UNIT 6 ALKANES

Structure

6.1 INTRODUCTION

Alkanes are saturated aliphatic hydrocarbons. You have already learnt in your previous classes that the saturated aliphatic hydrocarbons have the general formula, C_nH_{2n+2}, Because of their zig-zag patterns due to the tetrahedral geometry of sp^3 hybridised carbon, carbon atoms which are close together often join up with expulsion of two hydrogen atoms to form a ring. Such ring compounds are referred to as cyclic aliphatic hydrocarbons, also called alicyclic hydrocarbons or cycloalkanes which have the general formula, C_nH_{2n}.

Alkanes are also known as **paraffins**. The name paraffin comes from two Latin words, "Paraum and affinis", which mean "little affinity". This name was suggested because these alkanes are inert toward reagents such as acids, alkalies oxidising and reducing agents. However, under suitable conditions, alkanes undergo different types of reactions like halogenation, pyrolysis, aromatisation, etc. Many of these reactions proceed through the formation of highly reactive free radicals.

In this unit, first we shall discuss composition and fractionation of petroleum, as it is the main source of alkanes. Then we shall discuss the preparation, physical properties and spectral properties of alkenes. Finally, we shall study some chemical reactions of alkanes and cycloalkanes.

Objectives

After studying this unit, you should be able to :

- describe the composition and fractionation of petroleum,
- define octane number and cetane number,

- discuss the physical properties of alkanes,
- list the characteristic spectral peaks of alkanes in uv, ir, nmr and mass spectra,
- list the methods for preparation of alkanes and cycloalkanes,
- discuss the important chemical reactions of alkanes and cycloalkanes.

6.2 PETROLEUM : A SOURCE OF ALKANES

Petroleum is an oily, viscous inflammable and usually dark coloured liquid. The origin of the mixture of alkanes occurs abundantly in various natural deposits in the earth.

The biggest oil-producing country of the world is the USA. The other major oil producing countries are **Russia, Venezuela, Iran,** Gulf countries, Romania, Nyammar, Pakistan and India.

Petroleum is an oily, thick inflammable and usually dark coloured liquid. The origin of the word petroleum is from the Latin words petra (rock) and oleum (oil), as it is found in abundance near the surface of the earth trapped by rock structure.

Petroleum industry in India has made headway only after independence. In the last 30 years, petroleum production and refining levels have increased by more than 100 times whereas the consumption has increased by around 15 times. It is worth mentioning that even with this increased productivity, only two-thirds of our needs are satisfied.

Petroleum can be separated into various fractions known as gasoline, naphtha, kerosene, etc. In the following section, we will study the composition of petroleum in detail.

6.2.1 Compositon of petroleum

Liquefied petroleum gas (LPG) contains a mixture of propane and butane.

The composition of petroleum varies with the locality of its occurrence but all samples contain mixtures of alkanes ranging in size from methane with only one carbon atom to long chain hydrocarbon containing upto 40 carbon atoms. Cyclohexane, naplthene and other aromatic hydrocarbons are also present in small amounts. In addition to hydrocarbons, oxygen, nitrogen and sulphur containing compounds as well as metallic constituents may also be present. In fact, as many as 500 compounds have sometimes been detected in a single sample of petroleum.

Natural gas is found along with petroleum whose major components are methane (80%) and ethane (10%). The remaining 10% being a mixture of higher hydrocarbons. Besides hydrocarbons, natural gas also contains carbon dioxide and nitrogen.

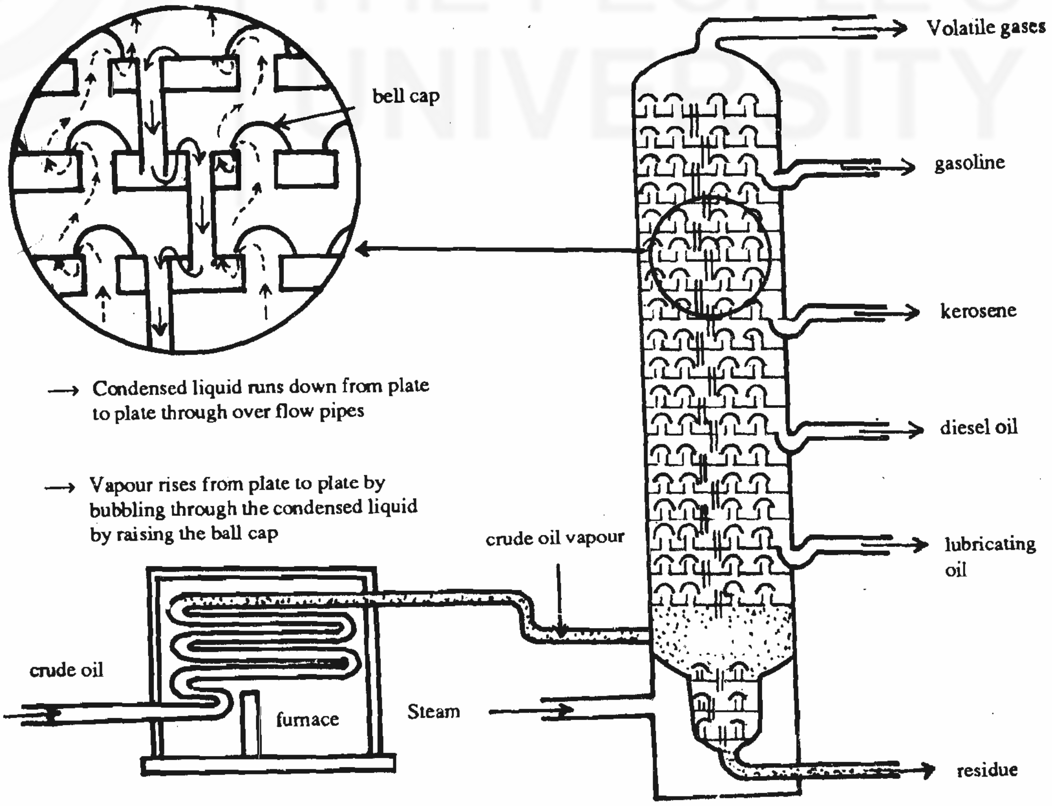


Fig. 6.1 : Fractionation of Petroleum

The petroleum obtained directly from the ground is not readily usable, since it is a mixture of many compounds. Separating the crude petroleum into useful components is called **refining**. The first step in refining is fractional distillation.

6.2.2 Fractionation of Petroleum

The first step in the refining of petroleum involves its separation into fractions of different boiling ranges by fractional distillation. Crude petroleum is heated in a furnace at 650 K and the hot liquid is then passed through a flash chamber where the low boiling fractions are volatilised by lowering the pressure. The vapours are then passed through a tall bubble tower. This tower is filled with horizontal stainless steel trays. Each tray is provided with chimneys covered with a loose cap called **bell cap** (Fig. 6.1). As the vapours ascend, they become gradually cooler and, therefore, various fractions condense at different heights. The higher boiling fractions condense in the lower portion of the tower. This permits the separation of crude petroleum vapours into a number of fractions, each condensing within a definite temperature range. Each fraction is a mixture of different hydrocarbons. Therefore, it has to be purified prior to use.

The important petroleum fractions along with their boiling ranges and chief uses are given in Table 6.1.

Tabe 6.1 : Fractionation of Petroleum

Name	B.P. (K)	Approximate composition	Uses
Natural gas		C_1-C_4	Refinery and domestic fuel
Light petrol	293-373	C_5-C_7	Solvent
Benzine	343-363	C_6-C_7	Dry cleaning
Ligroin	353-393	C_6-C_8	Solvent
Petrol (gasoline)	343-473	C_6-C_{11}	Motor fuel
Kerosene (paraffin oil)	473-573	C_{12}-C_{16}	Lighting
Gas oil (heavy oil)	above 573	C_{13}-C_{18}	Fuel oil
Lubricating oil (mineral oil)	above 573	C_{16}-C_{20}	Lubricants
Greases, Vaseline, Petroleum	above 573	C_{18}-C_{22}	Pharmaceutical preparations
Paraffin wax (hard wax)	above 573	C_{20}-C_{30}	Candles, waxed paper, etc.
Residue (asphaltic bitumen)	above 573	C_{30}-C_{40}	Asphalt tar, petroleum coke

6.2.3 Synthetic Petroleum

With the development of civilization and the growth of industry, the demand of gasoline and petroleum products is increasing day by day. The natural resources are limited and it is feared that they will soon be exhausted. Keeping this in mind, the chemists have tried different methods of manufacturing synthetic fuels. Following processes have shown some promise.

Bergius Process. In this process, finely powdered coal is hydrogenated in presence of catalysts, such as tin and lead to give a mixture of liquid hydrocarbons. During this process, the carbon rings in coal undergo fission to give smaller fragments which are then hydrogenated to open chain and cyclic hydrocarbons. Gasoline (bp upto 473 K) and kerosene (bp upto 573 K) are obtained on fractional distillation of hydrogenation products.

Fischer-Tropsch Process. This method was developed in 1923 by two German chemists, Franz Fischer and Hans Tropsch. Water gas, which is a mixture of carbon monoxide and hydrogen, is obtained by the reaction of steam with red hot coke. The water gas is mixed with half its volume of hydrogen and the catalyst used in the process is a mixture of cobalt (100 parts), thoria (5 parts), magnesia (8 parts) and kieselguhr (100 parts). This water was when hydrogenated and passed over a catalyst at 470-870 K under 1-10 atm pressure yields crude petroleum.

$$nCO + mH_2 \longrightarrow \text{Mixture of hydrocarbons} + H_2O$$

The crude oil obtained is refined by the fractional distillation process as described earlier.

6.2.4 Octane Number

The most commonly used fuel for automobiles is gasoline. Not all fuel are equally good. Let us see how we can differentiate between good quality and bad quality fuels. This can be done by comparing their octane numbers. Octane number is a measure of the quality of gasoline : the higher the octane number, the better the fuel.

The 2, 2, 4-trimethylpentane (iso-octane), which is considered a good fuel, is given an octane number of 100 whereas *n*-heptane, a very poor fuel, is given an octane number of zero. Mixture of these two compounds are used to define octane numbers between 0 and 100. Octane number is the percentage of 2, 2, 4-trimethylpentane present in a mixture of 2, 2, 4-trimethylpentane and *n*-heptane which has similar ignition properties as the fuel under examination. For example, a fuel that performs as well as a 1 : 1 mixture of 2, 2, 4-trimethylpentane and *n*-heptane has an octane number 50. Commercial gasoline has octane number 81, 74 and 65 for the premium, regular and third grade gasoline. Good quality motor fuels used in modern automobiles have octane number in the 87-95 range.

It has been observed that :

- branching of the hydrocarbon chain increases octane number
- octane number decreases as the chain length increases
- unsaturated hydrocarbons have higher octane number than saturated hydrocarbons
- cycloalkanes have higher octane number than the corresponding acyclic alkanes.

Various additives, such as tetraethyllead, $(C_2H_5)_4Pb$ and *tert*-butyl methyl ether, $(CH_3)_3COCH_3$, are used to boost the octane number of gasoline. The use of tetraethyllead is being curtailed for environmental reasons.

6.2.5 Cetane Number

The working of diesel engine differs from that of gasoline engine. In diesel engines, fuels having a lower octane number are much more useful than those having a higher octane number. In other words, the straight chain hydrocarbons constitute a superior fuel than the branched chain hydrocarbons. Quality of diesel fuel is expressed in terms of a number called **cetane number**.

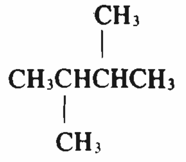
The hexadecane (cetane, $C_{16}H_{34}$), considered a good fuel, is given a cetane number 100 whereas α-methylnaphthalene, a very poor fuel, is given a cetane number zero. Cetane number is defined as the percentage of hexadecane in a mixture of hexadecane and α- methylnaphthalene which has similar ignition properties as the fuel under examination. Good quality diesel fuel required for modern diesel engine have cetane number greater than 45.

SAQ 1

State which compound has best octane rating in each of the following pairs.

a) $CH_3(CH_2)_4CH_3$; $CH_3CH_2CH_2CH_3$

b)

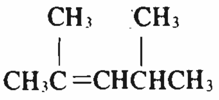


$CH_3\underset{CH_3}{CH}\overset{CH_3}{CH}CH_3$

; $CH_3(CH_2)_4CH_3$

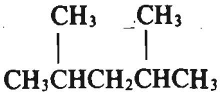
c) $CH_2{=}CHCH_2CH_3$; $CH_3CH_2CH_2CH_3$

d)



$CH_3\overset{CH_3}{C}{=}CH\overset{CH_3}{C}HCH_3$

;

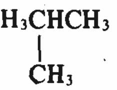
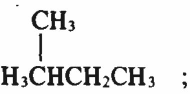
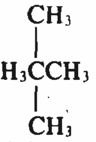


$CH_3\overset{CH_3}{CH}CH_2\overset{CH_3}{CH}CH_3$

6.3 PHYSICAL PROPERTIES

Covalent bonds of an alkane molecule are either carbon-carbon bonds or bonds between carbon and hydrogen atoms that differ very little in electronegativity. Therefore, the alkane molecule is either nonpolar or very weakly polar. Their physical constants like boiling points, densities, etc., increase with increase in the number of carbon atoms. Except for the first few members, the boiling point increases by 20 to 30 degrees for each CH_2 unit that is added to the chain. Boiling point of a covalent substance depends upon the intermolecular forces. Intermolecular forces, in turn, depend upon the number of electrons, surface area of the molecule and its dipole moment. The intermolecular forces increase with the increase in the number of electrons or in the value of the dipole moment and surface. area. The stronger the intermolecular forces, the higher the boiling point. In a particular series, with the increase in the number of carbon atoms, the surface area increases and hence, the intermolecular forces and boiling points also increase. Branching in a chain reduces the surface area and, therefore, decreases the boiling point.

	$CH_3CH_2CH_2CH_3$ butane	$CH_3(CH_2)_3CH_3$ pentane
BP (K)	273	309

	 $CH_3\underset{\underset{\textstyle CH_3}{\vert}}{C}HCH_3$ 2-methyl propane	 $CH_3\overset{\overset{\textstyle CH_3}{\vert}}{C}HCH_2CH_3$; 2-methyl butane	 $CH_3\overset{\overset{\textstyle CH_3}{\vert}}{\underset{\underset{\textstyle CH_3}{\vert}}{C}}CH_3$ 2, 2-dimethyl propane
BP (K)	261	245	276.5

Unlike boiling points, the melting points of alkanes do not show a regular increase. It has been found that molecules with an odd number of carbon atoms have lower melting point than those with an even number of carbon atoms. A possible explanation is given here. The carbon atoms in alkanes are sp^3 hybridised state with a bond angle of 109°28′. The terminal carbon atoms in a carbon chain with an odd number of carbon atoms lie on the same side, whereas those in a carbon chain with an even number of carbon atoms lie on the opposite site. This means that the packing efficiency and the interaction between the molecules in the solid state is less in alkanes containing an odd number of carbon atoms as compared to those with an even number of carbon atoms. This is reflected in the lower melting points of alkanes with odd number of carbon atoms. The maximum density of alkane is about 0.8, thus, all alkanes are lighter than water. Alkanes are soluble in nonpolar solvents but insoluble in polar solvents.

Terminal carbon atoms in a carbon chain with 5 carbon atoms (odd numbered) lying on the same side.

Terminal carbon atoms in a carbon chain with 4 carbon atoms (even numbered) lying on the opposite side.

SAQ 2

Fill in the blanks :

a) Alkane molecules are very weakly polar or nonpolar because there is very little .... difference between the carbon and hydrogen atoms.

b) Boiling point of alkanes .... with the increase in the length of the carbon chain.

c) Branching in the carbon chain .... the boiling point.

d) Alkanes are soluble in .... solvents.

6.4 SPECTRAL PROPERTIES

Uv spectroscopy is not of much help in the characterisation of alkanes, since the alkanes do not show any absorption band above 200 nm.

In the infrared (ir) spectra of alkanes, the position of C-H stretching band depends on whether the hydrogen atom is attached to a primary, secondary or tertiary carbon atom. Thus, we have the following regions :

— CH_3 2975-2950 and 2885-2860 cm^{-1}

$\underset{\vert}{\overset{\vert}{—CH_2}}$ 2940-2915 and 2870-2845 cm^{-1}

$\underset{\vert}{\overset{\vert}{—CH}}$ 2900-2880 cm^{-1}

Some C—H deformation absorption frequencies are —CH_3, 1470-1435 and 1385-1370 cm^{-1}

and $>CH_2$, 1480-1440 cm^{-1}. Two useful skeletal vibrations are : $(CH_3)_2CH$-, 1175-1165 cm^{-} and $(CH_3)_3C$-, 1255-1245 cm^{-1}. It is thus possible to detect the presence of these groups in a molecule.

The nmr spectra of alkanes give characteristic signals at, δ 0.9 (CH_3), δ 1.4 ($-\overset{|}{C}H_2$) and δ 1.5 ($-\underset{|}{\overset{|}{C}}H$).

Let us now examine the mass spectra of alkanes. The stability of the radical ions can also be presumed in the order *tert* >*sec* >*p*, hence, the fission of bonds in alkanes occurs preferentially at the branched carbon atom. When alternative fissions can occur, it is the heaviest side chain that is eliminated preferentially. Since alkyl radical ions are formed, all those with ^1H and ^{12}C will give peaks of odd masses in their mass spectra. In particular, alkanes give a series of peaks separated by 14 mass units (CH_2). The relative abundances of these peaks is usually the greatest for $C_3H_7^+$(43), $C_4H_9^+$(57) and $C_5H_{11}^+$(71), and decreases fairly regularly for the larger masses.

6.5 PREPARATION OF ALKANES AND CYCLOALKANES

Alkanes are generally obtained from natural sources : petroleum and natural gas. However, synthetic methods are more practical when a pure alkane is required. Alkanes can be prepared from : (a) alkenes or alkynes, (b) alkyl halides, and (c) carboxylic acids. You have already studied about the preparation of alkanes and cycloalkanes in your earlier classes. Here we recall only the important methods. General methods for the preparation of alkanes and cycloalkanes are summarised in Table 6.2.

Table 6.2 : Reaction for the preparation of alkane and cycloalkanes

ALKANES

Wurtz reaction

$$2RX + 2Na \longrightarrow RR + 2NaX$$

Kolbe's electrolytic method

$$R'COOK + RCOOK \longrightarrow \underbrace{R'R + 2CO_2}_{\text{at anode}} + \underbrace{H_2 + 2KOH}_{\text{at cathode}}$$

Hydrogenation of unsaturated hydrocarbons

$$RCH=CHR + H_2 \xrightarrow{\text{catalyst}} RCH_2CH_2R$$

Reduction of alkyl halides

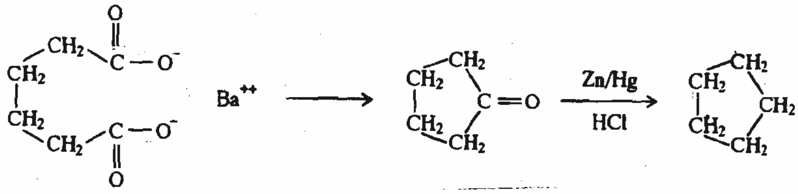
$$RX \xrightarrow[\text{agent}]{\text{reducing}} RH$$

$$RX + Mg \xrightarrow{\text{ether}} RMgX \xrightarrow[H_2O]{H^+} RH + Mg(OH)X$$

Decarboxylation of carboxylic acids

$$RCOONa + NaOH \longrightarrow RH + Na_2CO_3$$

CYCLOALKANES



Now let us study these methods in brief.

6.5.1 Wurtz Reaction

In the Wurtz reaction, an alkyl halide is treated with sodium in the presence of dry ether. The result is the joining of the two alkyl groups from two molecules of alkyl halide with the loss of halogens.

$$2RX + 2Na \longrightarrow RR + 2NaX$$

This reaction is useful only when two identical alkyl halide molecules are used. When a mixture of two different alkyl halides is used, a mixture of three different alkane is obtained. For example, if you take a mixture of bromomethane and bromoethane, you will get three different products, viz.,

$$CH_3Br + C_2H_5Br + 2Na \longrightarrow CH_3\text{-}C_2H_5 + 2NaBr$$
$$CH_3Br + CH_3Br + 2Na \longrightarrow CH_3\text{-}CH_3 + 2NaBr$$
$$C_2H_5Br + C_2H_5Br + 2Na \longrightarrow C_2H_5\text{-}C_2H_5 + 2NaBr$$

The separation of such a mixture into individual alkane is quite difficult. Thus, the Wurtz reaction between two different alkyl halides is normally useless in practice. When a single alkyl halide is used, the synthesised hydrocarbon contains an even number of carbon atoms. In other words, we can say that Wurtz reaction is suitable for the preparation of only those alkanes which contain an even number of carbon atoms. As shown above, the main difficulty with the Wurtz reaction is the formation of many side products when an alkane with odd number of carbon atoms is desired.

6.5.2 Kolbe's Electrolytic Method

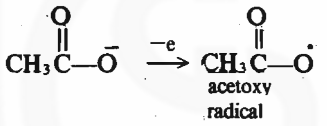
When a concentrated solution of sodium or potassium salt of a carboxylic acid is electrolysed, an alkane is formed. The method is known as Kolbe's electrolytic method.

$$RCOOK + RCOOK + H_2O \longrightarrow \underset{\text{at anode}}{RR + 2CO_2} + \underset{\text{at cathode}}{H_2 + 2KOH}$$

The following mechanistic pathway illustrates this method :

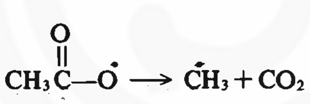
$$CH_3COOK \longrightarrow \dot{C}H_3COO^- + K^+$$

at cathode



$$CH_3\overset{O}{\overset{\|}{C}}\text{—}\bar{O} \xrightarrow{-e} CH_3\overset{O}{\overset{\|}{C}}\text{—}\dot{O}$$

acetoxy radical



$$CH_3\overset{O}{\overset{\|}{C}}\text{—}\dot{O} \longrightarrow \dot{C}H_3 + CO_2$$

$$\dot{C}H_3 + \dot{C}H_3 \longrightarrow CH_3 - CH_3$$

At cathode

$$2Na^+ \xrightarrow{+2e} 2Na \xrightarrow{2H_2O} 2NaOH + H_2$$

$$2H_2O + 2\bar{e} \longrightarrow H_2 + 2\bar{O}H$$

In case a mixture of salts of two carboxylic acids is electrolysed, a mixture of alkanes is formed:

$$R'COOK + R''COOK \longrightarrow \begin{matrix} R'R' \\ R'R'' + CO_2 + H_2 + KOH \\ R''R''. \end{matrix}$$

This reaction has limited synthetic applications because of the formation of many side products as a result of other reactions of the free radicals formed.

6.5.3 Hydrogenation of Unsaturated Hydrocarbons

Alkanes or cycloalkanes can be prepared by hydrogenation of unsaturated hydrocarbons using platinum or palladium as a catalysts. The general reaction for the reduction of alkene is :

$$\underset{\text{alkane}}{RCH{=}CHR} + H_2 \xrightarrow{\text{Pt or Pd}} \underset{\text{alkane}}{RCH_2CH_2R'}$$

$$\underset{\text{alkyne}}{RC{\equiv}CR} + 2H_2 \xrightarrow{\text{Pt or Pd}} \underset{\text{alkene}}{RCH_2CH_2R}$$

Hydrogenation of an alkene can also be carried out by using nickel catalyst but relatively higher temperature and pressure are required for this reaction. This reaction is called **Sabatier-Senderens' reaction.** An example is given below :

$$\underset{\text{1-propene}}{CH_3CH{=}CH_2} + H_2 \xrightarrow{Ni} \underset{\text{propane}}{CH_3CH_2CH_3}$$

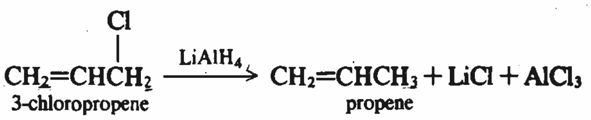
This is a very useful synthetic method and the yield is nearly 100%.

6.5.4 Reduction of Alkyl Halides

Alkanes can also be prepared by the reduction of alkyl halides by various methods. Reducing agents like zinc and acetic acid and zinc-copper couple give good yields of alkanes.

$$RX \xrightarrow[\text{agent}]{\text{Reducing}} RH$$

Lithium aluminium hydride, $LiAlH_4$, is an excellent reducing agent. Though it reduces many unsaturated functional groups, such as CO, C≡N, etc., it does not attack isolated double bond or triple bond. Dry ether is the commonly used solvent. For example,



$$\underset{\text{3-chloropropene}}{CH_2{=}CH\overset{\overset{\displaystyle Cl}{|}}{C}H_2} \xrightarrow{LiAlH_4} \underset{\text{propene}}{CH_2{=}CHCH_3} + LiCl + AlCl_3$$

Alkyl halide in ether reacts with magnesium to form alkylmagnesium halide (Grignard reagent) which, on treatment with water or dilute acid, decomposes to give alkanes. We will take up the preparation and properties of Grignard reagents in Unit 11 of this course.

$$RX + Mg \xrightarrow{\text{ether}} \underset{\text{Grignard reagent}}{RMgX} \xrightarrow[H_2O]{H^+} RH + Mg(OH)X$$

Soda lime is a mixture of NaOH and CaO. The active ingredient is NaOH, CaO helps in keeping the reaction mixture porous.

6.5.5 Decarboxylation of the Carboxylic Acids

Alkanes may be prepared through decarboxylation of carboxylic acids by heating a mixture of the sodium salt of a carboxylic acid with soda lime.

$$RCOONa + NaOH \longrightarrow RH + Na_2CO_3$$

This process of eliminating CO_2 from a carboxylic acid is known as decarboxylation. The alkanes so produced contain one carbon atom less than the original acid. The new hydrogen atom in the product is derived from soda lime.

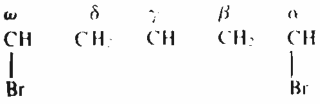
Although methane is obtained from ethanoic acid in good yield, other acids give only 10-20% of the corresponding hydrocarbon.

Sometimes decarboxylation of the acid itself is more effective than that of its salt. The direct decarboxylation of a carboxylic acid can be carried out by heating it with an organic base, such as pyridine using copper chromite ($CuO.Cr_2O_3$) as catalyst.

$$\underset{\text{propanoic acid}}{CH_3CH_2COOH} + \underset{\text{pyridine}}{C_5H_5N} \xrightarrow{CuO.Cr_2O_3} \underset{\text{ethane}}{CH_3CH_3} + CO_2$$

Next we discuss two methods of preparation of cycloalkanes.

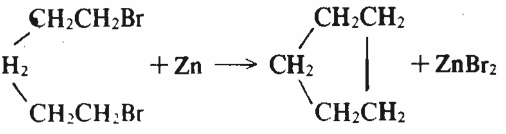
In common names Greek letters have long been used to designate position on a carbon skeleton, relative to a functional group.



1, 5-dibromopentane
(α, ω-dibromopentane)

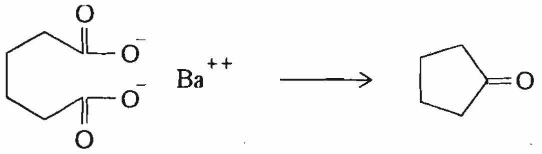
6.5.6 Preparation of Cycloalkanes

i) When 1, 5-dihalogen derivatives of alkanes are treated with sodium or zinc, the corresponding cycloalkane is formed, e.g., 1, 5-dibromopentane would form the cyclopentane :



1, 5-dibromopentane cyclopentane

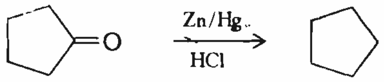
ii) When the calcium or barium salt of a dicarboxylic acid is distilled, a cyclic ketone is formed, e.g., barium adipate gives cyclopentanone



Salt of dicarboxylic acid

cyclopentanone

A cyclic ketone can be reduced into the corresponding cycloalkane using zinc amalgam and concerntrated hydrochloric acid (Clemmensen reduction). You will study Clemmensen reduction in detail in Unit 14.



cyclopentanone

cyclopentane

SAQ 3

Write the equation showing synthesis of the following alkanes from the starting materials indicated. Write your answer in the space given below :

a) Cyclohexane from cyclohexene

....

....

b) Undecane from the sodium salt of dodecanoic acid, $CH_3(CH_2)_{10}COOH$

....

....

c) Cyclopropane from 1, 3-dibromopropane

....

....

d) Butane from 1-chlorobutane

....

....

6.6 REACTIONS OF ALKANES

Alkanes are relatively unreactive to most of the common reagents. It is difficult to define the terms "reactive" and "unreactive", since a compound may be reactive under one set of conditions and unreactive under another. This reactivity or unreactivity may be explained by considering the nature of C—C and C—H bonds present in their molecules. Since the electronegativities of carbon and hydrogen do not differ appreciably, the bonded electrons in C—H are more or less equally shared between them. Thus, C—H bonds encountered in alkanes are almost nonpolar and the same is true of C—C bonds. Thus, polar and ionic reagent find no sites to attack an alkane molecule. Alkanes undergo mainly substitution reactions, which can be explained using free radical chain mechanism. These reactions take place in the presence of uv light or at a high temperature or in the presence of certain free radical initiators such as peroxides. In substitution reactions, one or more of the H atom(s) of alkanes are substituted by halogen or some other groups. Some important reactions of alkanes are given in Table 6.3.

The chemical reactions which take place in the presence of light are called photochemical reactions.

Table 6.3 : Reactions of alkanes

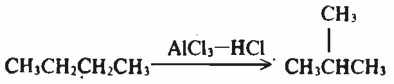
Halogenation

$$RH + X_2 \xrightarrow[\text{or } \Delta]{h\nu} RX + HX$$

Nitration

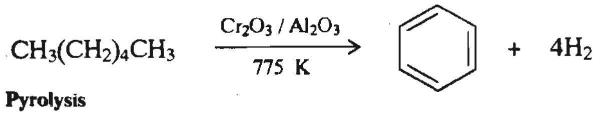
$$RH + HNO_3 \longrightarrow RNO_2 + H_2O$$

Isomerisation



$$CH_3CH_2CH_2CH_3 \xrightarrow{AlCl_3-HCl} CH_3\overset{\overset{\displaystyle CH_3}{|}}{C}HCH_3$$

Aromatisation



$$CH_3(CH_2)_4CH_3 \xrightarrow[775\ K]{Cr_2O_3 / Al_2O_3} C_6H_6 + 4H_2$$

Pyrolysis

$$CH_3CH_2CH_3 \longrightarrow CH_4 + CH_2=CH_2$$
$$\downarrow$$
$$CH_3CH=CH_2 + H_2$$

Combustion

$$CH_3CH_2CH_2CH_2CH_3 + 8O_2 \longrightarrow 5CO_2 + 6H_2O + 2549\ kJ\ mol^{-1}$$

Let us discuss these reaction in detail.

6.6.1 Halogenation

Halogenation of alkane is one of the most important reactions of alkanes. It is defined as the replacement of hydrogen atom(s), from an alkane molecule, by halogen atom(s).

$$RH + X_2 \xrightarrow{\Delta/h\nu} RX + HX$$

The reaction does not take place in dark but a vigorous reaction occurs when the mixture of alkane and halogen is exposed to light or heated to a high temperature. But in most cases, the reaction is of limited synthetic value because a mixture of products is obtained. Multiple substitutions may occur. For example, chlorination of methane produces a mixture of chloromethane, dichloromethane, trichloromethane and tetrachloromethane

$$CH_4 + Cl_2 \xrightarrow{h\nu} \underset{\text{chloromethane}}{CH_3Cl}$$

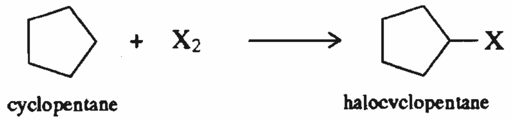
$$CH_3Cl + Cl_2 \xrightarrow{h\nu} \underset{\text{dichloromethane}}{CH_2Cl_2}$$

$$CH_2Cl_2 + Cl_2 \xrightarrow{h\nu} \underset{\text{trichloromethane}}{CHCl_3}$$

$$CHCl_3 + Cl_2 \xrightarrow{h\nu} \underset{\text{tetrachloromethane}}{CCl_4}$$

The yield of the monosubstituted product may increase by using an excess of alkane.

Similarly, a cycloalkane reacts with halogen to give halocycloalkane, e.g.,



The mechanism of halogenation is supposed to involve the following steps :

In the first step, the halogen molecule undergoes homolysis forming free radicals. This step is called chain initiation :

i) $X_2 \xrightarrow{h\nu/\Delta} 2\dot{X}$

In the next step, the halogen atom abstracts a hydrogen atom from the alkane molecule thereby producing an alkyl radical.

ii) $RH + \dot{X} \longrightarrow HX + \dot{R}$

The alkyl radical on collision with another molecule of halogen abstracts a halogen atom from it generating a molecule of the alkyl halide and a halogen atom. These two steps are called propagation. They are repeated in sequence till the reactants are consumed.

iii) $X_2 + \dot{R} \longrightarrow RX + \dot{X}$

Finally, the above chain may be terminated by coupling of any two radicals. This step is known as termination.

iv) $\dot{X} + \dot{X} \longrightarrow XX$
$\dot{R} + \dot{X} \longrightarrow RX$
$\dot{R} + \dot{R} \longrightarrow RR$

The order of reactivity of halogen in halogenation of alkanes is :

$F_2 > Cl_2 > Br > I_2$

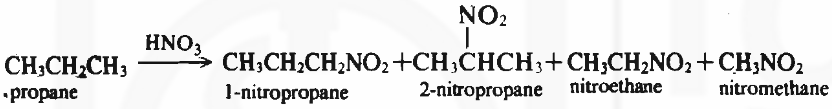
However, the flourination reaction is too violent to be practical, and iodine actually does not react at all.

6.6.2 Nitration

Alkanes, especially the higher member, can be nitrated with nitric acid at a temperature of 675-775 K. Like halogenation, it is a also free radical reaction.

$RH + HNO_3 \longrightarrow RNO_2 + H_2O$

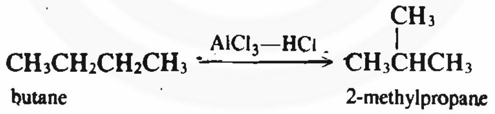
In this reaction, the product is usually a mixture of nitroalkanes including those with smaller carbon chain than the parent alkane.



$$\underset{\text{propane}}{CH_3CH_2CH_3} \xrightarrow{HNO_3} \underset{\text{1-nitropropane}}{CH_3CH_2CH_2NO_2} + \underset{\text{2-nitropropane}}{CH_3\overset{\overset{NO_2}{|}}{C}HCH_3} + \underset{\text{nitroethane}}{CH_3CH_2NO_2} + \underset{\text{nitromethane}}{CH_3NO_2}$$

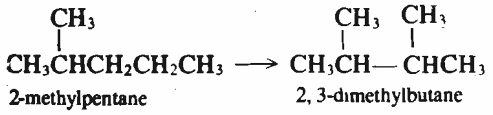
6.6.3 Isomerisation

The molecular rearrangement of one compound into another compound or into more than one compounds is called isomerisation. The straight chain alkanes are converted into branched chain isomers in the presence of aluminium chloride and hydrogen chloride.



$$\underset{\text{butane}}{CH_3CH_2CH_2CH_3} \xrightarrow{AlCl_3—HCl} \underset{\text{2-methylpropane}}{CH_3\overset{\overset{CH_3}{|}}{C}HCH_3}$$

Similarly, other less branched alkanes isomerise to more branched ones. Thus,

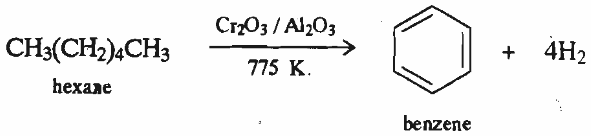


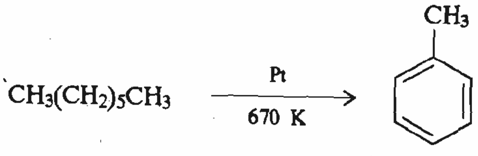
$$\underset{\text{2-methylpentane}}{CH_3\overset{\overset{CH_3}{|}}{C}HCH_2CH_2CH_3} \longrightarrow \underset{\text{2, 3-dimethylbutane}}{CH_3\overset{\overset{CH_3}{|}}{C}H—\overset{\overset{CH_3}{|}}{C}HCH_3}$$

Isomerisation is used to increase the branched chain content of lower alkanes produced by cracking; you have studied in subsec. 6.2.4 that branched chain alkanes are more valuable than straight chain alkanes as a motor fuel.

6.6.4 Aromatisation

This is a process of converting aliphatic or alicyclic compounds to aromatic hydrocarbons. Alkanes with six or more carbon atoms, when heated strongly under pressure in the presence of a catalyst, give aromatic hydrocarbons. This process involves cyclisation, isomerisation and dehydrogenation. Aromatisation of gasoline increases their octane number from 40 to 95 because unsaturated hydrocarbons are better fuels.





toluene

Catalytic aromatisation in the presence of platinum is sometimes referred to as platforming or hydroforming. This process also constitutes a valuable method for commercial production of these hydrocarbons.

6.6.5 Pyrolysis

This is a process of decomposing an organic substance by heating it to high temperature in the absence of oxygen. The word **pyrolysis** is taken from the Greek words **pyro** (fire) and **lysis** (disintegration). The pyrolysis of alkanes, particularly where petroleum is concerned, is known as **cracking**. When an alkane is heated to about 775-875 K, it decomposes into smaller molecules. For example, on cracking propane, the possible products are :

$$\underset{\text{propene}}{CH_3CH{=}CH_2} + H_2 \longleftarrow \underset{\text{propane}}{CH_3CH_2CH_3} \longrightarrow \underset{\text{methane}}{CH_4} + \underset{\text{ethene}}{CH_2{=}CH_2}$$

Large quantities of high boiling fractions of petroleum are converted into low boiling gasoline by cracking. Propene and hydrogen are produced from propane as a result of fission of C – H linkages. In the case of higher alkanes, fission of C – C linkages occurs more readily. The presence of catalysts like oxides of chromium, vanadium and molybdenum, however, accelerates the fission of C – H linkage. Pyrolysis in the presence of a catalyst is used in the manufacture of alkenes.

The mechanism of cracking is still obscure, but it is believed to be a **free radical** as illustrated below :

$$\begin{tikzcd}
CH_3CH_2CH_3 \arrow[r] \arrow[d] & CH_3CH_2\dot{C}H_2 + \dot{H} \arrow[r] & CH_3CH{=}CH_2 + H_2 \\
CH_3\dot{C}H_2 + \dot{C}H_3 \arrow[rr] & & CH_2{=}CH_2 + CH_4
\end{tikzcd}$$

The products formed during cracking of alkanes depends upon : (i) the structure of alkane, (ii) the pressure employed, and (iii) the presence or absence of a catalyst.

6.6.6 Combustion

Alkanes burn in excess of air or oxygen to give carbondioxide and water. This reaction is known as combustion and is the most important of all their reactions. Combustion is highly exothermic and accounts for their use as valuable fuels. It is a free radical chain reaction and requires a very high temperature for its initiation. Once the reaction is started, the subsequent chain-carrying steps proceed readily with the evolution of a large amount of energy. For example, the heat of combustion of pentane is 2549 kJ mol^{-1}.

$$CH_3CH_2CH_2CH_2CH_3 + 8O_2 \longrightarrow 5CO_2 + 6H_2O + 2549 \text{ kJ mol}^{-1}$$

The large quantity of heat evolved can be a source of extensive power. Hence the use of petrol, diesel etc., as fuels in internal combustion engines. The burning of alkanes also produces **carbon black**, which is used in the manufacture of Indian ink, printer's ink, black pigments and as a filler in rubber.

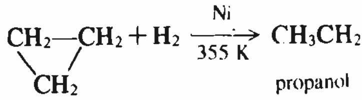
6.6.7 Reactions of Small Ring Compounds

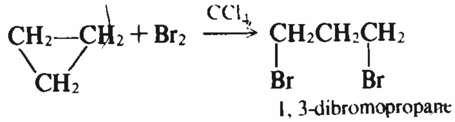
Let us now study the reactions characteristic of small ring compounds, such as cyclopropane and cyclobutane.

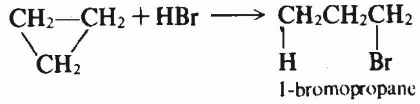
Besides, the free radical substitution reactions that are characteristic of cycloalkanes and of alkanes, in general, cyclopropane and, to some extent, cyclobutane undergo certain addition reactions. You will recall from your previous classes that the bonding in cyclopropane and cyclobutane is not as strong as that in higher homologues. Hence, the bonds in cyclopropane and cyclobutane are vulnerable to attack by certain reagents. These addition reactions destroy

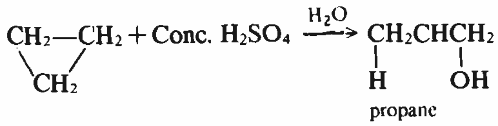
The sp^3 orbitals of the carbon atoms in cyclopropane cannot undergo complete overlap with each other because the angles between the carbon atoms of cyclopropane are geometrically required to be 60°. The ring sigma bonds of cyclopropane are, therefore, less stable than sp^3 sigma bonds that have the normal tetrahedral angle.

the cyclopropane and cyclobutane ring system, and yield open chain products. Some examples are given below :



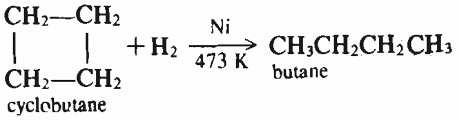






In each of these reactions, a carbon-carbon bond is broken and the two atoms of the reagent appear at the terminal carbon atoms.

Cyclobutane does not undergo most of the ring opening reactions of cyclopropane; it gets hydrogenated under vigorous conditions.



So you can see that cyclobutane undergoes addition reactions less readily than cyclopropane,

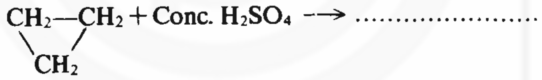
SAQ 4

Complete the following reactions :

a) $CH_3CH_3 + Cl_2 \xrightarrow{h\nu}$ ....

b) $CH_3CH_3 + HNO_3 \longrightarrow$ ....

c)



d) $CH_3(CH_2)_5CH_3 \xrightarrow[670\,K]{Pt}$ ....

6.7 SUMMARY

In this unit you have learnt that :

- Alkanes are compounds of the general formula C_nH_{2n+2}. Cycloalkanes contain a ring of carbon atoms and have the general formula C_nH_{2n}.
- The chief source of alkanes is petroleum.
- The performance of gasoline for internal combustion engines is rated by octane number. Cetane number is a measure of the quality of diesel.
- Alkanes are nonpolar compounds. Their physical constants like boiling point, density, etc., increase with increase in the number of carbon atoms. Branching in the chain decreases the boiling point.
- Alkanes are prepared by : (i) Wurtz reaction, (ii) Kolbe's electrolytic method, (iii) hydrogenation of unsaturated hydrocarbons, (iv) decarboxylation of carboxylic acids, (v) reduction of alkyl halides, and (vi) hydrolysis of Grignard reagents.
- The main reaction of alkanes is combustion; head for power production is its chief outcome.

- Halogenation of alkanes gives multiple substitution. The order of reactivity of halogens is $F_2 > Cl_2 > Br_2$. Iodine does not react at all.
- An alkane can be converted into its corresponding branched chain isomer in the presence of aluminium chloride and hydrogen chloride.
- When an alkane is heated to a high temperature (at about 875 K), it decomposes into small molecules. This process is known as pyrolysis.
- When alkanes with six or more carbon atoms are heated under pressure in the presence of a catalyst, aromatic hydrocarbons are produced.

6.8 TERMINAL QUESTIONS

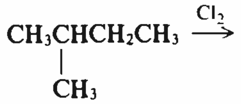
1) Give the products of the following reactions :

a) $CH_3CH_2Br + CH_3CH_2Br \xrightarrow{Na}$

b) $CH_3CH_2CH_3 \xrightarrow{LiAlH_4}$

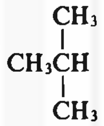
c) $CH_3CH{=}CHCH_2Cl \xrightarrow{H_2/Pt}$

d) $CH_3CH_3 + Cl_2 \xrightarrow{h\nu}$

e) 

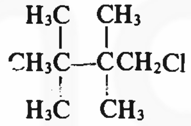
$CH_3\underset{\substack{|\\ CH_3}}{C}HCH_2CH_3 \xrightarrow{Cl_2}$

2) Starting with $CH_2{=}CHCH_2Br$ or $(CH_3)_3CCl$, how would you prepare the following compounds:

a) 

$CH_3\overset{\substack{CH_3\\ |}}{\underset{\substack{|\\ CH_3}}{C}}H$

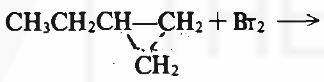
b) $CH_3(CH_2)_4CH_3$

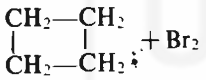
c) 

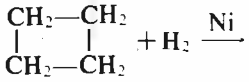
$CH_3\overset{\substack{H_3C\\ |}}{\underset{\substack{|\\ H_3C}}{C}}-\overset{\substack{CH_3\\ |}}{\underset{\substack{|\\ CH_3}}{C}}CH_2Cl$

3) Write the equation to show Wurtz reaction :

4) Complete the following equations:

a) 

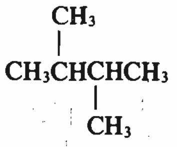
b) 

c) 

6.9 ANSWERS

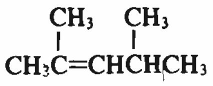
Self Assessment Questions

1) a) $CH_3CH_2CH_2CH_3$

b) 

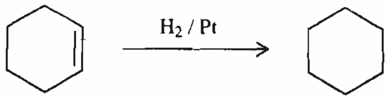
$CH_3\overset{\substack{CH_3\\ |}}{C}H\underset{\substack{|\\ CH_3}}{C}HCH_3$

c) $CH_2{=}CHCH_2CH_3$

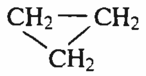
d) 

$CH_3\overset{\overset{CH_3}{|}}{C}=CH\overset{\overset{CH_3}{|}}{C}HCH_3$

2) a) electronegativity
   b) increases
   c) decreases
   d) nonpolar

3) a) 

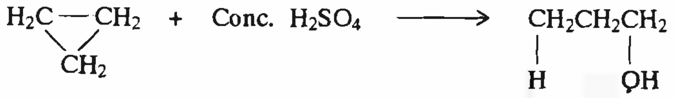
b) $CH_3(CH_2)_{10}COOH + C_5H_5N \xrightarrow{CuO.Cr_2O_3} CH_3(CH_2)_9CH_3$

c) $BrCH_2CH_2CH_2Br + Zn \longrightarrow$  $+ ZnBr_2$

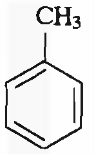
d) $CH_3CH_2CH_2Cl \xrightarrow{LiAlH_4} CH_3CH_2CH_3$

4) a) $CH_3CH_3 + Cl_2 \xrightarrow{h\nu} CH_3CH_2Cl$

b) $CH_3CH_3 + HNO_3 \longrightarrow CH_3CH_2NO_2$

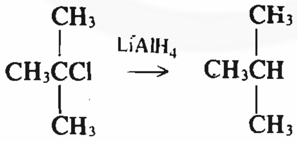
c) 

$\underset{\underset{H}{|}}{CH_2}CH_2\underset{\underset{OH}{|}}{CH_2}$

d) $CH_3(CH_2)_5CH_3 \xrightarrow[670\ K]{Pt}$ 

Terminal Questions

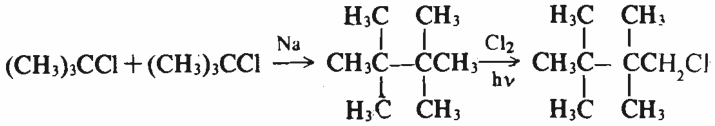
1) a) $CH_3CH_2CH_2CH_3$
   b) No reaction
   c) $CH_3CH_2CH_2CH_2Cl$
   d) CH_3CH_2Cl
   e) No reaction

2) a) 

$CH_3\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}Cl \xrightarrow{LiAlH_4} CH_3\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}H$

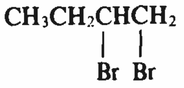
b) $CH_2{=}CHCH_2Br + CH_2{=}CHCH_2Br \xrightarrow{Na} CH_2{=}CHCH_2CH_2CH{=}CH_2$

$\xrightarrow{H_2/Pt} CH_3(CH_2)_4CH_3$

c) 

$(CH_3)_3CCl + (CH_3)_3CCl \xrightarrow{Na} CH_3\underset{\underset{H_3C}{|}}{\overset{\overset{H_3C}{|}}{C}}-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}CH_3 \xrightarrow[h\nu]{Cl_2} CH_3\underset{\underset{H_3C}{|}}{\overset{\overset{H_3C}{|}}{C}}-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}CH_2Cl$

3) $CH_3Br + CH_3Br \xrightarrow{2Na} CH_3CH_3 + 2NaBr.$

4) a) 

$CH_3CH_2\underset{\underset{Br}{|}}{CH}\underset{\underset{Br}{|}}{CH_2}$

b) No reaction
c) $CH_3CH_2CH_2CH_3$

UNIT 7 ALKENES

Structure

7.1 INTRODUCTION

In Unit 1, we mentioned briefly about the alkenes. In this unit, we shall discuss their chemistry in detail. Ethene, the simplest alkene, was known to chemists in the eighteenth century and was obtained in pure form in 1795. Alkenes, also called olefins, are hydrocarbons which contain one or more carbon-carbon double bond(s). Since alkenes evidently contain less than the maximum number of hydrogen atoms, they are referred to as **unsaturated hydrocarbons**.

Alkenes are often found as plant products and in petroleum. Many alkenes are biologically active compounds. For example, ethene induces ripening in fruit.

In this unit, we will discuss structure of alkenes, their spectral and physical properties, different methods for their preparation and finally, we will study their important chemical reactions.

Objectives

After studying this unit, you should be able to :

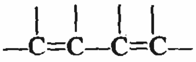
- classify the types of alkenes,
- explain the structure of monoenes and dienes,
- list their spectral and physical properties,
- list the different methods for their preparation, and
- write down the important chemical reactions of alkenes.

7.2 CLASSIFICATION OF ALKENES

Alkenes can be classified on the basis of the number of double bonds present in the molecule. Hydrocarbons containing one carbon-carbon double bond are called monoenes. The monoenes have the general formula C_nH_{2n}.

Hydrocarbons containing two double bonds are called diolefins or alkadienes or dienes. They have the general formula C_nH_{2n-2} and are isomeric with alkynes. Trienes have three double bonds and tetraenes have four double bonds. The term polyene is used for hydrocarbons containing more than four double bonds.

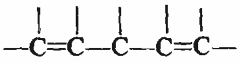
Dienes are divided into three main classes depending on the relative positions of the two double bonds in the molecule : isolated or non-conjugated dienes, conjugated dienes and cumulated dienes. In conjugated dienes, the two double bonds are separated by a single bond. A typical conjugated diene skeleton is given below :



$-\overset{|}{C}=\overset{|}{C}-\overset{|}{C}=\overset{|}{C}-$

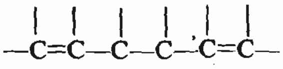
conjugated diene

In isolated dienes, the two double bonds are separated by at least two single bonds for which two typical skeletons are given below :



$-\overset{|}{C}=\overset{|}{C}-\overset{|}{C}-\overset{|}{C}=\overset{|}{C}-$

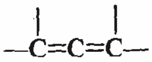
isolated diene
(two single bonds between
two double bonds)



$-\overset{|}{C}=\overset{|}{C}-\overset{|}{C}-\overset{|}{C}-\overset{|}{C}=\overset{|}{C}-$

isolated diene
(three single bonds between
two double bonds)

In cumulated dienes, there are two double bonds around the same carbon atom; a typical skeleton is given below :



$-\overset{|}{C}=C=\overset{|}{C}-$

cumulated diene (allene)

Compounds that contain cumulated double bonds are known but are very uncommon. The conjugated dienes are the most important among the dienes. They show certain reactions that are not shown by monoenes or other dienes. Thus, in this unit, we shall concentrate our attention on monoenes and conjugated dienes.

Structure of Monoenes and Dienes

The carbon-carbon double bond is both an important structural unit and an important functional group in organic chemistry. The shape of the organic molecule is influenced by the presence of the double bond which is also the site of most of the chemical reactions that alkenes undergo. So it is necessary to understand the structure of these molecules.

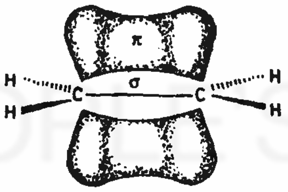


Fig. 7.1 : Orbital picture of ethene.

Carbon-carbon double bond is the distinguishing feature of the monoenes and dienes. You have already studied about the bonding of monoenes in Unit 1 of this course and learnt that the carbon atoms involved in double bond formation are sp^2 hybridised. The bond angle around the sp^2 hybridised carbon atoms is 120° (Fig. 7.1). Bonding in dienes with isolated double bonds is similar to monoenes. Thus here we shall discuss π bonds in conjugate and cumulated systems.

Let us consider 1, 3-butadiene as an example of a conjugated diene,

$CH_2{=}CHCH{=}CH_2$

1, 3-butadiene

Each of the four carbon atoms of butadiene contains an unhybridised p-orbital. The sideways overlap of unhybridised p-orbitals gives rise to two localised π bonds, i.e., the bonds between C_1 and C_2 and C_3 and C_4 (Fig. 7.2). The four carbon atoms and the six hydrogen atoms of butadiene lie in the same plane so that there is a certain amount of overlapping between the electron clouds of the p-orbitals of C_2 and C_3. This give rise to completely delocalised π-orbitals spread over all the four carbon atoms. It is this delocalisation of π electrons which imparts stability to 1, 3-butadiene.

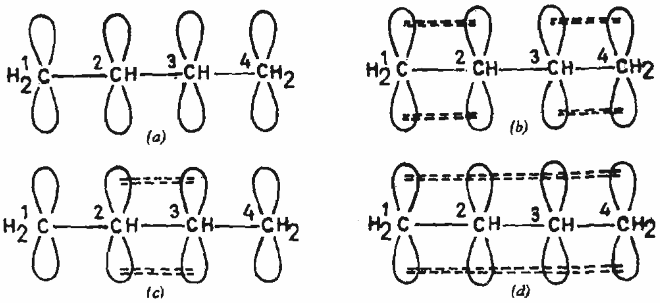


Fig. 7.2 : Orbital structure of 1, 3-butadiene

In the allene molecule, the central carbon atom is *sp* hybridised while the terminal carbon atoms are sp^2 hybridised. The central carbon atom forms a σ bond with each of the terminal sp^2 hybridised carbon atom. The remaining two *p*-orbitals of this carbon form two π bonds by sideways overlapping with the *p*-orbitals of the terminal carbon atoms (Fig. 7.3).

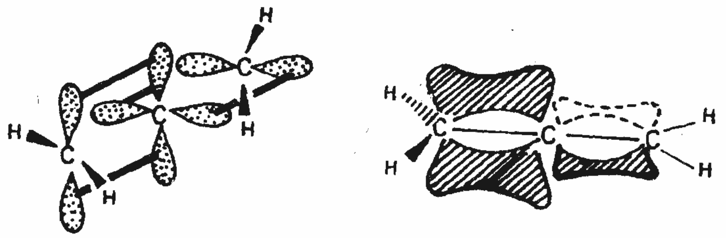


Fig. 7.3 : Molecular orbital picture of allene.

SAQ 1

Fill in the blank in the spaces given below :

a) Dienes are isomeric with ....

b) Polyenes contain more than .... double bonds.

c) Double bonds that alternate with single bond are .... dienes.

d) In allene the central atom is .... hybridised and the terminal atoms are .... hybridised.

7.3 PHYSICAL PROPERTIES

In general, the physical properties of alkenes are similar to those of the corresponding alkanes. Like alkanes, the boiling points of a homologous series of alkenes increase 20-30 K per CH_2 group except for the very small homologues. Like alkanes, branching in an alkene also lowers the boiling point. Lower alkenes, from ethene to butene, are colourless gases, higher ones, from C_5-C_{15}, are liquids and the rest are solids at room temperature.

Alkenes are slightly more soluble in water than the corresponding alkanes because the π-electrons are attracted to the partially positive hydrogen of the water molecules.

7.4 SPECTRAL PROPERTIES

In the uv spectrum, although the ethylenic chromophore shows an absorption band below 200 nm, yet it is not of much practical value as measurement of uv spectrum in this region is influenced by the absorption of air and solvent molecules.

The ir spectra are quite useful for structure determination of alkenes. The unsymmetrical alkenes are polar and absorb in the region between 1600 and 1700 cm^{-1}, whereas the symmetrical ones, being nonpolar, do not absorb in this region. Further, depending upon the substituent, one or more bands of medium intensity appear in the region between 3000 and 3100 cm^{-1} for >C=C—H stretching. The *cis*- and *trans*-isomers of the type RCH=CHR may be distinguished by C—H deformation frequencies. The *cis*-isomer absorbs at 675-730 cm^{-1} and the *trans*-isomer at 960-975 cm^{-1}

In the ir spectra of allenes, a band near 1950 cm^{-1} appears for the C=C stretching vibration. The strong band at 850 cm^{-1} arises from >C=CH_2 wagging and is characteristic of allene. The characteristic —C=C— stretching frequencies in conjugated systems is lower and appears around 1600 cm^{-1}

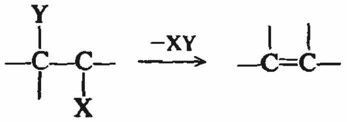
In the nmr spectra, the chemical shifts of olefinic protons are shifted towards lower field than those of alkane protons. The exact position of absorption depends on the location of the double bond in the hydrocarbon chain. In general, proton on the terminal alkenyl carbon absorb near δ 4.7 ppm, while the protons on the nonterminal carbon absorb slightly farther downfield at δ 5.3 ppm. The protons α to a double bond ($CH_2CH = CHCH_2$) appear at δ 2.06 ppm.

In conjugated dienes, the olefinic protons are more deshielded and consequently resonance due to these protons occurs downfield. In conjugated dienes, the signal due to $CH_2=$ protons appears at δ 5.3-5.7 ppm and that due to H—C=C proton at δ 6.0-6.5 ppm. In the nmr spectra of the allenes, the alkene hydrogen give rise to signals at δ 5.7-4.7 ppm.

In the mass spectra of alkenes, the molecular ion peak is usually distinct. The fragmentation of interest for alkenes is the allylic cleavage.

7.5 PREPARATION OF ALKENES.

Synthetically, alkenes are prepared by introducing a double bond in saturated hydrocarbons through elimination of atoms or groups from two adjacent carbon atoms. The result is the formation of a double bond between these two carbon atoms.



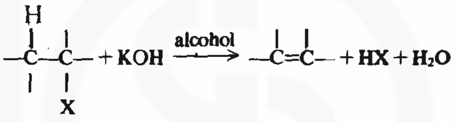
$$-\overset{Y}{\underset{|}{\overset{|}{C}}}-\underset{X}{\underset{|}{C}}- \xrightarrow{-XY} -\overset{|}{C}=\overset{|}{C}-$$

Elimination

Alkenes can be prepared from alkyl halides, alcohol and ketones and through cleavage reactions. Some important methods for the preparation of alkenes are summarised in Table 7.1.

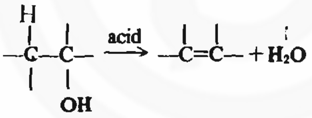
Table 7.1 : Preparation of alkenes

Dehydrohalogenation of Alkyl Halides



$$-\overset{H}{\underset{|}{\overset{|}{C}}}-\underset{X}{\underset{|}{\overset{|}{C}}}- + KOH \xrightarrow{alcohol} -\overset{|}{C}=\overset{|}{C}- + HX + H_2O$$

Dehydration of Alcohols

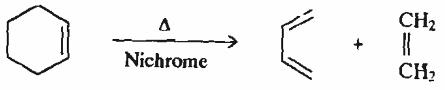


$$-\overset{H}{\underset{|}{\overset{|}{C}}}-\underset{OH}{\underset{|}{\overset{|}{C}}}- \xrightarrow{acid} -\overset{|}{C}=\overset{|}{C}- + H_2O$$

Wittig Reaction

$$-\overset{|}{C}=O + \text{Wittig reagent} \longrightarrow -\overset{|}{C}=\overset{|}{C}-$$

Retro Diels-Alder Reaction



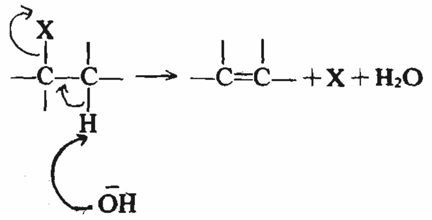
Let us discuss each method in detail.

7.5.1 Dehydrohalogenation of Alkyl Halides

Alkyl halides are converted into alkenes by dehydrohalogenation. Dehydrohalogenation involves elimination of the halogen atom together with a hydrogen atom from an adjacent carbon atom. The elimination is brought about by treating the alkyl halide with a strong base. Thus, bromoethane yields ethene when treated with potassium hydroxide in alcoholic solution.

$$\underset{\text{bromoethane}}{CH_3CH_2Br} \xrightarrow[C_2H_5OH]{KOH} \underset{\text{ethane}}{CH_2{=}CH_2} + HBr + H_2O$$

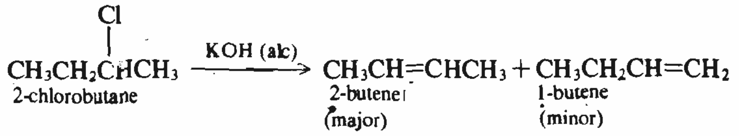
The function of hydroxide ion is to abstract hydrogen from the carbon atom next to the halogen bearing carbon. The carbon halogen bond then cleaves resulting in double bond formation.



Ease of hydrohalogenation of alkyl halides is : *tert* >*sec* >*p*

The alkyl halides, in which halogen is attached to a terminal carbon, yield a single alkene but alkyl halides in which the halogen atom is attached to a nonterminal carbon atom and both adjacent position have hydrogen atoms yield a mixture of alkenes.

$$\underset{\text{chlorobutane}}{CH_3CH_2CH_2CH_2Cl} \xrightarrow{\text{KOH (alc)}} \underset{\text{1-butene}}{CH_3CH_2CH{=}CH_2}$$



$$\underset{\text{2-chlorobutane}}{CH_3CH_2\overset{\displaystyle Cl}{\overset{|}{C}}HCH_3} \xrightarrow{\text{KOH (alc)}} \underset{\text{(major)}}{\underset{\text{2-butene}}{CH_3CH{=}CHCH_3}} + \underset{\text{(minor)}}{\underset{\text{1-butene}}{CH_3CH_2CH{=}CH_2}}$$

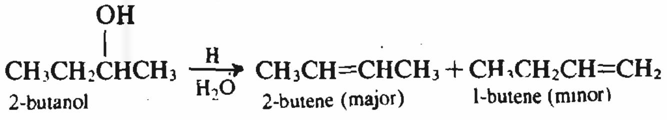
In the first reaction, chlorobutane can lose hydrogen only from C_2; therefore, it gives only one product, i.e., 1-butene. However, in the second reaction, 2-chlorobutene can lose hydrogen from any of the two-β-carbon atoms and, hence, it gives a mixture of 2-butene (80%) and 1-butene (20%). Now you may ask why 2-butene is the major product? Dehydrohalogenation follows Saytzeff rule which says that the more highly substituted alkene is the dominant product. You will study Saytzeff rule in detail in Unit 11.

7.5.2 Dehydration of Alcohols

An alcohol is converted into an alkene by dehydration, i.e., elimination of a molecule of water. Dehydration requires the presence of an acid and the application of heat. The alcohol is heated with sulphuric or phosphoric acid to a temperature as high as 475 K. Dehydration is also brought about by passing the alcohol vapour over alumina (Al_2O_3) at 625-675 K, e.g.,

$$\underset{\text{ethanol}}{CH_3CH_2OH} \xrightarrow[475\text{ K}]{95\%\ H_2SO_4} \underset{\text{ethene}}{CH_2{=}CH_2}$$

In the case of secondary and tertiary alcohols other than 2-propanol, there exists the possibility of the formation of more than one alkenes. For example, in 2-butanol, hydrogen elimination can occur either from C_1 or C_2. The direction and the rate of reaction again follow the Saytzeff rule and hence 2-butene, the more substituted alkene, is the major product and 1-butene the minor one.

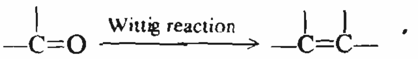


$$\underset{\text{2-butanol}}{CH_3CH_2\overset{\displaystyle OH}{\overset{|}{C}}HCH_3} \xrightarrow[H_2O]{H} \underset{\text{2-butene (major)}}{CH_3CH{=}CHCH_3} + \underset{\text{1-butene (minor)}}{CH_3CH_2CH{=}CH_2}$$

The ease of dehydration of various alcohols has been found to follow the order :
tert >*sec* >*p*

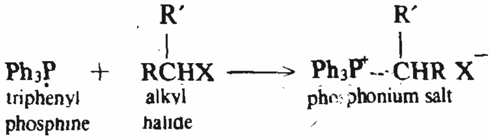
7.5.3 Wittig Reaction

In 1954, George Wittig reported a method of synthesising alkenes from carbonyl compounds. This reaction is applicable to aldehyde and ketones and leads to replacement of carbonyl oxygen by the group=CRR′ (where R ane R′ are hydrogen or alkyl group).



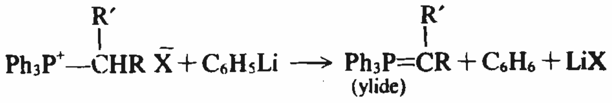
$$-\overset{|}{C}{=}O \xrightarrow{\text{Wittig reaction}} -\overset{|}{C}{=}\overset{|}{C}-$$

There are two main steps in Wittig reaction. In the first step, the nucleophilic reagent triphenylphosphine reacts with primary or secondary alkyl halide to give phosphonium salt.



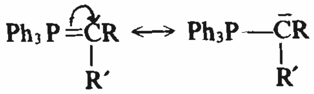
$$\underset{\text{triphenyl phosphine}}{Ph_3P} + \underset{\text{alkyl halide}}{\overset{\displaystyle R'}{\overset{|}{RCHX}}} \longrightarrow \underset{\text{phosphonium salt}}{Ph_3\overset{+}{P}-\overset{\displaystyle R'}{\overset{|}{C}}HR\ \overset{-}{X}}$$

This phosphonium salt further reacts with a strong base, which abstracts a weakly acidic α-hydrogen to give alkylidenetriphenylphosphorane (the phosphorous ylide) commonly known as the **Wittig reagent**.



$$Ph_3P^+\text{—}\overset{R'}{\overset{|}{C}}HR\ \bar{X} + C_6H_5Li \longrightarrow \underset{\text{(ylide)}}{Ph_3P{=}\overset{R'}{\overset{|}{C}}R} + C_6H_6 + LiX$$

The phosphorous ylide has a hybrid structure and it is the negative charge on carbon that is responsible for their characteristic reactions.

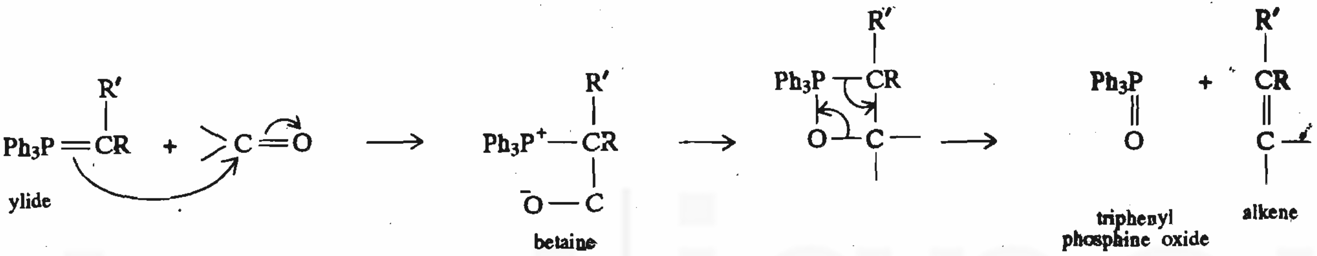


$$Ph_3P{=}\underset{R'}{\underset{|}{C}}R \longleftrightarrow Ph_3\overset{+}{P}\text{—}\underset{R'}{\underset{|}{\bar{C}}}R$$

The resulting phosphorus ylide attacks the carbonyl carbon to form **betaine** which often undergoes elimination spontaneously to yield alkene.

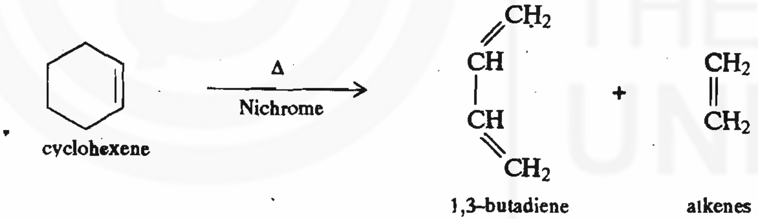
Betaine :
A molecule having non-adjacent opposite charges.

The mechanism of the Witting reaction has been the subject of much discussion, but evidence is now strongly in favour of formation of an Intermediate betaine followed by ring closure and then fission.



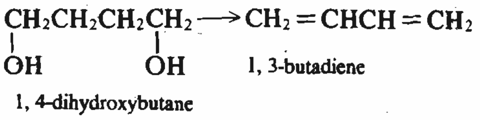
7.5.4 Preparation of Dienes

Retro Diels-Alder Reaction : Dienes are usually prepared by the adaptation of the methods used to make simple alkenes. However, 1, 3-butadiene is prepared by passing vapours of cyclohexene over heated nichrome (Ni-Cr-Fe) alloy.



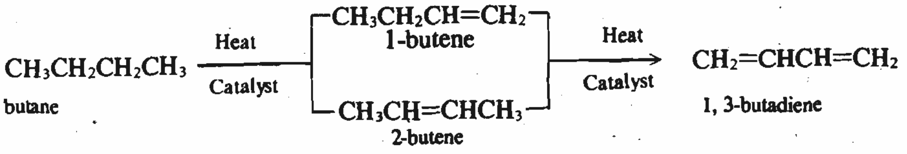
This reaction is also known as the retro Diels-Alder reaction as it is the reversal of the Diels-Alder reaction which you will study in section 7.6.9.

Other Methods for Preparation of Dienes : As stated above, dienes are usually prepared by adaptation of the method used to make simple alkenes. For example, 1, 4-dihydroxybutane on treatment with sulphuric acid gives 1, 3-butadiene.



$$\underset{\text{1, 4-dihydroxybutane}}{\underset{OH}{\underset{|}{C}}H_2CH_2CH_2\underset{OH}{\underset{|}{C}}H_2} \longrightarrow \underset{\text{1, 3-butadiene}}{CH_2=CHCH=CH_2}$$

1, 3-Butadiene can also be prepared from butane by the cracking process using Cr_2O_3, as illustrated below :



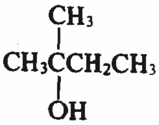
$$\underset{\text{butane}}{CH_3CH_2CH_2CH_3} \xrightarrow[\text{Catalyst}]{\text{Heat}} \left[\begin{array}{c} \underset{\text{1-butene}}{CH_3CH_2CH{=}CH_2} \\ \\ \underset{\text{2-butene}}{CH_3CH{=}CHCH_3} \end{array}\right] \xrightarrow[\text{Catalyst}]{\text{Heat}} \underset{\text{1, 3-butadiene}}{CH_2{=}CHCH{=}CH_2}$$

SAQ 2

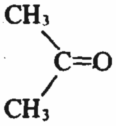
Write equations for the preparation of alkene from the following starting material. If there is more than one product indicate the major one.

a) 
$\mathrm{CH_3CH_2\overset{\overset{Br}{|}}{C}HCH_3}$

....

b) 
$\mathrm{CH_3\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}CH_2CH_3}$

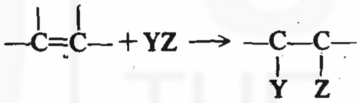
....

c) 

....

7.6 REACTIONS OF ALKENES

The double bond consists of a strong σ bond and a weak π bond; so most of the reactions of alkenes would involve the breaking of this weaker bond.

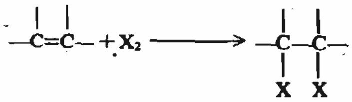

$$-\overset{|}{C}=\overset{|}{C}- + YZ \longrightarrow -\underset{\underset{Y}{|}}{C}-\underset{\underset{Z}{|}}{C}-$$

In addition reactions of alkene, the π-bond is broken and the electron pair comprising it, is used in the formation of two new σ bonds. Thus, two sp^2 hybridised carbon atoms are rehybridised to sp^3 carbons. Compounds containing π bonds are usually of higher energy than those having σ bonds. Consequently, addition reactions are usually exothermic processes.

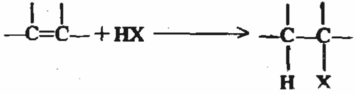
In the region of the double bond, there is a cloud of electrons above and below the plane of bonded atoms. The π electrons are loosely held by the nuclei and are thus easily available to electron-seeking reagent. Such reagents are called electrophilic reagents or electrophiles and the typical reaction of an alkene is the electrophilic addition. Some important reactions of alkenes are given in Table 7.2 and discussed below :

Table 7.2 : Reaction of alkenes

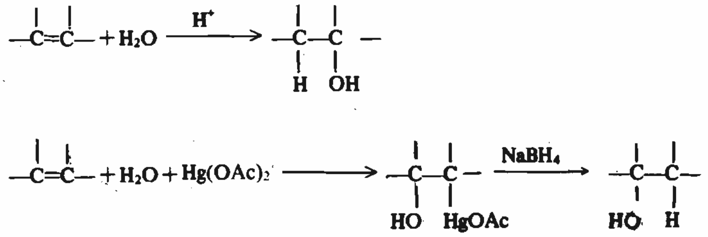
Halogenation


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

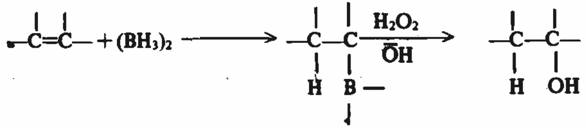
Addition of hydrogen halide


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

Addition of water

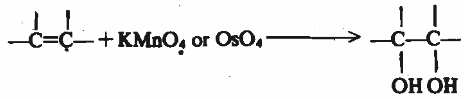


Hydroboration

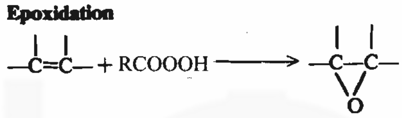


Ozonolysis

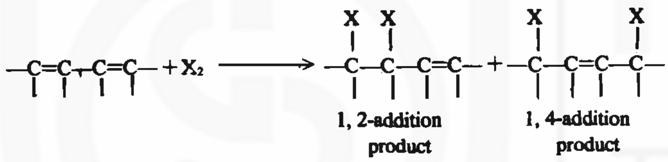
Hydroxylation



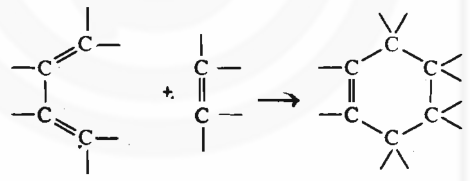
Epoxidation



Addition to conjugated diens



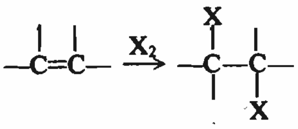
Diels-Alder Reaction



cyclohexene

7.6.1 Addition of Halogens

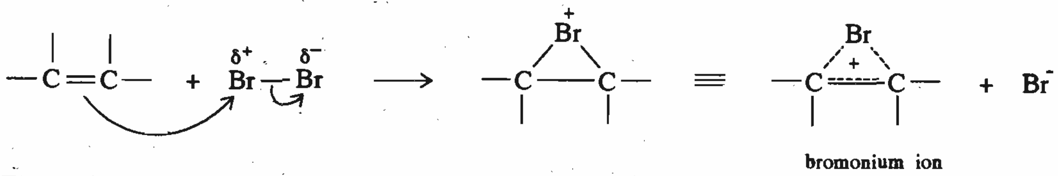
Halogens are quite reactive towards alkenes. Treatment of alkenes with halogens gives 1, 2-dihalogenated alkenes.



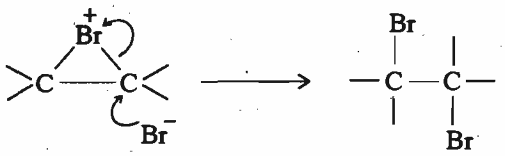
Bromine and chlorine are particularly effective electrophilic addition reagents. Fluorine tends to be too reactive and difficult to control for most laboratory procedures and iodine does not react with alkenes.

Mechanism

Although bromine is non-polar, it is nevertheless highly polarisable and, in the vicinity of the nucleophilic double bond, the bromine molecule becomes polarised and hence a partial positive charge (δ^+) develops on one bromine atom and a partial negative charge (δ^-) on the other. The π electrons of alkene attack the positive end of the polarised bromine molecule, displacing bromide ion and forming a cyclic bromonium ion.



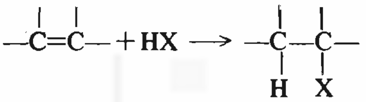
The cyclic structure shields one side of the molecule and, for this reason, Br⁻ attacks from the opposite side of the erstwhile double bond to give *trans* product. This process is known as *trans* addition. This steric course of the reaction is important in case of alkenes which can give rise to different isomeric products.



Addition of bromine is extremely useful for detection of carbon-carbon double bond. Rapid decolourisation of bromine solution serves as a test for the presence of the carbon-carbon double bond in a compound.

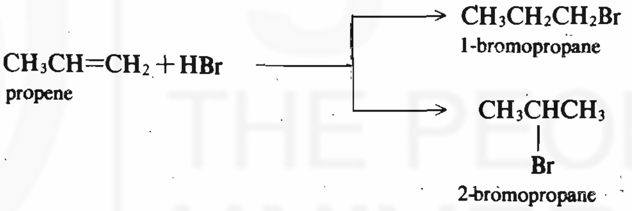
7.6.2 Hydrohalogenation

An alkene is converted by hydrogen halide (halogen acid) into the corresponding alkyl halide,



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

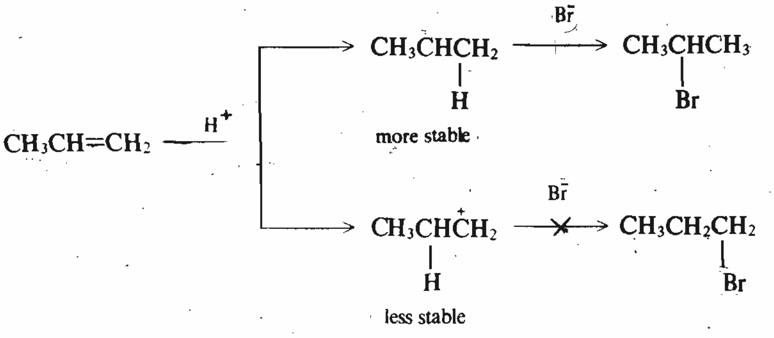
As long as the alkene is symmetrical, we get only one product. In case of unsymmetrical alkene, the position of attachment of nucleophile is governed by the nature of substituents. Addition of HBr to propene should give two products, i.e., 1-bromopropane and 2-bromopropane.



However, only one product, 2-bromopropane, is produced. Such reactions are called **regiospecific** reactions. To explain the exclusive formation of the product, the Russian chemist Markownikoff formulated a rule know after him as Markownikoff's rule, which states that addition of a hydrogen halide to an unsymmetrical alkene takes place in such a way that the negative part of the reagent goes to that carbon atom of the alkene which carries the lesser number of hydrogen atoms.

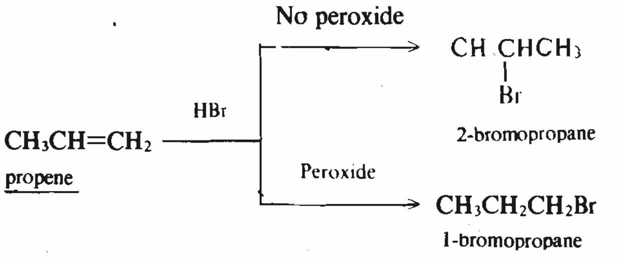
Regiospecific : Only one of the two direction of addition is observed.

Markownikoff's rule can be explained on the basis of the relative stabilities of carbocations which are of the order of tertiary, > secondary > primary. Accordingly, the more substituted carbocation is formed as an intermediate in preference to the less substituted one. For example, in the addition of H^+ to propene, there exists the possibility of the formation of either a primary or a secondary carbocation. Since, the secondary carbocation is more stable, addition of H^+ gives exclusively 2-bromopropane via the more stable intermediate.



Peroxide effect

You must be under the impression that addition to alkene always give Markownikoff's product. But it is not so. After an extensive study of the mechanism of addition of HBr to alkene, Kharasch and Mayo found that in the presence of peroxide the product obtained was not the one predicted by Markownikoff's rule but it was contrary to the Markownikoff's rule. Such additions are sometimes referred to as anti-Markownikoff additions. Since the reversal of the addition reaction is brought about in the presence of peroxides, it is known as the peroxide effect. For example, the addition of hydrogen bromide to propene in the presence of peroxides give 1-bromopropane rather than 2-bromopropane.

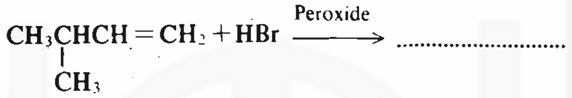


The reaction intermediate in such additions is a free radical rather than a carbocation. The mechanism is somewhat similar to that of halogenation of an alkane, which will be dealt in the "Organic Reaction Mechanism" course.

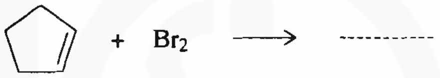
SAQ 3

Complete the following reaction

a) $CH_3CH_2CH=CH_2 + HCl \longrightarrow$ ....

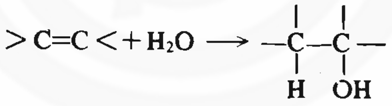
b) 

$$CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}HCH=CH_2 + HBr \xrightarrow{\text{Peroxide}} \text{..............................}$$

c) 

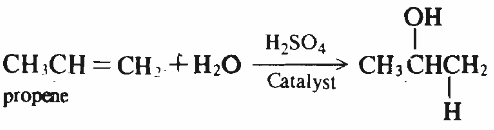
7.6.3 Addition of Water

Addition of H_2O to alkene is known as hydration of alkene. This reaction occurs when H_2O adds to alkenes in the presence of an acid catalyst to yield an alcohol,



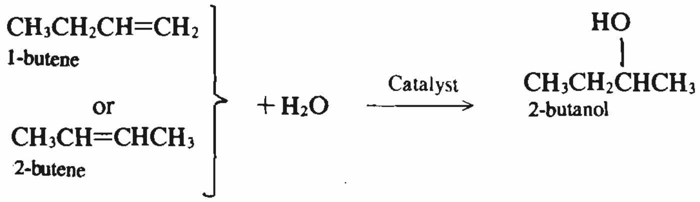
$$>C=C< + H_2O \longrightarrow -\underset{H}{\overset{|}{\underset{|}{C}}}-\underset{OH}{\overset{|}{\underset{|}{C}}}-$$

Like hydrogenation, addition of H_2O to unsymmetrical alkene follows Markownikoff's rule :

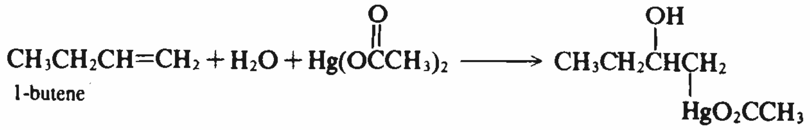


$$\underset{\text{propene}}{CH_3CH=CH_2} + H_2O \xrightarrow[\text{Catalyst}]{H_2SO_4} CH_3\overset{OH}{\overset{|}{\underset{\underset{H}{|}}{C}}}HCH_2$$

2-propanol

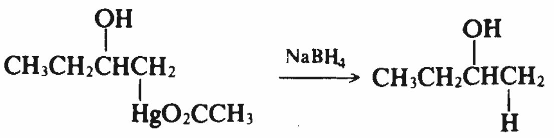


Another method used to accomplish Markownikoff's hydration of an alkene is **oxymercuration-demercuration**. Alkene reacts with mercuric acetate in the presence of water to give hydroxy-mercurial compounds which on reduction accomplishes demercuration and produces an alcohol. The product of oxymercuration is usually reduced with sodium borohydride (NaBH). Oxymercuration-demercuration reaction usually give better yield of alcohols than the addition of water with H_2SO_4–



$$CH_3CH_2CH{=}CH_2 + H_2O + Hg(O\overset{O}{\overset{\|}{C}}CH_3)_2 \longrightarrow CH_3CH_2\overset{OH}{\overset{|}{C}H}\underset{HgO_2CCH_3}{\underset{|}{C}H_2}$$

1-butene



$$CH_3CH_2\overset{OH}{\overset{|}{C}H}\underset{HgO_2CCH_3}{\underset{|}{C}H_2} \xrightarrow{NaBH_4} CH_3CH_2\overset{OH}{\overset{|}{C}H}\underset{H}{\underset{|}{C}H_2}$$

2-butanol

7.6.4 Hydroboration

When an alkene reacts with borane, addition to the carbon-carbon double bond takes place to yield an organoborane a compound with a carbon-boron bond. The reaction is known as **hydroboration**. This reaction is very facile and requires only few seconds for completion at 273 K and gives organoboranes in very high yield.

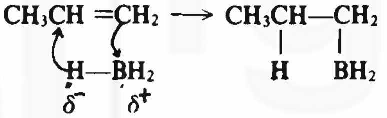
Borane (BH_3) itself is unknown but its dimer, diborane (B_2H_6) behaves as if it were the hypothetical monomer $(BH_3)_2$.

$$CH_2{=}CH_2 + (BH_3)_2 \longrightarrow CH_3CH_2{-}BH_2$$

Since BH_3 has three hydrogen, addition occurs three times to produce trialkylborane product e.g.

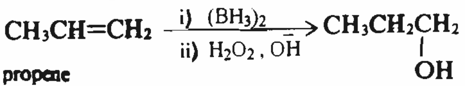
$$CH_2{=}CH_2 + CH_3CH_2{-}BH_2 \longrightarrow (CH_3CH_2)_2BH$$
$$CH_2{=}CH_2 + (CH_3CH_2)_2BH \longrightarrow (CH_3CH_2)_3B$$

Hydroboration reaction is described as anti-Markownikoff's addition. This is true only in literal sense, because hydrogen is the electronegative portion of the molecule instead of the electropositive portion.



As shown above the hydrogen (as a hydride ion, H^-) goes to more substituted carbon. The result appears to be anti-Markownikoff's addition.

Organoborane are generally not isolated but are instead used directly as reactive intermediates for further synthetic reaction. For example, oxidation of organoborane by alkaline H_2O_2 gives corresponding alcohol.



$$CH_3CH{=}CH_2 \xrightarrow[ii)\ H_2O_2,\ \bar{O}H]{i)\ (BH_3)_2} CH_3CH_2\underset{OH}{\underset{|}{C}H_2}$$

propene

1-propanol

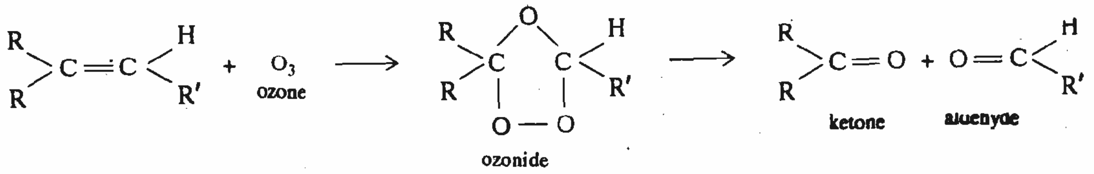
Treatment of organoboranes with a carboxylic acid leads to alkane,

$$\underset{\text{1-propene}}{CH_3CH{=}CH_2} \xrightarrow[ii)\ (CH_3)COOH]{i)\ (BH_3)_2} \underset{\text{propane}}{CH_3CH_2CH_3}$$

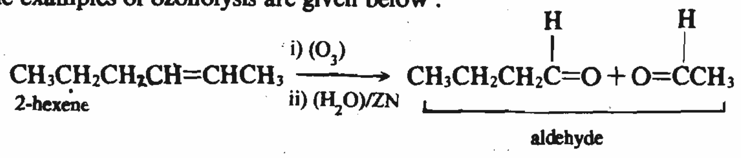
7.6.5 Ozonolysis

In all the reactions of alkenes studied so far, the carbon skeleton of the starting material was left intact. We have seen the conversion of the carbon-carbon double bond into new functional groups (halide, alcohol, etc.) by adding different reagents, but the carbon skeleton was not broken or rearranged. Ozonolysis is a cleavage reaction, i.e. a reaction in which the double bond is completely broken and alkene molecule is converted into two smaller molecules.

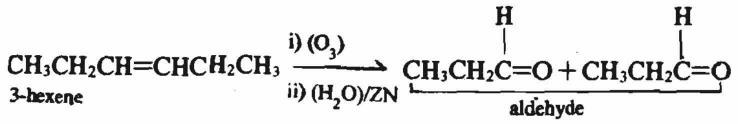
Ozonolysis consists of two separate reactions, the first is oxidation of alkene by ozone to give an ozonide; and the second is reduction of the ozonide to yield cleavage product.



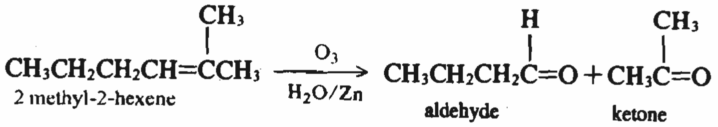
Some examples of ozonolysis are given below :



$$\underset{\text{2-hexene}}{\mathrm{CH_3CH_2CH_2CH{=}CHCH_3}} \xrightarrow[\text{ii) }(H_2O)/ZN]{\text{i) }(O_3)} \underbrace{\mathrm{CH_3CH_2CH_2\overset{\overset{H}{|}}{C}{=}O + O{=}\overset{\overset{H}{|}}{C}CH_3}}_{\text{aldehyde}}$$



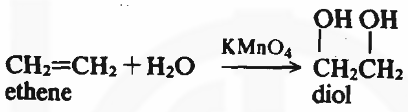
$$\underset{\text{3-hexene}}{\mathrm{CH_3CH_2CH{=}CHCH_2CH_3}} \xrightarrow[\text{ii) }(H_2O)/ZN]{\text{i) }(O_3)} \underbrace{\mathrm{CH_3CH_2\overset{\overset{H}{|}}{C}{=}O + CH_3CH_2\overset{\overset{H}{|}}{C}{=}O}}_{\text{aldehyde}}$$



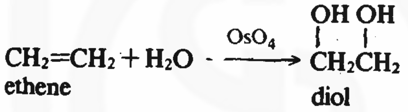
$$\underset{\text{2 methyl-2-hexene}}{\mathrm{CH_3CH_2CH_2CH{=}\overset{\overset{CH_3}{|}}{C}CH_3}} \xrightarrow[H_2O/Zn]{O_3} \underset{\text{aldehyde}}{\mathrm{CH_3CH_2CH_2\overset{\overset{H}{|}}{C}{=}O}} + \underset{\text{ketone}}{\mathrm{CH_3\overset{\overset{CH_3}{|}}{C}{=}O}}$$

7.6.6 Hydroxylation

Alkenes are readily hydroxylated (addition of hydroxyl groups) to form a dihydroxy compound (diol) known as glycols. The most popular reagent used to convert an alkene to diol is cold alkaline aqueous solution of potassium permanganate or osmium tetroxide.



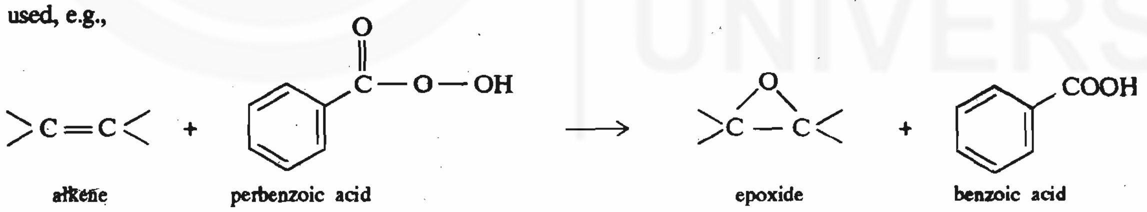
$$\underset{\text{ethene}}{\mathrm{CH_2{=}CH_2}} + \mathrm{H_2O} \xrightarrow{KMnO_4} \underset{\text{diol}}{\mathrm{\overset{\overset{OH}{|}}{C}H_2\overset{\overset{OH}{|}}{C}H_2}}$$



$$\underset{\text{ethene}}{\mathrm{CH_2{=}CH_2}} + \mathrm{H_2O} \xrightarrow{OsO_4} \underset{\text{diol}}{\mathrm{\overset{\overset{OH}{|}}{C}H_2\overset{\overset{OH}{|}}{C}H_2}}$$

7.6.7 Epoxidation

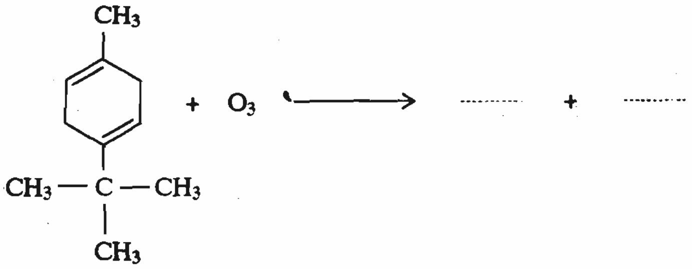
The double bond in alkene is converted into epoxide by means of peracids. Perbenzoic acid ($C_6H_5COO_2H$), monoperphthalic acid ($HO_2CC_6H_4COO_2H$) and *p*-nitroperbenzoic acid have been used, e.g.,



SAQ 4

Predict the products of the following reactions :

a)



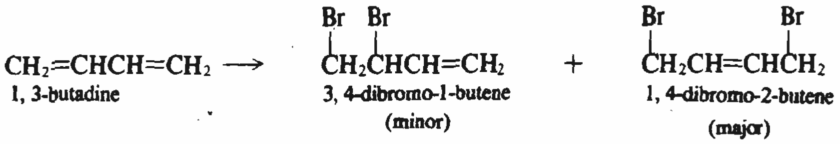
b)

$$\mathrm{CH_3\overset{\overset{CH_3}{|}}{C}{=}CH_2 + CH_3\overset{\overset{O}{\|}}{C}OOH} \longrightarrow \text{..............}$$

c) $CH_3CH{=}CH_2 \xrightarrow[H_2O]{KMnO_4}$ ....

7.6.8 Addition to Conjugated Diene

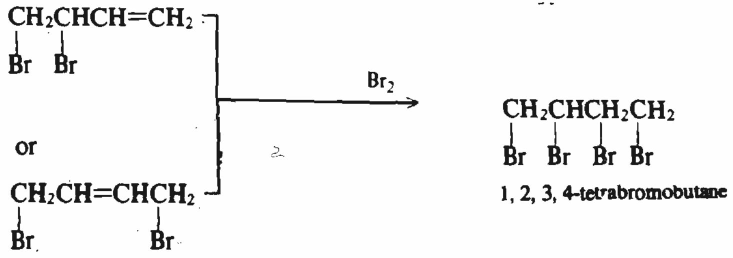
Alkadienes with conjugated system of double bonds undergo abnormal addition reactions, e.g., when 1, 3-butadiene is treated with bromine, two dibromo derivatives are obtained. One of these is 3, 4-dibromo-1-butene (due to 1:2 addition) and the other is 1, 4-dibromo-2-butene (due to 1:4 addition), a major product.



$$CH_2{=}CHCH{=}CH_2 \longrightarrow \overset{Br}{C}H_2\overset{Br}{C}HCH{=}CH_2 + \overset{Br}{C}H_2CH{=}CH\overset{Br}{C}H_2$$

1, 3-butadine — 3, 4-dibromo-1-butene (minor) — 1, 4-dibromo-2-butene (major)

With an excess of bromine, the 1, 4 addition as well as the 1, 2-addition products would yield the same 1, 2, 3, 4-tetrabromobutane.

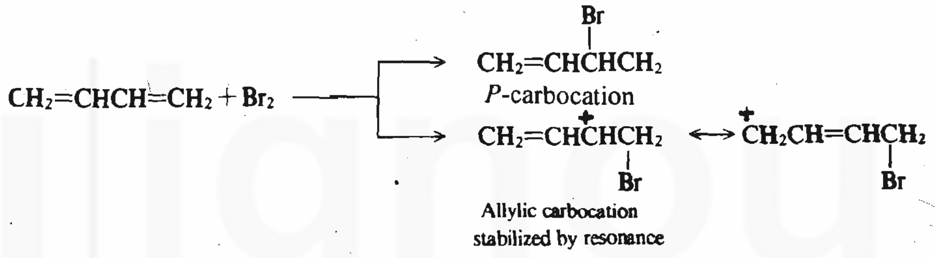


$$\left.\begin{array}{l}\underset{Br}{C}H_2\underset{Br}{C}HCH{=}CH_2\\ \text{or}\\ \underset{Br}{C}H_2CH{=}CH\underset{Br}{C}H_2\end{array}\right] \xrightarrow{Br_2} \underset{Br}{C}H_2\underset{Br}{C}H\underset{Br}{C}H_2\underset{Br}{C}H_2$$

1, 2, 3, 4-tetrabromobutane

Mechanism

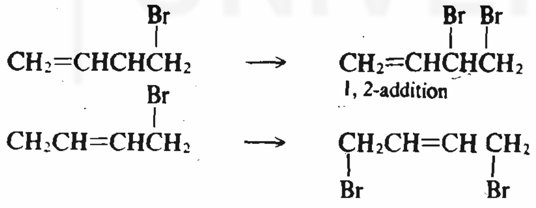
The mechanism of halogenation of 1, 3-butadiene is illustrated below :



$$CH_2{=}CHCH{=}CH_2 + Br_2 \longrightarrow \begin{cases} CH_2{=}CH\overset{Br}{C}H\overset{+}{C}H_2 \quad P\text{-carbocation}\\ CH_2{=}CH\overset{+}{C}H\underset{Br}{C}H_2 \longleftrightarrow \overset{+}{C}H_2CH{=}CH\underset{Br}{C}H_2 \end{cases}$$

Allylic carbocation stabilized by resonance

Bromine may attach itself to either C_1 or C_2. The addition of the bromine atom at C_2 would give rise to an unstable primary localized carbocation. But the bromine addition at C_1 results in the formation of resonance stabilized allylic cation. This also explains the enhanced reactivity of dienes over isolated ethylenic double bonds. When the allylic, carbocation is attacked by bromine ion (Br^-) to complete the electrophilic addition reaction, the attack can occur at either C_1 or C_3, since both share the positive charge. The result is a mixture of 1, 2- and 1, 4-addition products, the latter formed in excess since it has the more highly substituted double bond and is hence more stable.



$$CH_2{=}CH\overset{Br}{C}HCH_2 \longrightarrow CH_2{=}CH\overset{Br}{C}H\overset{Br}{C}H_2$$

1, 2-addition

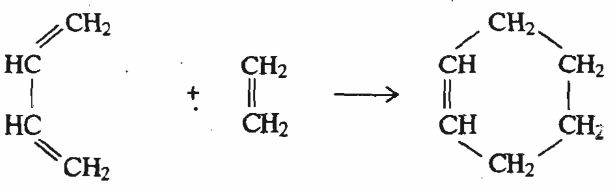
$$CH_2CH{=}CH\overset{Br}{C}H_2 \longrightarrow \underset{Br}{C}H_2CH{=}CH\,\underset{Br}{C}H_2$$

1,4-addition.

7.6.9 Diels-Alder Reaction

Diels and Alder jointly received the 1950 Noble prize for their work in this area.

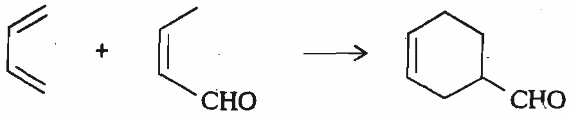
In Diels-Alder reaction, a conjugated diene is treated with an unsaturated compound called the dienophile (diene-lover) to yield a cyclic system. This reaction is named after the German chemists, Diel and Alder. It is a very useful reaction for synthesising cyclic systems. The simplest Diels-Alder reaction is the reaction of 1, 3-butadiene with ethene to yield cyclohexene. The resulting product (here cyclohexene) is called the adduct:



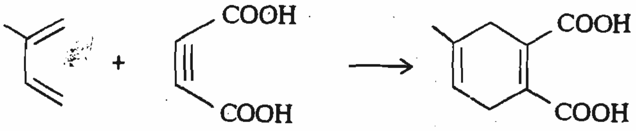
1, 3-butadiene — ethene — cyclohexene

This is a very slow reaction and it occurs only under conditions of heat and pressure. Diels-Alder additions take place most rapidly and give the highest yield if the alkene component has electron withdrawing groups or the diene has electron donating groups. The reaction has wide scope because triple bonded systems also may be used as dienophiles. Some important examples of Diels-Alder reaction are given below :

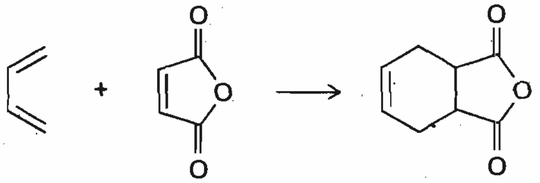
i)



ii)



iii)



SAQ 5

a) Write the structure of all possible carbocation intermediates in the addition of HI to 2, 4-hexadiene.

....

b) Which carbocation, of the above problem, would you expect to be more stable?

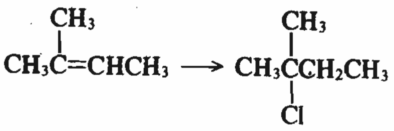
....

7.7 SUMMARY

- Hydrocarbons containing one carbon-carbon double bond are known as monoene or olefins. Hydrocarbons containing two double bonds are known as alkedienes or dienes. Dienes are divided into three classes, i.e., conjugated dienes, isolated dienes and cumulated dienes.
- In general, the physical properties of alkenes are similar to the corresponding alkanes.
- Alkenes are generally prepared by the elimination of atoms or groups from the adjacent carbon atoms. Two such reactions are dehydrohalogenation of alkyl halides and dehydration of alcohols. The ease of dehydrohalogenation of alkyl halide or dehydration of alcohol is :
  tert >sec >p
- Alkenes can also be prepared from aldehydes or ketones by Wittig reactions.
- Dienes are prepared by retro Diels-Alder reactions.
- The main reactions of alkenes are electrophilic addition reactions. These reactions include addition of halogen, addition of alkyl halide, addition of water, etc.
- Alkenes can be oxidised by ozone, permanganate and osmium tetroxide. Alkenes on ozonolysis give aldehydes or ketones and on oxidation give 1, 2-diol.
- Addition of halogen to conjugated dienes give normal 1, 2-addition product as a minor product and abnormal 1, 4-addition product as a major product.
- Alkenes undergo Diels-Alder reaction.

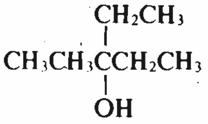
7.8 TERMINAL QUESTIONS

1) Give a structural formula for the carbocation intermediate that leads to the principle product in the following reaction :

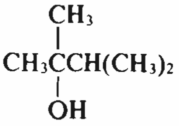


$$CH_3\overset{\overset{CH_3}{|}}{C}=CHCH_3 \longrightarrow CH_3\underset{\underset{Cl}{|}}{\overset{\overset{CH_3}{|}}{C}}CH_2CH_3$$

2) Identify the alkene obtained on hydration/dehydrohalogenation of each of the following compounds:

a) 

$$\mathrm{CH_3CH_3\overset{\displaystyle CH_2CH_3}{\underset{\displaystyle OH}{C}}CH_2CH_3}$$

b) 

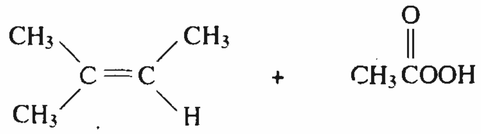
$$\mathrm{CH_3\overset{\displaystyle CH_3}{\underset{\displaystyle OH}{C}}CH(CH_3)_2}$$

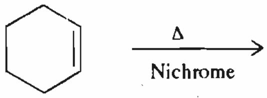
c) $CH_3CH_2CH_2Br$

3) Give the product formed when HBr reacts with 2-methyl-2-butene is presence of peroxide and in absence of peroxide.

4) Arrange the following alkenes in order of decreasing stability.
$R_2C{=}CR_2$; $R_2C{=}CH_2$; $CH_2{=}CH_2$; $R_2C{=}CHR$; $RHC{=}CHR$; $RCH{=}CH_2$.

5) Complete the following reactions :

a) 

b) 

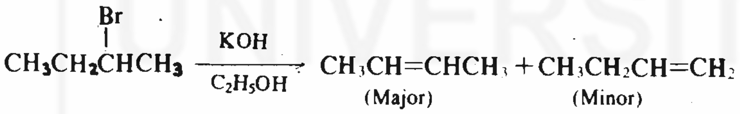
c) $CH_3CH{=}CH_2 + H_2O \xrightarrow[273\ K]{KMnO_4}$

d) $CH_2{=}CHCH{=}CH_2{+}HBr \longrightarrow$

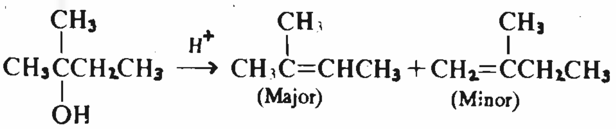
7.9 ANSWERS

Self Assessment Questions

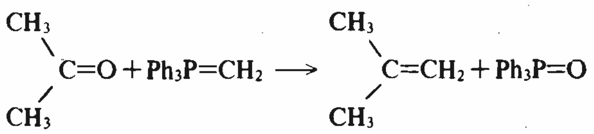
1) a) alkyne
b) four
c) conjugated
d) *sp*; *sp*^{2}

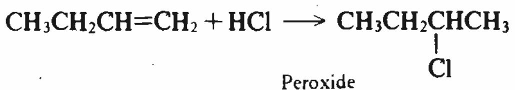
2) a) 

$$\mathrm{CH_3CH_2\overset{\displaystyle Br}{C}HCH_3 \xrightarrow[C_2H_5OH]{KOH} \underset{(Major)}{CH_3CH{=}CHCH_3} + \underset{(Minor)}{CH_3CH_2CH{=}CH_2}}$$

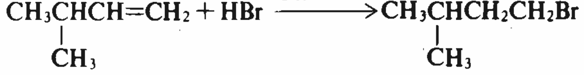
b) 

$$\mathrm{CH_3\overset{\displaystyle CH_3}{\underset{\displaystyle OH}{C}}CH_2CH_3 \xrightarrow{H^+} \underset{(Major)}{CH_3\overset{\displaystyle CH_3}{C}{=}CHCH_3} + \underset{(Minor)}{CH_2{=}\overset{\displaystyle CH_3}{C}CH_2CH_3}}$$

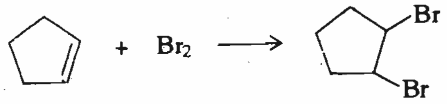
c) 

3) a) 

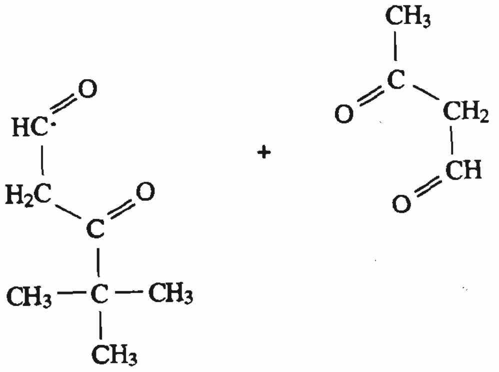
$$\mathrm{CH_3CH_2CH{=}CH_2 + HCl \longrightarrow CH_3CH_2\underset{\displaystyle Cl}{C}HCH_3}$$

b) 

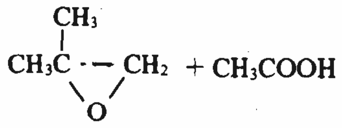
$$\mathrm{CH_3\underset{\displaystyle CH_3}{C}HCH{=}CH_2 + HBr \xrightarrow{Peroxide} CH_3\underset{\displaystyle CH_3}{C}HCH_2CH_2Br}$$

c) 

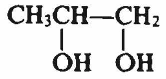
4) a)



b)



c)


$$\underset{OH}{CH_3CH}-\underset{OH}{CH_2}$$

5) a) $CH_3CH{=}CHCH{=}CHCH_3 \xrightarrow{H^+} CH_3CH_2\overset{+}{C}HCH{=}CHCH_3 + CH_3\overset{+}{C}HCH_2CH{=}CHCH_3$

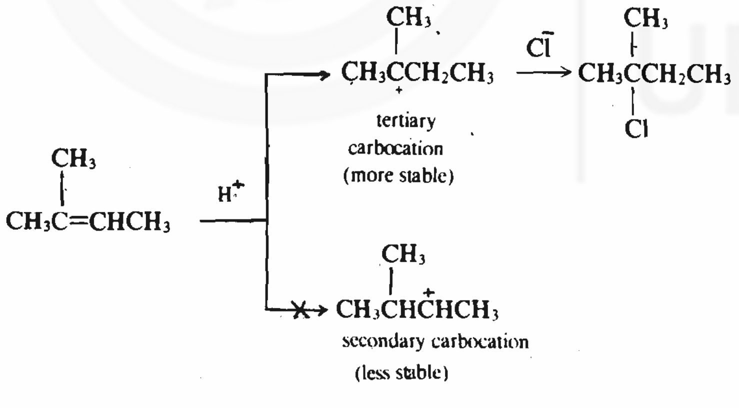
(Addition of H⁺ to the other double bond gives identical intermediate)

b) The first carbocation shown would be more stable because it is resonance stabilized allytic carbocation, i.e.,

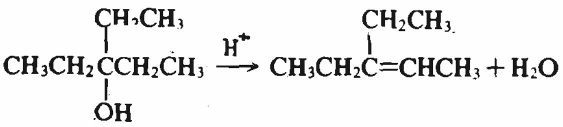
$$CH_3CH_2\overset{+}{C}H-CH{=}CHCH_3 \longleftrightarrow CH_3CH_2CH{=}CH-\overset{+}{C}HCH_3$$

Terminal Questions

1)

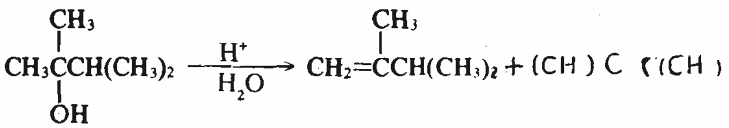


2) a)


$$CH_3CH_2\underset{OH}{\overset{CH_2CH_3}{C}}CH_2CH_3 \xrightarrow{H^+} CH_3CH_2\overset{CH_2CH_3}{C}{=}CHCH_3 + H_2O$$

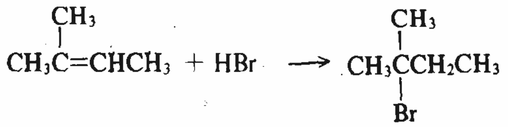
The hydroxyl group is located on carbon that bear three equivalent ethyl substituents in the starting alcohol. Elimination can occur in either of the three equivalent direction to give the same alkene.

b)


$$CH_3\underset{OH}{\overset{CH_3}{C}}CH(CH_3)_2 \xrightarrow[H_2O]{H^+} CH_2{=}\overset{CH_3}{C}CH(CH_3)_2 + (CH\ )\ C\ \ (CH\ )$$

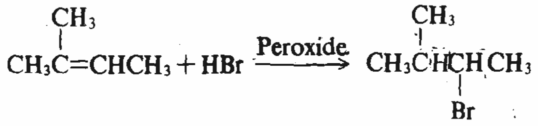
c) $CH_3CH_2CH_2Br \xrightarrow[C_2H_5OH]{KOH} CH_3CH{=}CH_2$

3) The addition of HBr in absence of peroxide gives Markownikoff's product,



$$CH_3\overset{CH_3}{C}{=}CHCH_3 + HBr \longrightarrow CH_3\underset{Br}{\overset{CH_3}{C}}CH_2CH_3$$

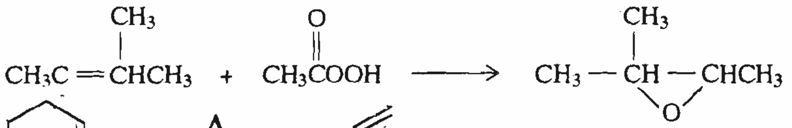
The addition of HBr in the presence of peroxide gives anti-Markownikoff's product, i.e.:



$$CH_3\overset{CH_3}{C}{=}CHCH_3 + HBr \xrightarrow{Peroxide} CH_3\overset{CH_3}{C}H\underset{Br}{C}HCH_3$$

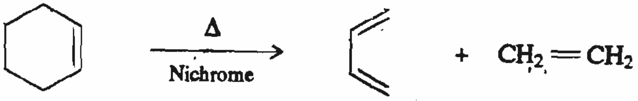
4) $R_2C{=}CR_2 > R_2C{=}CHR > R_2C{=}CH_2, RCH{=}CHR > RCH{=}CH_2 > CH_2{=}CH_2$

5) a)

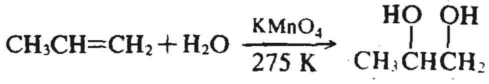


$$CH_3\overset{CH_3}{C}{=}CHCH_3 + CH_3\overset{O}{\overset{\|}{C}}OOH \longrightarrow CH_3-\overset{CH_3}{CH}-CHCH_3$$

b)

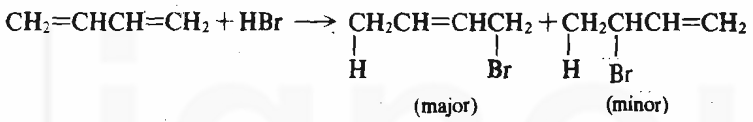


c)



$$CH_3CH{=}CH_2 + H_2O \xrightarrow[275\ K]{KMnO_4} CH_3\overset{HO}{C}H\overset{OH}{C}H_2$$

d)



$$CH_2{=}CHCH{=}CH_2 + HBr \longrightarrow \underset{H}{C}H_2CH{=}CH\underset{Br}{C}H_2 + \underset{H}{C}H_2\underset{Br}{C}HCH{=}CH_2$$

UNIT 8 ALKYNES

Structure

8.1 INTRODUCTION

In the previous two units, you have studied the chemistry of alkanes and alkenes. We shall now study another kind of hydrocarbon known as alkynes which contain carbon-carbon triple bond.

Ethyne, CH≡CH, the simplest alkyne, was burnt in the miners' lamps before electric lamps were developed. It is used in oxyacetylene torches for cutting and welding metals. It is extensively used as a fuel gas. In industry, it is the starting material for the preparation of many important chemicals, e.g., ethanoic acid, chloroethene (vinyl chloride), propanone, butanol, ethanol, etc.

A large number of naturally occurring compounds containing triple bonds have been isolated from plant kingdom. For example, a triyne from safflower has considerable activity against nematodes and evidently forms part of the plant's chemical defence against infestation.

You will see in this unit that the carbon-carbon triple bond reacts with many of the reagents that reacts with alkenes. You will also study the most unique aspect of the chemistry of alkynes, the acidity of terminal alkynes.

Objectives

After studying this unit, you should be able to :

- list the various kinds of alkynes,
- list the physical and spectral properties of alkynes,
- explain the various methods for the preparation of alkynes,
- explain the acidity of terminal alkynes.
- explain the chemical reactions of alkynes.

8.2 TYPES OF ALKYNES

Alkynes, also known as acetylenes, constitute the homogenous series of open chain unsaturated hydrocarbons that contain one or more carbon-carbon triple bond. Alkynes may be of two types : terminal and internal. In the terminal alkynes, the triple bond lies at the end of the carbon chain and in the internal alkynes, the triple bond lies anywhere except at the terminal position.

$CH_3C{\equiv}CH$	$CH_3CH_2C{\equiv}CCH_2CH_3$	$CH_3C{\equiv}CC{\equiv}CCH_3$
1-propyne (terminal alkyne)	3-hexyne (internal alkyne)	2,4-hexadiyne (internal alkyne)

8.3 PHYSICAL PROPERTIES

The increase in boiling point with increase in molecular weight is due to increased London forces, as discussed in Block 1 of this course.

Fractional distillation is the method of separating the components in a liquid mixture using the difference in their boiling points.

The physical properties of alkynes are similar to those of corresponding alkenes. They are all colourless and odourless (except ethyne). The first three members, i.e., ethyne, propyne and 1-butyne, are gases at room temperature; the next eight members are liquids and the higher members are solids. The physical constants like melting points, boiling points and densities increase gradually with the increase in molecular weight. Alkynes have slightly higher boiling points than the corresponding alkenes and alkanes. Terminal alkynes have lower boiling points than the isomeric internal alkynes and can be separated by careful fractional distillation. Alkynes share with alkanes and alkenes the properties of low density and low water solubility. They are nonpolar and dissolve readily in typical organic solvents, such as diethyl ether, chlorinated hydrocarbons, etc.

8.4 SPECTRAL PROPERTIES

The alkynyl chromophore absorbs below 200 nm (π-π^* transition) in uv region which is often difficult to detect. Conjugation with a multiple bond, however, results in a bathochromic shift.

The ir absorption region of compounds with a triple bond depends on whether they contain alkyne hydrogen or not. Thus, in terminal alkynes, RC≡CH, there is one absorption band in the region of 3300-3100 cm^{-1} due to the C≡CH stretching, and another in the region of 2140-2100 cm^{-1} due to —C≡C— stretch. In the internal alkynes RC≡CR, there is absorption in the region of 2260-2190 cm^{-1} corresponding to the —C≡C— stretching.

The internal alkynes, RC≡CR, have no alkynyl hydrogen, therefore, they have no nmr absorption characteristics of alkynyl hydrogen. The terminal alkynes, RC≡CH, give an absorption signal between δ 2 and 3, characteristic of alkynyl proton. Thus, value for alkynyl proton is less than the value of alkenyl protons. Let us suggest an explanation for this.

The chemical shift of a particular proton depends on the magnetic field felt by it. As you know, the chemical shift as well as the magnetic field felt by a particular proton depends on :

- the electronegativity of the carbon atom to which the proton is attached,
- the way the proton is oriented to the neighbouring π electron cloud, if any.

The *sp* hybridised carbon in alkynes is more electronegative than the sp^2 hybridized carbon in alkenes. Hence, we could expect higher δ value for alkynyl protons than for alkenyl protons. But the orientation of the alkynyl proton to the π electron cloud is unfavourable for higher δ values, as compared to the alkenyl protons.

The mass spectra of an alkyne gives distinct molecular ion peak. However, the fragmentation is often complex and not easily interpreted.

8.5 PREPARATION OF ALKYNES

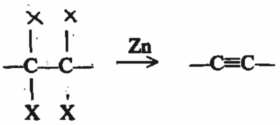
Organic synthesis makes use of two major reaction types : one is functional group transformation and the other is carbon-carbon bond forming reaction. Both these strategies are applied to the preparation of alkynes. In this unit, we shall discuss how alkynes are prepared by elimination reactions and by adding alkyl group(s) to the smaller ethyne unit. Some important methods of preparation of alkynes are outlined in Table 8.1.

Table 8.1 : Preparation of alkynes

Dehydrohalogenation of dihalide

$$-\overset{H}{\underset{X}{C}}-\overset{H}{\underset{X}{C}}- \xrightarrow[-2HX]{\text{Base}} -C\equiv C-$$

Dehalogenation of tetrahalide



$$-\overset{X}{\underset{X}{C}}-\overset{X}{\underset{X}{C}}- \xrightarrow{Zn} -C\equiv C-$$

Alkylation of ethyne

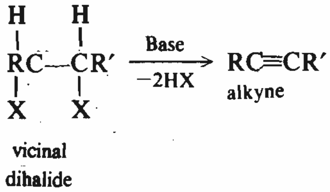
$$-C\equiv CH \xrightarrow{Na/NH_3} -C\equiv \overset{-}{C}:\overset{+}{Na} \xrightarrow{RX} -C\equiv CR$$

8.5.1 Dehydrohalogenation of Dihalides

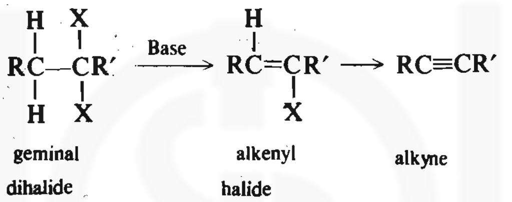
You have already seen in Unit 7 that an alkene can be prepared by the elimination of HX from an alkyl halide. Similarly, an alkyne can be prepared by the elimination of two molecules of HX from a dihalide. The dihalide may be of the geminal or vicinal type.

Geminal dihalide : One in which both the halogen atoms are substituted on the same carbon atom.

Vicinal dihalide : One in which halogen atoms are substituted on adjacent carbon atoms.

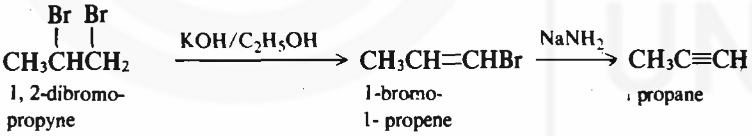


$$\underset{\text{vicinal dihalide}}{R\overset{H}{\underset{X}{C}}-\overset{H}{\underset{X}{C}}R'} \xrightarrow[-2HX]{\text{Base}} \underset{\text{alkyne}}{RC\equiv CR'}$$



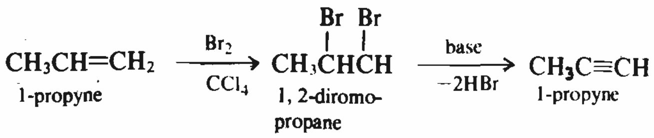
$$\underset{\text{geminal dihalide}}{R\overset{H}{\underset{H}{C}}-\overset{X}{\underset{X}{C}}R'} \xrightarrow{\text{Base}} \underset{\text{alkenyl halide}}{R\overset{H}{C}=\underset{X}{C}R'} \longrightarrow \underset{\text{alkyne}}{RC\equiv CR'}$$

Since an alkyne contains a triple bond as compared to the double bond in alkenes, two molecules of HX must be eliminated. Therefore, stronger conditions are required to remove the second HX molecule. For example, when 1, 2-dibromopropane reacts with a strong base, a two-fold elimination occurs and as a result a propyne is produced.



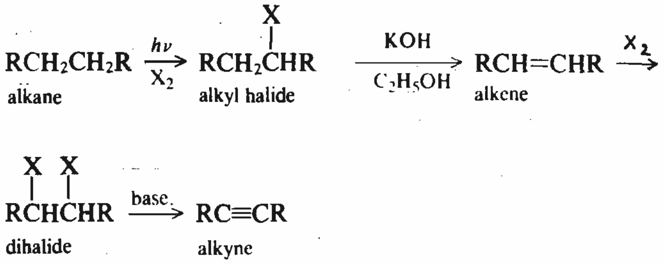
$$\underset{\text{1, 2-dibromo-propyne}}{CH_3\overset{Br}{C}H\overset{Br}{C}H_2} \xrightarrow{KOH/C_2H_5OH} \underset{\text{1-bromo-1- propene}}{CH_3CH=CHBr} \xrightarrow{NaNH_2} \underset{\text{propane}}{CH_3C\equiv CH}$$

You have studied in Unit 7 that dihalides are prepared by the addition of halogen to an alkene. Thus, the overall sequence of halogenation-dehydrohalogenation provides an excellent method for going from an alkene to an alkyne, e.g.,



$$\underset{\text{1-propyne}}{CH_3CH=CH_2} \xrightarrow[CCl_4]{Br_2} \underset{\text{1, 2-diromo-propane}}{CH_3\overset{Br}{C}H\overset{Br}{C}H} \xrightarrow[-2HBr]{\text{base}} \underset{\text{1-propyne}}{CH_3C\equiv CH}$$

You may recall that alkenes can be prepared by elimination reactions of alkyl halides, which again, can be obtained from alkanes. Thus, we can say that alkane can serve as a starting material for the preparations of alkynes.



$$\underset{\text{alkane}}{RCH_2CH_2R} \xrightarrow[X_2]{h\nu} \underset{\text{alkyl halide}}{RCH_2\overset{X}{C}HR} \xrightarrow[C_2H_5OH]{KOH} \underset{\text{alkene}}{RCH=CHR} \xrightarrow{X_2}$$

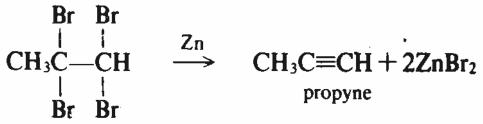
$$\underset{\text{dihalide}}{R\overset{X}{C}H\overset{X}{C}HR} \xrightarrow{\text{base}} \underset{\text{alkyne}}{RC\equiv CR}$$

Different bases can be used for dehydrohalogenation; sodium amide is preferred, since it usually gives a higher yield.

The two-fold dehydrohalogenation follows the same mechanism as the dehydrohalogenation of alkyl halide to alkenes mentioned in Unit 7.

8.5.2 Dehalogenation of Tetrahalides

Alkyne can also be prepared by dehalogenation of tetrahalides. For example, propyne is formed when the vapours of 1, 1, 2, 2-tetrabromopropane are passed over heated zinc.



$$CH_3CBr_2{-}CHBr_2 \xrightarrow{Zn} CH_3C\equiv CH + 2ZnBr_2$$

propyne

1, 1, 2, 2-
tetrabromopropane

This reaction does not have any synthetic importance, since the tetrahalides themselves are usually prepared from alkynes. However, it provides a method for the purification of alkynes.

8.5.3 Alkylation of Ethyne

Reactions that lead to the attachment of an alkyl group to a molecular fragment are called alkylation.

In this sub-section, we shall see how alkynes are prepared by combining smaller units to build larger carbon chains. One of these structural units is ethyne itself. By attaching alkyl group to ethyne, more complex alkynes can be prepared. For example,

$$HC\equiv CH \xrightarrow{Na/NH_3} HC\equiv\overset{-}{C}\colon \overset{+}{Na}$$

sodium ethynide

$$HC\equiv\overset{-}{C}\colon \overset{+}{Na} + ICH_2CH_2CH_2CH_3 \longrightarrow HC\equiv C(CH_2)_3CH_3 + NaI$$

1-iodobutane 1-hexyne (86% yield)

Alkylation is a two-step process. In the first step, ethyne reacts with sodium amide to give an sodium ethynide ion, the conjugated base of ethyne.

In the second step, sodium ethynide ion attacks the C-1 carbon atom of 1-iodobutance and pushes out the iodide ion, yielding the terminal alkyne, 1-hexyne, giving an overall 86% yield.

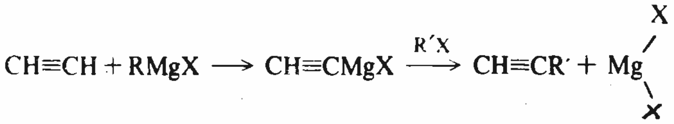
Again, 1-hexyne can itself be converted into an alkynide anion, and can be alkylated a second time to yield an internal alkyne. A different alkyl halide can be used this time.

$$CH_3(CH_2)_3C\equiv CH \xrightarrow[2.\ CH_3CH_2Br]{1.\ NaNH_2} CH_3(CH_2)_3C\equiv CCH_2CH_3$$

1-hexyne 3-octyne

This reaction gives good yields of alkyne only with primary alkyl bromides and iodides.

Alkylation can also be carried out by reacting ethyne and Grignard reagent, followed by the action of an alkyl halide,



$$CH\equiv CH + RMgX \longrightarrow CH\equiv CMgX \xrightarrow{R'X} CH\equiv CR' + Mg\begin{smallmatrix}X\\X\end{smallmatrix}$$

SAQ 1

Suggest a method for preparation of the following alkynes starting with ethyne. Use any alkyl halide needed.

a) 2-Heptyne

....

b) 3-Heptyne

....

8.6 ACIDITY OF ALKYNES

You have already studied the Bronsted-Lowry theory of acids and bases in Unit 5 of this course. According to Bronsted and Lowry, an acid is a species that donates H^+. In fact, any compound containing a hydrogen atom can act as an acid under suitable conditions. Acid strength can be measured by measuring dissociation constants and expressing the result as values. Strong acids have lower pKa values than weak acids.

Hydrocarbons are usually not regarded as acids. Nevertheless, we can consider the removal of a proton from a hydrocarbon by a very strong base.

$$\geq CH + B^- \longrightarrow \geq \bar{C}: + BH$$

In this equation, the hydrocarbon acts as a Bronsted acid (carbon acid) and the conjugated base is a **carbon anion** or **carbanion.**

Approximate acidities of different types of aliphatic hydrocarbons have been measured and their pK_a values are given in Table 8.2.

Table 8.2 : Acidities of some hydrocarbons

Type	Example	pK_a
Alkane	$CH_4 \rightleftharpoons \bar{C}H_3 + H^+$	49
Alkene	$CH_2{=}CH_2 \rightleftharpoons CH_2{=}\bar{C}H + H^+$	44
Alkyne	$HC{\equiv}CH \rightleftharpoons HC{\equiv}\bar{C} + H^+$	25

From the data given in Table 8.2, we can see that there is a significant difference in the acidity of alkynes and other hydrocarbons. The order of acid strength of these hydrocarbons is :

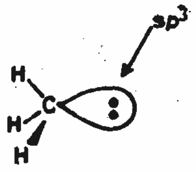
$$CH{\equiv}CH > CH_2{=}CH_2 > CH_3CH_3$$

Conversely, the decreasing order of basic strength of the conjugate anions resulting from these hydrocarbons should be :

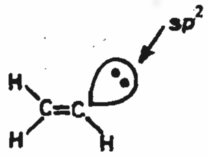
$CH_3\bar{C}H_2 >$	$CH_2{=}\bar{C}H >$	$CH{\equiv}\bar{C}$
alkanide anion	alkenide anion	alkynide anion

This decreasing order of acidities and basicities of hydrocarbons can be explained as follows :

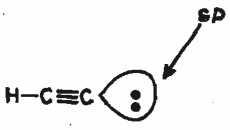
Conjugated bases of alkanes, alkenes and alkynes have an electron pair in sp^3, sp^2 and sp orbitals, respectively, i.e.,



alkanide anion



alkenide anion



alkynide anion

As we proceed from the alkanide anion to alkynide anion, the *s* character of the hybrid orbital increases and *p* character decreases. The alkanide anion (sp^3 hybridised) has 25% *s* character and 75% *p* character; alkenide anion (sp^2 hybridised) has 33.3% *s* character and 66.6% *p* character; and alkynide anion (*sp* hybridised) has 50% *s* character and 50% *p* character. You have already studied in your earlier classes that electrons in *s* orbital are closer to the nucleus than those in *p* orbitals. Since *s* character is maximum in alkynide anion and minimum in alkanide anion, the electron pair should be held most tightly in alkynide anion and most loosely in alkanide anion. Alkenide anion lies in between. In other words, the electron pair in alkynide anion should be least available for protonation. As you know, the basic strength is more if the electron pair is easily available for protonation.

Therefore, in the above series, alkynide anion is the weakest base and alkanide anion is the strongest base. Conversely, alkyne is the strongest acid and alkane the weakest acid.

This can be explained in another way also. On the basis of the above discussion, we can say that the *sp* hybridised carbon would attract the electrons pair constituting the C—H bond of an alkyne more than the sp^2 and sp^3 hybridised carbons in alkene and alkane; respectively. This implies that C—H bond in an alkyne would be more ionic and has a tendency to donate a proton (H^+). Hence, ethyne would be more acidic as compared to ethene or ethane.

Let us now compare its acidity with ammonia and water.

Addition of ethyne to sodamide in ether yields ammonia and sodium ethynide.

$$\underset{\text{stronger acid}}{HC\equiv CH} + \underset{\text{stronger base}}{\bar{N}H_2} \rightleftharpoons \underset{\text{weaker acid}}{H{-}NH_2} + \underset{\text{weaker base}}{HC\equiv\bar{C}}$$

$$\underset{\text{Acid}}{HA} \rightleftharpoons H^+ + \underset{\text{conjugate base}}{A^-}$$

The stronger the conjugate base, the weaker the acid and *vice-versa*.

The weaker acid, $H{-}NH_2$, is displaced from its salt by the stronger acid, $HC\equiv CH$. In other words, the stronger base, $\bar{N}H_2$ pulls the hydrogen ion away from ethyne to yield a weaker conjugate base, $HC\equiv\bar{C}$, since NH_2 holds the hydrogen ion more tightly than $HC\equiv\bar{C}$, ammonia must necessarily be a weaker acid than ethyne.

Addition of water to sodium ethynide forms sodium hydroxide and regenerates ethyne.

$$\underset{\text{stronger acid}}{H{-}OH} + \underset{\text{stronger base}}{HC\equiv\bar{C}\!:\overset{+}{Na}} \longrightarrow \underset{\text{weaker acid}}{HC\equiv C{-}H} + \underset{\text{weak base}}{NaOH}$$

The weaker acid, ethyne, is displaced from its salt by the stronger acid, H_2O. Thus, ethyne is a stronger acid than ammonia, but a weaker acid than water, i.e., the three compounds have the following order of acid strength :

$$H_2O > HC\equiv CH > NH_3$$

SAQ 2

Arrange the following bases in the increasing order of basic strength

$HC\equiv\bar{C}$, $\bar{O}H$, $\bar{N}H_2$

……………………………………………………………………………………………

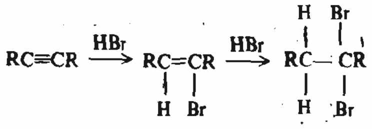
8.7 REACTIONS OF ALKYNES

Due to the presence of loosely held π electrons, alkynes undergo reactions similar to those of alkenes. You will see in this unit that some of the chemical characteristics of alkynes are similar to those of alkenes. Characteristic reactions of alkynes include electrophilic additions, reduction and oxidation. Some important reactions of alkynes are summarised in Table 8.3.

Table 8.3 : Reactions of alkynes

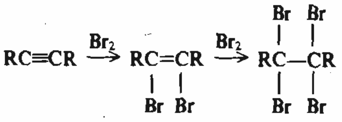
Electrophilic addition reactions

i)



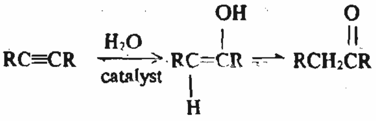
$$RC\equiv CR \xrightarrow{HBr} \underset{H\ \ \ Br}{RC=CR} \xrightarrow{HBr} \overset{H\ \ \ Br}{\underset{H\ \ \ Br}{RC-CR}}$$

ii)



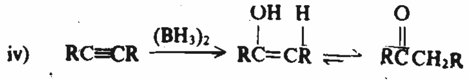
$$RC\equiv CR \xrightarrow{Br_2} \underset{Br\ \ Br}{RC=CR} \xrightarrow{Br_2} \overset{Br\ \ Br}{\underset{Br\ \ Br}{RC-CR}}$$

iii)



$$RC\equiv CR \xrightarrow[\text{catalyst}]{H_2O} \underset{H}{RC}=\overset{OH}{CR} \rightleftharpoons RCH_2\overset{O}{\overset{\|}{C}}R$$

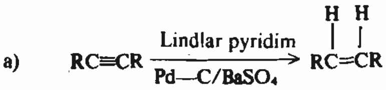
iv)



$$RC\equiv CR \xrightarrow{(BH_3)_2} R\overset{OH}{\overset{|}{C}}=\overset{H}{\overset{|}{C}}R \rightleftharpoons R\overset{O}{\overset{\|}{C}}CH_2R$$

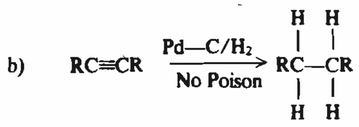
Hydrogenation

a)



$$RC\equiv CR \xrightarrow[Pd—C/BaSO_4]{\text{Lindlar pyridim}} R\overset{H}{\overset{|}{C}}=\overset{H}{\overset{|}{C}}R$$

b)



$$RC\equiv CR \xrightarrow[\text{No Poison}]{Pd—C/H_2} R\underset{H}{\underset{|}{\overset{H}{\overset{|}{C}}}}—\underset{H}{\underset{|}{\overset{H}{\overset{|}{C}}}}R$$

Ozonolysis

$RC\equiv CR \xrightarrow{O_3} RCOOH + HOOCR$

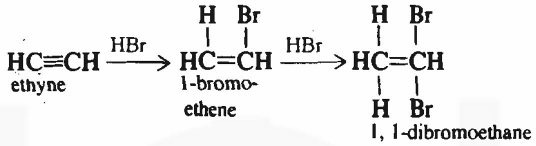
8.7.1 Electrophilic Addition

Electrophilic addition reactions are characteristic of alkynes. Some common electrophilic addition reactions are discussed below.

If one of the carbon atoms involved in double bond formation (with another carbon atom) carries a positive charge, then the species is called alkenyl cation.

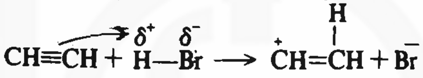
i) Hydrohalogenation

Halogen acid (HX) can add on the alkynes. The addition of halogen acid cannot take place in the dark, light or metalic halides. Like alkenes, the addition is in accordance with Markowniff's rule; for example, ethyne combines with hydrogen bromide to form first 1-bromoethene and then 1, 1-dibromoethane.



$$\underset{\text{ethyne}}{HC\equiv CH} \xrightarrow{HBr} \underset{\text{1-bromoethene}}{H\overset{H}{\overset{|}{C}}=\overset{Br}{\overset{|}{C}}H} \xrightarrow{HBr} \underset{\text{1, 1-dibromoethane}}{H\underset{H}{\underset{|}{\overset{H}{\overset{|}{C}}}}=\underset{Br}{\underset{|}{\overset{Br}{\overset{|}{C}}}}H}$$

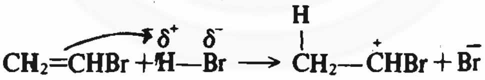
The mechanism of these reactions is the same as in the hydrohalogenation of alkenes, i.e.,



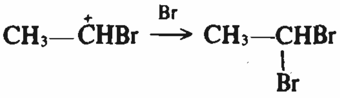
$$CH\equiv CH + \overset{\delta^+}{H}—\overset{\delta^-}{Br} \longrightarrow \overset{+}{C}H=\overset{H}{\overset{|}{C}}H + \bar{Br}$$

$$\overset{+}{C}H=CH_2 \xrightarrow{Br^-} BrCH=CH_2$$

Addition of another molecule of hydrogen bromide could give either $CH_3\overset{+}{C}HBr$ (a secondary carbocation) or $\overset{+}{C}H_2CH_2Br$ (a primary carbocation). Since the secondary carbocation is more stable than the primary carbocation, the reaction proceeds via the secondary carbocation to form 1, 1-dibromoethane. Thus



$$CH_2=CHBr + \overset{\delta^+}{H}—\overset{\delta^-}{Br} \longrightarrow \overset{H}{\overset{|}{C}}H_2—\overset{+}{C}HBr + \bar{Br}$$

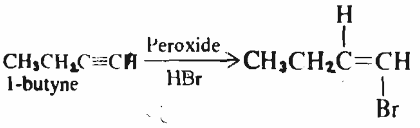


$$CH_3—\overset{+}{C}HBr \xrightarrow{Br} CH_3—\underset{Br}{\underset{|}{C}}HBr$$

Because of the electron-withdrawing nature of bromine atom, the availability of π electrons in 1-bromoethene is less than that in ethene. Hence, the electrophilic addition (of HBr) to 1-bromoethene is much slower than that to ethene.

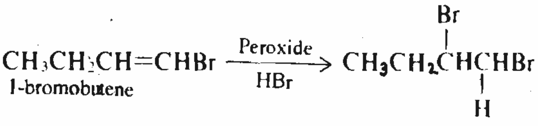
You may be aware that bromine atom is grouped as —I group. Recall what you have studied under inductive effect in Block 1

In the presence of free radical initiators such as peroxides, anti-Markownikoff addition of HBr is observed as with alkenes. For example, addition of HBr in the presence of peroxides to 1-butyne gives 1, 2-dibromobutane, as shown below :



$$\underset{\text{1-butyne}}{CH_3CH_2C\equiv CH} \xrightarrow[HBr]{\text{Peroxide}} CH_3CH_2\overset{H}{\overset{|}{C}}=\underset{Br}{\underset{|}{C}}H$$

1-bromobutene

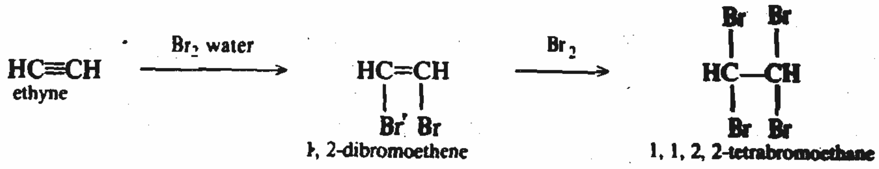


$$\underset{\text{1-bromobutene}}{CH_3CH_2CH=CHBr} \xrightarrow[HBr]{\text{Peroxide}} CH_3CH_2\overset{Br}{\overset{|}{C}}H\underset{H}{\underset{|}{C}}HBr$$

1, 2-dibromobutane

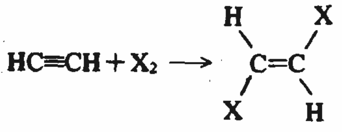
ii) Halogenation

Alkynes react with chlorine and bromine to yield tetrahaloalkanes. Two molecules of halogen add to the triple bond. A dihaloalkene is an intermediate and can be isolated using proper reaction conditions. Ethyne, for instance, on treatment with bromine water gives only 1, 2-dibromoethene whereas with bromine alone, it forms 1, 1, 2, 2-tetrabromoethane.



$$HC\equiv CH \xrightarrow{Br_2\ water} HBrC{=}CHBr \xrightarrow{Br_2} Br_2HC{-}CHBr_2$$

The addition of halogens to ethyne is stereoselective; the predominant product is the *trans* isomer.



$$HC\equiv CH + X_2 \longrightarrow HXC{=}CXH$$

trans product

SAQ 3

Write chemical equation for the reaction of propyne with each of the following reagents.

a) HCl

....

b) Cl_2

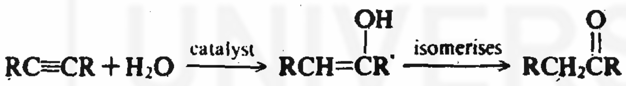
....

c) HBr (in presence of peroxide)

....

iii) Hydration

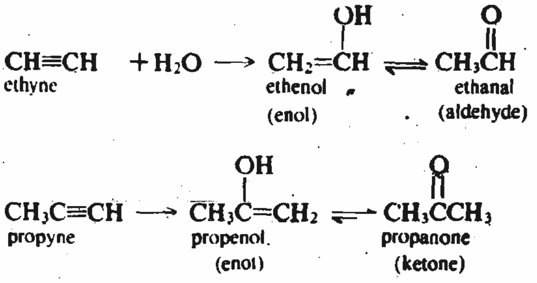
You have seen in Unit 7 that addition of a water molecule to an alkene gives an alcohol. Similarly, addition of a water molecule to an alkyne gives an enol. An enol has the —OH group attached to a double-bonded carbon atom.



$$RC\equiv CR + H_2O \xrightarrow{catalyst} RCH{=}C(OH)R \xrightarrow{isomerises} RCH_2C(=O)R$$

In fact, enols are very unstable and they isomerise (or tautomerise) to give aldehyde or ketones. The process by which enols are converted into aldehydes or ketones is called keto-enol isomerism or keto-enol tautomerism. For example, when ethyne undergoes hydration, it gives an aldehyde, i.e., ethanal; while, propyne gives a ketone, i.e.. propanone.

The arrow is longer towards aldehyde or ketone side showing the direction in which the equilibrium is favoured.

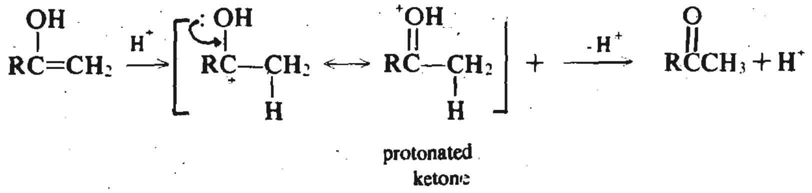


$$CH\equiv CH + H_2O \longrightarrow CH_2{=}CH(OH) \rightleftharpoons CH_3CHO$$

$$CH_3C\equiv CH \longrightarrow CH_3C(OH){=}CH_2 \rightleftharpoons CH_3COCH_3$$

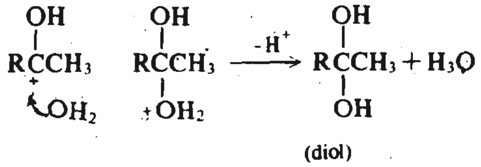
In case of unsymmetrical alkynes, addition of water takes place in accordance with Markownikoff's rule.

Enol is converted into an aldehyde or a ketone by a mechanism similar to the hydration of a double bond. The enol double-bond is protonated to give a carbocation. The carbocation in the example shown below is a protonated ketone. Instead of adding water, this ion loses a proton to give ketone.



$$R\overset{\overset{OH}{|}}{C}=CH_2 \xrightarrow{H^+} \left[R\overset{\overset{:OH}{|}}{\underset{+}{C}}-\underset{\underset{H}{|}}{CH_2} \longleftrightarrow R\overset{\overset{^+OH}{||}}{C}-\underset{\underset{H}{|}}{CH_2} \right] + \xrightarrow{-H^+} R\overset{\overset{O}{||}}{C}CH_3 + H^+$$

Now you may ask why carbocation is not attacked by water molecule to give a diol, i.e.,

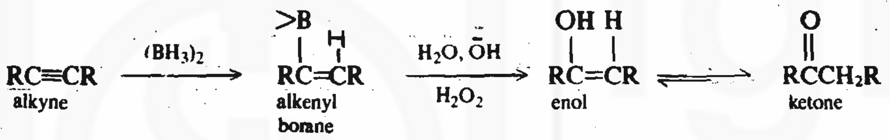


$$R\overset{\overset{OH}{|}}{\underset{+}{C}}CH_3 \quad R\overset{\overset{OH}{|}}{\underset{\underset{+OH_2}{|}}{C}}CH_3 \xrightarrow{-H^+} R\overset{\overset{OH}{|}}{\underset{\underset{OH}{|}}{C}}CH_3 + H_3O$$

This reaction does not occur, because it is reversible, and the equilibrium between the ketone and the corresponding diol in most cases favours formation of the ketone.

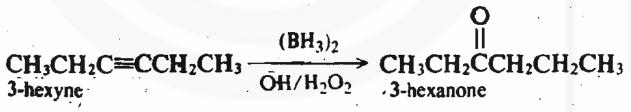
iv) **Hydroboration**

Addition of borane to alkynes gives alkenyl boranes, which can be oxidised by basic hydrogen peroxide to ketones via their enol.

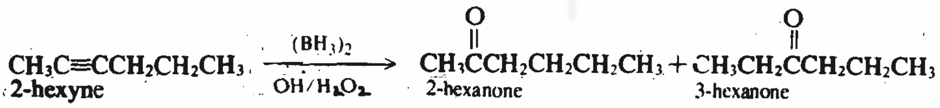


$$RC\equiv CR \xrightarrow{(BH_3)_2} R\overset{\overset{>B}{|}}{C}=\overset{\overset{H}{|}}{C}R \xrightarrow[H_2O_2]{H_2O,\,\bar{O}H} R\overset{\overset{OH}{|}}{C}=\overset{\overset{H}{|}}{C}R \rightleftharpoons R\overset{\overset{O}{||}}{C}CH_2R$$

The symmetrical internal alkynes give a single product while unsymmetrical internal alkynes give a mixture of both the possible ketones. For example, 3-hexyne gives 3-hexanone while 2-hexyne gives a mixture of 2-hexanone and 3-hexanone.



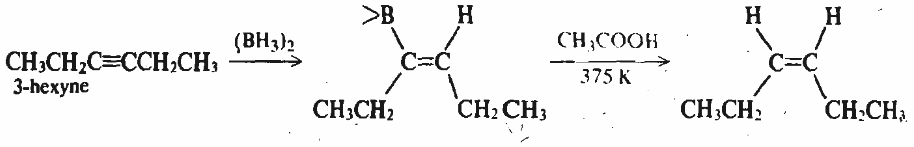
$$CH_3CH_2C\equiv CCH_2CH_3 \xrightarrow[\bar{O}H/H_2O_2]{(BH_3)_2} CH_3CH_2\overset{\overset{O}{||}}{C}CH_2CH_2CH_3$$



$$CH_3C\equiv CCH_2CH_2CH_3 \xrightarrow[\bar{O}H/H_2O_2]{(BH_3)_2} CH_3\overset{\overset{O}{||}}{C}CH_2CH_2CH_2CH_3 + CH_3CH_2\overset{\overset{O}{||}}{C}CH_2CH_2CH_3$$

The terminal alkynes on hydroboration give aldehydes.

Another reaction of organoboranes is **protonolysis**. That is, the alkenyl boranes, formed after the addition of borane to alkynes, on treatment with ethanoic acid yield *cis*-alkenes. This reaction sequence provides another method of converting alkynes to *cis*-alkenes.



$$CH_3CH_2C\equiv CCH_2CH_3 \xrightarrow{(BH_3)_2} (>B)(CH_3CH_2)C=C(H)(CH_2CH_3) \xrightarrow[375\,K]{CH_3COOH} (H)(CH_3CH_2)C=C(H)(CH_2CH_3)$$

cis 3-hexane

SAQ 4

Give the equation for hydroboration of a terminal alkyne.

....

....

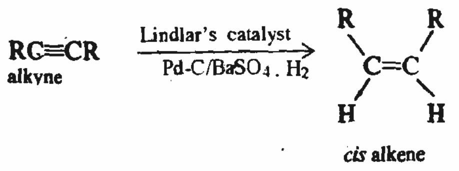
……

……

8.7.2 Hydrogenation

A catalyst mixed with a selective inhibiting agent is called a poisoned catalyst.

Like alkenes, alkynes undergo catalytic hydrogenation. The addition of hydrogen to an alkyne takes place in two steps. First addition results in the formation of an alkene; since an alkene can also undergo catalytic hydrogenation, the second addition gives an alkane. By using a calculated amount of hydrogen and a poisoned catalyst, hydrogenation can be stopped at the alkene stage. These catalysts **selectively** block the hydrogenation of alkenes.



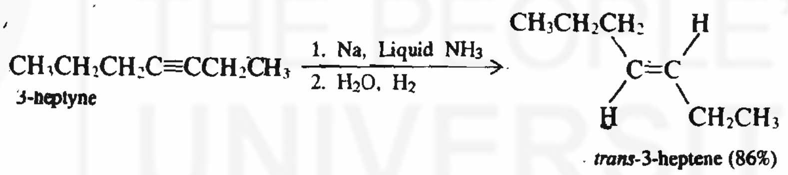
Stereoselective reaction is a reaction which yield predominantly one isomer.

This is a stereoselective addition reaction giving predominantly *cis* alkenes. In the absence of a poison, catalytic hydrogenation of an alkyne gives the alkane.

$$\underset{\text{alkyne}}{RC\equiv CR} \xrightarrow[\text{No Poison}]{H_2,Pd/C} \underset{\substack{\text{alkane}\\ \text{95\% yield}}}{RCH_2CH_2R}$$

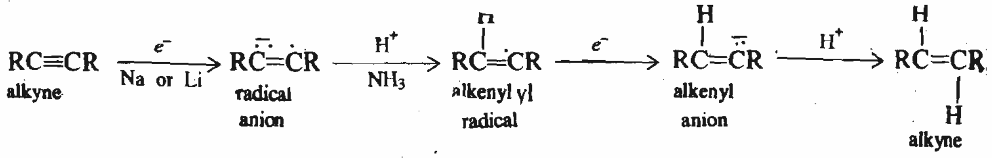
Now you can ask : can we modify the reduction of alkynes so as to get only *trans* alkenes. Th answer is yes; we can get only *trans* products, but with a different reducing agent and through a different mechanism.

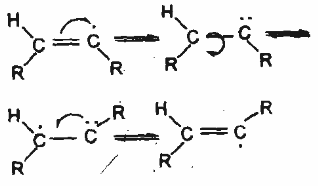
If we carry out the reduction of an alkyne with sodium metal or lithium metal in liquid ammonia, *trans* alkene is almost an exclusive product. For example, 3-heptyne is reduced to *trans* 3-heptene in the following way :



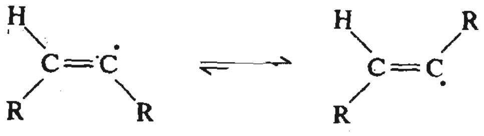
A radical anion has one centre with a negative charge and another, with an unpaired electron.

In the first step of this mechanism, the alkyne accepts one electron to give a radical anion. The radical anion is protonated by ammonia solvent to give an alkenyl radical; which gets further reduced by accepting another electron to give an alkenyl anion. This species is again protonated to give the alkene.



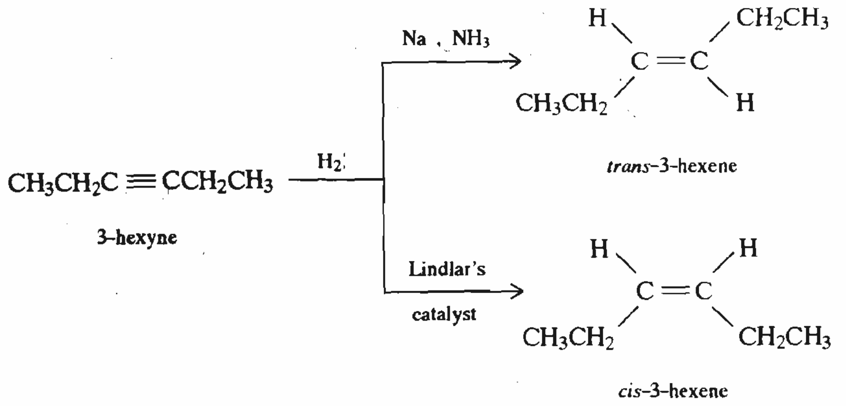


Formation of the *trans* alkene is due to the rapid equilibration of the intermediate alkenyl radical between the *cis*-and *trans*-forms. The equilibrium lies on the side of the more stable *trans* species.



cis radical (less stable) *trans* radical (more stable)

In other words, we can say reduction of alkyne to double bond can yield either *cis*-alkene or *trans*-alkene, depending upon the choice of the reducing agent.



SAQ 5

Suggest a method for the synthesis of the following compounds from 2-hexyne :

a) *cis*-2-hexene

....

....

b) *trans*-2-hexene

....

....

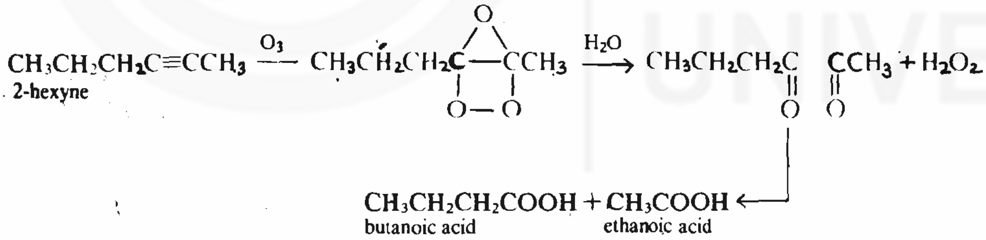
c) hexane

....

....

8.7.3 Ozonolysis

Reagents and reactions that lead to oxidative cleavage of alkenes also lead to cleavage of alkynes. Addition of ozone to an alkyne produces the ozonide. The ozonides on hydrolysis give 1, 2-dicarbonyl compounds, which undergo oxidative cleavage to carboxylic acids by hydrogen peroxide formed in the reaction. For example, 2-hexyne on ozonolysis gives butanoic and ethanoic acids.



Same products are obtained when alkynes are oxidised by alkaline permanganate and then hydrolysed using mineral acid.

$$\underset{\text{2-hexyne}}{CH_3CH_2CH_2C{\equiv}CCH_3} \xrightarrow[2.\ H^+]{1.\ KMnO_4\bar{O}H} \underset{\text{butanoic acid}}{CH_3CH_2CH_2COOH} + \underset{\text{ethanoic acid}}{CH_3COOH}$$

Oxidative cleavage reactions are used as a tool in structure determination. The carboxylic acids formed would tell us which of the carbon atoms were linked through the triple bond in the original alkyne.

In this context, by carbonyl components, we specifically refer to aldehydes or ketones or compounds having both the functional groups. In general, a carbonyl compound means aldehyde ketone, acid, ester or any of acid derivatives.

The steps for arriving at the structure of an alkyne using oxidation cleavage are given below :

* First write down the formulae of the acids side by side, such that —C—OH groups face each other, e.g., let us propose the structure of the alkyne which on oxidative cleavage gives :

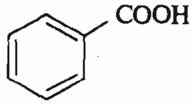
$$R\overset{O}{\overset{\|}{C}}OH \text{ and } HO\overset{O}{\overset{\|}{C}}R'$$

*combine the carbon chains omitting =O and —OH groups; place a triple bond between the carbon atoms which were earlier part of the carboxylic groups.

$RC \equiv CR'$

SAQ 6

Propose structures for alkynes that give the following products on oxidative cleavage :

a)  + CH_3COOH

....

3) How will you convert ?

a) 2-Bromopropane to propyne

b) 1-Bromopropane to 2-hexyne.

b) $CH_3(CH_2)_7COOH + HOOC(CH_2)_7COOH$

....

c) $2CH_3CH_2COOH$

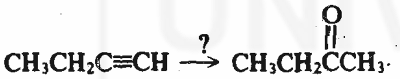
....

8.8 SUMMARY

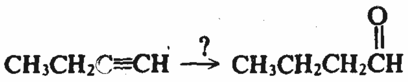
- Alkynes are the hydrocarbons with one or more carbon-carbon triple bond.
- Alkynes may be of two type, i.e., terminal or internal.
- Physical properties of alkynes are more or less similar to alkenes.
- Alkynes are prepared by alkylation of terminal alkynes or by a two-fold elimination of HX from dihalide or by dehalogenation of tetrahalides.
- Terminal alkynes are more acidic than alkanes or alkenes.
- Hydrohalogenation follows Markownikoff's rule.
- Halogens add to alkynes to give tetrahaloalkanes. Using proper reaction conditions dihaloalkene can be isolated.
- Hydration of an alkyne gives an unstable enol which tautomerises to give an aldehyde or a ketone.
- Hydroboration of alkynes may give ketones or aldehydes, depending on reaction conditions and the type of the alkyne.
- Hydrogenation of an alkyne in the presence of Pd, Pt or Ni catalyst yields an alkane. By using poisoned catalyst, the intermediate *cis*-alkene can be obtained. Reduction of an alkyne with sodium or lithium in liquid ammonia gives the *trans*-alkene.
- Ozonolysis of alkynes give carboxylic acids.

8.9 TERMINAL QUESTIONS

1) How would you carry out the following reactions ?

a) 

$CH_3CH_2C{\equiv}CH \xrightarrow{?} CH_3CH_2\overset{\overset{O}{\|}}{C}CH_3$

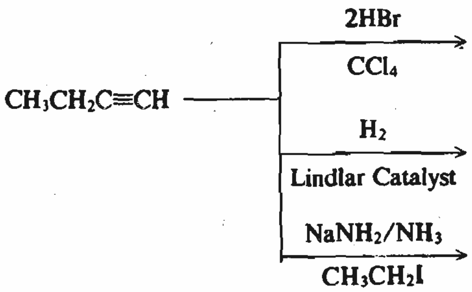
b) 

$CH_3CH_2C{\equiv}CH \xrightarrow{?} CH_3CH_2CH_2\overset{\overset{O}{\|}}{C}H$

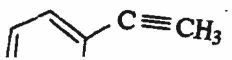
c) $CH_3CH_2C{\equiv}CHCH_3 \xrightarrow{?} CH_3CH_2COOH + CH_3COOH$

d) $CH_3CH_2CH_2CH{=}CH_2 \xrightarrow{?} CH_3CH_2CH_2C{\equiv}CH$

2) Predict the product of the following reactions of 1-butyne :



c) $CH_3CH_2CH_2C{\equiv}CCH_3 \xrightarrow{Pd/H_2} CH_3(CH_2)_4CH_3$

6) a) 

3) How will you convert ?
   a) 2-Bromopropane to propyne
   b) 1-Bromopropane to 2-hexyne.

4) **Suggest steps for the following transformations :**
   a) **2, 3-dibromopentane to *trans*-2-pentene**
   b) **3-methyl-1-butyne to *trans*-2-methyl-3-heptene**

5) Show, by writing appropriate chemical equations, how each of the following compounds could be converted to 1-hexyne ?
   a) **1, 2-Dibromohexane**
   b) **1-Hexene**
   c) **Hexane**

8.10 ANSWERS

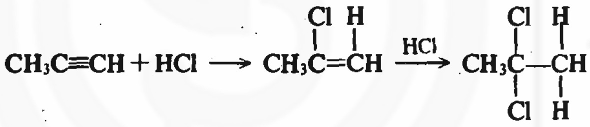
Self Assessment Questions

1) a)
$$CH\equiv CH \xrightarrow{NaNH_2\,.\,NH_3} HC\equiv\overset{-}{C}\overset{+}{Na}$$
$$HC\equiv\overset{-}{C}\overset{+}{Na} + CH_3(CH_2)_3Br \longrightarrow HC\equiv C(CH_2)_3CH_3$$
$$HC\equiv C(CH_2)_3CH_3 \xrightarrow{NaNH_2\,.\,NH_3} \overset{+}{Na}\overset{-}{C}\equiv C(CH_2)_3CH_3$$
$$\overset{+}{Na}\overset{-}{C}\equiv C(CH_2)_3CH_3 + CH_3Br \longrightarrow CH_3C\equiv C(CH_2)_3CH_3$$

b)
$$HC\equiv CH \xrightarrow[2.\ CH_3(CH_2)_2Br]{1.\ NaNH_2\,.\,NH_3} CH\equiv C(CH_2)_2CH_3$$
$$CH\equiv C(CH_2)_2CH_3 \xrightarrow[NH_3]{NaNH_2} \overset{+}{Na}\overset{-}{C}\equiv C(CH_2)_2CH_3$$
$$\overset{+}{Na}\overset{-}{C}\equiv C(CH_2)_2CH_3 + CH_3CH_2Br \longrightarrow CH_3CH_2C\equiv C(CH_2)_2CH_3$$

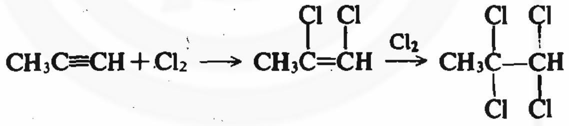
2) $\bar{O}H < HC\equiv\bar{C} < \bar{N}H_2$

3) a)



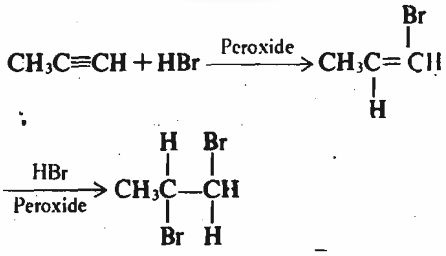
$$CH_3C\equiv CH + HCl \longrightarrow CH_3\overset{Cl}{\overset{|}{C}}=\overset{H}{\overset{|}{C}}H \xrightarrow{HCl} CH_3\underset{Cl}{\underset{|}{\overset{Cl}{\overset{|}{C}}}}-\underset{H}{\underset{|}{\overset{H}{\overset{|}{C}}}}H$$

b)



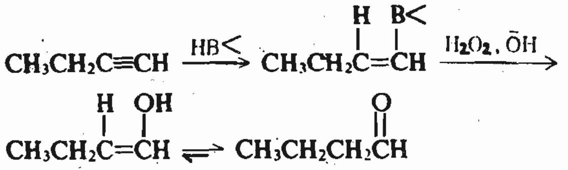
$$CH_3C\equiv CH + Cl_2 \longrightarrow CH_3\overset{Cl}{\overset{|}{C}}=\overset{Cl}{\overset{|}{C}}H \xrightarrow{Cl_2} CH_3\underset{Cl}{\underset{|}{\overset{Cl}{\overset{|}{C}}}}-\underset{Cl}{\underset{|}{\overset{Cl}{\overset{|}{C}}}}H$$

c)



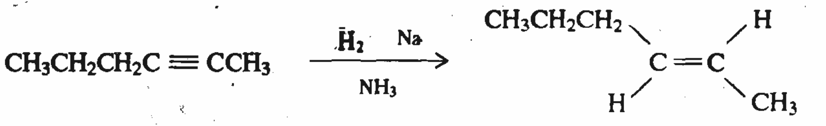
$$CH_3C\equiv CH + HBr \xrightarrow{Peroxide} CH_3\underset{H}{\underset{|}{C}}=\overset{Br}{\overset{|}{C}}H$$
$$\xrightarrow[Peroxide]{HBr} CH_3\underset{Br}{\underset{|}{\overset{H}{\overset{|}{C}}}}-\underset{H}{\underset{|}{\overset{Br}{\overset{|}{C}}}}H$$

4)

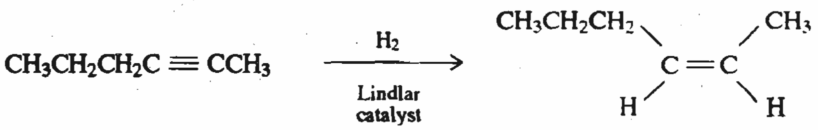


$$CH_3CH_2C\equiv CH \xrightarrow{HB<} CH_3CH_2\overset{H}{\overset{|}{C}}=\overset{B<}{\overset{|}{C}}H \xrightarrow{H_2O_2,\,\bar{O}H}$$
$$CH_3CH_2\overset{H}{\overset{|}{C}}=\overset{OH}{\overset{|}{C}}H \rightleftharpoons CH_3CH_2CH_2\overset{O}{\overset{||}{C}}H$$

5) a)

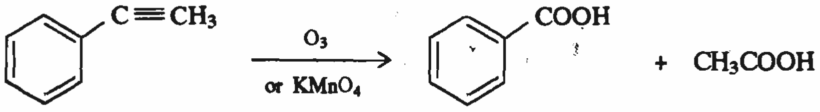


b)



c) $CH_3CH_2CH_2C{\equiv}CCH_3 \xrightarrow{Pd/H_2} CH_3(CH_2)_4CH_3$

6) a)

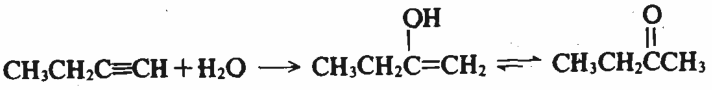


b) $CH_3(CH_2)_7C \equiv C(CH_2)_7COOH \xrightarrow[KMnO_4]{O_3 \text{ or}} CH_3(CH_2)_7COOH + HOOC(CH_2)_7COOH$

c) $CH_3CH_2C \equiv CCH_2CH_3 \xrightarrow[\text{or } KMnO_4]{O_3} CH_3CH_2COOH + CH_3CH_2COOH$

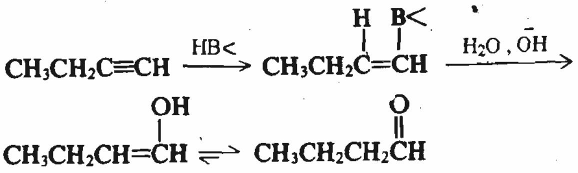
Answers to Terminal Questions

1) a)



$$CH_3CH_2C{\equiv}CH + H_2O \longrightarrow CH_3CH_2\overset{OH}{C}{=}CH_2 \rightleftharpoons CH_3CH_2\overset{O}{\overset{\|}{C}}CH_3$$

b)

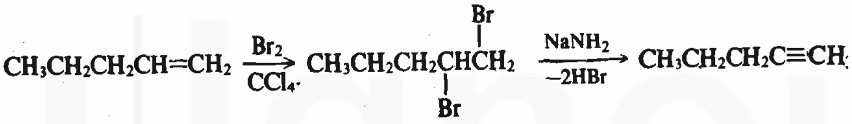


$$CH_3CH_2C{\equiv}CH \xrightarrow{HB<} CH_3CH_2\overset{H}{C}{=}\overset{B<}{CH} \xrightarrow{H_2O,\ \overset{-}{O}H}$$

$$CH_3CH_2CH{=}\overset{OH}{CH} \rightleftharpoons CH_3CH_2CH_2\overset{O}{\overset{\|}{C}}H$$

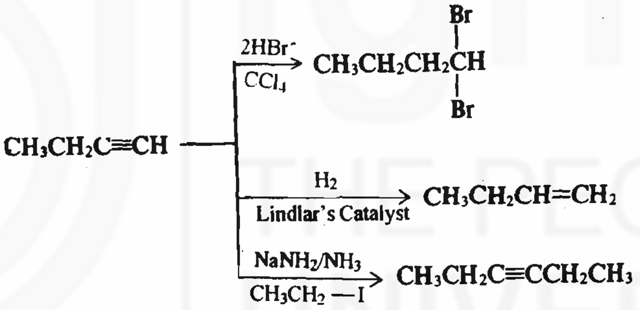
c) $CH_3CH_2CH_2C{\equiv}CCH_3 \xrightarrow[\text{or } KMnO_4]{O_3} CH_3CH_2COOH + CH_3COOH$

d)



$$CH_3CH_2CH_2CH{=}CH_2 \xrightarrow[CCl_4]{Br_2} CH_3CH_2CH_2\underset{Br}{CH}\overset{Br}{CH_2} \xrightarrow[-2HBr]{NaNH_2} CH_3CH_2CH_2C{\equiv}CH$$

2)

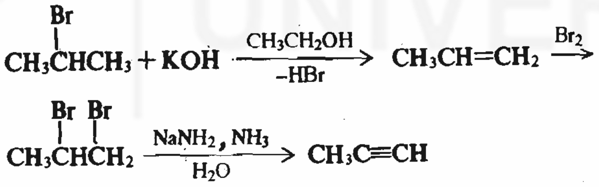


$$CH_3CH_2C{\equiv}CH \xrightarrow[CCl_4]{2HBr} CH_3CH_2CH_2\overset{Br}{\underset{Br}{CH}}$$

$$CH_3CH_2C{\equiv}CH \xrightarrow[\text{Lindlar's Catalyst}]{H_2} CH_3CH_2CH{=}CH_2$$

$$CH_3CH_2C{\equiv}CH \xrightarrow[CH_3CH_2-I]{NaNH_2/NH_3} CH_3CH_2C{\equiv}CCH_2CH_3$$

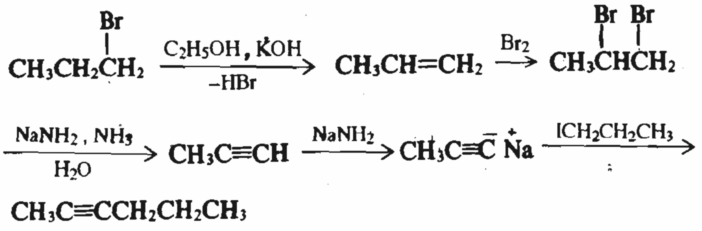
3) a)



$$CH_3\overset{Br}{CH}CH_3 + KOH \xrightarrow[-HBr]{CH_3CH_2OH} CH_3CH{=}CH_2 \xrightarrow{Br_2}$$

$$CH_3\overset{Br}{CH}\overset{Br}{CH_2} \xrightarrow[H_2O]{NaNH_2,\ NH_3} CH_3C{\equiv}CH$$

b)

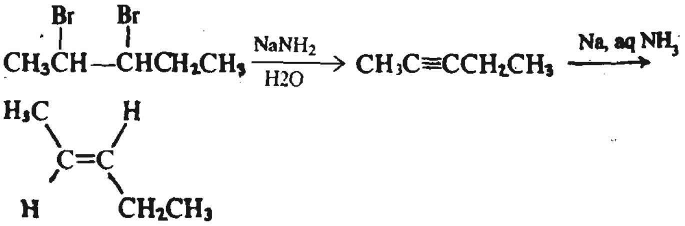


$$CH_3CH_2\overset{Br}{CH_2} \xrightarrow[-HBr]{C_2H_5OH,\ KOH} CH_3CH{=}CH_2 \xrightarrow{Br_2} CH_3\overset{Br}{CH}\overset{Br}{CH_2}$$

$$\xrightarrow[H_2O]{NaNH_2,\ NH_3} CH_3C{\equiv}CH \xrightarrow{NaNH_2} CH_3C{\equiv}\overset{-}{C}\overset{+}{Na} \xrightarrow{ICH_2CH_2CH_3}$$

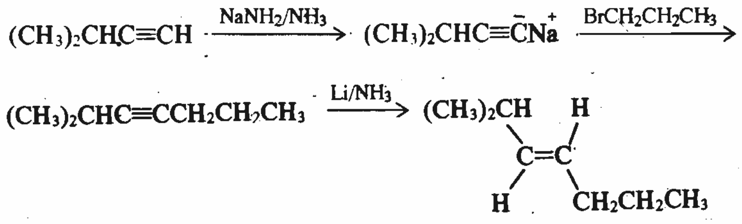
$$CH_3C{\equiv}CCH_2CH_2CH_3$$

4) a)



$$CH_3\overset{Br}{CH}-\overset{Br}{CH}CH_2CH_3 \xrightarrow[H2O]{NaNH_2} CH_3C{\equiv}CCH_2CH_3 \xrightarrow{Na,\ aq\ NH_3}$$

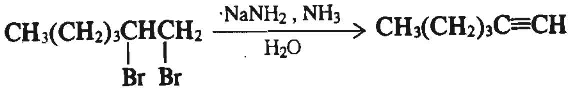
b)



$$(CH_3)_2CHC\equiv CH \xrightarrow{NaNH_2/NH_3} (CH_3)_2CHC\equiv\overset{-}{C}\overset{+}{Na} \xrightarrow{BrCH_2CH_2CH_3}$$

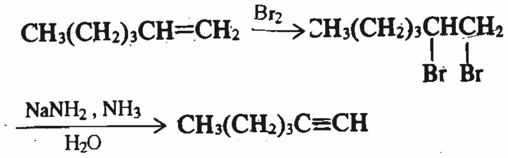
$$(CH_3)_2CHC\equiv CCH_2CH_2CH_3 \xrightarrow{Li/NH_3}$$

5) a)



$$CH_3(CH_2)_3\underset{Br}{CH}\underset{Br}{CH_2} \xrightarrow[H_2O]{NaNH_2,\ NH_3} CH_3(CH_2)_3C\equiv CH$$

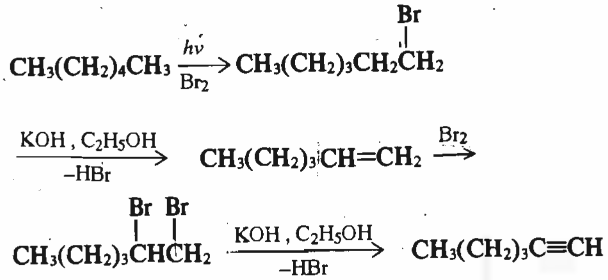
b)



$$CH_3(CH_2)_3CH{=}CH_2 \xrightarrow{Br_2} CH_3(CH_2)_3\underset{Br}{CH}\underset{Br}{CH_2}$$

$$\xrightarrow[H_2O]{NaNH_2,\ NH_3} CH_3(CH_2)_3C\equiv CH$$

c)



$$CH_3(CH_2)_4CH_3 \xrightarrow[Br_2]{h\nu} CH_3(CH_2)_3CH_2\overset{Br}{CH_2}$$

$$\xrightarrow[-HBr]{KOH,\ C_2H_5OH} CH_3(CH_2)_3CH{=}CH_2 \xrightarrow{Br_2}$$

$$CH_3(CH_2)_3\overset{Br}{CH}\overset{Br}{CH_2} \xrightarrow[-HBr]{KOH,\ C_2H_5OH} CH_3(CH_2)_3C\equiv CH$$

UNIT 9 AROMATIC HYDROCARBONS AND POLYNUCLEAR AROMATICS

Structure

9.1 INTRODUCTION

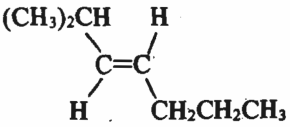
In the last three Units, we have discussed the chemistry of aliphatic hydrocarbons. Now we come to another class of compounds, namely, aromatic hydrocarbons.

Early in the development of organic chemistry, organic compounds were arbitrarily classified as either aliphatic or aromatic. The meaning of word "aliphatic" means fatty. The aliphatic compounds were so named because the first members of this class to be studied were the fatty acids. In addition to the aliphatic compounds, there were a large number of another type of compounds, which were also obtained from natural sources, e.g., resins, balsams, aromatic oils, etc. The structure of these compounds was unknown but they had one thing in common, a pleasant odour. Thus, these compounds were arbitrarily classified as aromatic compounds (Greek : **aroma** 'fragrant smell'). Now the word aromatic is used for benzene and related compounds. So the original meaning of the word aromatic (fragrant) has no longer any significance.

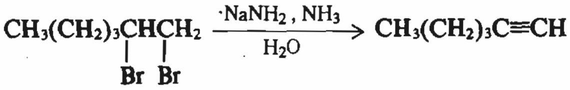
Benzene, the simplest of the aromatic compounds, was isolated by Michael Faraday in 1825 from the gas obtained by pyrolysis of whale oil. Later, in 1845, Holman discovered benzene in

b) $\mathrm{(CH_3)_2CHC{\equiv}CH} \xrightarrow{\mathrm{NaNH_2/NH_3}} \mathrm{(CH_3)_2CHC{\equiv}\overset{-}{C}\overset{+}{Na}} \xrightarrow{\mathrm{BrCH_2CH_2CH_3}}$

$\mathrm{(CH_3)_2CHC{\equiv}CCH_2CH_2CH_3} \xrightarrow{\mathrm{Li/NH_3}}$

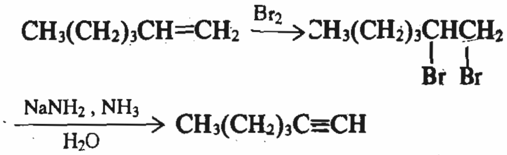


5) a)



$$\mathrm{CH_3(CH_2)_3\underset{\displaystyle |\atop Br}{CH}\underset{\displaystyle |\atop Br}{CH_2}} \xrightarrow[\mathrm{H_2O}]{\mathrm{NaNH_2,\ NH_3}} \mathrm{CH_3(CH_2)_3C{\equiv}CH}$$

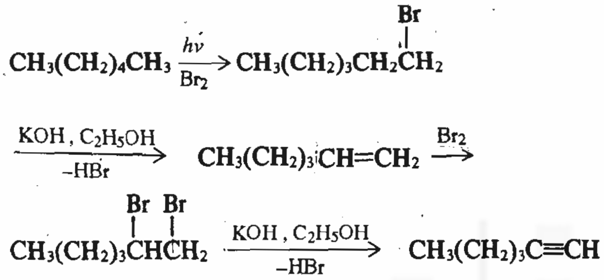
b)



$$\mathrm{CH_3(CH_2)_3CH{=}CH_2} \xrightarrow{\mathrm{Br_2}} \mathrm{CH_3(CH_2)_3\underset{\displaystyle |\atop Br}{CH}\underset{\displaystyle |\atop Br}{CH_2}}$$

$$\xrightarrow[\mathrm{H_2O}]{\mathrm{NaNH_2,\ NH_3}} \mathrm{CH_3(CH_2)_3C{\equiv}CH}$$

c)



$$\mathrm{CH_3(CH_2)_4CH_3} \xrightarrow[\mathrm{Br_2}]{h\nu} \mathrm{CH_3(CH_2)_3CH_2\overset{Br \atop \displaystyle |}{CH_2}}$$

$$\xrightarrow[\mathrm{-HBr}]{\mathrm{KOH,\ C_2H_5OH}} \mathrm{CH_3(CH_2)_3CH{=}CH_2} \xrightarrow{\mathrm{Br_2}}$$

$$\mathrm{CH_3(CH_2)_3\overset{Br \atop \displaystyle |}{CH}\overset{Br \atop \displaystyle |}{CH_2}} \xrightarrow[\mathrm{-HBr}]{\mathrm{KOH,\ C_2H_5OH}} \mathrm{CH_3(CH_2)_3C{\equiv}CH}$$

UNIT 9 AROMATIC HYDROCARBONS AND POLYNUCLEAR AROMATICS

Structure

9.1 INTRODUCTION

In the last three Units, we have discussed the chemistry of aliphatic hydrocarbons. Now we come to another class of compounds, namely, aromatic hydrocarbons.

Early in the development of organic chemistry, organic compounds were arbitrarily classified as either aliphatic or aromatic. The meaning of word "aliphatic" means fatty. The aliphatic compounds were so named because the first members of this class to be studied were the fatty acids. In addition to the aliphatic compounds, there were a large number of another type of compounds, which were also obtained from natural sources, e.g., resins, balsams, aromatic oils, etc. The structure of these compounds was unknown but they had one thing in common, a pleasant odour. Thus, these compounds were arbitrarily classified as aromatic compounds (Greek : **aroma** 'fragrant smell'). Now the word aromatic is used for benzene and related compounds. So the original meaning of the word aromatic (fragrant) has no longer any significance.

Benzene, the simplest of the aromatic compounds, was isolated by Michael Faraday in 1825 from the gas obtained by pyrolysis of whale oil. Later, in 1845, Holman discovered benzene in coal tar, which contains benzene and many of its derivatives.

Many compounds isolated from natural sources and many synthetic drugs are aromatic in nature. The local anaesthetic procaine and the tranquiliser diazepam (valium) are a few examples.

Benzene is carcinogenic and injurious to health. Prolonged exposure leads to bone-marrow depression. Benzene as a solvent should, therefore, be used carefully, avoiding evaporation in the open or inhaling its vapour.

Keeping in view the importance of aromatic compounds, we shall study the chemistry of benzene and its derivatives in this unit.

Objectives

After studying this unit, you should be able to:

- describe the isolation of benzene,
- list the important spectral peaks of benzene and its derivatives,
- explain the resonance energy of aromatic compounds,
- discuss the important reactions of aromatic compounds,
- explain the polynuclear hydrocarbons, and
- list the important reactions of polynuclear hydrocarbons.

9.2 ISOLATION OF BENZENE

Coal tar was once the chief source of benzene and its derivatives. Today, benzene and its derivatives can be extracted from petroleum in which they occur naturally. They are also prepared from the non-aromatic constituents of petroleum, which is now the main source. The most important such method is hydroforming or catalytic reforming.

Hydroforming or Catalytic Reforming

This method is based on dehydrogenation, cyclisation and isomerisation reactions. The aromatic compounds so obtained contain the same number of carbon atoms as the aliphatic starting materials. Hydroforming is carried out under high pressure and at temperatures of around 750-820 K in the presence of platinum catalyst. Following are some important examples of hydroforming :

$$\underset{\text{hexane}}{CH_3(CH_2)_4CH_3} \xrightarrow{\Delta} \underset{\text{benzene}}{C_6H_6} + 4H_2$$

$$\underset{\text{heptane}}{CH_3(CH_2)_5CH_3} \xrightarrow{\Delta} \underset{\text{toluene}}{C_6H_5CH_3} + 4H_2$$

$$\underset{\text{octane}}{CH_3(CH_2)_6CH_3} \xrightarrow{\Delta} \underset{\text{xylenes}}{C_6H_4(CH_3)_2} + \underset{\text{ethyl benzene}}{C_6H_5C_2H_5}$$

Note that a mixture $o-$, $m-$ and $p-$xylenes is referred to as xylenes.

Various hydrocarbons are separated by a selective solvent process, but since, benzene is obtained in much smaller amount than toluene and the xylenes, these are converted into benzene by heating with hydrogen under pressure in the presence of a metal oxide catalyst. This process is called hydrodealkylation.

$$\underset{\text{toluene}}{C_6H_5CH_3} + H_2 \xrightarrow{\text{Catalyst}} \underset{\text{benzene}}{C_6H_6} + \underset{\text{methane}}{CH_4}$$

9.3 SPECTRAL PROPERTIES

The presence of an aromatic ring in a compound is detectable by uv spectroscopy. Aromatic compounds show a series of absorption bands with fairly intense absorption near 205 nm and a less intense absorption in the 255-275 nm range. As the conjugation increases, λ_{max} also increases.

The ir spectrum is quite useful for recognising the presence of aromatic compounds. The ir spectrum gives a weak absorption band near 3030 cm^{-1} for aryl C—H stretching vibration. Absorption due to C=C stretching in benzene gives a series of four bands, generally between 1450 and 1600 cm^{-1}.

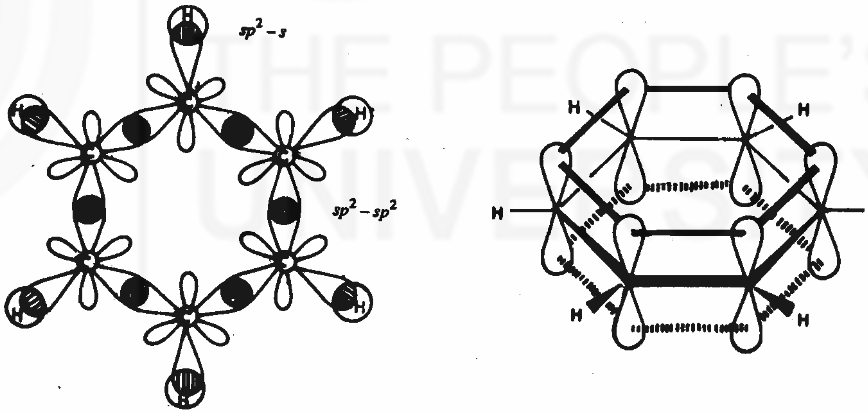
Because of a great deal of overlapping of the various bands in the region of 1225-970 cm^{-1}, this region is not very useful for identification purposes.

The nmr spectrum is a useful tool for the structure determination of benzene and its derivatives. Since all the six hydrogen atoms in benzene are equivalent, the nmr spectrum gives only one singlet at δ 7.27 ppm. Recall that olefinic protons appear at higher field values, generally at about δ 5.0 ppm. Electron-withdrawing substituents on the ring shift the absorption of adjacent protons further **downfield**, while electron-releasing groups shift absorption **upfield** from that of the unsubstituted benzene.

The mass spectrum of benzene gives prominent molecular ion peak (M^+). Also $M + 1$ and $M + 2$ peaks, due to ^{13}C and ^{2}H are observed. Benzene shows prominent peaks at m/z 78 $(C_6H_6)^+$, m/z 77 $(C_6H_5)^+$, m/z 53 $(C_4H_5)^+$, m/z 51 $(C_4H_3)^+$, m/z 50 $(C_4H_2)^+$ and m/z 39 $(C_3H_3)^+$. All these also occur in the mass spectra of nearly all benzene derivatives.

9.4 STRUCTURE OF BENZENE

Molecular Orbital Theory provides a description of benzene. According to this theory, benzene is a planar flat symmetrical molecule having the shape of a regular hexagon. The C—C—C bond angle has a value of 120°. Each carbon atom in the molecule is *sp*^{2} hybridised. Two orbitals of the *sp*^{2} hybridised carbon atom overlap with the other two orbitals of the adjacent carbon atom resulting in the formation of two σ bonds. The third orbital of each carbon atom overlaps and forms a σ bond with 1*s* orbital of hydrogen atom. Thus six carbon-carbon σ bonds are formed. Each carbon atom still has a *p* orbital perpendicular to the plane of the ring. The *p* orbital has two lobes one above and the other below the plane of the ring and because all *p* orbitals are equivalent, they overlap equally well with both the neighbouring *p* orbitals resulting in a delocalised doughnut shaped π orbital cloud above and below the ring. The picture that emerges out of this discussion is given below in Fig. 9.1.



σ- Skeleton

π-skeleton

Fig 9.1 : σ and π skeleton of benzene

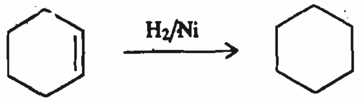
The benzene ring is a cyclic conjugated system and is usually represented as a regular hexagon with a circle inside the ring. This gives an idea of delocalisation of π-electrons.

9.5 RESONANCE AND AROMATICITY

You have already studied the basic concept of resonance in Unit 5 of this course. Here, we will discuss the resonance effect in aromatic compounds. The structures of a large number of organic compounds can be written with the help of simple bond diagrams, e.g., ethene as $CH_2{=}CH_2$, ethyne as $HC \equiv CH$, etc. There are, however, many compounds for which simple bond diagrams do not accurately describe these molecules, one of the examples being benzene. The structure of benzene (Fig 9.1) gives the impression that it is a cyclic compound of six carbon atoms containing three single and three double bonds. If this were so, you would expect two values of carbon-carbon bond lengths, viz., one for single bonds (nearly 154 pm as in ethane) and the other for double bonds (nearly 133 pm as in ethene). Experimental evidence through X-ray diffraction studies shows that all the six carbon-carbon bonds in benzene are equal and have a length of 139 pm, which is in between 133 and 154 pm. The explanation of this is as follows :

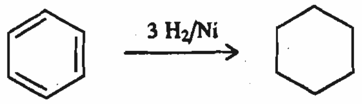
X-ray studies give the bond lengths and bond angle.

The heats of hydrogenation of cyclohexene and benzene determined experimentally are given below :



$\Delta H = -121$ kJ mol^{-1}

cyclohexene   cyclohexane



$\Delta H = -209$ kJ mol^{-1}

cyclohexatriene (benzene)   cyclohexane

The heat evolved when hydrogen is added to cyclohexene (having one C = C bond) is 121 kJ mol^{-1}. The expected value of the heat evolved when hydrogen is added to benzene (having three C=C bonds) should be 3 × 121 kJ mol^{-1} = 363 kJ mol^{-1}, but the experimental value is 209 kJ mol^{-1}. We can infer that benzene is more stable (having lower energy content) than the hypothetical molecule containing three isolated C=C bonds by 363—209 = 154 kJ mol^{-1}. This energy difference is called the resonance energy and is responsible for the stability of benzene compared to other unsaturated compounds which lack resonance stabilisation.

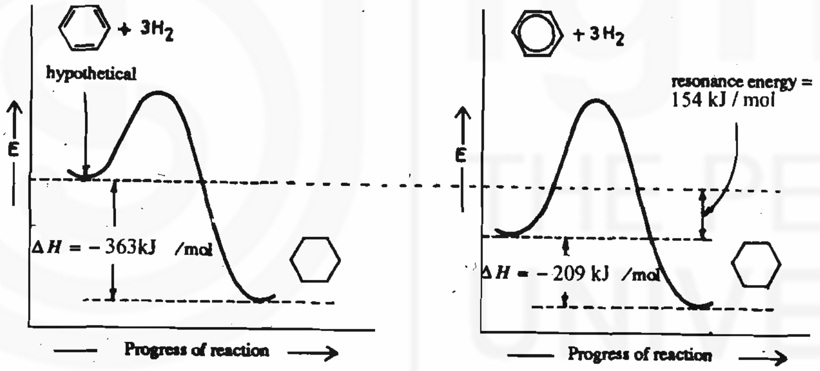
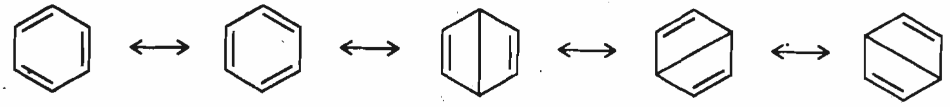


Fig. 9.2 Energy diagrams for the hydrogenation of cyclohexatriene (hypothetical) and benzene

We cannot write down a single structure for benzene which would encompass all its properties rather it is considered to be the resonance "hybrid" of the following hypothetical structures I-V



I   II   III   IV   V

These structures are called resonance structures or contributors or canonical forms. The two "Kekule" forms, I and II, are of lower energy (more stable) than the three "Dewar" forms, III to V. Structures I and II could be expected to "contribute" more to the hybrid than either III, IV or V, hence, the properties of benzene would be expected to resemble more closely to either I or II than to III, IV or V. Since I and II have the same energy, each would contribute to the hybird by the same amount. The symbol of resonance, double-headed arrow (⟷) does not indicate an equilibrium. The canonical structures I-V are hypothetical and do not have any physical existence. These structures differ in their electronic arrangement and arise due to shift of π electrons within the molecule.

Aromaticity

Perhaps you hav been wondering whether other cyclic compoundss with π electrons might also be considered aromatic, some of these systems are indeed aromatic, but not all of them. What structural features are necessary for a molecule to be aromatic?

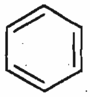
A German Physicist, Erich Hückel's in 1931, proposed the Hückel's rule. According to this rule, an aromatic molecule must be a cyclic conjugated species having $(4n + 2)$ π-electrons where n is an integer (n = 0, 1, 2, 3, ...). This means that only the ring with 2, 6, 10, 14, ... π electrons may be aromatic but a ring with 4, 8 or 12 π electrons may not be aromatic. Hückel's rule is also applicable to ionic species. Let us look at some of the evidence supporting the Hückel's rule.

1) Cyclobutadiene

no. of π-electrons = 4

$4n + 2$ π-electrons are required for aromaticity. Cyclobutadiene has 4 π-electrons, hence cyclobutadiene is not aromatic as it has 4 π-electrons and is highly unstable.

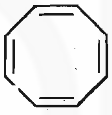
2) Benzene



no. of π-electrons = 6

Here the $4n + 2\pi$ rule can be applied as it has 6 π-electrons which are required for a single ring system. It is an excellent example of an aromatic system.

3) Cyclooctatetraene



no. of π-electrons = 8

It does not have $4n + 2$ π-electrons and thus is not aromatic.

Another reason why cyclooctatetraene is not aromatic is that it is not even fully conjugated. It is a tub shaped molecule and the neighbouring orbitals containing the π-electron do not have the necessary geometry for proper overlap.

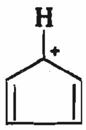
cyclooctatetrane

From the above example, it is clear that a flat planar geometry is required for proper overlap resulting in delocalisation of π-electrons which is a necessary condition for aromaticity.

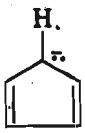
SAQ 1

Which of the following compound is aromatic?

a)



b)



c)

9.6 REACTIONS OF AROMATIC COMPOUNDS

Characteristic reactions of benzene involve substitution, in which the resonance-stabilised ring system is preserved. Why is this so? You may answer by saying that this is due to the resonance stabilisation of the benzene. But then the question arises, why then benzene enters into reactions at all, why is it not inert? This dual behaviour, the coexistence of stability and reactivity is due to the presence of the circulating π electrons in the benzene ring which, on one hand, keeps the carbon nuclei within bonding distance and, on the other, offers a site of attack to positively charged species.

Electrophilic substitution includes a wide variety of reactions, such as nitration, halogenation, sulphonation and the Friedel-Crafts reactions undergone by nearly all aromatic rings. Some important reactions are summarised in Table 9.1.

Table 9.1 Electrophilic aromatic substitution reactions

1) **Nitration**

$$ArH + HNO_3 \xrightarrow{H_2SO_4} ArNO_2 + H_2O$$

2) **Halogenation**

$$ArH + X_2 \xrightarrow{Fe} ArX + HX$$

3) **Suphonation**

$$ArH + SO_3 \xrightarrow{H_2SO_4} ArSO_3H + H_2O$$

4) **Friedel-Crafts alkylation**

$$ArH + RCl \xrightarrow{AlCl_3} ArR + HCl$$

5) **Friedel-Crafts acylation**

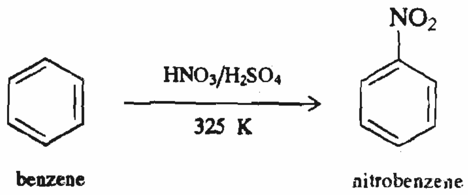
$$ArH + RCOCl \xrightarrow{AlCl_3} ArCOR + HCl$$

Note : Ar = C_6H_5-

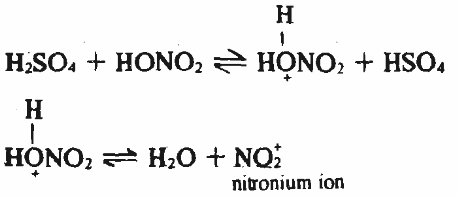
9.6.1 Nitration

Replacement of hydrogen by the nitro-group is known as **"Nitration"**.

Nitration of benzene can be carried out by the reaction of benzene with a mixture of concentrated nitric and sulphuric acids



The electrophile in this reaction is the nitronium ion, $\overset{+}{N}O_2$. It is generated by the reaction of H_2SO_4 with HNO_3.



$$H_2SO_4 + HONO_2 \rightleftharpoons H\underset{+}{\overset{H}{O}}NO_2 + HSO_4$$

$$H\underset{+}{\overset{H}{O}}NO_2 \rightleftharpoons H_2O + NO_2^+$$

nitronium ion

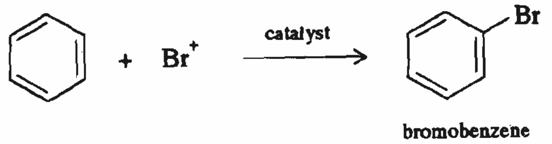
Further evidence for the participation of the nitronium ion comes from the fact that other species capable of producing nitronium ion, such as $\overset{+}{N}O_2\overset{-}{B}F_4$, $N\overset{+}{O}_2N\overset{-}{O}_3$ and $\overset{+}{N}O_2Cl\overset{-}{O}_4$ also nitrate benzenoid compound..

Nitration of benzene is an important reaction because the nitro group can be converted into other functional groups. We will discuss this in Unit 18 of Block IV.

9.6.2 Halogenation

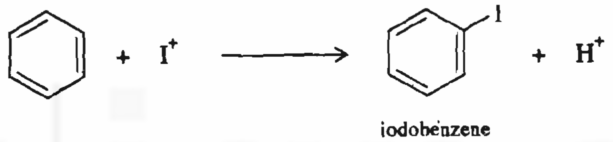
Benzene reacts with halogens in the presence of a catalyst ($FeBr_3$, $FeCl_3$) to yield halogen substituted products, i.e., aryl halides.

The main function of the catalyst is to partially or completely polarise the halogen-halogen bond, e.g.,



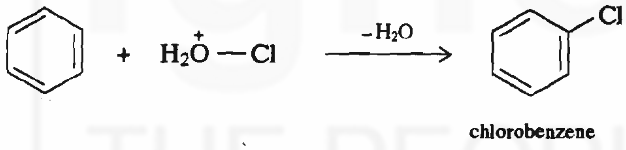
A typical reaction of aromatic halogenation is the bromination of benzene. As a general rule, fluorine is too reactive and a poor yield of fluorobenzene is obtained. Chlorine reacts smoothly and gives an excellent yield of chlorobenzene. Iodine itself is unreactive; however, iodination of benzene is carried out in the presence of oxidising agent such as hydrogen peroxide, H_2O_2, or copper salt such as $CuCl_2$. This oxidising agent oxidises molecular iodine to an electrophile I^+

$$I_2 + 2\,Cu^{++} \longrightarrow 2\,I^+ + 2\,Cu^+$$



Halogenation can also be affected by other reagents, such as hypochlorous or hypobromous acids in presence of strong acids.

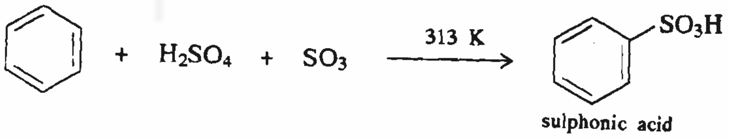
$$H-O-Cl + H^+ \longrightarrow H_2O^+-Cl$$



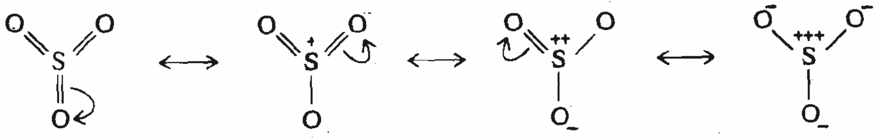
9.6.3 Sulphonation

Aromatic compounds in which the sulphonic group ($-SO_3H$) is directly attached to the benzene ring are called aromatic sulphonic acids. Replacement of hydrogen from benzene by the sulphonic group is called sulphonation. It is another example of electrophilic substitution reaction. Sulphonation is usually accomplished using sulphuric acid or fuming sulphuric acid ($H_2SO_4 + SO_3$) containing varying proportions of sulphur trioxide.

$2H_2SO_4 \longrightarrow SO_3 + HSO_4^- + H_2O$



The reactive electrophile is neutral SO_3, as is evident from its structure given below:



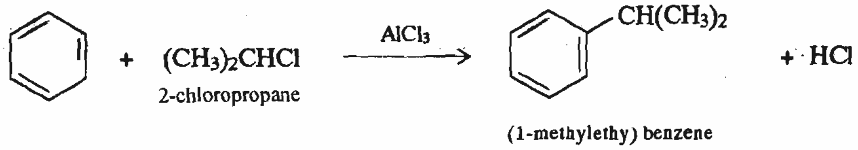
Unlike the other electrophilic substitution reaction of benzene, sulphonation is a highly reversible reaction and the direction depends on the reaction conditions. Sulphonation is favoured in the presence of concentrated or fuming sulphuric acid, desulphonation in hot, dilute aqueous acids.

9.6.4 Friedel-Crafts Alkylation

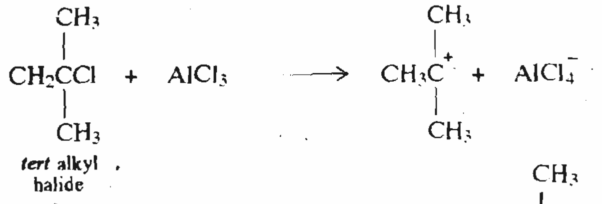
Complex substituted aromatic compounds are almost always synthesised from the simpler, readily available aromatic compounds. Since benzene is very common and easily available, chemists use it as starting material and introduce the desired substituents. You have already stuided the introduction of halogen, nitrogen and sulphur-based functional groups to the aromatic ring. Now you will study another important reaction, i.e., alkylation of aromatic ring.

Alkylation of benzene is the substitution of a ring hydrogen by an alkyl group in the ring. Reaction of the aromatic compounds with alkyl halides in the presence of anhydrous $AlCl_3$, as the catalyst gives alkylated products. This reaction is known as Friedel-Crafts alkylation. The reaction of 2-chloropropane with benzene in the presence of $AlCl_3$ to yield (1-methyl ethyl) benzene is a typical Friedel-Crafts alkylation reaction.

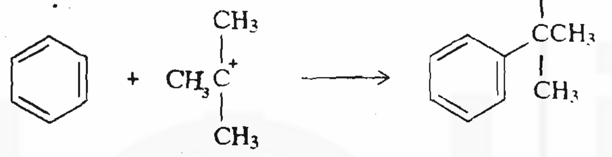
Friedel, a French chemist, and Crafts an American chemist developed this reaction in 1877.



The electrophile in the Friedel-Crafts reaction is R^+. This ion is formed when an alkyl halide reacts with a Lewis acid. Lewis acids such as $AlCl_3$, $FeCl_3$, $ZnCl_2$, $AlBr_3$, BF_3 etc. are used in Friedel-Crafts alkylation. In case of alkylation with tertiary alkyl halides, the electrophilic species is a free carbocation. However, in primary and secondary alkyl halides, it appears that instead of free carbocations, the electrophilic species is an alkyl halide-Lewis acid complex with positively polarised carbon.



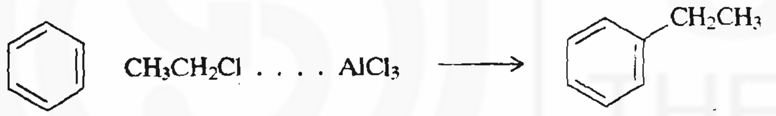
$$(CH_3)_3CCl + AlCl_3 \longrightarrow (CH_3)_3C^+ + AlCl_4^-$$



$$CH_3CH_2Cl + AlCl_3 \longrightarrow CH_3CH_2Cl \;\ldots\; AlCl_3$$

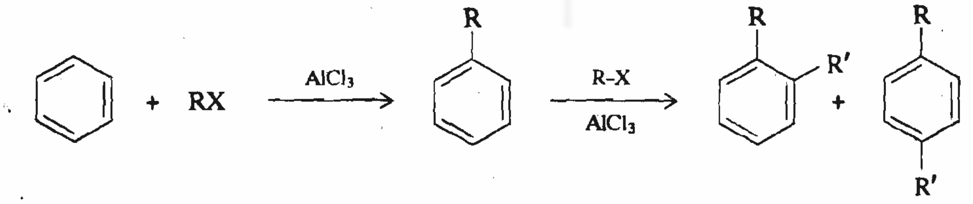
p alkyl halide

alkyl halide Lewis acid complex



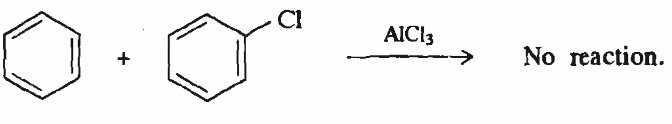
Though the Friedel-Crafts reaction is widely applicable in organic synthesis, it has some limitations as given below:

i) The main difficulty with the Friedel-Crafts alkylation is that the substitution of the first alkyl group activates the ring towards further substitution. We will discuss activation and deactivation in Sec. 9.7.2.

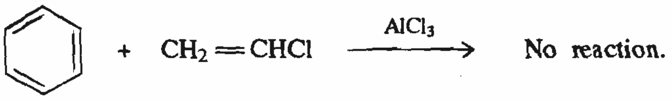


The best way of avoiding this second reaction is to use an excess of aromatic compound.

ii) Friedel-Crafts alkylations are limited to alkyl halides; aryl halides and alkenyl halides do not react. Aryl and alkenyl carbocations are too unstable to form under Friedel-Crafts reaction conditions.

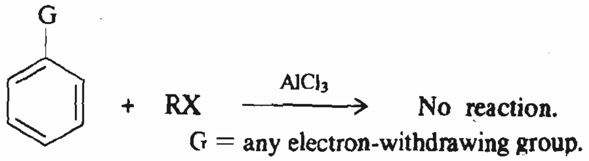


aryl halide

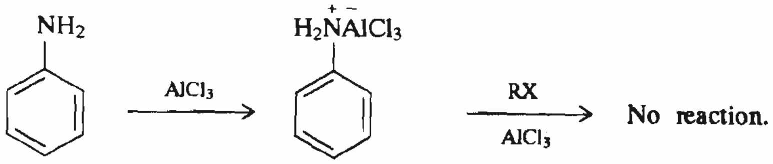


alkenyl halide

iii) If the aromatic compound has an electron withdrawing substituent, it does not undergo Friedel-Crafts alkylation; the deactivated ring is not reactive to attack carbocations.

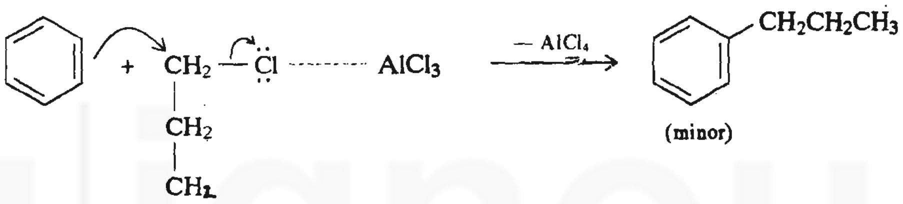


iv) Aromatic amines fail to undergo alkylation, probably because amino group forms a complex with Lewis acid. Since this complex has a positive charge on nitrogen, it deactivates the aromatic ring for electrophilic substitution.

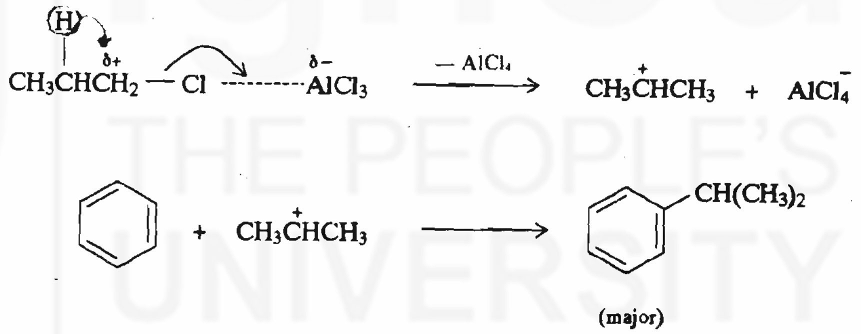


v) Sometimes during the alkylation, the attacking electrophile undergoes rearrangement by 1, 2 shift of H or R. For example, the alkylation of benzene with chloropropane leads to a mixture of propylbenzene and (1-methylethyl) benzene.

No rearrangement



Rearrangement

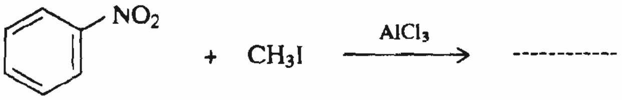


The mechanism is similar to alkylation with an alkyl halide and this reaction proceeds through the more stable carbocation intermediate.

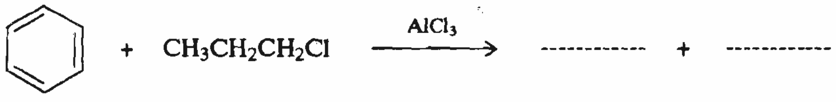
SAQ 2

Give the product(s) of the following reactions:

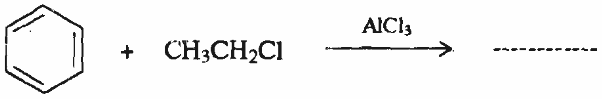
a)



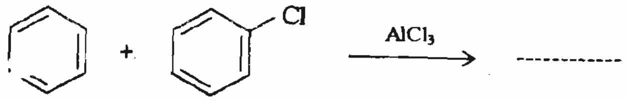
b)



c)

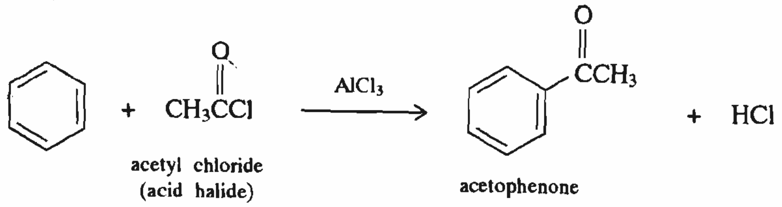


d)

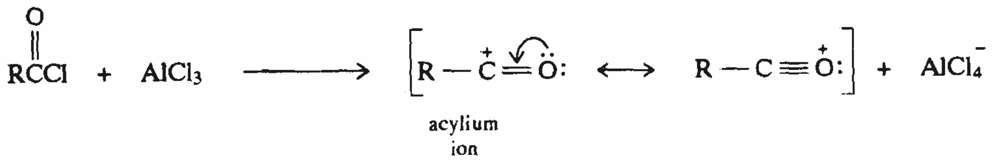


9.6.5 Friedel-Crafts Acylation

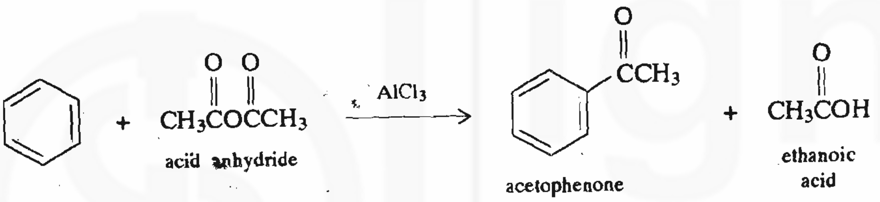
The $R\overset{O}{\overset{\|}{C}}$–group or $Ar\overset{O}{\overset{\|}{C}}$–group is called an acyl group. Substitution of an acyl group into an aromatic ring by the reaction with an acid chlorides in the presence of Lewis acid as catalyst is called an aromatic acylation reaction or Friedel-Crafts acylation. For example, the reaction of benzene with ethanoyl chloride (acetyl chloride) gives the ketone, phenylethanone (acetophenone).



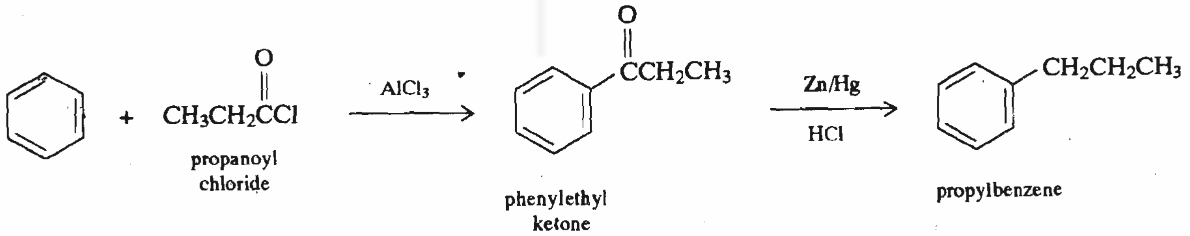
The mechanism of Friedel-Crafts acylation is similar to that of the other electrophilic aromatic substitution reactions The electrophile in this reaction is the resonance-stabilized carbocation, **acylium ion**. This ion is formed when the acid chloride reacts with the Lewis acid, $AlCl_3$.



Carboxylic acid anhydride can be used as alternative to acid chloride for the Friedel-Crafts acylation reaction.



Friedel-Crafts acylation reaction is a synthetically useful reaction. For example, the carbonyl group of the ketone produced by Friedel-Crafts acylation can be reduced to $>CH_2$ group by using zinc amalgam and hydrochloric acid. This method of reduction is known as Clemmensen reduction. By the combination of Friedel-Crafts acylation and Clemmensen reduction, an alkylbenzene may be prepared.

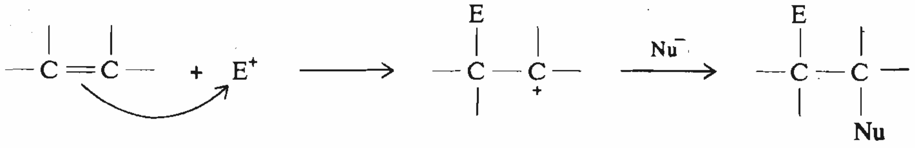


Unlike Friedel-Crafts alkylation, Friedel-Crafts acylation reactions are not accompanied by rearrangements within the acyl group. Moreover, there is no polysubstitution as the aromatic ring is deactivated after the introduction of the first acyl group.

9.6.6 Mechanism of Electrophilic Substitution

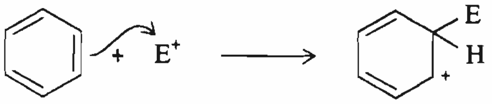
There are reasons to believe that all the electrophilic substitution reactions take place by similar mechanism. It is necessary to understand the principles of this mechanism. Thus, we will discuss the general electrophilic substitution mechanism by Using E^+ for electrophilies.

Before studying detailed mechanism, let us briefly recall what we have learnt about electrophilic addition to alkenes. Electrophilic attack on C=C gives carbocation intermediate which is then attacked by nucleophile to yield addition product.

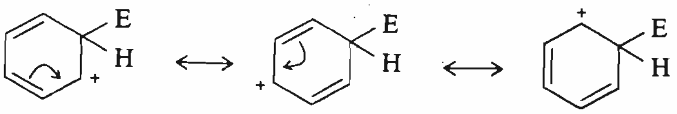


If a reaction takes place through a series of steps, the slowest step is called the rate-determining step (RDS).

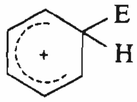
An electrophilic aromatic substitution reaction begins in a similar way. The π electrons of the ring attack on electrophile E^+, forming a σ bond with electrophile. In this process, the positive charge of the electrophile is to be transferred to the adjacent ring carbon atom which is called – carbocation. This is a slow step and is, therefore, the rate determining step.



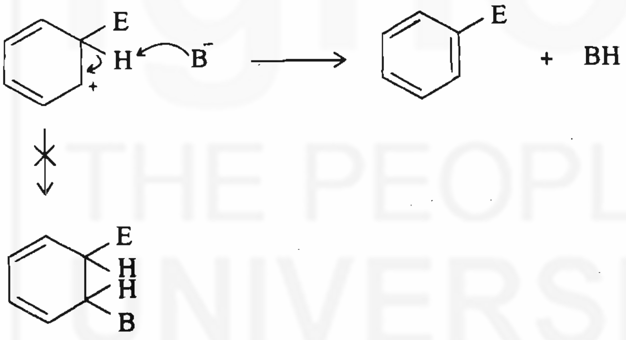
This carbocation is stabilized by resonance as shown below:



These three resonance structures of the intermediate are often combined and represented as follows:

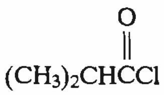


In the case of alkenes, you have seen that nucleophile attacks the carbocation to yield the addition product. Since, in the present case, the addition of the nucleophile would destroy the aromatic stabilisation of the benzene ring, this type of addition does not take place in aromatic carbocation. Instead, nucleophile acts as base and abstracts a ring proton yielding substituted aromatic product.

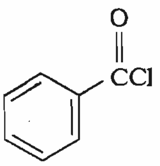


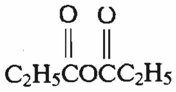
SAQ 3

Give the structure of the product expected from the reaction of each of the following compounds with benzene in the presence of $AlCl_3$.

a) 

$(CH_3)_2CH\overset{O}{\overset{\|}{C}}Cl$

b) 

c) 

$C_2H_5\overset{O}{\overset{\|}{C}}O\overset{O}{\overset{\|}{C}}C_2H_5$

SAQ 4

Write the mechanism of sulphonation of benzene using SO_3 as electrophile.

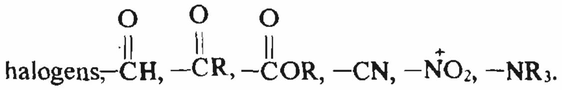
....

....

9.7 EFFECT OF SUBSTITUENTS ON REACTIVITY AND ORIENTATION

Benzene forms only one monosubstituted product by the electrophilic substitution. Let us see what happen when we carry out an electrophilic substitution on a substituted benzene. Studies have shown that the substituents affect the reactivity and the orientation in the benzene ring. Three possible disubstituted products, viz., *ortho, para* and *meta* can result. These three products are not formed at random; rather, a given substituent already attached to the benzene ring usuallly directs the position of the second substituent.

Thre are two types of substituents—one is electron-donating group, such as $-NR_2$, $-OH$, $-OR$, $-NHCOR$, and alkyl and other is electron-withdrawings group which include

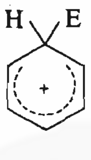


halogens, $-\overset{O}{\overset{\|}{C}}H$, $-\overset{O}{\overset{\|}{C}}R$, $-\overset{O}{\overset{\|}{C}}OR$, $-CN$, $-\overset{+}{N}O_2$, $-NR_3$.

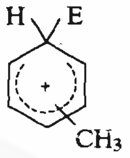
Now we will study the effect of substituents on reactivity and orientation.

9.7.1 Effect of Substituents on Reactivity

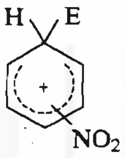
To compare the rates of electrophilic substitution in benzene, methyl substituted benzene (methyl benzene or toluene) and nitro substituted benzene (nitrobenzene) are compared in a reaction, say nitration. It is found that nitration of methyl benzene (toluene) is more facile than benzene whereas nitration of nitrobenzene is more difficult. In other words, benzene ring seems to be activated in toluene and deactivated in nitrobenzene. Let us see if we can explain this on the basis of intermediate carbocation formed.



I



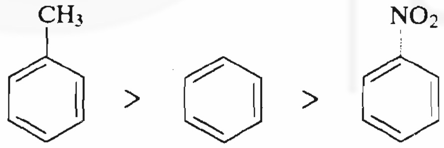
II



III

In the case of methylbenzene (II), the methyl group, which is an electron-donating group, tends to neutralise the charge on the carbocation, this dispersal of the charge stabilises the carbocation thus leading to faster reaction than benzene.

In case of nitrobenzene (III), the NO_2 group which is an electron-withdrawing group, tends to intensify the positive charge and destabilise the carbocation. Due to this effect, the rate of the reaction is slower than in benzene. Reactivity in electrophilic aromatic substitution depends, then, upon the tendency of a substituent group to release or withdraw electrons. A group that releases electrons activates the ring; a group that withdraws electrons deactivates the ring. Hence, the order of reactivity of the above compounds towards electrophilic substitution reaction is:



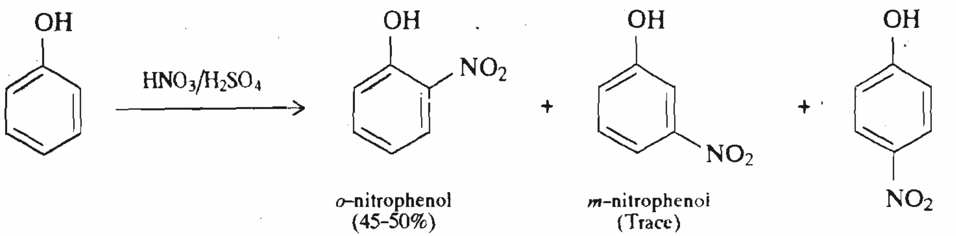
SAQ 5

Which compound would you expect to undergo aromatic nitration more readily, $C_6H_5-CH_3$ or $C_6H_5-CCl_3$? And why ?

....

9.7.2 Effect of Substituents on Orientation

The second effect of a substituent is to direct the position of the incoming substituent. Thus, for instance, nitration of phenol gives *ortho* and *para*-nitrophenol as major products.

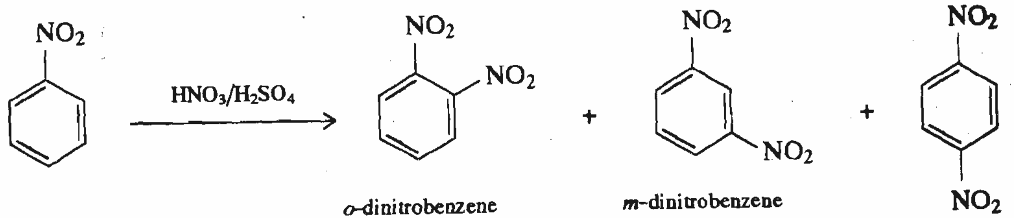


o-nitrophenol
(45-50%)

m-nitrophenol
(Trace)

p-nitrophenol
(45-50%)

On the other hand, nitration of nitrobenzene yields *meta* dinitrobenzene as a major product, i.e.,



o-dinitrobenzene (7%)

m-dinitrobenzene (91%)

p-dinitrobenzene (2%)

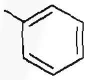
This shows that different substituents have different effect on substitution reaction. Thus substituents can be classified into three groups, i.e.,

- *ortho* and *para*-directing activator
- *meta*-directing deactivator
- *ortho* and *para*-directing deactivator

- No meta directing activators are known.

Table 9.2 lists some of the groups in each category.

Table 9.2 : Classification of directing effects for some common substituents

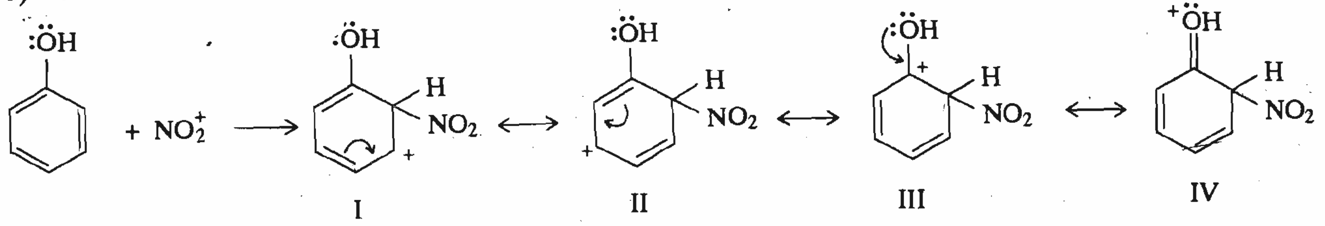
***Ortho*-and *para*-directing activators**	***Ortho*- and *para*-directing deactivators**	***Meta*-directing deactivators**
$-NH_2$	$-I$	$-N^+(CH_3)_3$
$-OH$	$-Br$	$-NO_2$
$-OCH_3$	$-Cl$	$-CN$
$-NHCOCH_3$	$-F$	$-\overset{O}{\overset{\parallel}{C}}CH_3$
		$-\overset{O}{\overset{\parallel}{C}}OCH_3$
$-CH_3$		
		$-\overset{O}{\overset{\parallel}{C}}OH$
		$-\overset{O}{\overset{\parallel}{C}}H$

Before we try to account for the orientation in electrophilic substitution, we should clarify our definitions of activating and deactivating. Activating groups activate all the positions of the ring. They are *ortho* and *para* directors because they activate *ortho* and *para* position much more than they do the *meta* position. Similarly, deactivating groups deactivates all position in the ring. They are *meta* directors because they deactivate the *ortho* and *para* position more than they deactivate the *meta* position. Thus, the effect of any group, whether activating or deactivating, is strongest at the *ortho* and *para* positions.

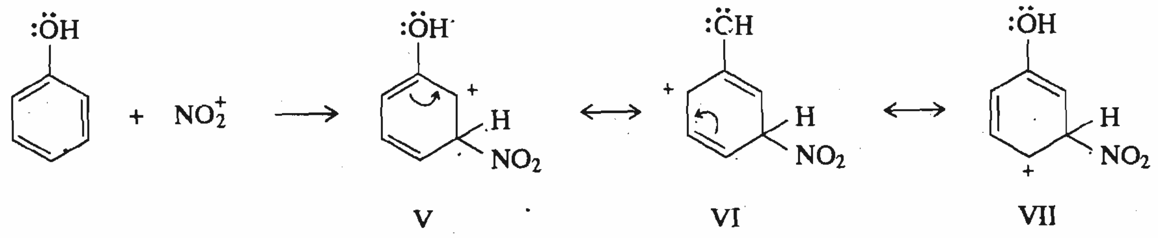
***Ortho* and *para*-directing activator :** To understand the orientation effect of the substituents, we have to first write all the possible resonance forms of the charged intermediates for each of the three possible reaction courses.

Reactions of NO_2^+ at the *para*, *meta* and *ortho* positions of phenol give the intermediates with the following resonance structures.

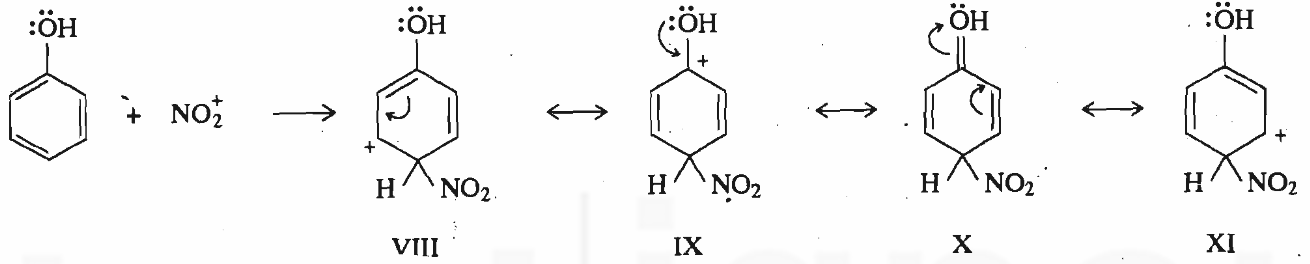
a) *Ortho*–Attack



b) *Meta*–Attack



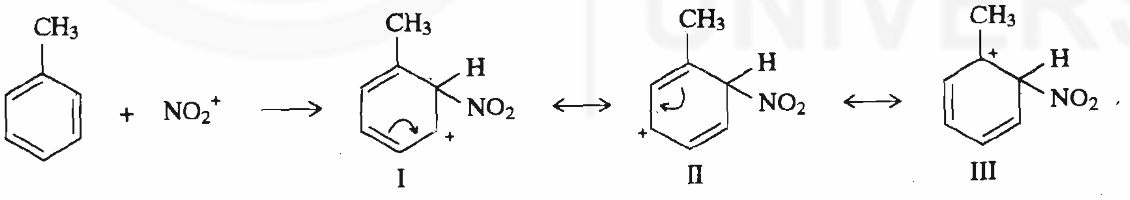
c) *Para*–Attack



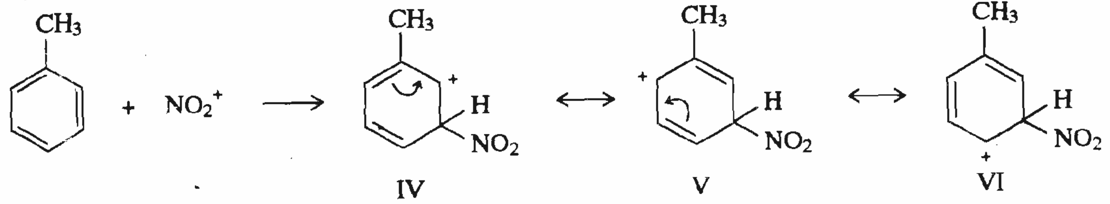
In case of *ortho* and *para* attacks, structures IV and X respectively show that the unshared electron pair of oxygen delocalize the positive charge on the carbocation and, hence, four resonance structures are possible. In the case of *meta* attack, since the charge cannot be delocalised onto the —OH group, the carbocation that is formed has only three resonance structures. Hence, carbocation formed by *ortho* and *para* attacks are more stable and, therefore, *ortho* and *para* nitrophenols are the major products.

Now take the example of electrophilic aromatic substitution on alkyl substituted benzene ring. Let us inspect the possible resonance structures of carbocation formed by the attack of the electrophile, $\overset{+}{N}O_2$, on toluene.

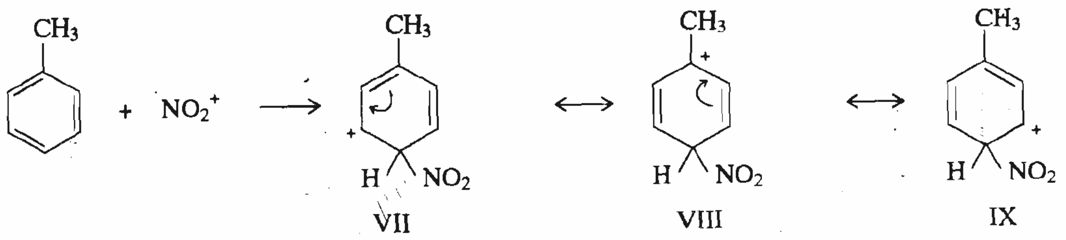
a) *Ortho*–Attack



b) *Meta*–Attack



c) *Para*–Attack



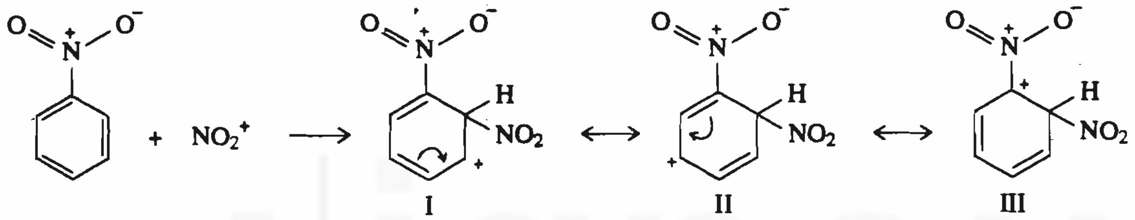
Structure III and VIII are additionally stabilized by inductive effect of methyl group.

As indicated above, in structures III and VIII, resulting from *ortho* and *para* attack respectively, the positive charge is located on the carbon atom to which the methyl group is attached. Because that structure has tertiary carbocation character, it is more stable than the others, in which the positive charge is at a secondary carbocation. On the other hand, *meta* attack produces an intermediate in which none of the resonance structures benefits from such tertiary carbocation stabilisation. Thus, electrophilic attack on a carbon located *ortho* or *para* to methyl group leads to a cationic intermediate that is more stable than the one derived by attack at the *meta* carbon. Substitution at *ortho*-and *para*-position is, therefore, preferred to *meta*-substitution.

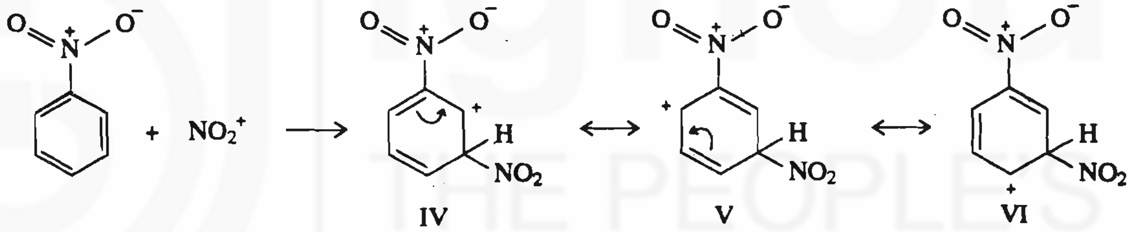
This can also be explained on the basis of inductive effect. The carbocation III and VIII formed by the *ortho*-and *para*-attack respectively, are stabilised by inductive effect of methyl group and, therefore, formed in major amount.

***Meta*-directing deactivators :** We can apply similar arguments to *meta*-directing groups. These groups are all electronegative groups without an unshared electron pair on an atom adjacent to the benzene ring. In all these cases, the benzene ring would be deactivated. Let us take the example of nitration of nitrobenzene. The possible resonance structures of the carbocation formed are :

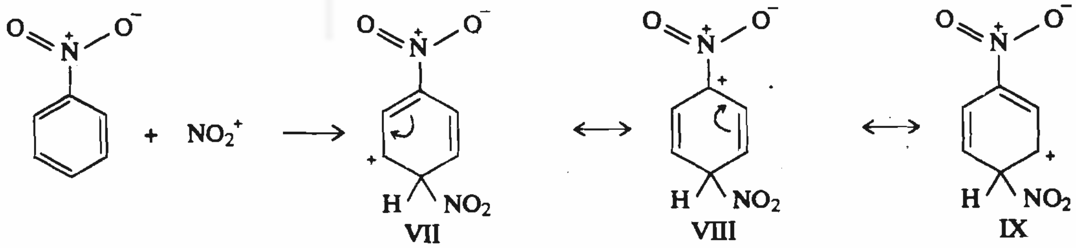
a) *Ortho*-Attack



b) *Meta*-Attack



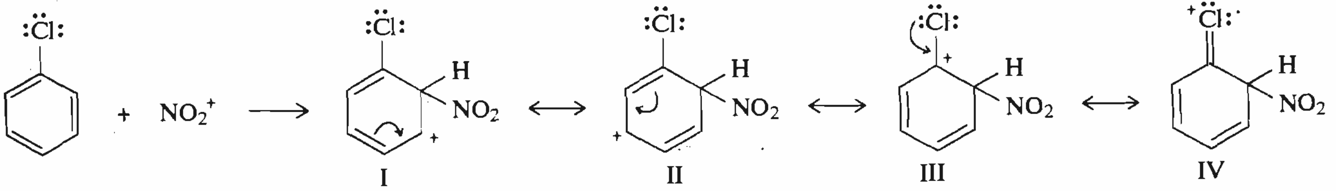
c) *Para*-Attack



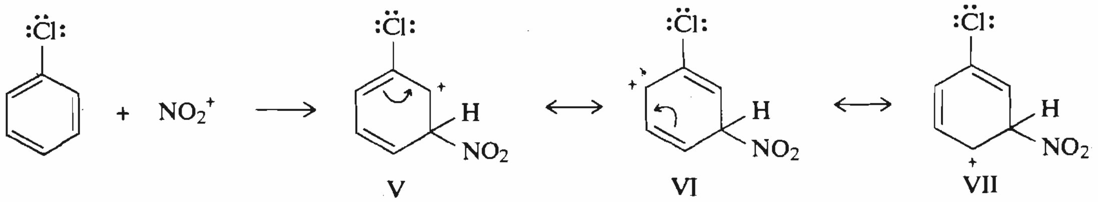
In all the three cases, carbocations formed have three resonance structures. But the structure III and VIII resulting from *ortho* and *para* respectively, are very unfavourable because the positive charge is placed directly on the carbon carrying the electron withdrawing group. A severe electrostatic repulsive interaction between the carbocation and the positive end of the $\overset{+}{N}O_2$ group strongly disfavours this carbocation. The carbocations formed by *meta* attack, have no such form with similar charges on adjacent atoms. Therefore, its transition state is the most stable, and attack at *meta*-position is preferred.

***Ortho* and *para* directing deactivator** : Halogens are unusual in their effect on electrophilic aromatic substitution. They are deactivating yet *ortho* and *para* directing. For understanding the orientation, consider the attack of electrophile at *ortho, meta* and *para* positions of chlorobenzene.

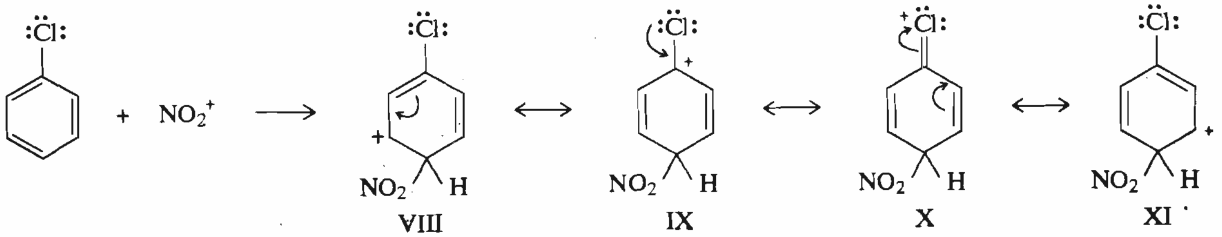
a) *Ortho*-Attack



b) *Meta*-Attack



c) *Para*-Attack



In structures III and IX, resulting from *ortho* and *para* attack, there is a positive charge on carbon bearing the halogen atom. Through its inductive effect, chlorine withdraws electrons, making this structure unstable. But there is another factor that one should not forget. It is known that halogen can share a lone pair of electrons and accommodate the positive charge, as shown in structures IV and X, for *ortho* and *para* attack, respectively. These structures are comparatively stable. No such structure is possible when the electrophile attack on *meta* position. Structures IV (in *ortho* attack) and X (in *para* attack) outweigh the instability rendered by structures III and IX. Therefore, attack at *ortho* and *para* position is prepared.

SAQ 6

Predict the major and minor products of the following:

a) Nitration of bromobenzene

....

b) Nitration of nitrobenzene

....

c) Bromination of nitrobenzene

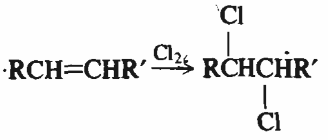
....

d) Chlorination of phenol

....

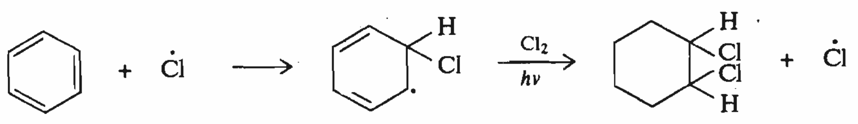
9.8 ADDITION REACTIONS OF BENZENE

You have already studied in Unit 7 that the chlorination of an alkene gives 1, 2-dichloroalkane.

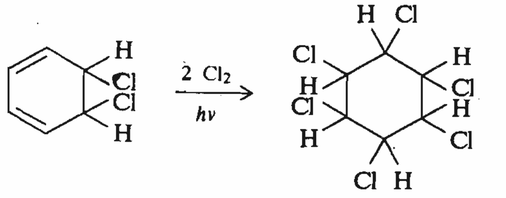


$$RCH{=}CHR' \xrightarrow{Cl_2} R\underset{\displaystyle Cl}{\overset{\displaystyle Cl}{CH}}CHR'$$

In contrast to this, the addition of chlorine to benzene takes place with some difficulty and produces several isomers of 1, 2, 3, 4, 5, 6-hexachlorocyclohexanes. When treated with chlorine or bromine in the presence of sunlight, benzene forms the hexahalides, $C_6H_6Cl_6$ and $C_6H_6Br_6$, respectively. The addition reaction proceed by the free radical mechanism.



$$Cl_2 \xrightarrow{h\nu} 2\,\dot{C}l$$

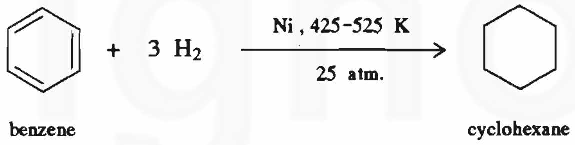


1,2,3,4,5,6-hexachlorocyclohexane

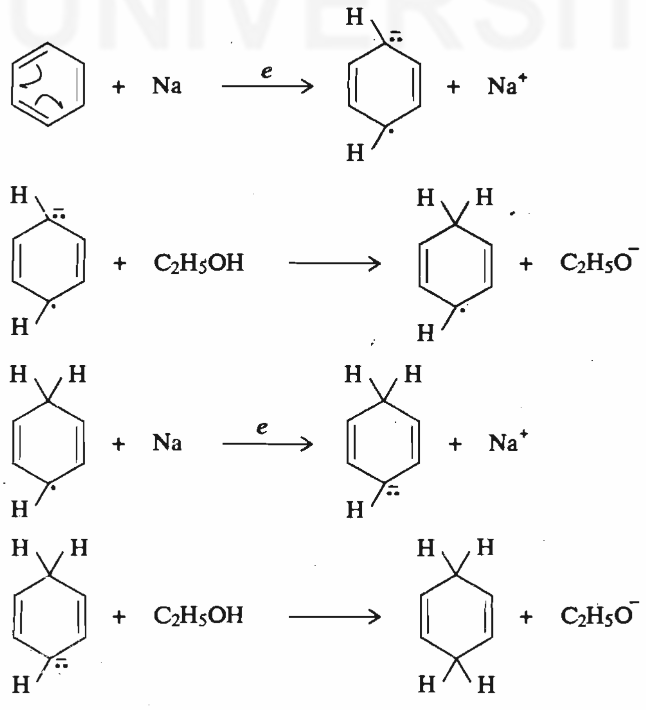
The 1, 2, 3, 4, 5, 6-hexachlorocyclohexane, theoretically can exist in eight stereoisomeric forms but only seven of these are known. One of the isomers, known as Gammexane, is a powerful insecticide. It is very stable and acts more quickly than D.D.T. All the isomers have shown to exist in the chair form.

9.9 REDUCTION

Hydrogenation of benzene at higher temperature and under pressure yields cyclohexane.



Although benzene is not reduced by metal and acid, or by sodium in ethanol, it is reduced by sodium in liquid ammonia in the presence of ethanol (**Birch reduction**) to give 1, 4-dihydrobenzene (cyclohexa-1, 4-diene). This reaction has also been shown to have a free radical mechanism.

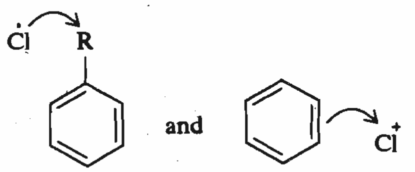


Lithium in anhydrous ethylamine, however, reduces benzene to cyclohexene and cyclohexane.

9.10 REACTIONS OF SIDE-CHAIN

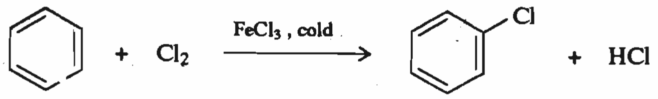
9.10.1 Substitution in the Side-chain

Alkylbenzene clearly offers two sites for attack by halogen: the ring and the side chain. We

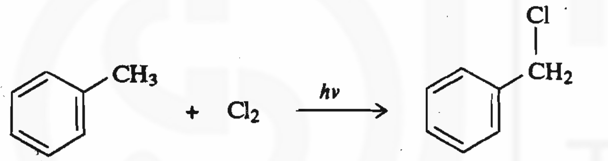


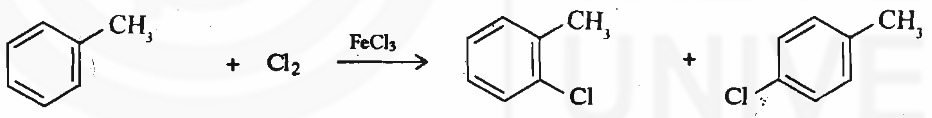
can control the position of attack by choosing the proper reaction conditions. Halogenation of alkanes requires condition under which halogen atoms are formed by homolyses of halogen molecules, that is, high temperature or light. Halogenation of benzene, on the other hand, involves transfer of positive halogen, which is promoted by Lewis acid catalyst like ferric chloride.

$$CH_4 + Cl_2 \xrightarrow{\text{Heat or light}} CH_3Cl + HCl$$



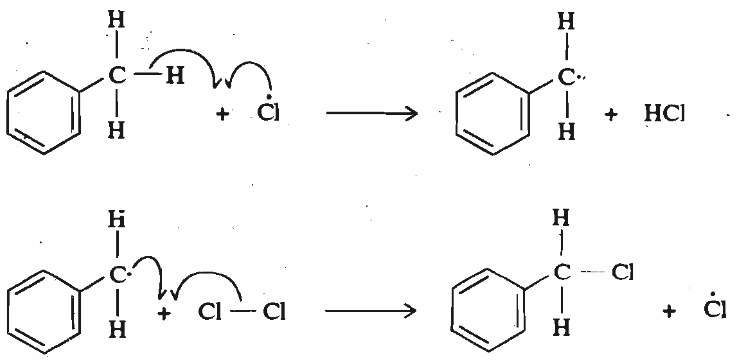
The position of attack in methylbenzene (toluene) would be decided by the nature of the attacking particle and by the condition employed. If the reaction is carried out in the presence of light, substitution occurs almost exclusively in the side chain. In the absence of light and in the presence of ferric chloride, substitution occurs mostly in the ring. For example:



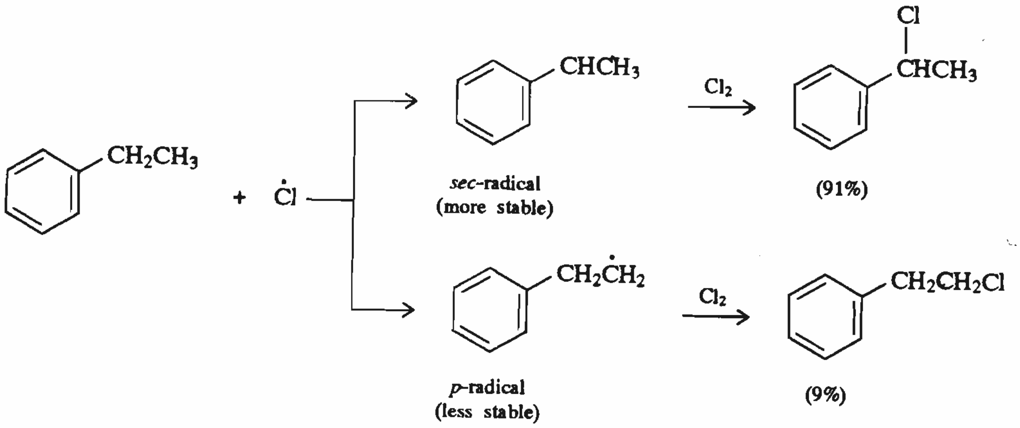


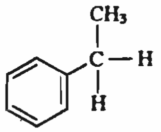
Chlorination of methylbenzene (toluene), in the presence of light, takes place via free radical chain mechanism as shown below:

$$Cl_2 \xrightarrow{h\nu} \cdot 2\ Cl$$

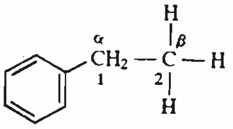


In alkyl benzenes with side chains larger than methyl, it is expected that the free radical substitution may take place on any of the side chain carbon atoms; so we must consider the likelihood of obtaining a mixture of isomers. For example, chlorination of ethylbenzene should give two isomeric products, 1-chloro-1-phenylethane and 2-chloro-1-phenylethane in equal amounts. But 1-chloro-1-phenylethane is the major (91%) product,



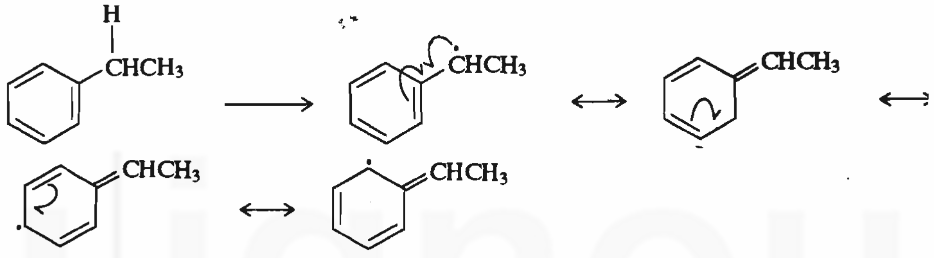


benzylic C — H bond



β-phenylethyl C — H bond

You can ask, why it is so. This is because the bond dissociation energy of benzylic C—H bond, $C_6H_5\overset{CH_3}{C}H—H$, (355 kJ mol⁻) is less than *β*-phenyl ethyl C—H bond, $C_6H_5—CH_2CH_2—H$ (435 kJ mol^{-1}). That means, less energy is required for the homolytic fission of benzylic C—H bond. In other words, benzyl radical is more stable. The greater stability of benzyl radical is delocalisation of the odd electron over the ring as shown below :

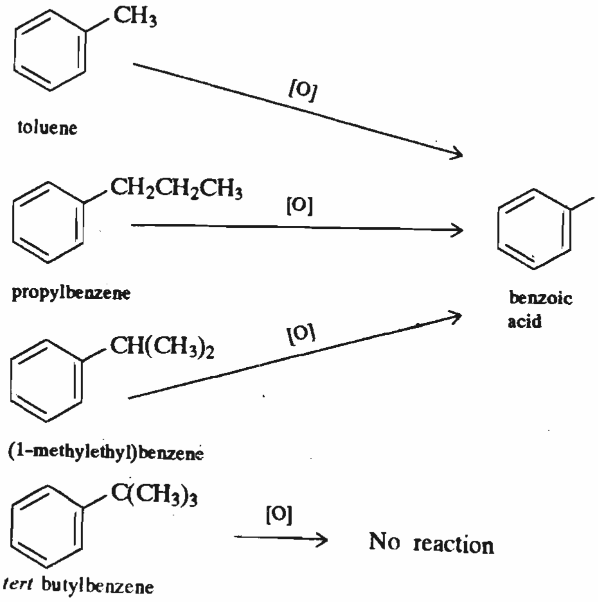


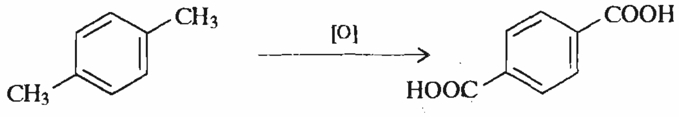
Since the benzylic radical formed is more stable, 1-chloro-1-phenylethane is the major product.

9.10.2 Oxidation of Side-chain

Although benzene and alkanes are quite unreactive towards the usual oxidising agents ($KMnO_4$, $K_2Cr_2O_7$ etc.), the benzene ring renders an aliphatic side chain quite susceptible to oxidation. The side chain, irrespective of its length, is oxidised to a carboxyl group (-COOH). Tertiary alkyl substituted aromatic compounds do not follow this reaction. For example, toluene, propylbenzene, (1-methylethyl) benzene are oxidised to benzoic acid in higher yields. *p*-Methyltoluene on oxidation gives terephthalic (benzene-1, 4-dicarboxylic) acid but tertiary butylbenzene is not effected.

The number and the position of the carboxylic groups produced indicate the number and position of alkyl chain attached to the aromatic ring.



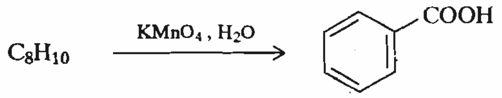


p-methyl toluene

This reaction is useful for two purposes:

- synthesis of carboxylic acids
- identification of alkylbenzenes

SAQ 7
Draw the structural formulas for the starting materials in the following reaction:

a) 

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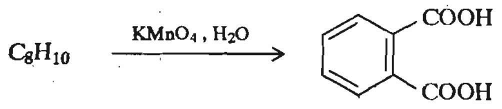
b) 

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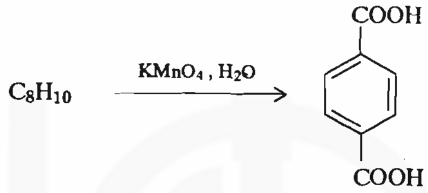
c) 

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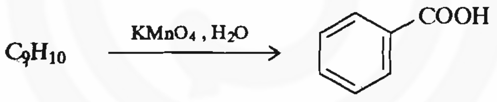
d) 

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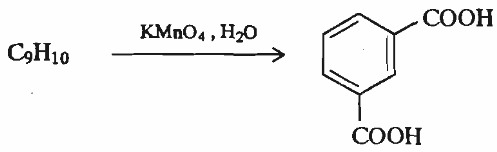
e) 

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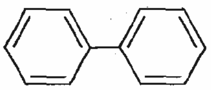
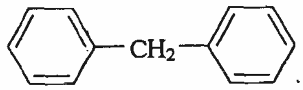
9.11 POLYNUCLEAR HYDROCARBONS

Polynuclear hydrocarbon is an assembly of more than one benzene ring in the molecule. Depending upon the mode of attachment of various rings, the polynuclear aromatic hydrocarbons may be classified into two broad classes: (i) isolated benzenoid hydrocarbon, and (ii) condensed or fused benzenoid hydrocarbons.

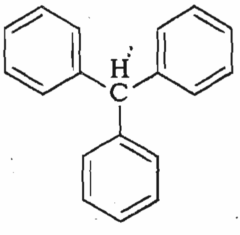
i) **Isolated benzenoid hydrocarbon:** In isolated systems, two or more rings are joined to each other either directly or through carbon chain. Some common examples are biphenyl, diphenylmethane and triphenylmethane.



biphenyl

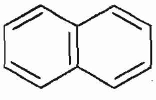


diphenylmethane

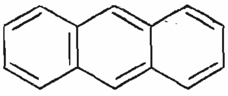


triphenylmethane

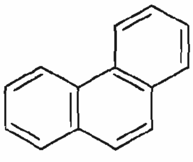
ii) **Condensed or fused benzenoid hydrocarbon:** The condensed or fused benzenoid hydrocarbons are those in which two or more benzene rings are fused together at the *ortho* position in such a way that each pair of rings shares two carbons. They include compounds like naphthalene, anthracene, phenanthrene etc.



naphthalene



antharacene



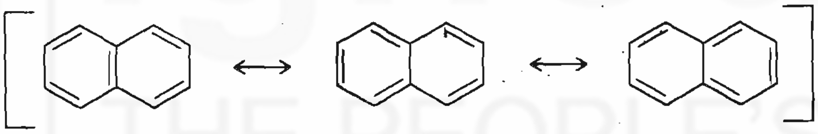
phenanthrene

The condensed polynuclear hydrocarbons is by far the larger and the more important group. A large number of them have been found to possess carcinogenic (cancer producing) activity. In this unit we will discuss the chemistry of naphthalene only.

9.11.1 Naphthalene

Naphthalene is the parent compound of polynuclear hydrocarbons. Naphthalene, m.p. 355 K, is a colourless volatile crystalline solid.

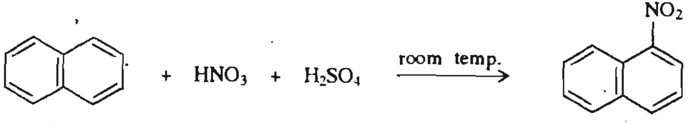
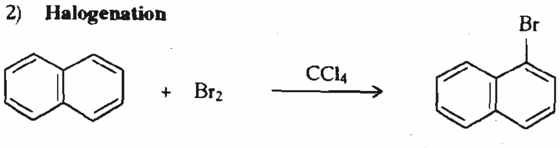
Naphthalene has three resonance hybrid structures. The bonds are not all of the same length, but are close to the benzene value of 139.7 pm.



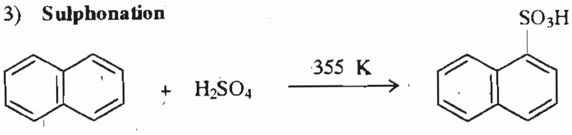
How can we explain the aromaticity of naphthalene? The above structure of naphthalene shows that it has 10 π electrons and 10 is the Huckel number which indicates that naphthalene should be an aromatic molecule.

Like benzene, naphthalene undergoes usual electrophilic substitution reactions. It also undergoes oxidation or reduction more readily than benzene. Some important reactions of naphthalene are given in Table 9.3.

Table 9.3 : Electrophilic substitution reactions of naphthalene

Reaction	Remarks
1) **Nitration**  1-nitronaphthalene	At higher temperatures, a mixture of 1, 5- and 1, 8-dinitronapthalene are formed
2) **Halogenation**  1-bromonaphthalene	1) 1-Chloronapthalene can form in presence of $FeCl_3$ 2) Only 1-substitution takes place

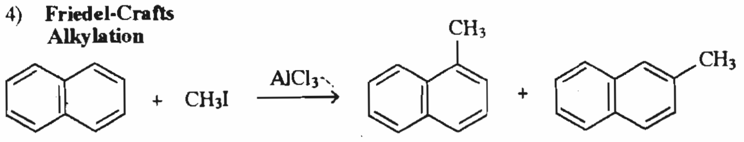
3) Sulphonation



1-naphthalenesulphonic acid

At 435 K, 2-naphalenesulphonic acid is the main product

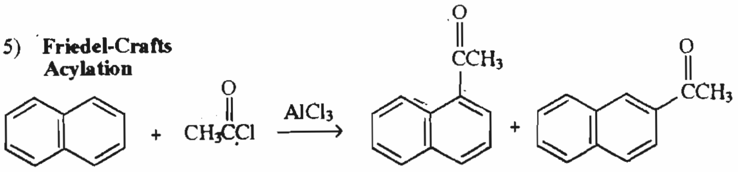
4) Friedel-Crafts Alkylation



1-methylnaphthalene 2-methylnaphthalene

The proportion of 1- and 2- substituted products depends on the size of the reagents

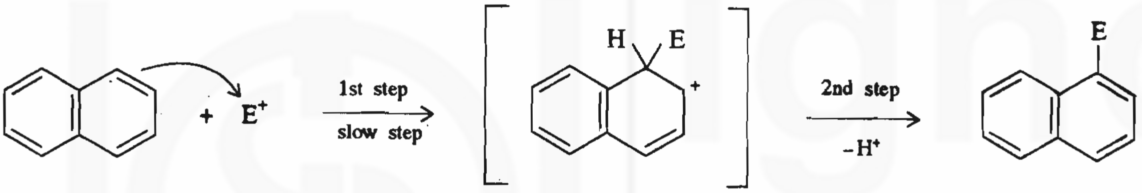
5) Friedel-Crafts Acylation



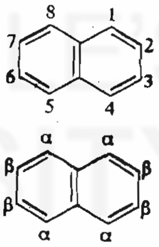
1-naphthyl methyl ketone 2-naphthyl methyl ketone

The proportion of 1- and 2- substituted products depends on the solvent used

Electrophilic substitution of naphthalene: Polynuclear hydrocarbons are more reactive towards electrophilic attack than benzene. Naphthalene undergoes a number of usual electrophilic substitution reactions, such as nitration, halogenation, sulphonation, Friedel-Crafts alkylation, Friedel-Crafts acylation, etc.



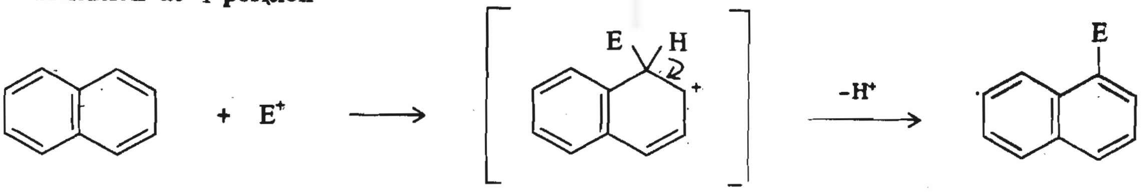
α-substituted product



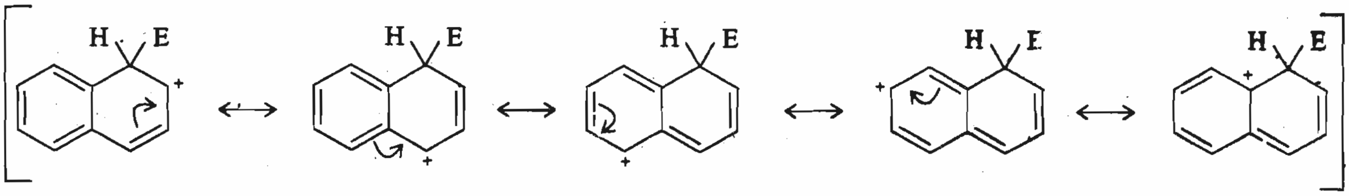
The mechanism for napthalene substitution reaction is similar to that of benzene substitution.

The first substituent goes to 1-position (α-position); that means, the 1-position is more reactive than the 2-position (β-position). You can ask why it is so. To understand this, let us examine the resonance structures of the two intermediate carbocations resulting from the respective attacks.

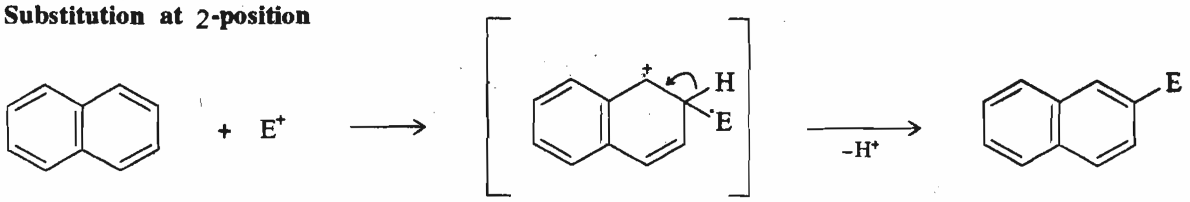
Substitution at 1-position



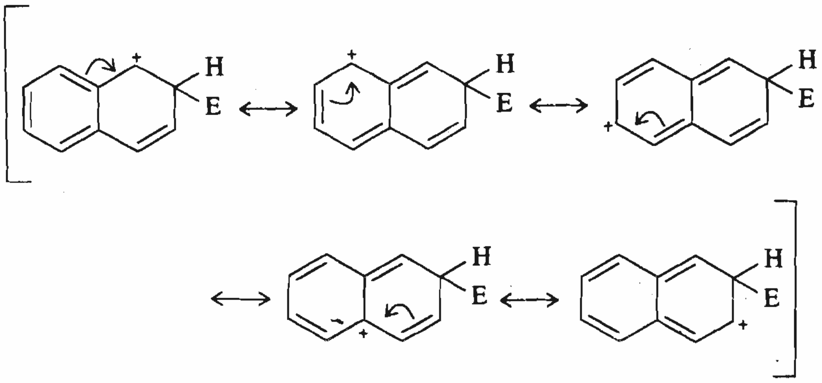
Resonance structure of carbocation



Substitution at 2-position

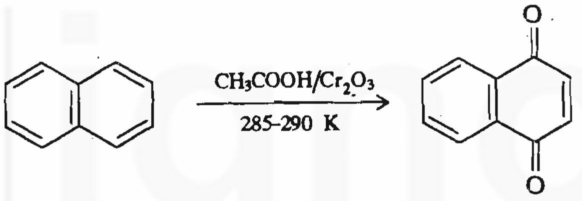


Resonance structure of carbocation



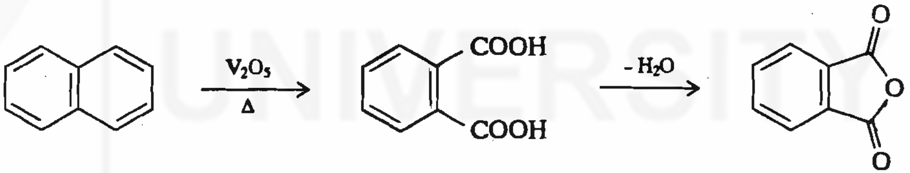
In both cases, the positive charge can be distributed to five different positions, but these carbocations are not equivalent in energy. In the first case, the first two structures have their benzene ring intact and are consequently more stable than the remaining three structures. In the second case, only one resonance structure has a benzenoid ring intact. The resulting resonance hybrid has higher energy in the second case than in the first case. The intermediate carbocation in the first case is more stabilised by resonance, and its transition state is of lower energy. For this reason the intermediate in the first case is formed faster and 1-position is more reactive.

Oxidation and reduction of nephthalene: Under controlled conditions, naphthalene is oxidised to 1, 4-naphthoquinone, but the yield is usually low.



1,4-naphthoquinone
(18-22%)

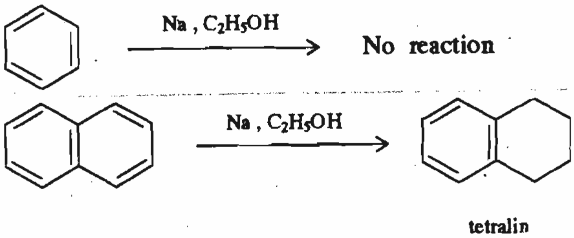
More vigorous oxidation results in the loss of one ring and yields phthalic anhydride. This reaction probably proceed through the formation of *ortho*-phthatic acid.



phthalic acid

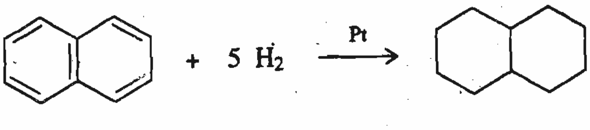
phthalic anhydride

Unlike benzene, naphthelene can be partially hydrogenated without heat and pressure, or which can be reduced with sodium and ethanol.



tetralin

For complete hydrogenation of napthelene, it requires heat and pressure just as in the case of benzene.



decalin

9.12 SUMMARY

- Coaltar is the chief source of aromatic hydrocarbons. Today, aromatic hydrocarbons are obtained by passing alkanes over platinum catalyst at 750-820 K. The process is called hydroforming or catalytic reforming.
- Unlike alkenes, benzene does not undergo electrophilic addition reactions, but it does undergo electrophilic substitution reactions, e.g., nitration, halogenation, sulphonation, Friedel-Crafts alkylation, Friedel-Crafts acylation, etc.
- In the presence of sunlight, benzene gives an additional product. For example, it gives benzenehexabromide and benzenehexachloride (gammaxene).
- Groups attached to the benzene ring affect the reactivity of the ring for further substitution and also determine the orientation of further substitution. Various substituents are classified into two groups. The electron-donating substituents, when attached to benzene, have *ortho* and *para* directing influence while electron-withdrawing substituents are *meta* directing.
- Alkylbenzenes offer two main areas for attack by halogen—the ring and the side chain. In the presence of light, halogen goes to side chain while, in the presence of acid catalyst, it goes to ring.
- In alkylbenzene, the entire side chain can be oxidised to carboxylic acid.
- Polynuclear hydrocarbons are made up of two or more benzene rings. There are two types of polynuclear hydrocarbons : isolated and condensed type.
- Polynuclear hydrocarbons undergo electrophilic substitution reaction. The 1-position of naphthalene is more reactive.
- Naphthalene also undergoes oxidation and reduction more readily than benzene.

9.13 TERMINAL QUESTIONS

1) Write equation to show how the following conversion takes place.
   a) Toluene to *m*-bromobenzonic acid
   b) Benzene to benzoic acid
   c) Benzene to *p*-nitrotoluene
   d) Benzene to *m*-nitroacetophenone

2) Write the chemical equation for the oxidation of the following compounds with hot $KMnO_4$.
   a) Butylbenzenes
   b) 1, 1-Dimethylethyl benzene
   c) 1, 3, 5-Trymethylbenzene

3) Rank the following compounds in the expected order of the reactivity towards Friedel-Crafts alkylation. Which of the following compound(s) are unreactive?
   a) Bromobenzene b) Toluene
   c) Phenol d) Aniline
   e) Nitrobenzene f) *p*-Bromotoluene

4) How do you convert benzene into the following compounds?
   a) Bromobenzene b) Benzenesulphonic acid
   c) Cyclohexane d) Ethylbenzene
   e) Hexachlorocyclohexane

5) Write the resonance structures of cation formed from $C_6H_5NH_2$ during :
   a) *ortho*-bromination b) *meta*-bromination
   c) *para*-bromination

6) Compound A, B and C are the three isomeric dibromobenzenes. Identify which is *ortho*, *para* and *meta* from the number of mononitration products.
   a) Compound A $\xrightarrow{HNO_3/H_2SO_4}$ two mononitration products

b) Compound B $\xrightarrow{HNO_3/H_2SO_4}$ three mononitration products

c) Compound C $\xrightarrow{HNO_3/H_2SO_4}$ one mononitration products

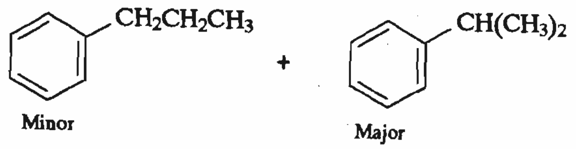
9.14 ANSWERS

Self Assessment Questions

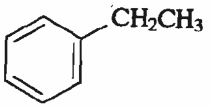
1) In compound a) one ring carbon in sp^3 hybridised and is not coplanar, hence it is not aromatic. Ion (b) contains sp^2 hybridised ring carbon atoms but does not follow Huckel's rule, hence it is not aromatic. Ion (c) is aromatic because it contains sp^2 hybridised ring atoms and follows Huckel's rule.

2) a) No reaction.

b)

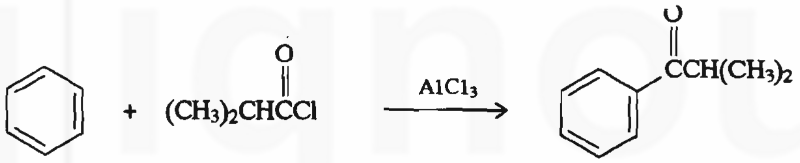


c)



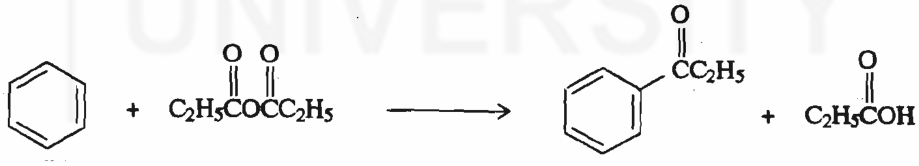
d) No reaction.

3) a)

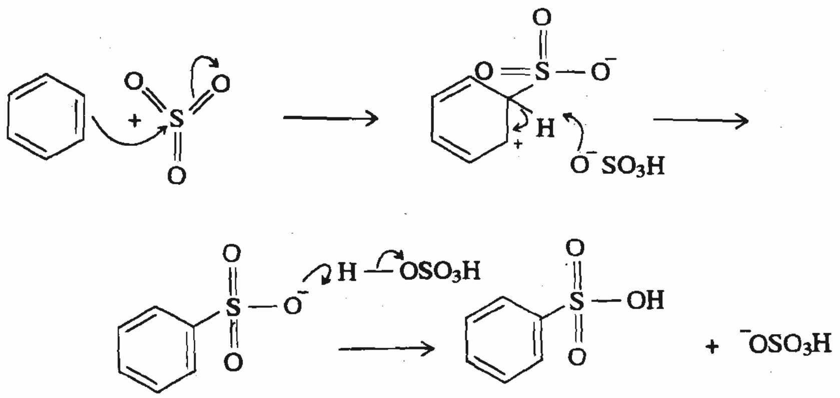


b)

c)

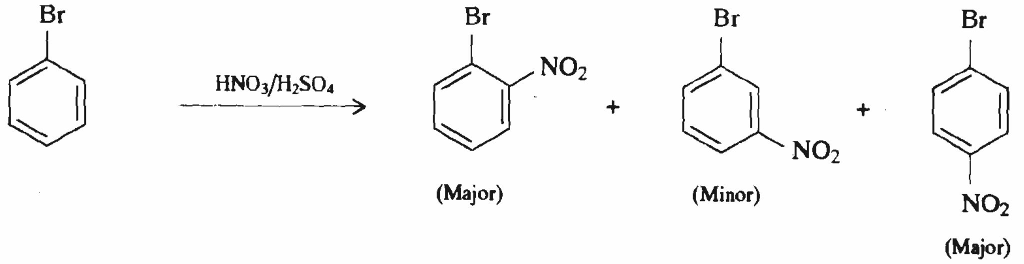


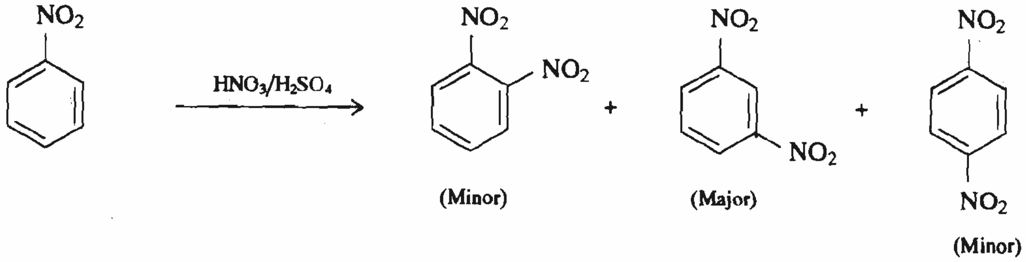
4)



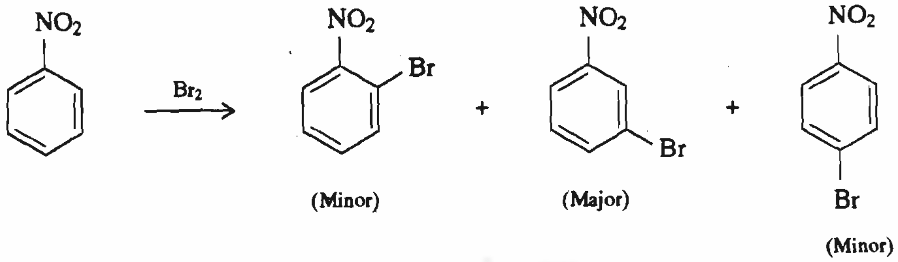
5) While the $-CH_3$ group is electron releasing and activates the ring, the CCl_3 group is strongly electron withdrawing because of the influence of the electronegative chlorine atoms and hence, deactivates the ring. Therefore, $C_6H_5CCl_3$ undergoes substitution more slowly.

6)

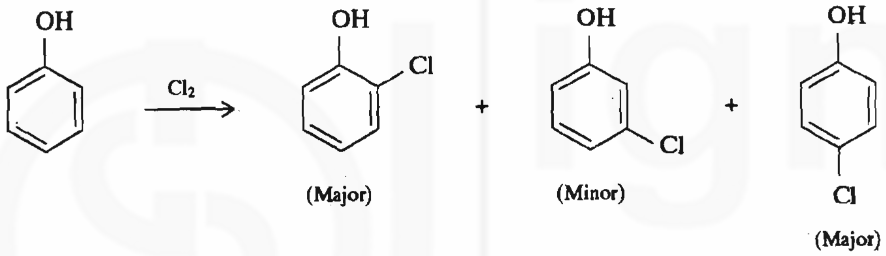

Br
HNO_3/H_2SO_4
Br
NO_2
(Major)
Br
NO_2
(Minor)
Br
NO_2
(Major)


NO_2
HNO_3/H_2SO_4
NO_2
NO_2
(Minor)
NO_2
NO_2
(Major)
NO_2
NO_2
(Minor)

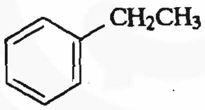
c)


NO_2
Br_2
NO_2
Br
(Minor)
NO_2
Br
(Major)
NO_2
Br
(Minor)

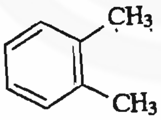
d)


OH
Cl_2
OH
Cl
(Major)
OH
Cl
(Minor)
OH
Cl
(Major)

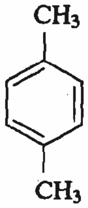
7) a)


CH_2CH_3

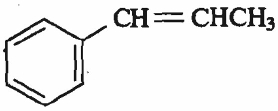
b)


CH_3
CH_3

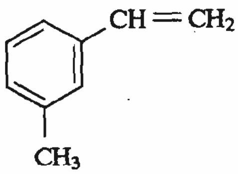
c)


CH_3
CH_3

d)

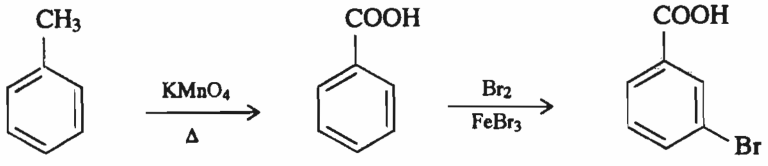

CH=CHCH$_3$

e)

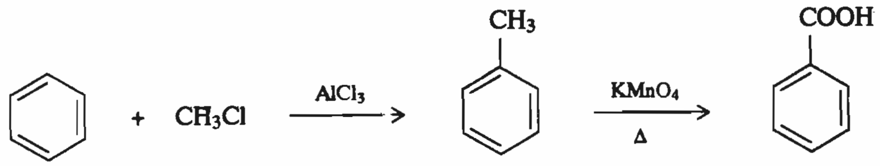

CH=CH$_2$
CH_3

Terminal Questions

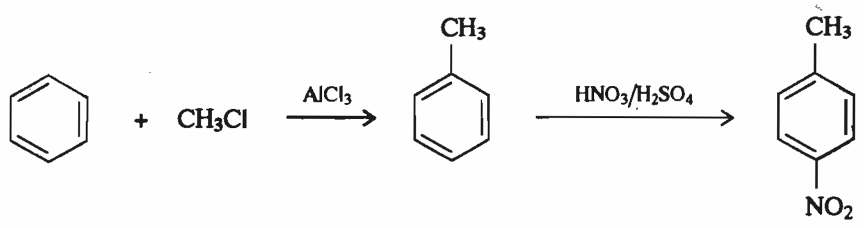
1) a)



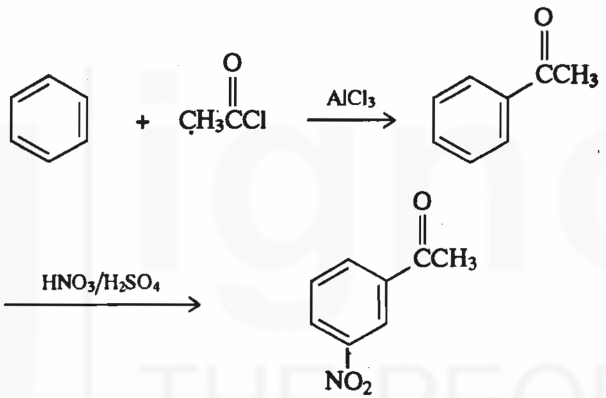
b)



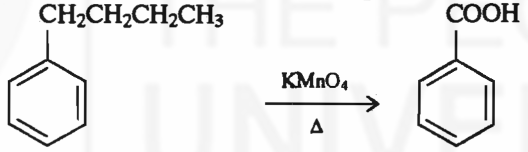
c)



d)



2) a)



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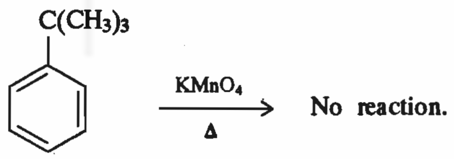
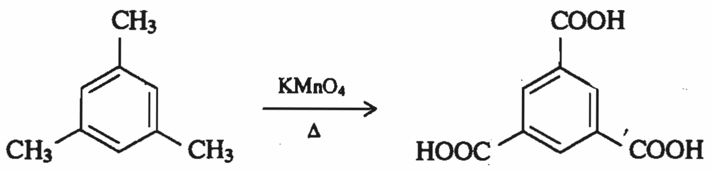


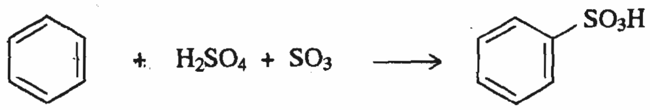
c)



3) Order of reactivity of the given compounds towards Friedel-Crafts alkylation is : Phenol > Toluene > *p*-Bromotoluene > Bromobenzene. Nitrobenzene and aniline are unreactive towards alkylation.

4) a)

b)



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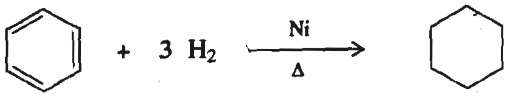
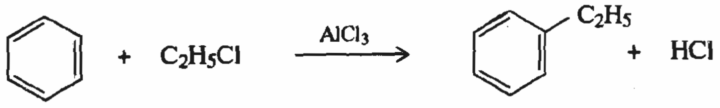
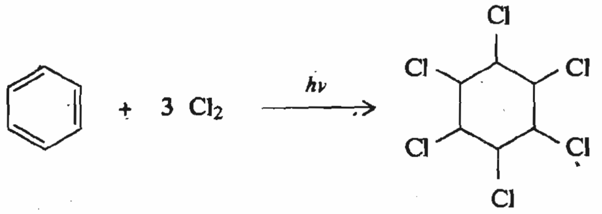


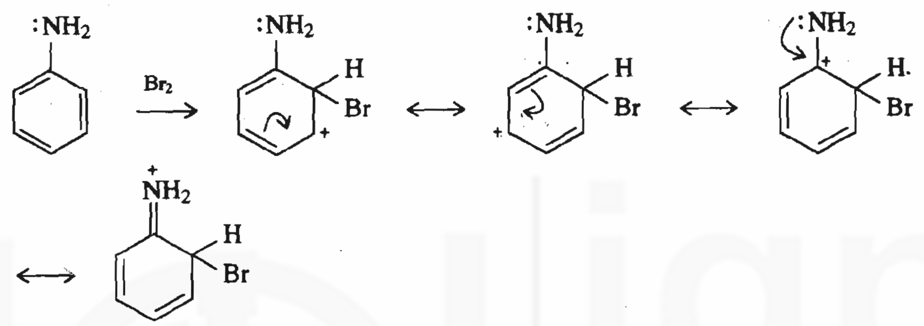
d)



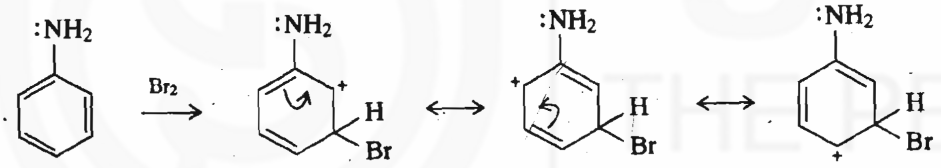
e)



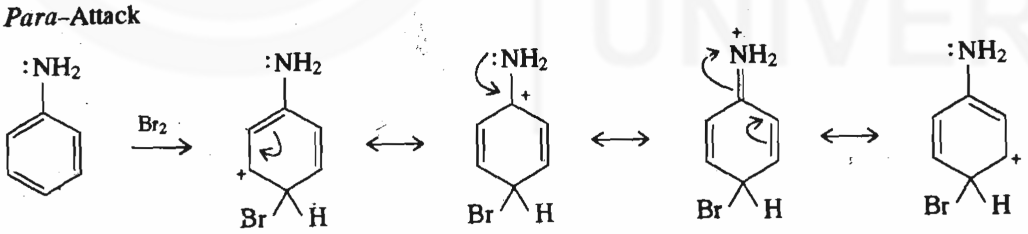
5) a) *Ortho*-Attack



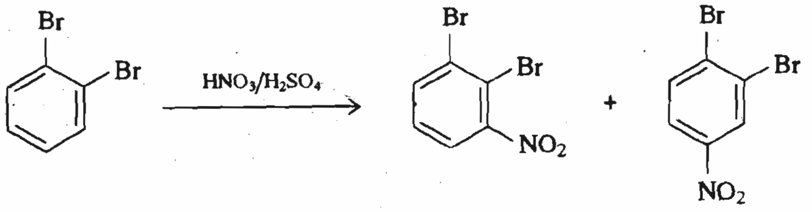
b) *Meta*-Attack



c) *Para*-Attack

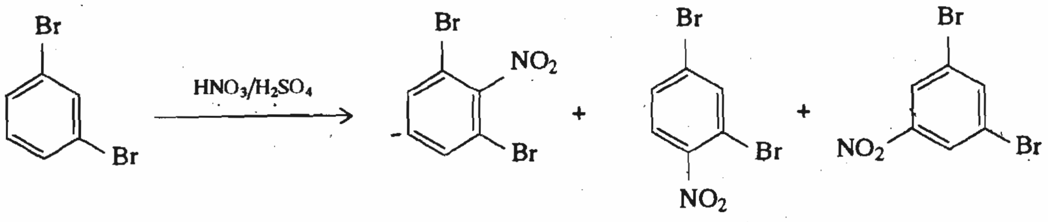


6) a)

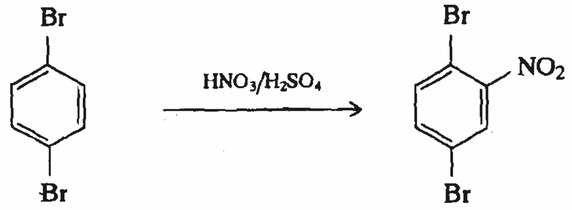


Only these two products are possible from *o*-dibromobenzene

b)



Three products are possible from *m*-dibromobenzene c)



Only one product is possible from *p*-dibromobenzene

On the basis of above reactions, we can say that :

Compound A is a *o*-dibromobenzene

Compound B is a *m*-dibromobenzene

Compound C is *p*-dibromobenzene.

UNIT 10 HETEROCYCLIC COMPOUNDS

Structure

10.1 INTRODUCTION

Our study of the cyclic systems upto this point was restricted to compounds in which the ring contains carbon atoms. Rings that contain, in addition to carbon, atoms of other elements in the ring are called heterocyclic. The hetero atoms that occur most frequently in heterocyclic rings are nitrogen, sulphur and oxygen. The rings in heterocyclic compounds may be saturated or unsaturated. Unsaturated heterocyclic systems may be aromatic or nonaromatic. Among aromatic heterocycles five and six-membered heterocyclic rings are most common.

In the biological world heterocyclic compounds are of wide occurrence and are often of critical physiological importance. Thus chlorophyll, the green pigment of leaves which catalyses photosynthesis is based on a heterocyclic framework. The same is true of haemin, which gives the red colour to our blood and functions as an oxygen carrier. Heterocyclic compounds form the sites of reaction in many enzymes and coenzymes. Heredity comes down, ultimately to the particular sequence of attachment of half a dozen heterocyclic rings to the long chains of nucleic acids.

The pyrrole ring is the basic unit of the porphyrin system which occurs, for example, in chlorophyll and in haemoglobin. From this unit, we can have some idea of the importance as well as the complexity of heterocyclic system.

Objectives

After studying this unit you should be able to :

- write down the name of some heterocyclic compounds,
- list the natural sources of furan, pyrrole, thiophene and pyridine,
- discuss the basic properties of heterocyclic compounds,
- list the different methods for the preparation of furan, pyrrole, thiophene and pyridene, and
- explain the chemical properties of these compounds.

10.2 NOMENCLATURE

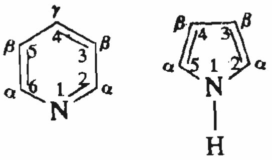
In this section, we shall discuss some of the rules adopted by IUPAC for naming heterocyclic compounds. The size of the ring as well as the numbers, kind and position of the hetero atom are specified by this system using a suitable prefix or suffix according to a set of rules given below:

i) The names of monocyclic compounds are derived by a prefix indicating the nature of the hetero-atom present, e.g. oxygen, oxa; sulphur, thia; nitrogen, aza. It may be noted that when the name contains two vowel a/e in a sequence then 'a' of the prefix is omitted.

ii) If the ring contains two or more identical hetero-atoms, the prefixes di, tri, etc. are used, e.g. dioxa, triaza. If the hetero atoms are different, oxygen takes precedence over sulphur and sulphur over nitrogen.

iii) The size of a five- and six-membered ring is indicated by the ending part, ole and ine, respectively.

iv) In monocyclic compounds, containing only one hetero atom, numbering starts with the hetro atom and proceeds in such a way that substituent gets the lowest numbered position and the numbering proceeds counter clockwise around the ring. In common names, Greek letters may also be used to designate ring position. The carbon adjacent to the hetero atom is the α-carbon, the next atom is β-carbon and then γ-carbon For example

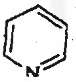


v) If the hetero atoms are different, then numbering starts at the atom cited first according to the rule in (ii) and proceeds round the ring in order of precedence.

vi) The state of hydrogenation is indicated by the prefix dihydro, tetrahydro, etc or by prefixing the name of the parent unsaturated compound with the symbol H preceded by a number indication the position of saturation.

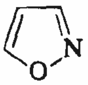
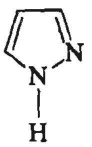
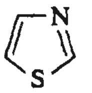
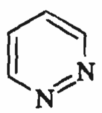
Nomenclature of some five and six membered unsaturated heterocyclic compounds is summarised in Table 10.1.

Table 10.1 : Naming of the five- and six- membered heterocyclic compounds

Name of the Hetero atom	Ring Size	Beginning part of the name	Ending part of the name	Example.
Nitrogen	5	aza	ole	aza + ole = azole, 
	6	aza	ine	aza + ine = azine, 
Oxygen	5	oxa	ole	oxa + ole = oxole, 
Sulphur	5	thia	ole	thia + ole = thiole, 

SAQ 1

Give the IUPAC of the following compounds.

a) 
b) 
, c) 
, d) 

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10.3 FIVE-MEMBERED HETEROCYCLIC COMPOUNDS

The three simplest five membered hetro cyclic compounds containing a hetero atom are furan (oxole), pyrrole (azole) and thiophene (thiole).

By looking at the structure of these compounds, you may say that they should have properties like those of conjugated dines. But these compounds do not show any such properties, rather these compounds are found to undergo electrophilic substitution reactions such as nitration, sulphonation, halogenation and the Friedel Crafts reaction with considerable ease. Thus, these compounds evidently have aromatic character. The heats of combustion of these compounds, are less than that of benzene 150.5 kJ mol^{-1}. The values are as follows: 66.8 kJ mol^{-1} for furan, 87.8 kJ mol^{-1} for pyrrole and 121.2 kJ mol^{-1} for thiophene.

In fact pyrrole, furan and thiophene are aromatic. These heterocycles are also planer pentagons consisting pf sp^2 hybridised carbon atoms (Fig. 10.1). Of the six π electrons required as per Hückel's rule for aromaticity the double account for four and the lone pair on the heteroatom for the remaining two.

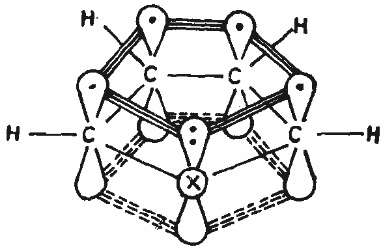


Fig. 10.1 : Orbital picture of Five-membered heterocycles.
X = O, S or N-H

10.3.1 Source

Pyrrole occurs in coal-tar and bone oil. It may be isolated from bone oil by washing the bone oil with dilute alkali to remove acidic substances, then with acid to remove strongly basic substances and finally by fractionating. Furan is extracted from coal tar and wood, especially pine-wood.

Bone Oil :
Product obtained by the destructive distillation of bones. It is a dark oily evil-smelling liquid.

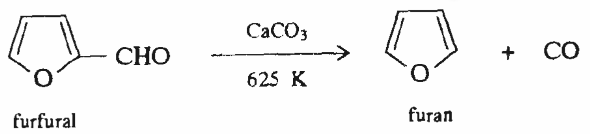
Thiophene occurs in coal tar and shale oil. Its boiling point (355 K) is close to that of benzene and hence it is difficult to separate from the benzene fraction, obtained from coal tar. Thiophene can be sulphonated more readily than benzene, and this property is used to separate the two compounds by repeatedly shaking benzene (from coal-tar) with cold concentrated sulphuric acid, so that water-soluble thiophenesulphonic acid is formed. When thiophenesulphonic acid is boiled with dilute hydrochloric acid or heated with steam. The $-SO_3H$ group is replaced by hydrogen to give thiophene.

Shale Oil :
Petroleum extracted from a kind of rock, known as shale. This rock is rich in hydrocarbons. Shale is subjected to destructive distillation where by the oil is released.

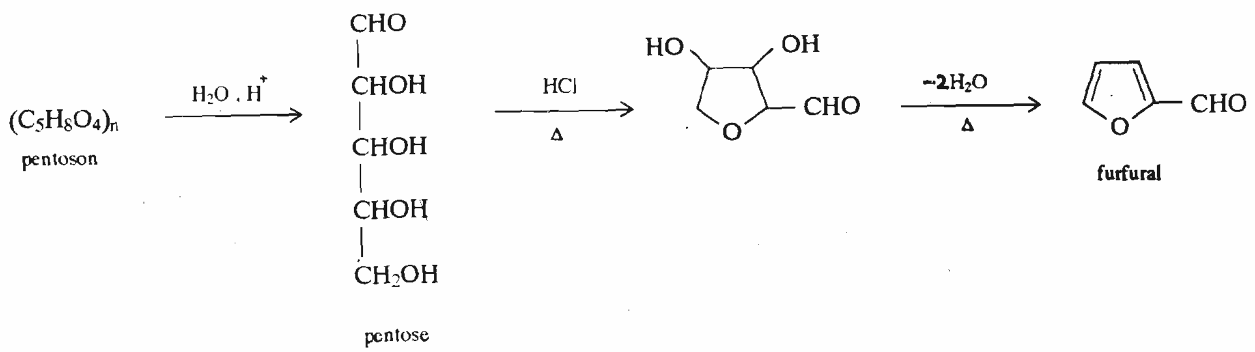
10.3.2 Preparation

As mentioned above, although pyrrole, furan and thiophene can be obtained from natural sources, the quantities are too small to fulfill our demands. The following method for large scale preparation of these compounds are, therefore, important.

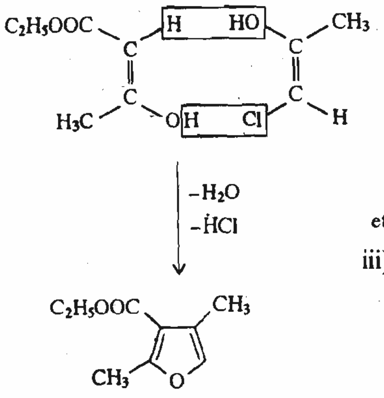
i) Furan is synthesised readily by decarbonylation (elimination of the CO group) of furfural.

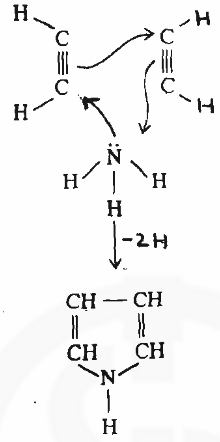


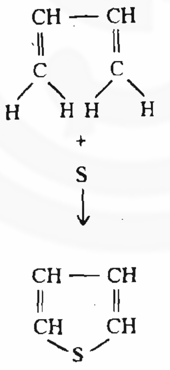
Furfural production is an interesting example of the use of industrial waste products. The hulls of rice and oats contain polymeric carbohydrates known as pentosans. Pentoses obtained from the polymeric material undergo subsequent dehydration and cyclisation to. yield furfural.

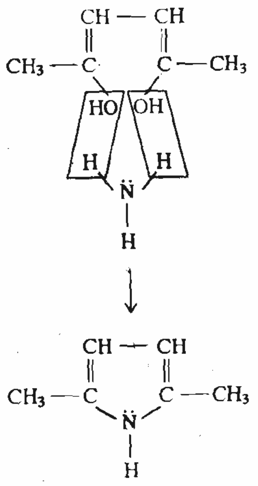


You can see that in many of the synthesis procedures, it is probable that ketonic compounds react through enol form. e.g.

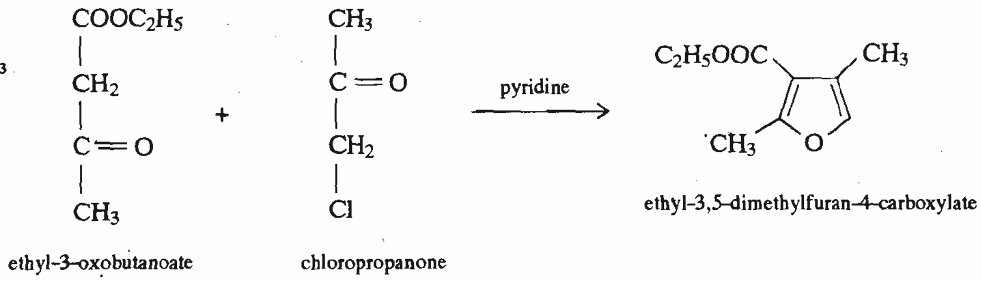




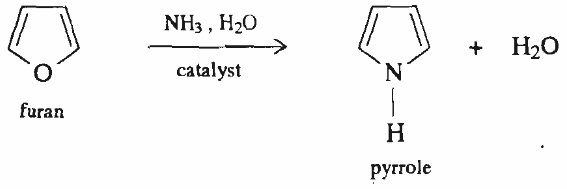




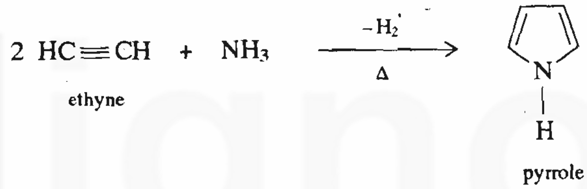
ii) An important method for laboratory preparation of substituted furans is the Fiest Benary synthesis in which a β-keto easter and an α-haloketone are reacted in presence of pyridine. For example, the enol form of ethyl 3-oxobutanoate (ethyl acetoacetate) and chloropropanone (chloroacetone) react as shown below to give ethyl 3, 5-dimethylfuran-4-carboxylate.



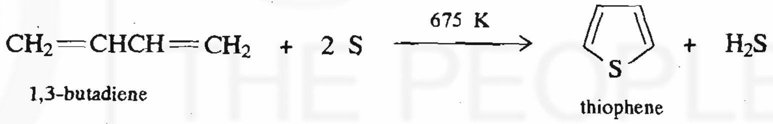
iii) Pyrrole is commercially produced from furan, ammonia and steam using alumina as catalyst at 675 K.



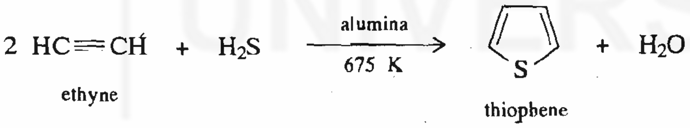
iv) Pyrrole is also produced when a mixture of ethyne and ammonia is passed through a red hot tube.



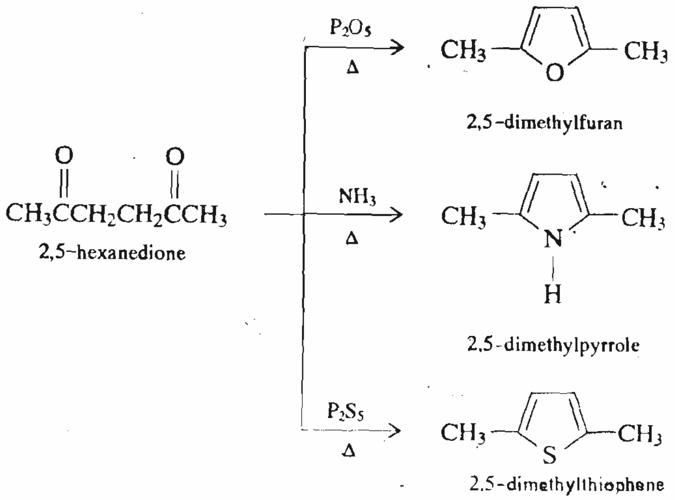
v) Thiophene is produced from C_4 hydrocarbons such as butane, butene or butadiene. Butadiene, formed initially through dehydrogenation of butane or butene by sulphur at 875 K is the probable precursor of thiophene.



vi) Thiophene is also produced commercially by passing a mixture of ethyne and H_2S over heated alumina,



vii) 1, 4-dicarbonyl compounds are useful starting materials for the synthesis of these heterocycles. If the dicarbonyl compound is heated with a dihydrating agent, e.g., P_2O_5, $ZnCl_2$ a furan is formed. If heated with a source of nitrogen or sulphur, pyrrole or thiophene are formed. These reactions are also known as Paal-Knorr methods.



10.3.3 Basic Character of Pyrrole

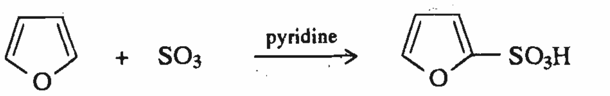
A lone pair of electrons on nitrogen is responsible for the basicity of nitrogen compounds. Pyrrole also has a lone pair of electrons on nitrogen and it, therefore, also acts as a base but it is a very weak base (K_b 2.5 × 10^{-14}). The reason for the weak basic character is that a lone pair of electrons on nitrogen is involved in the formation of the delocalised molecular orbital and is not available for the formation of a new bond with hydrogen. Furthermore, if a hydrogen is added to the nitrogen atom (through reaction with an acid), the resulting structure ceases to be aromatic. This makes the pyrrole cation extremely unstable. This is responsible for the absence of any significant basicity in pyrrole.

10.3.4 Reactions of Five-Membered Heterocyclic Compounds

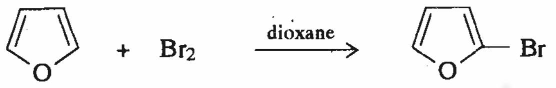
Five membered heterocyclic compounds undergo electrophilic substitution reduction, Diels-Alder and ring expansion reactions.

i) **Electrophilic Substitution Reaction**

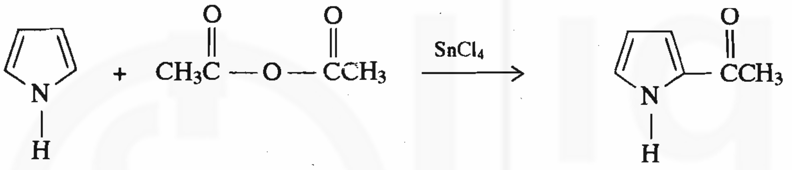
Like other aromatic compounds pyrrole, furan and thiophene commonly undergo electrophilic substitution reactions such as nitration, sulphonation, halogenation, Friedel Crafts acylation, e.g.,



2-furansulphonic acid



2-bromofuran

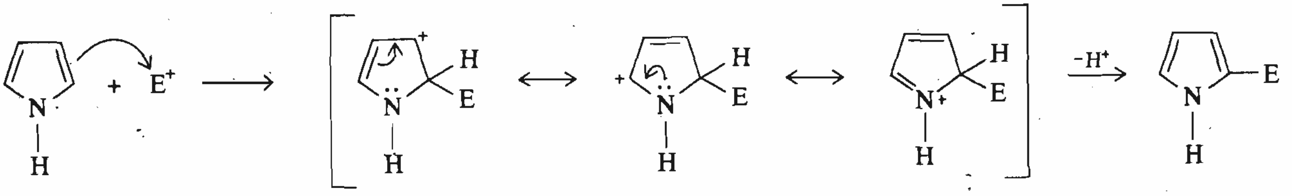


2-acetylpyrrole

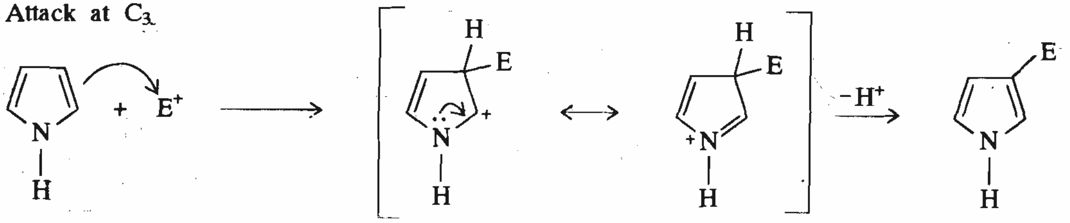
2-nitrothiophene

The attack of the electrophile in these heterocycles usually occurs at the C-2 (or β) position i.e., next to the hetero atom. In Unit 9 you have studied that you could account for orientation on the following basis : the controlling step is the attachment of electrophilic reagent to the aromatic ring, which takes place in such a way as to yield the most stable carbocation intermediate. Let us apply this approach to the reactions of pyrrole. Attack at position 2 of pyrrole yields a carbocation that is a hybrid of three structures, i.e., I, II and III whereas attack at position 3 yields carbocation which is a hybrid of only two structures, i.e., IV and V. The extra stabilisation of carbocation provided by structure III', in case of attack at position 2 makes positive charge at this position more stable. Thus, the attack at position 2 is favoured. Orientation of substitution in furan and thiophene can be accounted for in the same way.

Attack at C_2

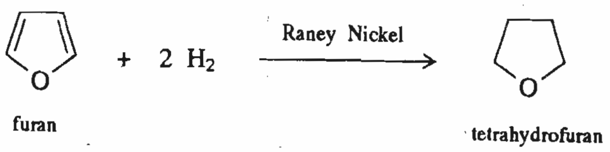


Attack at C_3

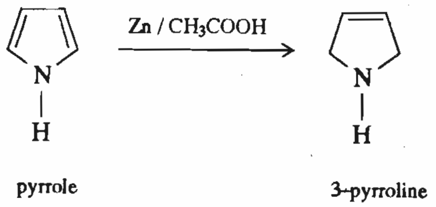


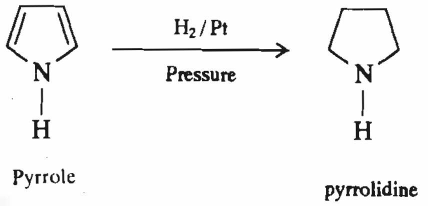
ii) Reduction

Tetrahydrofuran (THF) which is an industrially important solvent, results on catalytic reduction of furan over Raney Nickel catalyst.

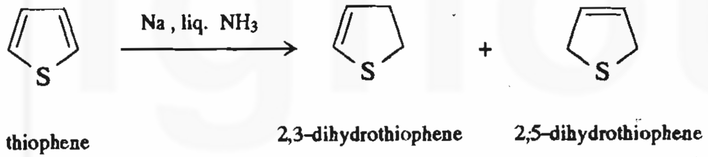


Mild reduction of pyrrole with zinc and ethanoic acid yields 3-pyrroline (2, 5 dihydro pyrrole). Catalytic reduction completely hydrogenates the ring system yielding pyrrolidine.

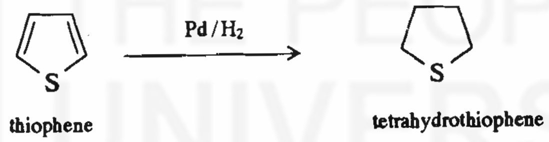




Birch reduction (with sodium in liquid ammonia) is used to obtain 2, 3 dihydrothiophene and 2, 5 dihydrothiophene.

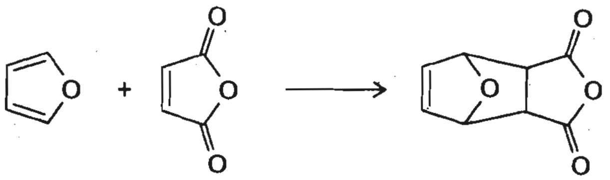


Tetrahydrothiophene is the product when a large amount of palladium is used as catalyst.

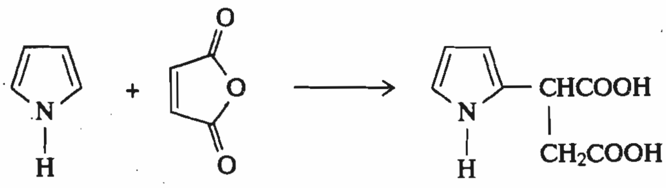


iii) Diels-Alder Reaction

Furan has sufficient diene character to undergo Diels-Alder reaction with maleic anhydride to form an addition product.



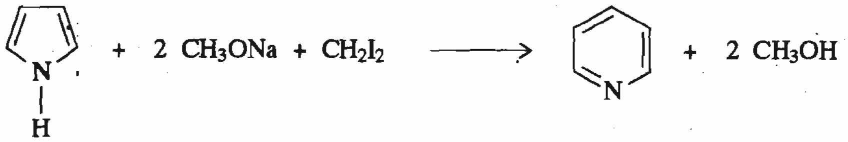
Pyrrole does not undergo Diels-Alder reaction on treatment with maleic anhydride. Rather a substitution product is obtained.



Thiophene does not undergo Diels-Alder reaction or substitution reaction with maleic anhydride.

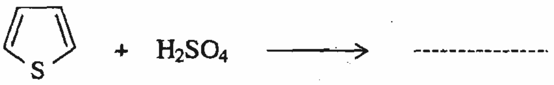
iv) **Ring Expansion Reaction**

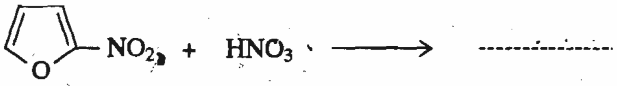
When treated with sodium methoxide and diiodomethane, pyrrole undergoes ring expansion forming pyridine.

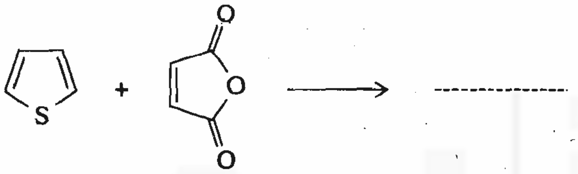


SAQ 2

Predict the product of the following reactions:







10.4 SIX-MEMBERED HETEROCYCLIC COMPOUNDS : PYRIDINE

Of the six membered aromatic heterocyclic compounds only nitrogen heterocycles, pyridine, is a stable aromatic compound. So in this unit, we shall study only pyridine.

Pyridine contains a six membered ring consisting of five carbon atoms and one nitrogen atom. The structure of pyridine has close resemblance to that of benzene. The molecule is planar with bond angles of 120°. All the five carbon atoms and the nitrogen atom are sp^2 hybridised. Each of the five carbon atoms and the nitrogen atom use their sp^2 orbital in forming bonds. Note that the lone pair of electrons in nitrogen atom is responsible for the basic character of pyridine. The six electrons in the unhybridised orbitals of carbon and nitrogen atoms are responsible for the formation of three double bonds (Fig. 10.2).

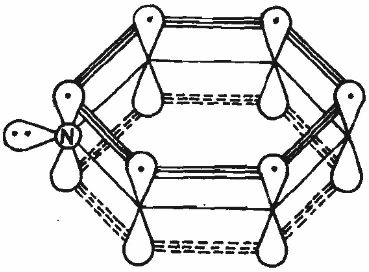


Fig. 10.2 : Orbital picture of pyridine.

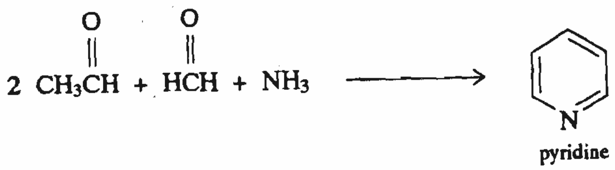
10.4.1 Source of Pyridine

Pyridine occurs in the light oil fraction of coal tar and in bone oil, and is a decomposition product of several alkaloids. Pyridine is obtained from light oil by treating it with dilute sulphuric acid. This dissolves pyridine and other basic substances. This solution is neutralised with sodium hydroxide and the liquid is repeatedly fractionated to get pyridine.

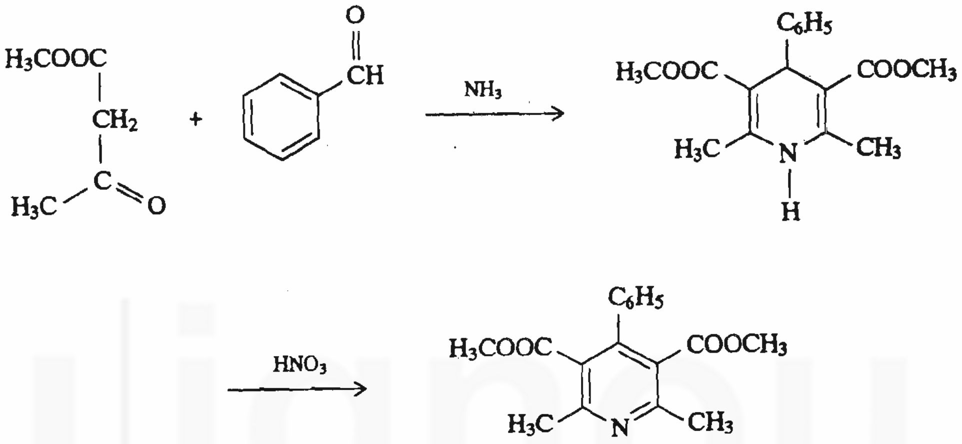
10.4.2 Preparation of Pyridine

Pyridine can be prepared by the following methods:

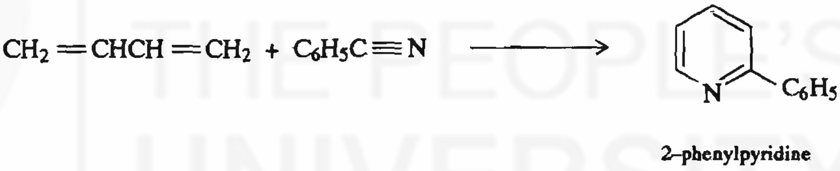
i) Pyridine is produced on a commercial scale by condensing methanal and ethanal in the presence of ammonia.



ii) In the laboratory pyridine is usually produced by the Hantzsch synthesis in which two moles of a β-keto easter combine with an aldehyde in presence of ammonia. The dihydropyridine produced initially is readily oxidised to aromatic product.



iii) Diels-Alder reaction is also used for the preparation of substituted pyridine using benzonitrile as the dienophile.



10.4.3 Basic Character of Pyridine

Pyridine is a base with $K_b = 2.3 \times 10^{-9}$. It has a pair of electrons in an sp^2 orbital which is available for sharing by a proton. In contrast to this, pyrrole ($K_b = 2.5 \times 10^{-14}$)can accept a proton only at the expense of its aromatic character. Hence, pyridine is much more basic than pyrrole.

Pyridine is, however, far less basic than the alkyl amines ($K_b = 10^{-14}$). This is so because the sp^2 hybridised nitrogen atom in pyridine is more electron attracting than the sp^3 hybridised nitrogen atom in aliphatic amines. Consequently, the lone pair is more tightly held in pyridine as compared to aliphatic amines and so is less available for protonation.

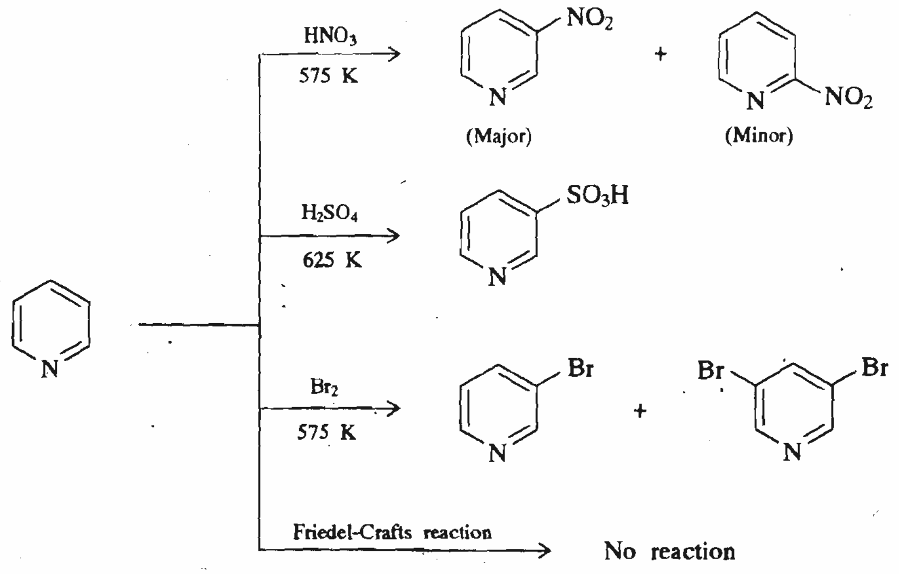
10.4.4 Reactions of Pyridine

Pyridine undergoes electrophilic and nucleophilic substitution reactions.

i) **Electrophilic Substitution**

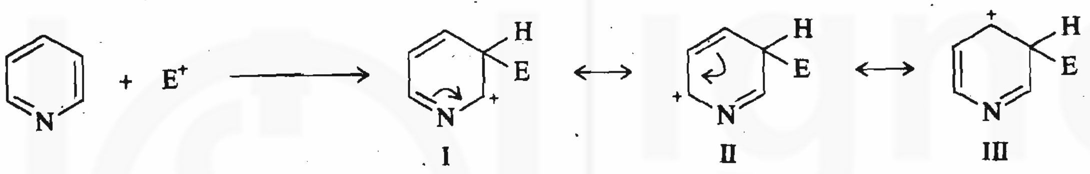
The pyridine ring is deactivated for electrophilic substitution as the electronegative nitrogen atom tends to attract the ring electrons towards itself. This effect is enhanced by protonation which occurs under the acidic reaction conditions.

It undergoes nitration, sulphonation and halogenation only under very vigorous conditions; these too in very poor yield. It does not undergo Friedel-Crafts reaction at all.

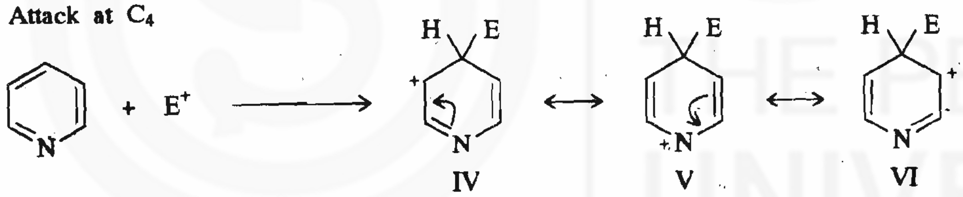


The substitution occurs chiefly at the 3-(or β) position as the transition state leading to substitution at this position is energetically more favourable; the intermediate positively charged species formed due to attack at 3-position is stabilised by three resonance structures, I to III.

Attack at C3



Attack at C4

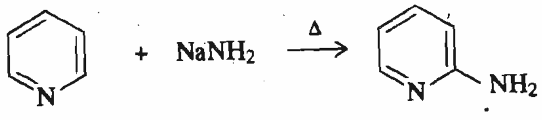


If the electrophile attacks at 4-position it results in a positive species which can be represented by three resonance structures, IV to VI. In one resonance structure (V) the positive charge is at the electronegative nitrogen atom. This greatly increases the energy of the transition state; hence, intermediate V is unstable. As a result, attack at 4-position is especially slow. No such structure is possible when the electrophile attacks 3-position, therefore substitution occurs predominantly at 3-position.

Attack at 2-position resembles attack at the 4-position just as *ortho* attack resembles *para* attack in the benzene series.

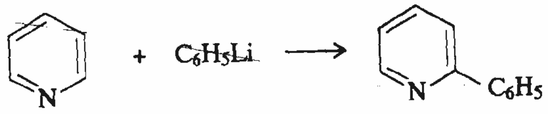
ii) Nucleophilic Substitution

Because of the presence of the electron withdrawing nitrogen atom, the reactivity of pyridine towards nucleophilic substitution is so great that even the powerfully basic hydride ion H^- can be displaced by the amide anion as in the following reaction.

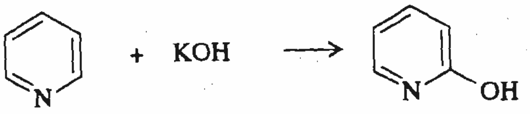


2-aminopyridine

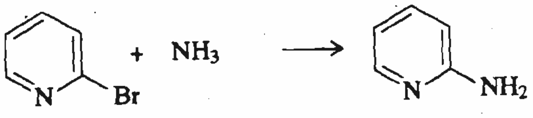
Other typical nucleophilic reactions of pyridine are :



2-phenylpyridine



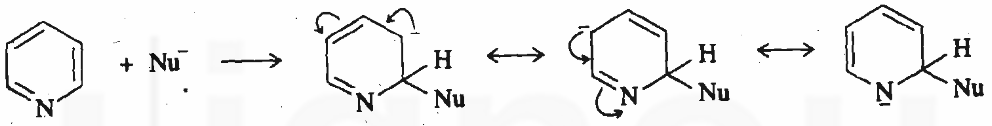
2-hydroxypyridine



2-aminopyridine

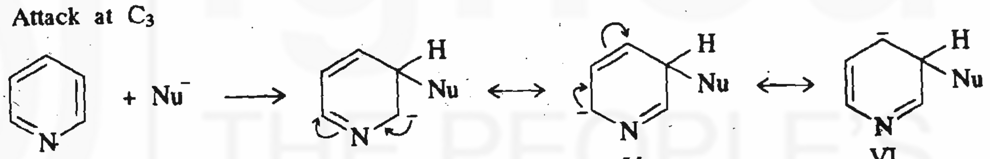
We have illustrated nucleophilic substitution at 2-position only, although such substitutiuon takes place to a large extent at 2- and 4-positions and not at 3-position. This can be explained through the following structures.

Attack at C_2



I II III

Attack at C_3

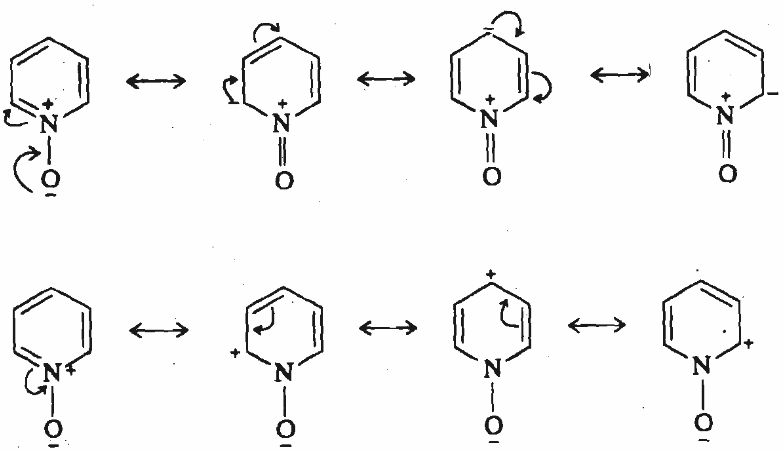


IV V VI

The attack of the nucleophile only at 2-position gives rise to resonance structures III where the negative charge resides on the electronegative nitrorgen atom; this is energetically favourable. We can apply similar arguments for the nucleophilic attack at 4-position. No such situation arises when nucleophile attacks 3-position. Thus the attack of the nucleophile occurs selectively on 2- and 4-positions of the pyridine ring.

iii) N-Oxides

Pyridine when treated with a peracid such as perethanoic acid or perbenzoic acid is converted into pyridine N-oxide. It can be depicted as a resonance hybrid of the following structures.



In some of the above structures, there is a decrease in electron density at various ring positions while in the others there is an increase in electron density. Thus pyridine N-oxide has been found to be more reactive towards both electrophilic and nucleophilic reagents than pyridine itself.

SAQ 3

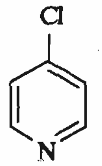
Predict the product(s) of the following reactions :

a) $2CH_3CHO + CH_2O + NH_3 \longrightarrow$

b) $C_5H_5N \xrightarrow[\text{reactions}]{\text{Friedel Crafts ;}}$

c) $C_5H_5N + Br_2 \longrightarrow$

d)



$+ \; NH_3 \longrightarrow$

10.5 SUMMARY

- Furan, pyrrole and thiophen and pyridine are important heterocycles.
- Heterocyclic compound generally occur in coal tar and bone oils.
- Pyrole acts as a weak base, its K_b value being 2.5×10^{-14}. Pyridine is a stronger base ($K_b 2.3 \times 10^{-9}$) than pyrrole but much weaker than aliphatic amine.
- Five-membered heterocyclic compounds can be prepared by the Paal-Knorr method and some other methods.
- Five membered heterocyclic compounds undergo electrophilic substitution reduction and Ring expansion reactions.
- Pyridine can be prepared by Hantzsch synthesis, Diels-Alder reaction and by condensing methanal and ethanal.
- The electrophilic substitution occurs predominantly at the 2-position.
- Pyridine undergoes electrophilic substitution as well as nucleophilic substitution reaction.
- Electrophilic substitution occurs predominantly at 3-position and nucleophilic substitution occurs prominantly at 2- and 4-positions of the pyridine ring.

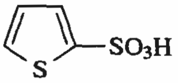
10.6 TERMINAL QUESTIONS

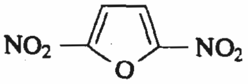
1) Arrange the following compounds in the increasing order of the basic strength.
   Pyridine, pyrrole and aliphatic amine
2) Write the structure for the product(s) obtained on treating furan with (a) maleic anhydride (b) catalytic reduction (c) $CH_3COONO_2^{+}$ (d) SO_3, pyridine.
3) Give the resonance structures for the intermediate in the reaction where electrophile E^+ attack on 2-position of pyridine.

10.7 ANSWERS

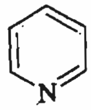
Self-Assessment Questions

1) a) 1, 2-Oxazole
   b) 1, 2-Diazole
   c) 1, 3-Thiazole
   d) 1, 2-Diazine

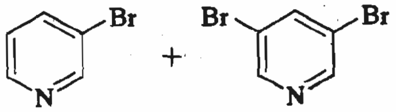
2) a) 

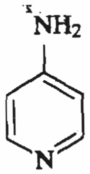
b) 

c) No reaction

3) a) 

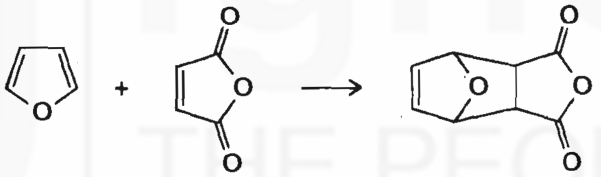
b) No reaction

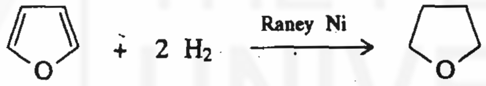
c) 

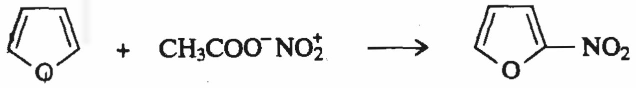
d) 

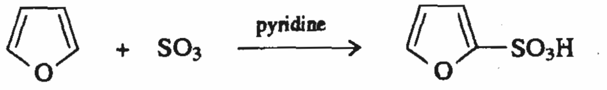
Terminal Questions

1) Aliphatic amine > pyridine > pyrrole

2) a) 

b) 

c) 

d) 

3)