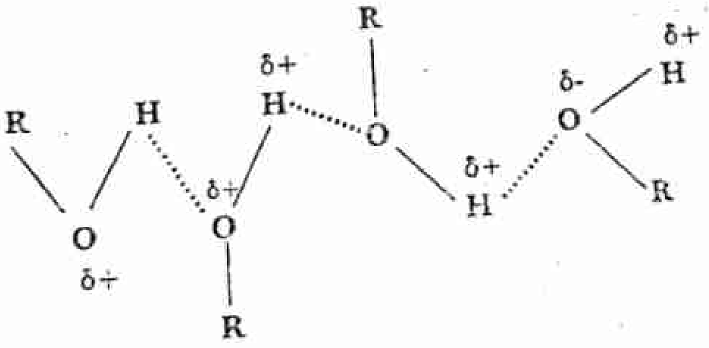
The lower members i.e. methanol to the butanols are liquids with distinct odour and burning taste. Higher members are waxy solids which are almost odourless.

Methanol to propanol are completely miscible with water. The butanols are not completely miscible with water. The higher alkanols are almost insoluble. The solubility of alkanols in water decreases as the hydrocarbon portion increases.

Alkanols have boiling points, which are considerably higher than those of alkanes of comparable relative molecular masses or those of alkoxyalkanes (ethers) with the same molecular formula, for example,

Butan-l-ol	$CH_3CH_2CH_2CH_2OH$	118°C
Ethoxyethane	$C_2H_5OC_2H_5$	35°C
Pentane	$CH_3CH_2CH_2CH_2CH_3$	36°C

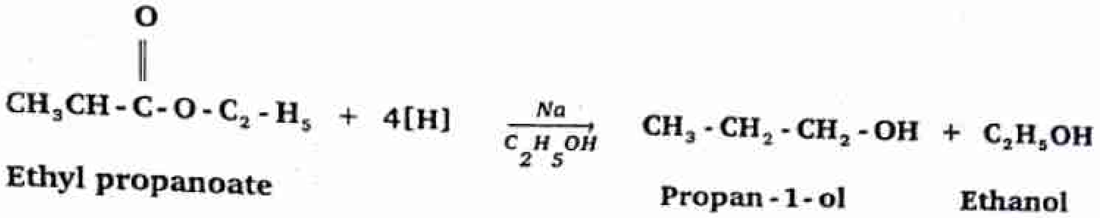
These differences arise because molecules of alkanols are associated through H-bonding.



ching reduces the boiling points of alkanols

$CH_3(CH_2)_2CH_2OH$	118°C	$CH_3CH_2CH_2OH$	97°C

only by the

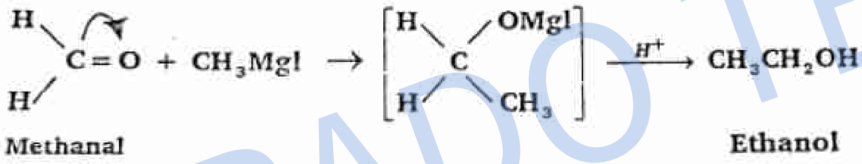


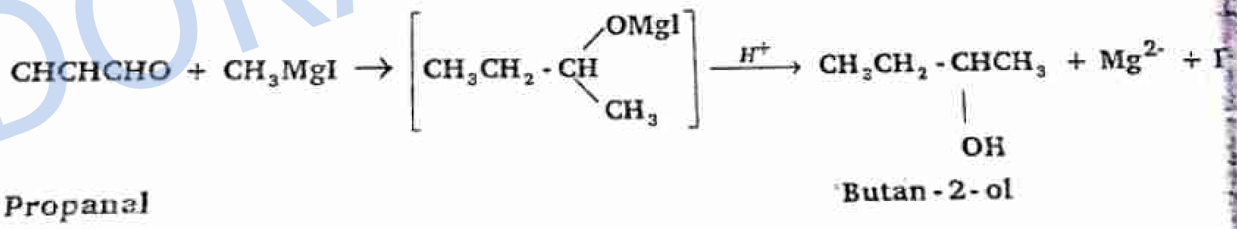
$$CH_3CH-\overset{\overset{O}{\|}}{C}-O-C_2-H_5 + 4[H] \xrightarrow[C_2H_5OH]{Na} CH_3-CH_2-CH_2-OH + C_2H_5OH$$

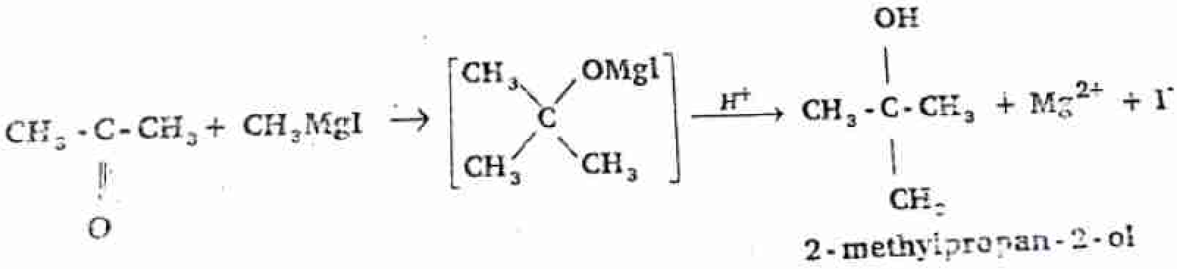
Ethyl propanoate Propan-1-ol Ethanol

4. Using Grignard Reagent

Alkanols may be prepared by reacting **Grignard reagent** and alkanal o alkanone and hydrolyzing the product with dilute mineral acid Grignard reagent is an organometallic compound with the gener formula RMgX or ArMgX where the carbon atom forming the bond wi magnesium carries a partial negative charge, for example $\overset{\delta-}{CH_2}-\overset{\delta++}{Mg}-\overset{\delta-}{Br}$. The reaction with methanal gives primary alkanol. Th reactions with other alkanals give secondary alkanols while wi alkanones tertiary alkanols are obtained.







Chapter 5

ALKYNES

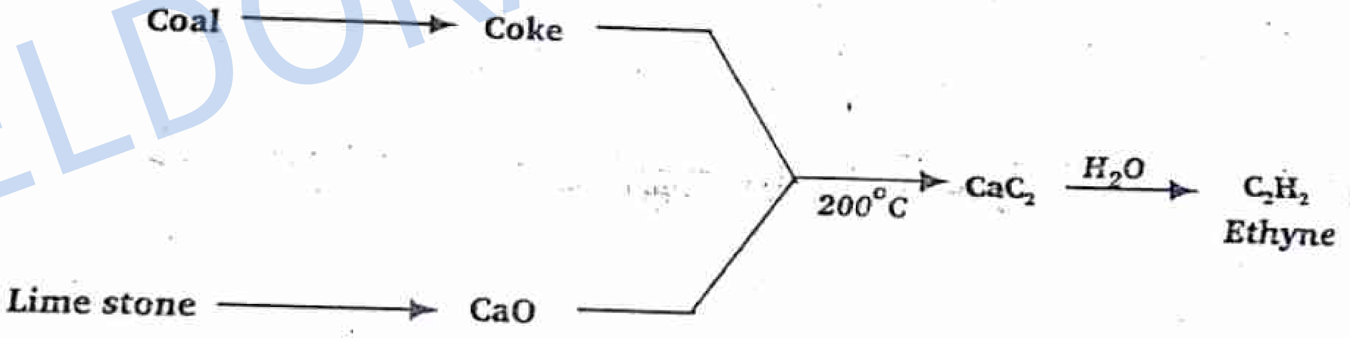
5.1. INTRODUCTION

The alkynes are unsaturated hydrocarbons containing carbon-carbon triple bond per molecule. They have the general molecular formula C_nH_{2n-2}. The first and best known member, ethyne, is a gas that is easily generated by the reaction between water and calcium dicarbide. The gas burns in oxygen to give a very hot and luminous flame. It has therefore, been used for a long time in welding and cutting metal scraps.

5.2. METHODS OF PREPARATION OF ALKYNES

1. From Calcium Dicarbide

Ethyne is manufactured by the action of water on calcium dicarbide. The calcium dicarbide is obtained by the reaction between coke and calcium oxide in the electric furnace. The coke and calcium oxide are themselves obtained in large quantities from coal and limestone respectively.

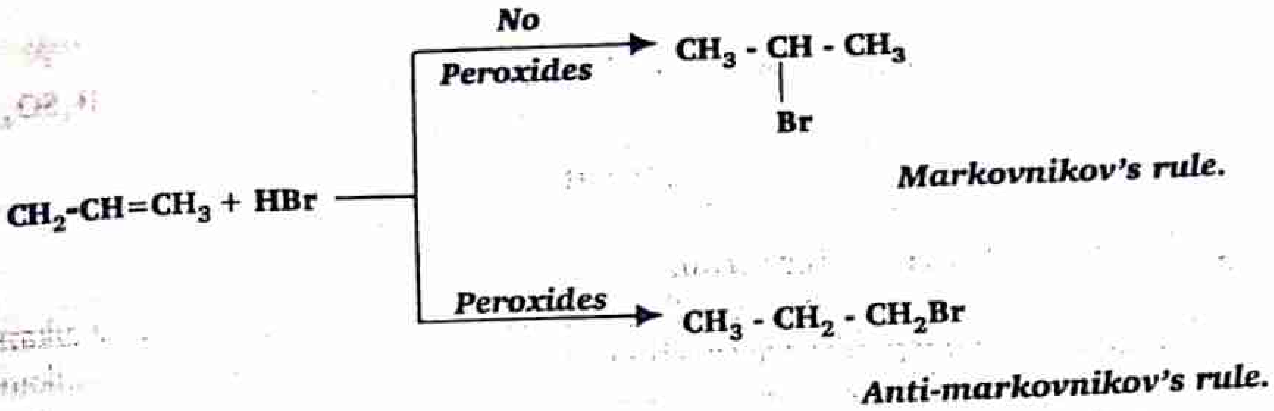


2. From Methane

The controlled partial oxidation of methane (from petroleum ad natural gas) using ai at about 1,500°C gives a mixture of ethyne, carbon (IV) oxide and hydrogen.

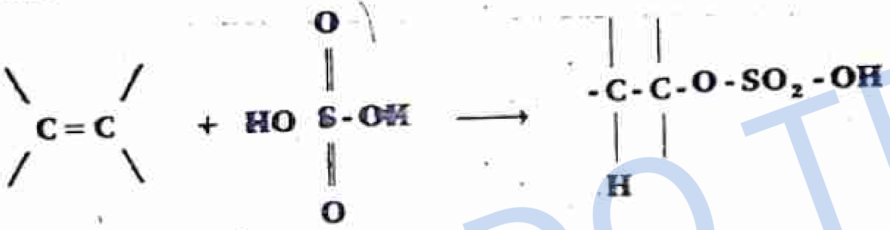
$$6CH_4 + O_2 \xrightarrow{1,500^\circ C} 2C_2H_2 + 2CO + 10H_2$$

This method is economically more feasible than the other method because of the us of the products, carbon (IV) oxide and hydrogen for the production of alkanols.



Addition of Tetraoxosulphate (VI) Acid

Alkenes react with cold concentrated tetraoxosulphate (VI) acid to form compounds of the general formula $ROSO_2OH$ alkyl hydrogen tetraoxosulphates. The products are formed by the addition of hydrogen ion and hydrogen tetraoxosulphate (VI) group, $-OSO_3H$ across the double bond. If the reaction is between the acid and unsymmetrical alkenes Markovnikov's rule is obeyed.



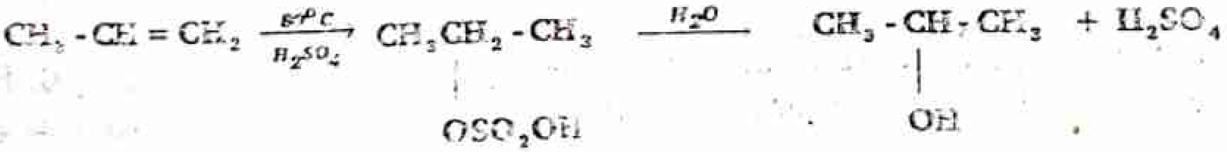
$$RCH=CH_2 + H_2SO_4 \longrightarrow \underset{\displaystyle OSO_2OH}{RCH}-CH_3$$

The reaction is carried out by bubbling gaseous alkenes into the acid or by stirring the iquid alkenes with the acid. The concentrations of the acid used depend on the alkene.

If the alkyl hydrogen tetraoxosulphate (VI) is hydrolysed with water an alkanol s obtained. This reaction therefore provides a route for the manufacture of alkanols from alkenes, which are obtained by cracking of petroleum.

Example

$$CH_2=CH_2 \xrightarrow[H_2SO_4]{95^0C} CH_3-CH_2-OSO_2OH \xrightarrow{H_2O} CH_3-CH_2-OH + H_2SO_4$$



$$CH_3-CH=CH_2 \xrightarrow[H_2SO_4]{80^0C} \underset{\displaystyle OSO_2OH}{CH_3CH_2}-CH_3 \xrightarrow{H_2O} CH_3-\underset{\displaystyle OH}{CH}-CH_3 + H_2SO_4$$

which are mainly physical. The standard physical methods are determination of vapour density, elevation of boiling point and depression of freezing point. These methods are described in physical chemistry textbooks. Mass spectrometers are also used in finding relative molecular masses.

The calculation of relative molecular masses is illustrated by the following example. Suppose the relative molecular mass of a compound with empirical formula C_2H_4NO is 116, *what is the molecular formula?*

$$(C_2H_4NO)_n = 116$$

$$[(12 \times 2) + (1 \times 4) + (14 \times 1) + (16 \times 1)]_n = 116$$

$$58n = 116$$

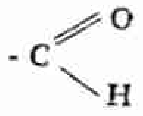
$$n = 2$$

molecular formula of the compound is $C_4H_8N_2O_2$.

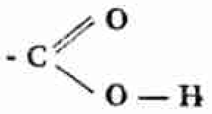
1.9. STRUCTURAL FORMULA

The structural formula of a compound shows the arrangement of the atoms in a molecule of the compound. Traditionally the procedure for the elucidation of the structure of a compound is to study its chemical behaviour. This labourous and wasteful method has been replaced by spectroscopic methods. The equipment used are however, expensive, but they give accurate result in a short time. The spectroscopic methods often used are infrared, ultra-violet and visible spectroscopy, nuclear magnetic resonance and mass spectroscopy.

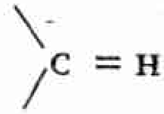
Apart from the carbon *"skeleton"* or framework of an organic compound, the functional groups attached to the framework are elucidated. The ***functional group*** is an atom or group of atoms which give an organic compound its characteristic chemical properties. For example all alkanols have the hydroxyl group, -OH, which is responsible for the chemical behaviour of alkanols. Examples of some functional groups are:



Alkanal group



Alkanoic acid group



Carbonyl group

1.10. STRUCTURAL ISOMERISM

Sometimes two or more structures are elucidated for the same molecular formula. Structural isomerism is the existence of two or more compounds with the same molecular formula but different structures. The different compounds are called *isomers*. For example, C_4H_{10} can be represented by

1 joule is an S.I. unit of work or energy. Work is derived from

$$\begin{aligned} W &= \text{Force x Distance in direction of force} \\ &= \text{Mass x acceleration x displacement} \end{aligned}$$

$1J = 1(kgms^{-2})(m)$.

$1kg = 1000g$

$1m = 100cm$

Therefore, $1J = kg(ms^{-2})(m)$

$$\begin{aligned} &= 1000g\ (100cms^{-2})100cm \\ &= 10^7gcm^2s^2 \\ &= 10^7 ergs \end{aligned}$$

Example 3

Convert a velocity of 80km/h to S.I. unit.

Solution

$1km = 1000m$

$1h = 60 \times 60s$

Therefore 80km/h

$$= 80000m/60 \times 60s$$

$$= \frac{80000}{60 \times 60} m/s$$

$$= 22.2\ m/s$$

Example 4

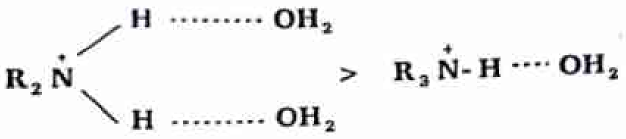
Convert an acceleration of $10ms^{-2}$ to a value in kmh^{-2}

Solution

$$1m = \frac{1}{1000} km$$

$$1s = \frac{1}{60 \times 60} h$$

by protonation can be associated with the solvent (water) i.e. solvation and become stabilised. The greater the number of hydrogen atoms attached to nitrogen in the cation, the greater the possibility of powerful solvation through hydrogen bonding with the solvent.



Thus along the series ammonia, primary amine, secondary amine and tertiary amine, inductive effect will tend to increase the basic strength but progressively less stabilization of the cation by hydration will occur. Stabilization of the cation decreases the basic strength. The net effect of introducing successive alkyl groups becomes progressively smaller and an actual change over occurs from secondary amine to tertiary amine. This makes tertiary amine the least basic. However, when the basic strength is measured in solvents in which hydrogen bonding cannot take place, the order of basic strength is tertiary amine > secondary amine > primary amine. For example in chlorobenzene, the order of basic strength of butylamines is tributylamine > dibutylamine > butylamine. But in water their pk_b, values are 3.39, 1.71 and 4.13 respectively.

2. Formation of Salts

Primary, secondary and tertiary amines like ammonia form salts with strong acids. Formation of salts is used to separate amines from non-basic compounds. The amine is regenerated by basification.

$$CH_3\text{-}NH_2 + HCl \rightarrow CH_3\overset{+}{N}H_3Cl^-$$

Methyl ammonium chloride

$$CH_3\overset{+}{N}H_3Cl^- + NaOH \rightarrow CH_3NH_2 + NaCl + H_2O$$

$$C_6H_5NH_2 + HCl \rightarrow C_6H_5\overset{+}{N}H_3Cl^-$$

Phenylammonium chloride

3. Alkylation

Primary and secondary amines react with halogenoalkanes to give further N-substituted derivatives. Primary amines form secondary amines, while secondary amines form tertiary amines.

HE WHO FELLOWSHIPS WITH THE HOLY SPIRIT IS A REFLECTOR OF SUCCESS FOR THE HOLY SPIRIT IS THE AUTHOR OF SUCCESS.

~ELDORADO TECH