UNIT 15

Hydrocarbons

SYLLABUS

Classification of hydrocarbons, alkanes and cycloalkanes.

Nomenclature, conformations of alkanes, cycloalkanes (ethane, propane, butane and cyclohexane), 3D structures and 2D projections (Sawhorse and Newmann)

Alkenes and alkynes—nomenclature, geometrical isomerism in alkenes, stability of alkenes, general methods of preparation, physical properties, chemical reactions reactivity, mechanism of electrophilic addition, reactions in alkenes, Markownikov's rule, peroxide effect, acidic character of alkynes, polymerization reactions.

Dienes—Concept of delocalization of electrons, addition reactions in dienes (1, 2 and 1, 4-addition),

Aromatic hydrocarbons—Benzene and its homologoues, Isomerism, nomenclature, sources of aromatic hydrocarbons (coal and petroleum), structure of benzene, resonance, delocalization, concept of aromaticity—an elementary idea. Chemical reactions of benzene— mechanism of electrophilic substitution reactions. Directive influence of substituents and their effect on reactivity, polynuclear hydrocarbons and their toxicity.

Petroleum and petrochemicals— Composition of crude oil, fractionation, uses of different fractions, quality of gasoline, LPG, CNG, Cracking and reforming, petrochemicals.

15.1. Introduction

The simplest organic compounds containing carbon and hydrogen only are called hydrocarbons. These are widely distributed in nature in the form of petroleum, natural gas and coal. Thus, *hydrocarbons are considered to be the parent organic compounds while all other compounds are thought to have been derived from them by replacement of one or more of their hydrogen atoms by appropriate functional groups.* In this unit, we shall discuss the different types of hydrocarbons, their structures, shapes, physical and chemical properties.

15.2. Classification of Hydrocarbons

On the basis of structure, hydrocarbons can be broadly divided into the following two types :

1. *Acyclic or open chain hydrocarbons*

2. *Cyclic or closed chain hydrocarbons*

1. Acyclic or open chain hydrocarbons. These compounds contain open chains of carbon atoms in their molecules. They are also called *aliphatic hydrocarbons*. These are further classified into the following three categories :

(*i*) Alkanes, (*ii*) Alkenes and (*iii*) Alkynes

This classification is primarily based upon the type of the carbon-carbon bonds present in their molecules. For example,

An alkane *has only carbon-carbon single bonds.* For example,

CH_3-CH_3 $CH_3-CH_2-CH_3$

Ethane Propane

$CH_3-CH_2-CH_2-CH_3$

Butane

An alkene *has one carbon-carbon double bond*. For example,

$CH_2=CH_2$ $CH_2-CH=CH_2$

Ethene Propene

$CH_3-CH=CH-CH_3$

But-2-ene

(*formerly* 2-butene)

An alkyne *has one carbon-carbon triple bond.* For example,

$CH\equiv CH$ $CH_3-C\equiv CH$

Ethyne Propyne

$CH_3-C\equiv C-CH_3$

But-2-yne

(*formerly 2-butyne*)

2. Cyclic or closed chain hydrocarbons. These compounds contain closed chains or rings of carbon atoms in their molecules. They are further divided into the following two clases :

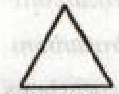
(*a*) *Alicyclic hydrocarbons*

(*b*) *Aromatic hydrocarbons*

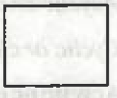
(*a*) **Alicyclic hydrocarbons.** Hydrocarbons which contain a ring of three or more carbon atoms and have properties similar to those of aliphatic hydrocarbons are called **alicyclic hydrocarbons.** These are further divided into the following three categories ?

(*i*) *cycloalkanes* (*ii*) *cycloalkenes* and (*iii*) *cycloalkynes*

(**i**) **Cycloalkanes.** *Saturated alicyclic hydrocarbons in which all the carbon atoms are joined by single covalent bonds are called* **cycloalkanes.** For example,

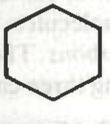


Cyclopropane



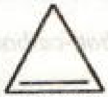
Cyclobutane

Cyclopentane



Cyclohexane

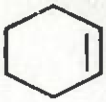
(*ii*) **Cycloalkenes.** *Unsaturated alicyclic hydrocarbons which contain one carbon-carbon double bond are called cycloalkenes.* For example,



Cyclopropene

Cyclobutene

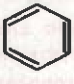
Cyclopentene



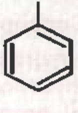
Cyclohexene

(*iii*) **Cycloalkynes.** *Unsaturated alicyclic hydrocarbons which contain one carbon-carbon triple bond are called* **cycloalkynes.** For example, cyclopentyne, cyclohexyne, cycloheptyne, cyclooctyne, cyclononyne etc. However, cyclopentyne and cyclohexyne are highly strained and unstable, cyclooctyne is strained but somewhat stable while cyclononyne and higher cycloalkynes are unstrained and hence are quite stable.

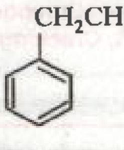
(*b*) **Aromatic hydrocarbons – Arenes.** *Hydrocarbons and their alkyl, alkenyl and alkynyl derivatives which contain one or more benzene rings either fused or isolated in their molecules are called* **aromatic hydrocarbons.** They are also called **arenes (aromatic alkenes).** Further, since these compounds resemble benzene in almost all of their properties, they are also called **benzenoid compounds.** For example,



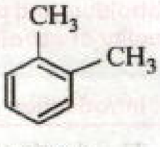
Benzene



Toluene



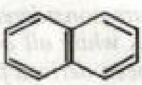
Ethylbenzene



o-Xylene

Arenes may also contain two or more isolated or fused rings. For example,

Diphenyl



Naphthalene

Anthracene

The above classification of hydrocarbons is summarized in Fig. 15.1.

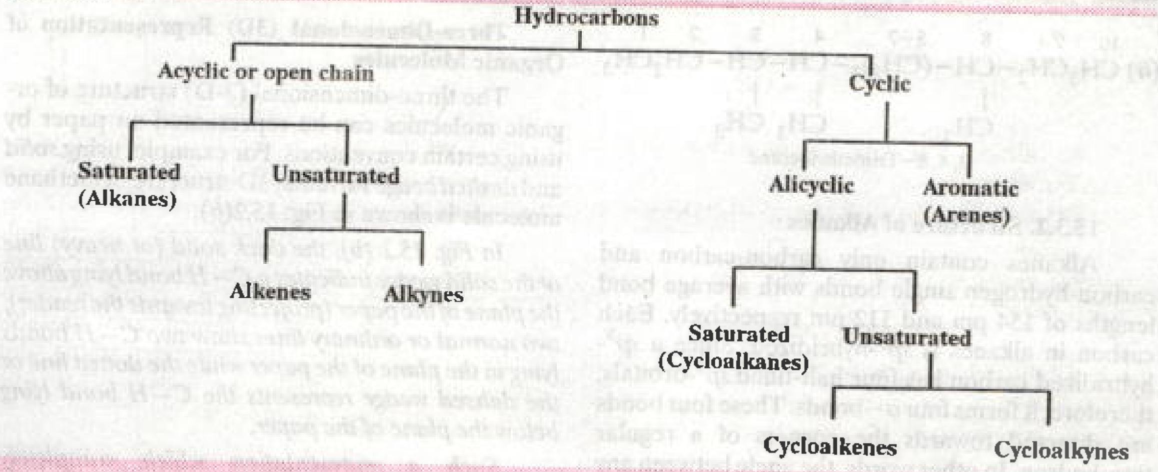


FIGURE 15.1. Classification of hydrocarbons.

PART I

ALKANES AND CYCLOALKANES

15.3. Alkanes

We have discussed above that saturated hydrocarbons can be either acyclic or cyclic. *The acyclic saturated hydrocarbons are called* **paraffins** (Latin : *parum* = little, *affinis* = affinity) since they are relatively unreactive towards most of the reagents such as acids, bases, oxidising and reducing agents. However, under drastic conditions, *i.e.*, at high temperature and pressure alkanes do undergo different types of reactions like halogenation, nitration, sulphonation, pyrolysis etc.

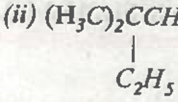
15.3.1. Nomenclature of Alkanes

In the IUPAC system, they are called *alkanes*. Their general formula is C_nH_{2n+2} where n = 1, 2, 3, ... etc. The nomenclature of alkanes has already been discussed in unit 14. However, for purpose of recapulation, the IUPAC names of some alkanes is given below :

No. of carbon atoms	Formula	IUPAC name
1	CH_4	Methane
2	C_2H_6	Ethane
3	C_3H_8	Propane
4	C_4H_{10}	Butane
5	C_5H_{12}	Pentane
6	C_6H_{14}	Hexane
10	$C_{10}H_{22}$	Decane
11	$C_{11}H_{24}$	Undecane
12	$C_{12}H_{26}$	Dodecane
13	$C_{13}H_{28}$	Tridecane
14	$C_{14}H_{30}$	Tetradecane
20	$C_{20}H_{42}$	Eicosane
30	$C_{30}H_{62}$	Triacontane

EXAMPLE 15.1. *Assign IUPAC name to the following structures :*

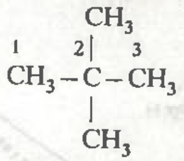
(i) $(H_3C)_4C$ *(ii)*



$(H_3C)_2\underset{\underset{C_2H_5}{|}}{C}CH_2C(CH_3)_3$

(N.C.E.R.T.)

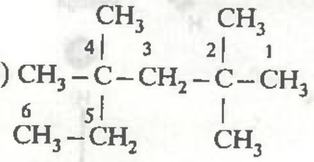
Solution. *(i)*



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

2, 2–Dimethylpropane

(ii)



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

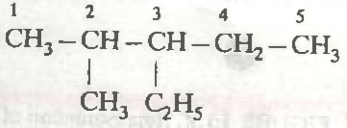
2, 2, 4, 4–Tetramethylhexane

EXAMPLE 15.2. *Write the structures for the alkanes having the following IUPAC names.*

(i) 3-Ethyl-2-methylpentane

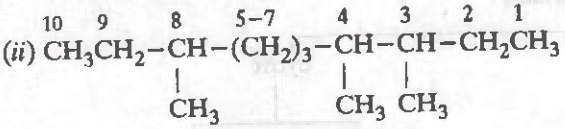
(ii) 3, 4, 8-Trimethyldecane. (N.C.E.R.T.)

Solution. *(i)*



$\overset{1}{CH_3}-\underset{\underset{CH_3}{|}}{\overset{2}{CH}}-\underset{\underset{C_2H_5}{|}}{\overset{3}{CH}}-\overset{4}{CH_2}-\overset{5}{CH_3}$

3–Ethyl–2–methylpentane



$$(ii)\ \overset{10}{C}H_3\overset{9}{C}H_2-\underset{\underset{CH_3}{|}}{\overset{8}{C}H}-\overset{5-7}{(CH_2)_3}-\underset{\underset{CH_3}{|}}{\overset{4}{C}H}-\underset{\underset{CH_3}{|}}{\overset{3}{C}H}-\overset{2}{C}H_2\overset{1}{C}H_3$$

3, 4, 8–Trimethyldecane

15.3.2. Structure of Alkanes

Alkanes contain only carbon-carbon and carbon-hydrogen single bonds with average bond lengths of 154 pm and 112 pm respectively. Each carbon in alkanes is sp^3-hybridized. Since a sp^3-hybridized carbon has four half-filled sp^3-orbitals, therefore, it forms four σ–bonds. These four bonds are directed towards the corners of a regular tetrahedron. In other words, the angle between any two adjacent bonds is 109° 28′ (*tetrahedral angle*). Thus, *alkanes have tetrahedral structures.*

Let us now discuss the structure of the simplest alkane, *i.e.*, methane (CH_4). In methane molecule, carbon lies at the centre of the tetrahedron while the four hydrogens are present at the corners or vertices of the regular tetrahedron. This implies that each face of the tetrahedron is an equilateral triangle and has three bonds as shown in Fig. 15.2 (*a*).

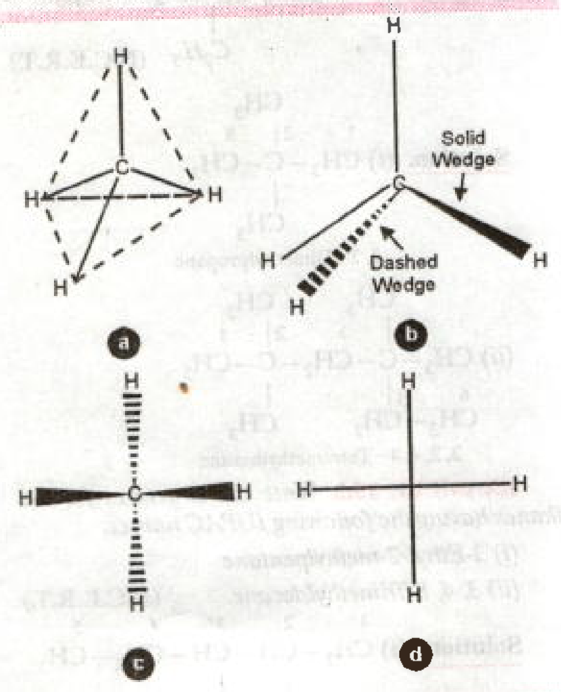


FIGURE 15.2. Representation of methane molecule (a) tetrahedral (b) three-dimensional, *i.e.*, 3D (c) another 3D view (d) two-dimensional, *i.e.*, 2D or Fisher Projection formula.

Three-Dimensional (3D) Representation of Organic Molecules

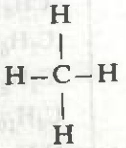
The three-dimensional (3-D) structure of organic molecules can be represented on paper by using certain conventions. For example, using *solid* and *dashed bedge* formula, 3D structure of methane molecule is shown in Fig. 15.2(*b*).

In Fig. 15.2 (b), the thick solid (or heavy) line or the solid wedge indicates a C – H bond lying above the plane of the paper (projecting towards the reader), two normal or ordinary lines show two C – H bonds lying in the plane of the paper while the dotted line or the dahsed wedge represents the C – H bond lying below the plane of the paper.

Such a representation which completely describes the actual positions of various atoms of a molecule in space is called a **spatial formula** or **three dimensional** *i.e.*, **3 D-structure.**

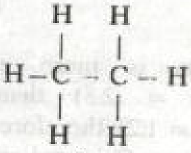
Projection Formulae. To represent three dimentional structures on a two-dimensional surface, (*i.e.* a paper), *Emil Fischer*, a German Chemist in 1891 introduced a simple method. The three-dimensional structure is oriented in such a manner that the *vertical bonds are directed away from you and horizontal bonds are directed towards you* as shown in Fig. 15.2(*c*). The molecule is then projected using a ray of light in the plane of the paper in form of a cross. The carbon atom lies at the centre of the cross but is not shown. Such planar representations of three dimensional structures are called **Fischer Projection Formulae.** Thus, Fig. 15.1(*d*) represents the two-dimensional (*i.e.* 2 D) or Fischer Projection formula of methane molecule. Besides Fischer projection formula, Newmann projection and Sawhorse projection formulae have also been used. Details of these representations will be discussed in **Sec. 15.5.**

Sometimes in the planar representation of molecules, the carbon atom at the centre is included as shown below :



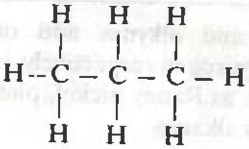
$$H-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-H$$

Such a representation is usually called as **graphic** or **displayed formula** or **line bond diagrams.** Although such formulae do not reveal the tetrahedral geometry of the molecule, they are commonly used for most purposes since they are easy to draw. However, it must be remembered that a graphic formula is just a simplified form of the real structure shown in Fig. 15.2 (*b*). Similarly, we can represent ethane (C_2H_6) and propane (C_3H_8) by the following graphic formulae :



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

Ethane



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

Propane

Sometimes, **condensed formulae**, instead of graphic formulae, are also used. For example,

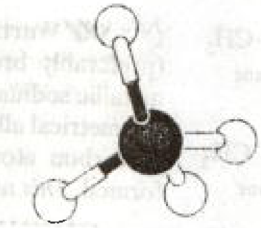
CH_3-CH_3 Ethane $CH_3-CH_2-CH_3$ Propane

ADD TO YOUR KNOWLEDGE

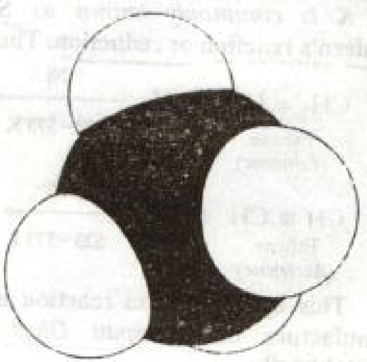
Molecular Models

Molecular models are extensively used for a better visualization and perception of 3D structures of organic molecules. These are made up of wood, plastic or metal and are commercially available. These are mainly of three types : (*i*) *Framework models* (*ii*) *Ball and stick models* and (*iii*) *Space filling models* as shown below :

Framework Model



Ball and Stick Model



Space Filling Model

In **framework models**, the atoms themselves are not shown but only the bonds connecting the atoms of a molecule are shown. *This type of model is used only to study the pattern of bonds in a molecule while ignoring the size of the atoms.*

In the **ball-and-stick model** both the atoms and bonds are shown. Whereas ball represent the atoms but sticks denote the bonds. Unsaturated compounds containing C = C and C ≡ C bonds are better represented using springs instead of sticks.

In **space filling models**, bonds are not shown but emphasis is laid on the relative size of each atom depending upon its *van der Waals' radius.* In other words, these models convey the volume occupied by each atom in the molecule.

15.3.3. Methods of Preparation of Alkanes

We have discussed above that petroleum is a valuable source for the large scale preparation of a number of hydrocarbons including alkanes. But many alkanes are not available from petroleum or we might need only a small amount of a pure alkane for our laboratory use. In such cases, we usually prepare them by laboratory methods of preparation. Some of the laboratory methods of preparation of alkanes are discussed below :

From Unsaturated Hydrocarbons. *The process of addition of hydrogen to an unsaturated compound in presence of a catalyst is called hydrogenation or reduction.*

Alkenes and alkynes add one and two molecules of hydrogen respectively, in presence of a catalyst such as Raney nickel, platinum or palladium to form alkanes.

eQ. $$\underset{\text{Alkene}}{RCH=CHR'} + H_2 \xrightarrow[\text{or Pt or Pd}]{\text{Raney Ni}} \underset{\text{Alkane}}{RCH_2-CH_2R'}$$

dQ $$\underset{\text{Alkyne}}{RC\equiv CR'} + 2\,H_2 \xrightarrow[\text{or Pt or Pd}]{\text{Raney Ni}} RCH_2-CH_2R'$$

(where R and R' may be H or same or different alkyl groups)

With platinum, palladium and Raney* nickel hydrogenation proceeds smoothly and quantitatively at ordinary temperatures and pressures. However, with ordinary nickel relatively higher temperatures (*ca.* 523–573 K) are often required. *This hydrogenation of unsaturated hydrocarbons using ordinary nickel at a temperature of about 523–573 K is commonly known as* **Sabatier and Sendern's reaction or reduction.** Thus,

eQ $$\underset{\substack{\text{Ethene}\\ (\textit{Ethylene})}}{CH_2=CH_2} + H_2 \xrightarrow[523-573\text{ K}]{\text{Ni}} \underset{\text{Ethane}}{CH_3-CH_3}$$

dQ $$\underset{\substack{\text{Ethyne}\\ (\textit{Acetylene})}}{CH\equiv CH} + 2H_2 \xrightarrow[523-573\text{ K}]{\text{Ni}} \underset{\text{Ethane}}{CH_3-CH_3}$$

This hydrogenation reaction is used in the manufacture of *Vanaspati Ghee* from edible vegetable oils.

✓ **From Alkyl halides.** Alkyl halides can be converted into alkanes by any one of the following methods :

(i) Through Grignard reagents. Alkyl halides especially, bromides and iodides react with magnesium metal in presence of dry ethoxyethane (diethyl ether) to form alkylmagnesium halides. These are commonly known as **Grignard reagents** after the name of their discoverer *Victor Grignard* who was awarded the Nobel Prize in Chemistry in 1912 for the discovery of these versatile reagents.

$$\underset{\text{Alkyl halide}}{R-X} + Mg \xrightarrow{\text{Dry ether}} \underset{\text{Grignard reagent}}{R-Mg-X}$$

e.g., $$\underset{\substack{\text{Bromoethane}\\ (\textit{Ethyl bromide})}}{CH_3CH_2-Br} + Mg \xrightarrow{\text{Dry ether}} \underset{\substack{\text{Ethylmagnesium}\\ \text{bromide}}}{CH_3CH_2MgBr}$$

Since carbon is more electronegative (Electronegativity = 2.5) than magnesium (Electronegativity = 1.2), therefore, C–Mg bond is quite polar. Hence, Grignard reagents readily react with compounds containing *active hydrogens* such as water, acids, alcohols, ammonia, amines, etc. to form alkanes. For example,

GQ $$\underset{\substack{\text{Ethylmagnesium}\\ \text{bromide}}}{CH_3CH_2MgBr} + H_2O \longrightarrow \underset{\text{Ethane}}{CH_3CH_3} + Mg(OH)Br$$

Q
Q $$\underset{\substack{\text{Methyl–}\\ \text{magnesium}\\ \text{iodide}}}{CH_3MgI} + \underset{\text{Methanol}}{CH_3OH} \longrightarrow \underset{\text{Methane}}{CH_4} + Mg(OCH_3)I$$

✓ **Wurtz reaction.** When an alkyl halide (preferably bromide or iodide) is treated with metallic sodium in presence of dry diethyl ether, a symmetrical alkane, containing double the number of carbon atoms present in the alkyl group, is formed. *This reaction is called* **Wurtz reaction.**

$$\underset{\text{Alkyl halide}}{R-\boxed{X + 2Na + X}-R} \xrightarrow{\text{Dry ether}} \underset{\text{Alkane}}{R-R} + 2NaX$$

e.g., $$\underset{\substack{\text{Bromomethane}\\ (\textit{Methyl bromide})}}{CH_3-\boxed{Br + 2Na + Br}-CH_3} \xrightarrow{\text{Dry ether}} \underset{\text{Ethane}}{CH_3-CH_3} + 2NaBr$$

$$\underset{\substack{\text{Iodoethane}\\ (\textit{Ethyl iodide})}}{CH_3CH_2-\boxed{I + 2Na + I}-CH_2CH_3} \xrightarrow{\text{Dry ether}} \underset{\text{Butane}}{CH_3CH_2-CH_2CH_3} + 2NaI$$

Thus, *Wurtz reaction is a convenient method for the preparation of symmetrical alkanes (R–R), i.e., alkanes containing an even number of carbon atoms.*

✓*Raney nickel is an active form of nickel and is obtained by treating Ni–Al alloy with NaOH when Al dissolves leaving nickel in the finely divided state.

However, if two different alkyl halides are used to prepare an alkane with odd number of carbon atoms, a mixture of three alkanes is actually produced. This is due to the reason that the two alkyl halides in addition to reacting with each other also react amongst themselves giving a mixture of three alkanes as illustrated below :

$$\underset{\substack{\text{Iodomethane}\\ (\textit{Methyl iodide})}}{CH_3-I} + 2Na + \underset{\substack{\text{Iodoethane}\\ (\textit{Ethyl iodide})}}{I-CH_2CH_3} \xrightarrow{\text{Dry ether}} \underset{\text{Propane}}{CH_3-CH_2CH_3} + 2NaI$$

$$CH_3-I + 2Na + I-CH_3 \xrightarrow{\text{Dry ether}} \underset{\text{Ethane}}{CH_3-CH_3} + 2NaI$$

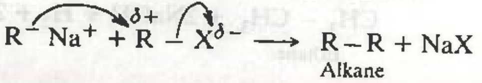
$$CH_3CH_2-I + 2Na + I-CH_2CH_3 \xrightarrow{\text{Dry ether}} \underset{\text{Butane}}{CH_3CH_2-CH_2CH_3} + 2NaI$$

The boiling points of these alkanes are very close and hence they cannot be separated by fractional distillation. It is because of this drawback that *Wurtz reaction is used for the synthesis of only symmetrical alkanes and not for the preparation of unsymmetrical alkanes, i.e., alkanes containing odd number of carbon atoms.*

Mechanism. Two different mechanisms have been suggested for the Wurtz reaction.

(*a*) *Through intermediate formation of an organometallic compound*

$$R-X + 2Na \longrightarrow \underset{\text{Alkyl sodium}}{R^-Na^+} + NaX$$



$$R^- Na^+ + \overset{\delta+}{R}-X^{\delta-} \longrightarrow \underset{\text{Alkane}}{R-R} + NaX$$

(*b*) *Through intermediate formation of free radicals*

$$R-X + Na \longrightarrow \underset{\text{Free radical}}{\dot{R}} + Na^+X^-$$

$$2\dot{R} \longrightarrow \underset{\text{Alkane}}{R-R}$$

(iii) Corey-House reaction. Wurtz reaction does not give good yields of unsymmetrical alkanes, *i.e.*, alkanes containing odd number of carbon atoms. However, Corey-House reaction can be used to prepare both symmetrical and unsymmetrical alkanes in good yields. In this reaction, the alkyl halide is first treated with lithium metal in dry ether to form alkyllithium which is then allowed to react with cuprous iodide to yield lithium dialkyl copper. Lithium dialkyl copper thus obtained on subsequent treatment with a suitable alkyl halide gives the desired alkane.

$$\underset{\text{Alkyl halide}}{R-X} + 2Li \xrightarrow{\text{Dry ether}} \underset{\text{Alkyllithium}}{R-Li} + LiX$$

$$2R-Li + CuI \longrightarrow \underset{\substack{\text{Lithium dialkyl-}\\ \text{copper}}}{R_2CuLi} + 2LiI$$

$$R_2CuLi + R'-X \longrightarrow \underset{\text{Alkane}}{R-R'} + \underset{\text{Alkyl copper}}{RCu} + LiX$$

(where R and R′ may be same or different alkyl groups)

e.g.
$$\underset{\text{Ethyl bromide}}{CH_3-CH_2-Br} + 2Li \xrightarrow{\text{Dry ether}} CH_3-CH_2-Li + LiBr$$

$$\underset{\text{Ethyllithium}}{2CH_3-CH_2-Li} + CuI \longrightarrow \underset{\text{Lithium diethylcopper}}{(CH_3-CH_2)_2CuLi} + LiI$$

$$(CH_3-CH_2)_2CuLi + \underset{n-\text{Propyl bromide}}{CH_3CH_2-CH_2-Br} \xrightarrow{\text{Dry ether}} \underset{n-\text{Pentane}}{CH_3CH_2CH_2CH_2CH_3} + \underset{\text{Ethylcopper}}{CH_3CH_2Cu} + LiBr$$

(iv) Reduction of Alkyl halides. Alkanes can also be prepared by the reduction of alkyl halides preferably bromides and iodides. This reduction can be carried out in number of different ways as discussed below :

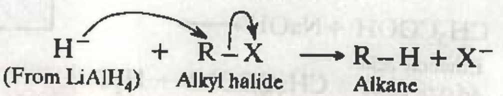
(*a*) *Reduction by dissolving metals such as Zn and CH_3COOH or HCl, Zn and NaOH or Zn – Cu couple and alcohol.*

$$\underset{\text{Alkyl halide}}{R-X} \xrightarrow{\text{Zn/HCl}} R-H + HX$$

e.g.,
$$\underset{2-\text{Bromobutane}}{CH_3CH_2-CHBr-CH_3} \xrightarrow{\text{Zn/HCl}} \underset{\text{Butane}}{CH_3CH_2-CH_2CH_3} + HBr$$

The reduction occurs by transfer of electrons and not by nascent hydrogen as originally believed.*

(*b*) *Reduction by chemical reagents such as $LiAlH_4$, $NaBH_4$ and Ph_3SnH.*



$$\underset{(\text{From LiAlH}_4)}{H^-} + \underset{\text{Alkyl halide}}{R-X} \longrightarrow \underset{\text{Alkane}}{R-H} + X^-$$

---

*(*i*) $Zn \rightarrow Zn^{2+} + 2e^-$ (*ii*) $R-X + e^- \rightarrow \dot{R} + X^-$ (*iii*) $\dot{R} + e^- \longrightarrow R:^-$ (*iv*) $R:^- + C_2H_5OH \rightarrow R-H + C_2H_5O^-$.

1° and 2° alkyl halides are readily reduced to alkanes by $LiAlH_4$ but 3° alkyl halides mainly undergo dehydrohalogenation. On the other hand, $NaBH_4$ reduces 2° and 3° alkyl halides but not 1° whereas triphenyltin hydride (Ph_3SnH) reduces all the three types of alkyl halides.

(ii) *Catalytic hydrogenolysis* implies cleavage of a sigma bond with H_2 in presence of a catalyst. The best catalyst is Pd – C but Raney Ni has also been effective provided it is used in large excess.

$$\underset{\text{Bromoethane}}{CH_3CH_2-Br} + H_2 \xrightarrow{Pd-C} \underset{\text{Ethane}}{CH_3-CH_3} + HBr$$

(iii) *Reduction with HI and red P.* Alkyl iodides are readily reduced to the corresponding alkanes by heating with conc. HI in presence of red P at 423 K.

$$\underset{\substack{\text{Iodoethane}\\ (\textit{Ethyl iodide})}}{CH_3CH_2-I} + HI \xrightarrow{423\text{ K/red P}} \underset{\text{Ethane}}{CH_3-CH_3} + I_2$$

The purpose of red phosphorus is to remove the iodine liberated in the reaction, otherwise it would react with the alkane to give back the alkyl iodide.

$$2P + 3I_2 \longrightarrow 2PI_3$$

10 **3. From carboxylic acids.** Alkanes can be prepared from carboxylic acids by the following two methods :

(*i*) Decarboxylation, and
(*ii*) Kolbe's electrolytic method

(i) Decarboxylation.

The process of removal of a molecule of CO_2 from an organic compound is called decarboxylation.

When a carboxylic acid is heated with soda-lime (NaOH + CaO in the ratio 3 : 1) at about 630 K, a molecule of CO_2 is lost and an alkane with one carbon atom less than the carboxylic acid is formed.

$$\underset{\text{Carboxylic acid}}{R-COOH} + NaOH \longrightarrow R-COONa + H_2O$$

$$R-COONa + NaOH \xrightarrow{CaO,\ 630\text{ K}} \underset{\text{Alkane}}{R-H} + Na_2CO_3$$

e.g.,
$$\underset{\substack{\text{Ethanoic acid}\\ (\textit{Acetic acid})}}{CH_3COOH} + NaOH \longrightarrow \underset{\text{Sod. acetate}}{CH_3COONa} + H_2O$$

$$CH_3COONa + NaOH \xrightarrow{CaO,\ 630\text{ K}} \underset{\text{Methane}}{CH_4} + Na_2CO_3$$

Similarly,
$$\underset{\substack{\text{Propanoic acid}\\ (\textit{Propionic acid})}}{CH_3CH_2COOH} + 2NaOH \xrightarrow[630\text{ K}]{CaO} \underset{\text{Ethane}}{CH_3-CH_3} + Na_2CO_3 + H_2O$$

NaOH alone could have been used in the above reaction but soda- lime is preferred because of the following two reasons :

(*i*) CaO permits the reaction to be carried out at a relatively higher temperature to ensure complete decarboxylation.

(*ii*) CaO keeps NaOH dry because it is quite *hygroscopic* (absorbs moisture from air) in nature.

In the laboratory, methane is prepared by heating a mixture of sodium acetate and soda lime (in the ratio of 1 : 4) in a copper tube (Fig. 15.3.) and the methane produced is collected by the downward displacement of water.

10 **(ii) Kolbe's electrolytic method.** When a concentrated aqueous solution of the sodium or potassium salt of a mono carboxylic acid is electrolysed, an alkane is produced as shown below :

$$2\,RCOONa + 2H_2O \xrightarrow{\text{Electrolysis}} \underset{\text{Alkane}}{R-R} + 2NaOH + H_2 + 2CO_2$$

e.g.,
$$\underset{\text{Sod. ethanoate}}{2\,CH_3COONa} + 2H_2O \xrightarrow{\text{Electrolysis}} \underset{\text{Ethane}}{CH_3-CH_3} + 2NaOH + H_2 + 2CO_2$$

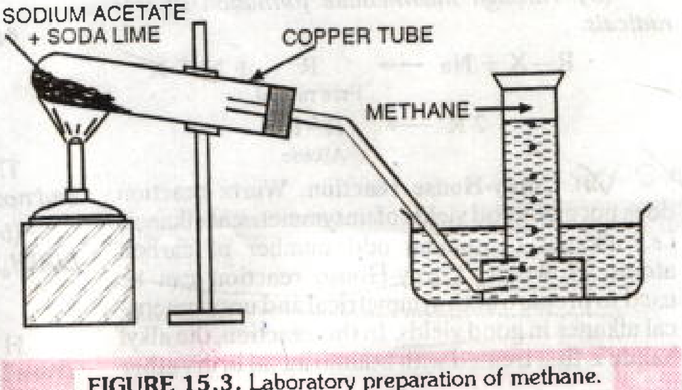


FIGURE 15.3. Laboratory preparation of methane.

This reaction is believed to occur through the following steps :

$$2\,CH_3COONa \xrightarrow{\text{Ionization}} 2\,CH_3COO^- + 2Na^+$$

$$2\,H_2O \overset{\text{Ionization}}{\rightleftharpoons} 2OH^- + 2H^+$$

At anode : $2\,CH_3COO^- - 2e^- \longrightarrow$

$$\underset{(unstable)}{[2\,CH_3COO]} \longrightarrow \underset{\text{Ethane}}{CH_3-CH_3} + 2CO_2$$

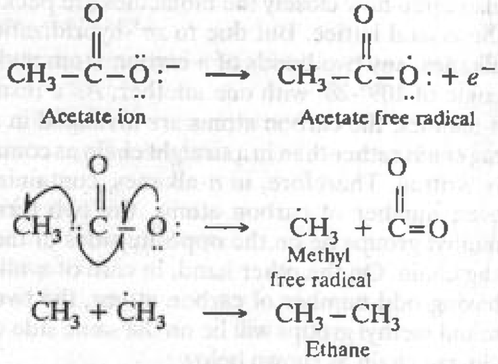
At cathode : Since the discharge potential of H^+ ions is lower than that of Na^+ ions, therefore, H^+ ions are preferentially discharged to produce H_2 while Na^+ ions remain in solution. Thus,

$$2H^+ + 2e^- \longrightarrow [2H] \longrightarrow H_2$$

Kolbe's reaction laid the foundation for the development of organo-electrochemistry.

Limitation. Like Wurtz raction, this is also used to prepare only alkanes with even number of carbon atoms and not alkanes with odd number of carbon atoms.

Mechanism. Kolbe's reaction occurs by free radical mechanism as shown below :



$$CH_3-\overset{O}{\overset{\|}{C}}-\ddot{O}:^- \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-\dot{O}: + e^-$$

$$CH_3-\overset{O}{\overset{\|}{C}}-\ddot{O}: \longrightarrow \dot{C}H_3 + \overset{O}{\overset{\|}{C}}=O$$

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

4. By the action of water on beryllium and aluminium carbide. Both these carbides on treatment with water methane.

$$\underset{\substack{\text{Beryllium}\\\text{carbide}}}{Be_2C} + 4\,H_2O \longrightarrow \underset{\text{Methane}}{CH_4} + 2\,Be(OH)_2$$

$$\underset{\substack{\text{Aluminium}\\\text{carbide}}}{Al_4C_3} + 12\,H_2O \longrightarrow 3\,CH_4 + 4\,Al(OH)_3$$

15.3.5. Physical Properties of Alkanes

The physical properties of alkanes such as boiling point, melting point, density and solubility depend upon the *intermolecular forces of attraction*. Since alkanes are almost non-polar molecules, therefore, these intermolecular forces of attraction are of *van der Waals type* which mainly depend upon the shape and hence the structure of the molecule. The magnitude of these forces of attraction depend upon the surface area of contact between adjacent molecules. Greater the surface area, stronger are the van der Waal's forces of attraction. In the light of these arguments, let us now discuss the variation in physical properties of alkanes.

1. Boiling points. Amongst the straight chain alkanes, the first four members (C_1-C_4) are gases, the next thirteen are liquids (C_5-C_{17}) and the higher members (C_{18} onwards) are colourless waxy solids.

The boiling points of straight chain alkanes increase fairly regularly with increase in their molecular mass. On the average, the boiling point generally increases by 20 – 30K for the addition of each carbon atom or a CH_2 group to the chain. The difference in boiling points is, however, greater for the lower homologues than for the higher homologues.

This regular increase in the boiling points of straight chain alkanes with increase in the carbon content (Fig. 15.4) is due to a corresponding *increase in the molecular size and hence the surface area of the molecules. As a result, the magnitude of the van der Waals forces of attraction goes up and hence the boiling point increases accordingly.*

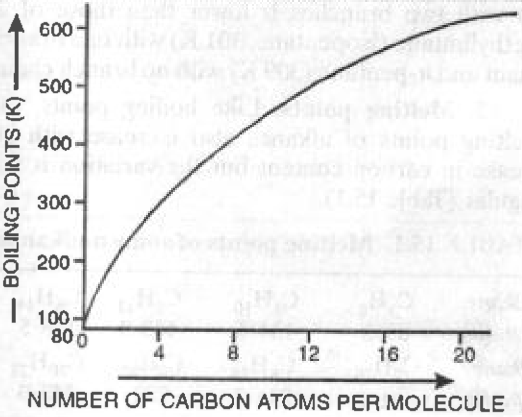
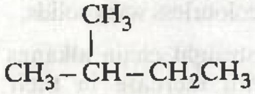


FIGURE 15.4. Increase in the boiling points of n-alkanes with the increase in the number of carbon atoms per molecule of the homologous series.

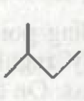
Amongst isomeric alkanes, *the branched chain isomer has invariably the lower boiling point than the corresponding n-alkane.* This is due to the reason that with branching the shape of the molecule tends to approach that of a sphere. *As a result, the surface area of the branched isomer decreases. Due to lesser surface area of these molecules, the van der Waals* *forces of attraction operating between their molecules become comparatively weaker* and hence lesser amount of energy is required to overcome them. As a result, *the boiling points of branched chain isomers are lower than those of the corresponding n-alkanes.*

$CH_3CH_2CH_2CH_2CH_3$ or 

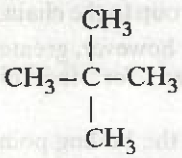
n–Pentane (*no branching*)
(*b.p.* = 309 K, *m.p.* = 143·3 K)



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

or 

Isopentane (*one branch*)
(*b.p.* = 301 K, *m.p.* = 113·1 K)



$CH_3-C(CH_3)_2-CH_3$

or 

Neopentane (*two branches*)
(*b.p.* = 282.5 K, *m.p.* = 256·4 K)

Further, it has been observed that greater the branching, lower is the boiling point of the branched isomer. For example, the boiling point of 2, 2-dimethylpropane (neopentane, 282.5 K) with two branches is lower than those of 2-methylbutane (isopentane, 301 K) with one branch chain and *n*-pentane (309 K) with no branch chain.

2. Melting points. Like boiling points, the melting points of alkanes also increase with increase in carbon content but the variation is not regular (Table 15.1).

TABLE 15.1. Melting points of some n-alkanes

Alkane	C_3H_8	C_4H_{10}	C_5H_{12}	C_6H_{14}
m.p. (K)	85·3	134·6	143·3	178·5
Alkane	C_7H_{16}	C_8H_{18}	C_9H_{20}	$C_{10}H_{22}$
m.p. (K)	182·4	216·2	222	243·3

When the melting points of *n*-alkanes are plotted against the number of carbon atoms present in them, a sawtooth pattern (Fig. 15.5.) is obtained.

From Fig. 15.4, it is clear that alkanes with even number of carbon atoms have higher melting points than those with an odd number of carbon atoms. This property is commonly known as **alternation effect** and can be explained as follows :

The melting point of a substance depends not only upon the size and shape of the molecules but also upon how closely the molecules are packed in the crystal lattice. But due to sp^3-hybridization in alkanes, any two bonds of a carbon atom make an angle of 109°-28′ with one another. As a result, in *n*-alkanes, the carbon atoms are arranged in a *zig-zag chain* rather than in a straight chain as commonly written. Therefore, in *n*-alkanes, containing an even number of carbon atoms, the two terminal methyl groups lie on the opposite sides of the zig-zag chain. On the other hand, in case of *n*-alkanes having odd number of carbon atoms, the two terminal methyl groups will lie on the same side of the zig-zag chain as shown below :

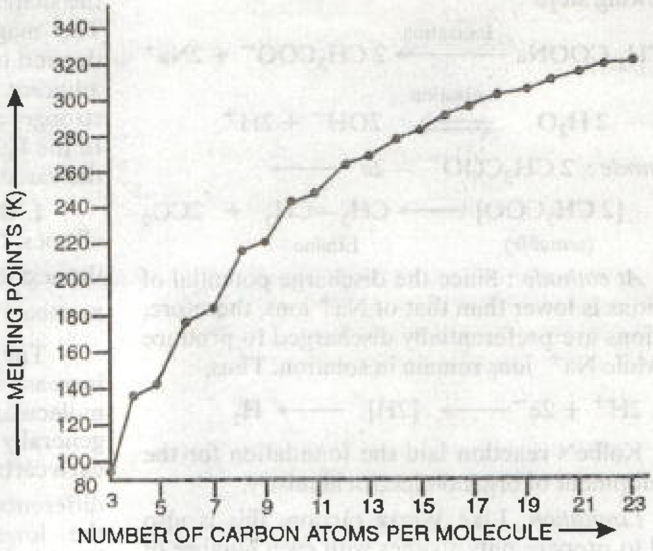
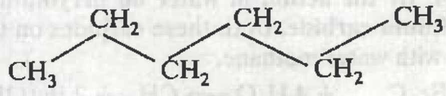
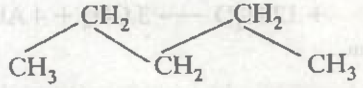


FIGURE 15.5. Increase in the melting points of n-alkanes with the increase in the number of carbon atoms per molecule of the homologous series.



n–Hexane
(*Even number of carbon atoms, higher melting point*)



(*Odd number of carbon atoms, lower melting point*)

Thus, it is clear that *n*-alkanes with even number of carbon atoms are more symmetrical than those containing odd number of carbon atoms and hence pack closely in the crystal lattice. In other words, vander Waals forces of attraction are much stronger in *n*-alkanes having even number of carbon atoms than those having odd number of carbon atoms. Therefore, *n–alkanes with even number of carbon atoms have much higher melting points than the next lower n-alkane with odd number of carbon atoms.* For example, *n*-butane with four (even) number of carbon atoms melts at 138 K while propane with three (odd) number of carbon atoms melts at 85.3 K. Similarly, *n*- hexane melts at 178.5 K while the next lower alkane, *i.e.*, *n*–pentane melts at 143.3 K.

It may be noted that such an alternation effect is not observed in boiling points since in the liquid state, the conformations of the molecules are not fixed but keep on changing as a result of collisions.

3. Solubility. *'Like dissolves like' is the general rule of solubility.* In the light of this rule, *alkane which are predominantly non-polar are insoluble in polar solvents such as water, alcohol etc. but are highly soluble in non-polar solvents such as petroleum ether, benzene, carbon tetrachloride etc.*

4. Density. The densities of alkanes increase with increase in the molecular masses till the limiting value of about 0.8 g cm^{-3} is reached. This means that *all alkanes are lighter than water.*

15.3.6. Chemical Reactions of Alkanes

The reactivities of various hydrocarbons are directly related to their structures. We have already discussed in Unit 14 that alkanes are saturated hydrocarbons. These contain only C – C and C – H, σ-bonds. Since these bonds are quite strong, *alkanes are the least reactive of all the hydrocarbons. It is because of this relative inertness that alkanes are also called* **paraffins** (Latin : *parum* = little, *affinis* = affinity or reactivity).

Some important chemical reactions of alkanes are discussed below :

1. Substitution reactions

> ***A reaction in which a hydrogen atom of a hydrocarbon is replaced by an atom or a group of atoms is called a substitution reaction.***

Alkanes, because of having only C – C and C – H sigma bonds undergo only substitution reactions. Some important substitution reactions of alkanes are discussed below.

(a) Halogenation of Alkanes. Halogenation of an alkane is carried out by treating it with a suitable halogen in presence of ultraviolet light or by heating the reaction mixture to 520 – 670 K.

The order of reactivity of different halogens in these reactions is :

$$F_2 > Cl_2 > Br_2 > I_2$$

(i) Chlorination. During chlorination of methane, all the four hydrogen atoms are replaced one by one to form a mixture of products. For example,

$$\underset{\text{Methane}}{CH_4} + Cl_2 \xrightarrow[520-670\ K]{h\nu\ \text{or}} \underset{\substack{\text{Chloromethane}\\ (\textit{Methyl chloride})}}{CH_3Cl} + HCl$$

$$\underset{\text{Chloromethane}}{CH_3Cl} + Cl_2 \xrightarrow[520-670\ K]{h\nu\ \text{or}} \underset{\substack{\text{Dichloromethane}\\ (\textit{Methylene chloride})}}{CH_2Cl_2} + HCl$$

$$\underset{\substack{\text{Dichloro–}\\ \text{methane}}}{CH_2Cl_2} + Cl_2 \xrightarrow[520-670\ K]{h\nu\ \text{or}} \underset{\substack{\text{Trichloromethane}\\ (\textit{Chloroform})}}{CHCl_3} + HCl$$

$$\underset{\substack{\text{Trichloro–}\\ \text{methane}}}{CHCl_3} + Cl_2 \xrightarrow[520-670\ K]{h\nu\ \text{or}} \underset{\substack{\text{Tetrachloromethane}\\ (\textit{Carbon tetrachloride})}}{CCl_4} + HCl$$

(ii) Brominaion. Bromine reacts with alkanes in a similar manner but less readily.

$$\underset{\text{Ethane}}{CH_3 - CH_3} + Br_2 \xrightarrow[520-670\ K]{h\nu} \underset{\text{Bromoethane}}{CH_3 - CH_2 - Br} + HBr$$

(iii) Iodination. The reaction of iodine with alkanes is reversible because the hydrogen iodide formed as a by-product is a moderate reducing agent and hence reduces the iodoalkane back to alkane.

$$CH_4 + I_2 \rightleftharpoons \underset{\substack{\text{Iodomethane}\\ (\textit{Methyl Iodide})}}{CH_3 - I} + HI$$

Thus, direct iodination of alkanes cannot be brought about. However, the iodination can be carried out in presence of an oxidising agent such as iodic acid (HIO_3), nitric and (HNO_3) or mercuric oxide (HgO) which converts HI to I_2 as it is formed :

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

$$2HNO_3 + 2HI \longrightarrow 2H_2O + 2NO_2 + I_2$$

$$HgO + 2HI \longrightarrow HgI_2 + H_2O$$

(iv) Fluorination of alkanes is too vigorous to be controlled under ordinary conditions. Furthermore, fluorination brings about extensive rupture of C – C and C – H bonds leading to a mixture of products. Thus, fluorination of alkanes with pure fluorine is of little practical use. However, fluorina-

tion of alkanes can be carried out by diluting fluorine with an inert gas such as nitrogen or argon. Alternatively, alkyl fluorides are more conveniently prepared indirectly by heating suitable chloroalkanes with inorganic fluorides such as AsF_3, SbF_3, AgF, Hg_2F_2 etc. For example,

$$\underset{\text{Chloroethane}}{2CH_3CH_2-Cl} + Hg_2F_2 \longrightarrow \underset{\text{Fluoroethane}}{2CH_3CH_2-F} + Hg_2Cl_2$$

This reaction is called **Swarts reaction.**

ADD TO YOUR KNOWLEDGE

Even monohalogenation of higher alkanes (propane and higher members) gives a mixture of all the possible isomeric haloalkanes. For example,

$$\underset{\text{Propane}}{CH_3-CH_2-CH_3} \xrightarrow[298\text{ K}]{Cl_2,\ h\nu} \underset{\text{1-Chloropropane (45\%)}}{CH_3-CH_2-CH_2-Cl} + \underset{\text{2-Chloropropane (55\%)}}{CH_3-CHCl-CH_3}$$

The relative amounts of these isomeric haloalkanes, however, depends upon

(*i*) nature of halogen (Cl_2 or Br_2) and

(*ii*) number and type of hydrogens (1°, 2° or 3°) being substituted.

In general, the ease of substitution of various hydrogens follows the sequence :

3° > 2° > 1° but their relative rates vary with the nature of the halogen. For example with Cl_2, the relative rate of substitution of 3°, 2° and 1° hydrogens at 298 K is 5 : 3·8 : 1 while with Br_2, it is 1600 : 82 : 1 at 400 K.

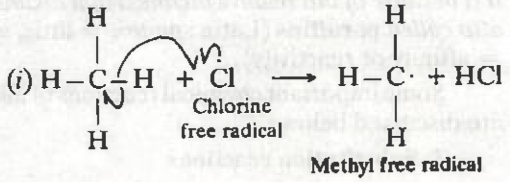
Mechanism of halogenation. Halogenation of alkanes occurs by a *free radical mechanism.* Each free radical reaction consists of three steps :

Let us illustrate the mechanism of halogenation of alkanes by considering the chlorination of methane.

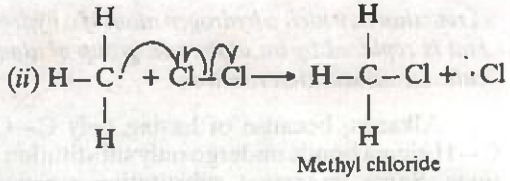
(*a*) **Chain initiation.** When a mixture of CH_4 and Cl_2 is heated to 520-670 K in dark or is subjected to UV light at room temperature, Cl_2 absorbs energy and undergoes homolytic fission producing chlorine free radicals.

$$Cl-Cl \xrightarrow[\text{Homolytic fission}]{520-670\text{ K or UV light}} \underset{\text{Chlorine free radical}}{2\dot{C}l}$$

(*b*) **Chain propagation.** Each propagation step consists of two reactions. In the first reaction, the ·Cl attacks the CH_4 molecule and abstracts a hydrogen atom forming $\cdot CH_3$ and a molecule of HCl as shown in reaction (*i*). In the second reaction, $\cdot CH_3$ thus produced reacts further with a molecule of Cl_2 forming a molecule of methyl chloride and another ·Cl as shown in reaction (*ii*). The newly formed ·Cl reacts with another molecule of CH_4 (reaction (*i*)) to produce another molecule of HCl and another $\cdot CH_3$. This $\cdot CH_3$ can again repeat reaction (*ii*) and so on. Thus, the sequence of reactions depicted in equations (*i*) and (*ii*) is repeated over and over again and the chain gets propagated. In other words, a single photon of light absorbed by Cl_2 can bring about the conversion of a large number of CH_4 molecules into CH_3Cl. Such reactions are called **chain reactions.**



$$(i)\ \mathrm{H-\overset{H}{\underset{H}{C}}-H + \dot{C}l \longrightarrow H-\overset{H}{\underset{H}{C}}\cdot + HCl}$$



$$(ii)\ \mathrm{H-\overset{H}{\underset{H}{C}}\cdot + Cl-Cl \longrightarrow H-\overset{H}{\underset{H}{C}}-Cl + \cdot Cl}$$

When sufficient amount of methyl chloride has been formed, the ·Cl produced in reaction (*ii*) has a greater chance of colliding with a molecule of CH_3Cl rather than a molecule of CH_4. If such a collision occurs, a new free radical ($\cdot CH_2Cl$) is produced (reaction (*iii*)) which may subsequently react with Cl_2 producing a molecule of CH_2Cl_2 (reaction (*iv*)) and another ·Cl. This process continues till all the hydrogen atoms of methane are replaced by halogen atoms (reactions (*v*), (*vi*), (*vii*) and (*viii*)).

(*iii*) $CH_3Cl + \cdot Cl \longrightarrow \cdot CH_2Cl + HCl$

(*iv*) $\cdot CH_2Cl + Cl_2 \longrightarrow CH_2Cl_2 + \cdot Cl$

(*v*) $CH_2Cl_2 + \cdot Cl \longrightarrow \cdot CHCl_2 + HCl$

(*vi*) $\cdot CHCl_2 + Cl_2 \longrightarrow CHCl_3 + \cdot Cl$

(*vii*) $CHCl_3 + \cdot Cl \longrightarrow \cdot CCl_3 + HCl$

(*viii*) $\cdot CCl_3 + Cl_2 \longrightarrow CCl_4 + \cdot Cl$

(*c*) **Chain termination.** The chain reactions discussed above may come to a halt if two of the same or different free radicals combine amongst themselves without producing new free radicals. Some of the possible chain termination steps are :

$$\cdot Cl + \cdot Cl \longrightarrow Cl-Cl$$

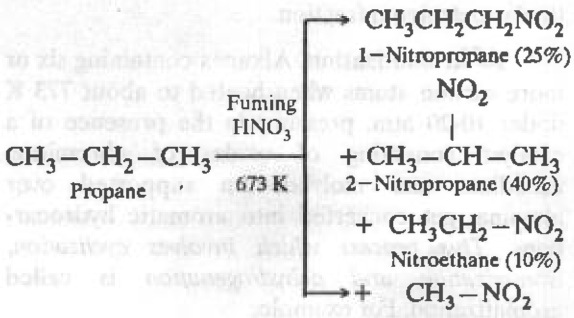
$$\cdot CH_3 + \cdot CH_3 \longrightarrow CH_3-CH_3$$

$$\cdot CH_3 + \cdot Cl \longrightarrow CH_3-Cl$$

B **Nitration.** *The process of replacement of a hydrogen atom by a nitro* ($-NO_2$) *group is called nitration.* At ordinary temperatures, alkanes do react with HNO_3. However, when a mixture of an alkane and fuming HNO_3 vapours are heated at 423–673K under pressure (*vapour phase nitration*), alkanes undergo nitration giving a mixture of nitroalkanes resulting through cleavage of carbon-carbon bonds. For example,

$$\underset{\text{Methane}}{CH_3-H} + \underset{(Fuming)}{HNO_3} \longrightarrow \underset{\substack{\text{Nitromethane}\\(low\ yield)}}{CH_3-NO_2} + H_2O$$

$$\underset{\text{Ethane}}{CH_3-CH_3} \xrightarrow[673\text{ K}]{\text{Fuming }HNO_3} \underset{\text{Nitroethane (80\%)}}{CH_3CH_2-NO_2} + \underset{\text{Nitromethane (20\%)}}{CH_3-NO_2}$$



$$\underset{\text{Propane}}{CH_3-CH_2-CH_3} \xrightarrow[673\text{ K}]{\text{Fuming }HNO_3} \underset{\text{1-Nitropropane (25\%)}}{CH_3CH_2CH_2NO_2} + \underset{\text{2-Nitropropane (40\%)}}{CH_3-\overset{NO_2}{\overset{|}{C}H}-CH_3} + \underset{\text{Nitroethane (10\%)}}{CH_3CH_2-NO_2} + \underset{\text{Nitromethane (25\%)}}{CH_3-NO_2}$$

+ Other oxidation products (CO_2, NO_2, H_2O etc.)

The order of reactivity of different hydrogens in this reaction is : 3° > 2° > 1°.

Mechanism. The reaction occurs by the following *free radical mechanism* :

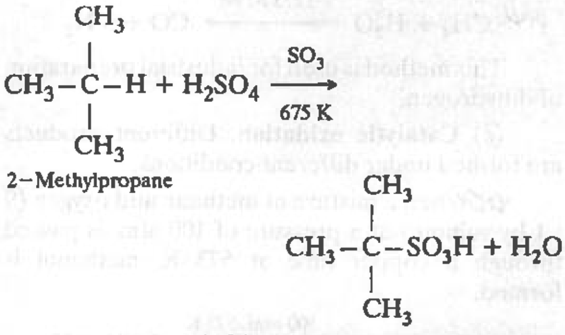
$$HO-NO_2 \xrightarrow[\text{Homolytic fission}]{423-673\text{ K}} H\dot{O} + N\dot{O}_2$$

$$R-H + OH \longrightarrow R\cdot + H_2O$$

$$R\cdot + NO_2 \longrightarrow \underset{\text{Nitroalkane}}{R-NO_2}$$

Sulphonation. *Substitution of a hydrogen atom of an alkane by sulphonic acid group* ($-SO_3H$) *is called sulphonation.* **It is carried out by heating an alkane with fuming sulphuric acid ($H_2SO_4 + SO_3$) at 675–725 K. Branched chain and higher *normal* alkanes (containing six or more carbon atoms) undergo sulphonation to give alkanesulphonic acids. The ease of substitution is 3° > 2° > 1°.**

$$\underset{n\text{-Hexane}}{CH_3(CH_2)_4CH_3} + H_2SO_4 \xrightarrow[675\text{ K}]{SO_3} \underset{n\text{-Hexanesulphonic acid}}{CH_3(CH_2)_4CH_2-SO_3H} + H_2O$$



$$\underset{\text{2-Methylpropane}}{CH_3-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-H} + H_2SO_4 \xrightarrow[675\text{ K}]{SO_3} \underset{\text{2-Methylpropane-2-sulphonic acid}}{CH_3-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-SO_3H} + H_2O$$

Mechanism. Like nitration, sulphonation also occurs by a *free- radical mechanism*.

$$HO-SO_3H \xrightarrow[\text{Homolytic fission}]{673\text{ K}} H\dot{O} + \dot{S}O_3H$$

$$R-H + \dot{O}H \longrightarrow \dot{R} + H_2O$$

$$R\cdot + \cdot SO_3H \longrightarrow \underset{\text{Alkanesulphonic acid}}{R-SO_3H}$$

OG **II. Oxidation. Some important oxidation reactions of alkanes are as follows :**

(*a*) Complete oxidation or combustion. On heating, alkanes readily burn in air or oxygen producing CO_2 and H_2O. This process is called combustion.

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O; \quad \Delta_cH^\circ = -890 \text{ kJ mol}^{-1}$$

$$2CH_3-CH_3 + 7O_2 \longrightarrow 4CO_2 + 6H_2O; \quad \Delta_cH^\circ = -1555 \text{ kJ mol}^{-1}$$

Since the process of combustion is accompanied by liberation of large amount of heat, therefore, alkanes which are the constituents of LPG, gasoline, kerosene oil, and diesel are widely used as fuels.

(*b*) **Incomplete combustion.** (*i*) If the combustion of alkanes is carried out in limited supply of air or oxygen, CO is produced along with unburnt carbon in the form of carbon black or soot.

$$\underset{(limited)}{CH_4 + 3O_2} \longrightarrow 2CO + 4H_2O$$

$$\underset{(limited)}{CH_4 + O_2} \longrightarrow \underset{\text{Carbon black}}{C} + H_2O$$

Carbon black is used in the preparation of black inks, paints, polishes etc.

(*ii*) *Reaction with steam.* Methane reacts with steam at 1273 K in presence of nickel as catalyst forming CO and H_2.

$$CH_4 + H_2O \xrightarrow{1273 \text{ K, Ni}} CO + 3H_2$$

This method is used for industrial preparation of dihydrogen.

(*c*) **Catalytic oxidation.** Different products are formed under different conditions.

(*i*) When a mixture of methane and oxygen (9 : 1 by volume) at a pressure of 100 atm. is passed through a copper tube at 573 K, methanol is formed.

$$\underset{\text{Methane}}{2CH_4} + O_2 \xrightarrow[\text{Cu tube}]{100 \text{ atm. } 573 \text{ K}} \underset{\text{Methanol}}{2CH_3OH}$$

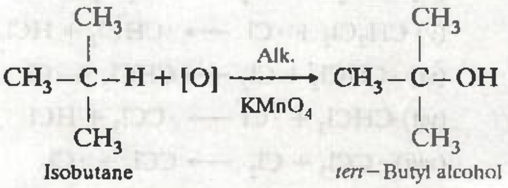
(*ii*) When a mixture of methane and oxygen under pressure is passed over heated molybdenum oxide, it is oxidised to methanal.

$$\underset{\text{Methane}}{CH_4} + O_2 \xrightarrow[\Delta, \text{ pressure}]{Mo_2O_3} \underset{\text{Methanal}}{HCHO} + H_2O$$

(*iii*) *Higher alkanes on oxidation in presence of silver oxide give carboxylic acids.*

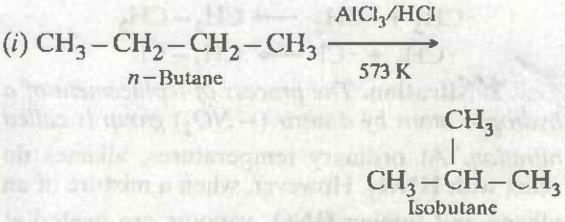
$$\underset{\text{Alkane}}{2R-CH_3} + 3O_2 \xrightarrow[\Delta]{Ag_2O} \underset{\text{Carboxylic acid}}{2RCOOH} + 2H_2O$$

(*iv*) In general, oxidising agents such as $KMnO_4$, $K_2Cr_2O_7$ etc. have no effect on alkanes. However, alkanes containing a tertiary hydrogen can be oxidised to the corresponding alcohols.

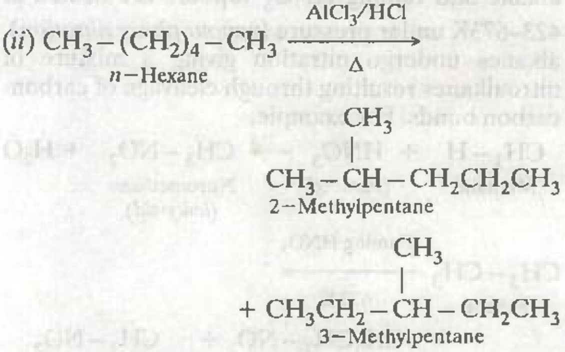


$$\underset{\text{Isobutane}}{(CH_3)_3C-H} + [O] \xrightarrow[KMnO_4]{\text{Alk.}} \underset{tert\text{-Butyl alcohol}}{(CH_3)_3C-OH}$$

IV. Isomerization. When *n*-alkanes are heated with anhydrous aluminium chloride and hydrogen chloride at 573 K under a pressure of about 35 atmospheres, they are converted into branched chain alkanes. For example,



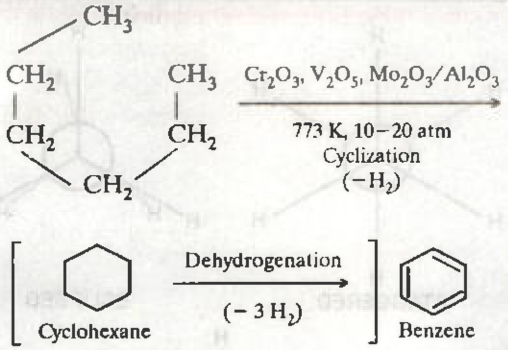
$$(i)\ \underset{n\text{-Butane}}{CH_3-CH_2-CH_2-CH_3} \xrightarrow[573 \text{ K}]{AlCl_3/HCl} \underset{\text{Isobutane}}{CH_3-\overset{\displaystyle CH_3}{\overset{|}{C}H}-CH_3}$$



$$(ii)\ \underset{n\text{-Hexane}}{CH_3-(CH_2)_4-CH_3} \xrightarrow[\Delta]{AlCl_3/HCl} \underset{2\text{-Methylpentane}}{CH_3-\overset{\displaystyle CH_3}{\overset{|}{C}H}-CH_2CH_2CH_3} + \underset{3\text{-Methylpentane}}{CH_3CH_2-\overset{\displaystyle CH_3}{\overset{|}{C}H}-CH_2CH_3}$$

The process of isomerization has been of great utility for increasing the *octane* number of a particular petroleum fraction.

V. Aromatization. Alkanes containing six or more carbon atoms when heated to about 773 K under 10-20 atm. pressure in the presence of a catalyst consisting of oxides of chromium, vanadium and molybdenum supported over alumina, get converted into aromatic hydrocarbons. *This process which involves cyclization, isomerization and dehydrogenation* is called aromatization. For example,



0 A81

Under similar conditions heptane gives toluene and octane gives mixture of *o*-, *m*- and *p*-xylenes.

15.3.7. Uses of Alkanes

(*i*) Methane in form of natural gas is used for running scooters, cars, buses etc. L.P.G. (mixture of butane and isobutane) is used as a fuel in homes as well as in industry.

(*ii*) Methane is used to make carbon black which is used in the manufacture of printing inks, paints and automobile tyres.

(*iii*) Catalytic oxidation of alkanes gives alcohols, aldehydes and carboxylic acids.

(*iv*) Higher alkanes in form of gasoline, kerosene oil, diesel, lubricating oils and paraffin wax are widely used.

(*v*) Methane is used for the manufacture halogen containing compounds such as CH_2Cl_2, $CHCl_3$, CCl_4 etc. are used as solvents both in laboratory and industry.

15.4. Stereoisomerism

Isomers which have the same structural formula but have different relative arrangement of atoms or groups in space are called **stereoisomers** (Greek : *stereo* = space, meros = part) and the *phenomenon is called* **stereoisomerism.**

Since each different spatial arrangement of atoms which characterises a particular stereoisomer is called configuration, therefore, *stereoisomers have the same molecular structure but different configurations.*

Stereoisomerism is of the following three types :

(*i*) *Conformational isomerism*

(*ii*) *Optical isomerism and*

(*iii*) *Geometrical isomerism.*

Let us now discuss conformational isomerism in alkanes.

15.5. Conformations of Alkanes

It has already been stated in Unit 5 that a sigma (or single covalent) bond between two carbon atoms is formed by overlap of sp^3-hybrid orbitals of each carbon along their internuclear axis. Therefore, the electron distribution within the molecular orbital (MO) thus formed is *cylindrically symmetrical* along the internuclear axis as shown in Fig. 15.6. Due to this cylindrical symmetry of σ-MO's, *rotation about carbon-carbon single bond is almost free* (as it requires very little energy for rotation). As a result of this almost free rotation, the molecules of an alkane can have different shapes, *i.e.*, different relative arrangements of their atoms in space.

FIGURE 15.6. A cylindrically symmetric MO (of a single bond) obtained by overlapping of sp^3-hybrid orbitals of two carbon atoms.

The infinite number of momentary arrangements of the atoms in space which result through rotation about a single bond are called conformations or rotational isomers or simply rotamers.

Let us now apply the concept of free rotation to ethane propane and *n*-butane molecules and discuss their conformations.

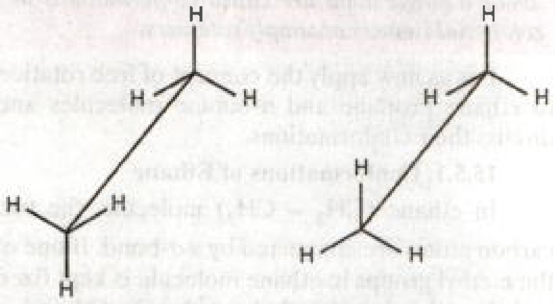
15.5.1. Conformations of Ethane

In ethane ($CH_3 - CH_3$) molecule, the two carbon atoms are connected by a σ-bond. If one of the methyl groups in ethane molecule is kept fixed and the other is rotated about the C–C bond, a large number of momentary arrangements of the hydrogen atoms on one carbon atom with respect to the hydrogen atoms on the other carbon atom in space are obtained. These infinite number of momentary arrangements of atoms in space represent conformations of ethane. In all these conformations, the basic structure of ethane molecule and various bond angles and bond lengths remain the same.

Out of the infinite number of possible conformations of ethane, only two extreme conformations, *i.e.*, staggered and eclipsed are important. All other conformations lying in between these two conformations known as *gauche* or *skew* conformations.

Two-dimensional or 2 D-representation of Conformations. We have already discussed that three-dimensional structures can be represented on a two-dimensional (*i.e.* 2 D) surface with the help of **Fischer Projections. One serious drawback** of these projection formulae is *that they represent the molecule in the unfavourable eclipsed conformation.* However, while discussing the reactions of a molecule, it is usually desirable to depict the molecule in its actual staggered form rather than in the hypothetical eclipsed form as shown in the Fischer projection. Therefore to overcome this difficulty, the conformations of a molecule are usually represented by the following two methods :

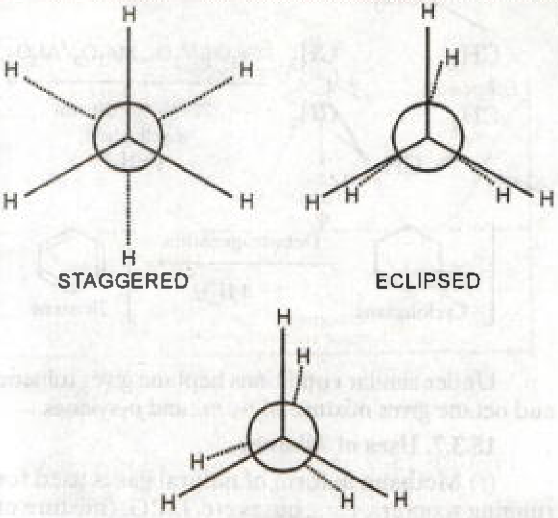
(*i*) **Sawhorse Formulae.** This is a simple method of representing three dimensional formulae on paper. The molecule is viewed slightly from above and from the right and projected on the paper. The bond between the two carbon atoms is drawn diagonally and is slightly elongated for clarity. The lower left hand carbon is considered to be towards the front and the upper right hand carbon towards the back. The Sawhorse representation for staggered and eclipsed conformations of ethane are shown in Fig. 15.7.



STAGGERED ECLIPSED

FIGURE 15.7. Sawhorse representation for Staggered and Eclipsed conformations of ethane.

(*ii*) **Newman Projection Formulae.** Newman devised a simple and highly useful method of repesenting three dimensional formulae on paper. After his name, these are called **Newman Projections.** These projection formulae are obtained by viewing the molecule along the bond joining the two carbon atoms. The carbon atom near the eye is represented by a point and the three atoms or groups attached to it by three equally spaced (120°) radii. The carbon atom farther from the eye is designated by a circle and the three atoms or groups attached to it by three equally spaced radial extensions. The Newman projections for staggered, eclipsed and skew conformations of ethane are shown in Fig. 15.8.



STAGGERED ECLIPSED

SKEW

FIGURE 15.8. Newman projection formulae for Staggered, Eclipsed and Skew conformations of ethane.

Relative stability of Staggered and Eclipsed conformations of Ethane. In staggered conformation, each of the hydrogen atoms on the front carbon lies exactly in between each of the hydrogen atoms on the back carbon. In other words, in this conformation, any two hydrogen atoms on adjacent carbon atoms (non-bonded hydrogens) are as far apart as possible (internuclear H to H distance = 3·1 Å or 310 pm). As a result, the repulsions between the electron clouds of σ-bonds of two non-bonded hydrogen atoms is minimum. On the other hand, in eclipsed conformation, each of the hydrogen atoms on the back carbon lies exactly behind each of the hydrogen atoms on the front carbon. In other words, the non-bonded hydrogen atoms are quite close (2·29Å or 229 pm). As a result, the electron clouds of the σ-bonds of two non-bonded hydrogen atoms repel each other. This raises the energy of the eclipsed conformation relative to staggered conformation. Thus, the staggered conformation of ethane should be more stable than the eclipsed conformation. Experimentally, it has been found to be so. The staggered conformation of ethane is about 12·55 kJ mol^{-1} more stable than the eclipsed conformation.

The variation of energy of the conformations of ethane with rotation about the C – C single bond is shown in Fig. 15.9.

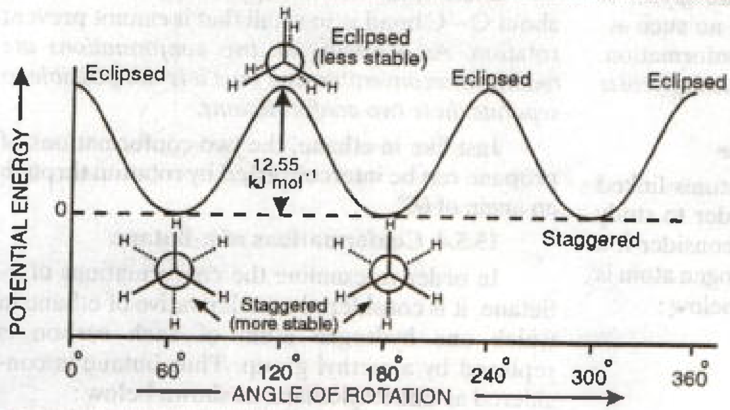


FIGURE 15.9. Variation of energy during rotation about C–C single bond in ethane molecule.

The energy difference of 12·55 kJ mol^{-1} between the staggered and eclipsed conformations is, in fact, the **energy barrier** to rotation about the C – C single bond in ethane. However, *this energy barrier is not large enough to prevent rotation*. Even at room temperature, the collisions of the molecules supply sufficient kinetic energy to overcome this energy barrier. Thus, *the two conformations are readily interconvertible. As a result, it is not possible to separate the two conformations of ethane. However, at any given moment, most of the ethane molecules would exist in the staggered conformation due to its minimum energy and maximum stability.*

15.5.2. Factors affecting stability of conformations

The relative stability of different conformations of a molecule depend upon the following three factors :

1. *Angle strain* **2.** *Torsional strain* **3.** *Non-bonded interactions.*

1. Angle strain. Every atom tends to have bond angles that match those of its bonding orbitals. For example, a sp^3-carbon has tetrahedral bond angles of 109°–28′. *Any deviation from the normal bond angles introduces angle strain in the molecule.* For example, in cyclopropane, the carbon atoms are sp^3-hybridized and thus should have bond angles of 109°–28′. But the actual < CCC bond angles are only 60°. Hence, *cyclopropane molecule has considerable angle strain.*

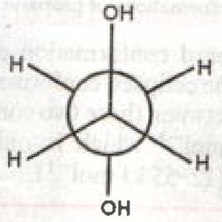
2. Torsional strain. Any pair of tetrahedral carbons attached to each other tend to have staggered bonds, *i.e.*, any ethane like portion of a molecule tends to have ethane like staggered conformation. *Any deviation from staggered conformation introduces torsional strain into the molecule. Thus, the instability of eclipsed conformation of ethane relative to staggered conformation is due to* **torsional strain** *and the energy barrier between the staggered and eclipsed conformations of ethane is called the* **torsional energy.**

3. Non-bonded interactions. *The atoms (or groups) present on adjacent carbon atoms are called* **non-bonded atoms** (*or groups*) and *the interactions between them* are called **non-bonded interactions.** These interactions may be either attractive or repulsive. These are generally of the following two types :

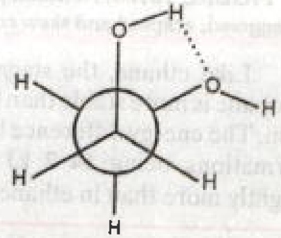
(*i*) **Steric strain.** If the two non-bonded atoms (or groups) just touch each other, *i.e.* are held together at a distance just equal to sum of their van der Waals radii, they attract each other. Conversely, *if the two non-bonded atoms or groups are brought closer than the sum of their van der Waals radii, they repel each other. Such repulsive interaction is called van der Walls strain or* **steric strain.** For example, gauche conformation of *n*-butane (refer to Fig. 15.13), is less stable than anti-conformation due to steric strain or van der Waals strain because both these conformations are free of torsional strain and angle strain.

(*ii*) **Dipole-dipole interactions.** It is reasonable to visualise that non-bonded atoms (or groups) tend to take positions which have most favourable dipole-dipole interactions. In other words, they tend to take up positions which minimize dipole-dipole repulsions or maximize dipole-dipole attractions.

Hydrogen bonding is a special kind of dipole-dipole interactions. To illustrate the effect of H-bonding on the relative stability of conformations, consider the *anti*- and *gauche* conformations of ethylene glycol as shown below :



Anti conformation

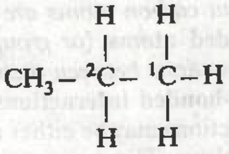


Gauche conformation is stabilized by H-bonding

Gauche conformation of ethylene glycol is stabilized by H-bonding but there are no such attractive interactions in the anti-conformation. Therefore, *gauche conformation of ethylene glycol is more stable than the anti-conformation.*

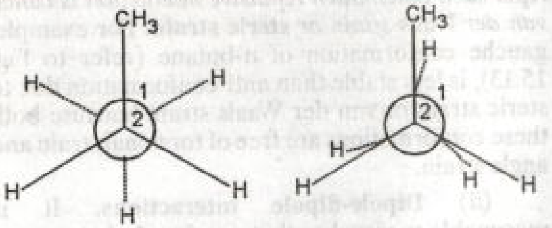
15.5.3. Conformations of Propane

Propane contains three carbon atoms linked to one another by single bonds. In order to study the conformations of propane, let us consider it a derivative of ethane in which one hydrogen atom is replaced by a methyl group as shown below :

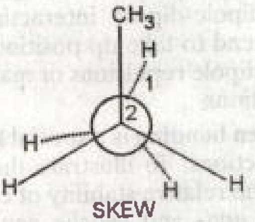


$$CH_3-\overset{H}{\underset{H}{{}^2C}}-\overset{H}{\underset{H}{{}^1C}}-H$$

If one of these carbon atoms (say C_2) is fixed and the other is rotated around the C_1-C_2 bond through an angle of 360°, an infinite number of conformations are theoretically possible. Out of these only two extreme conformations, *i.e.*, staggered and eclipsed are important. Their Newmann projections are shown in Fig. 15.10.



STAGGERED ECLIPSED



SKEW

FIGURE 15.10. Newman projection formulae for staggered, eclipsed and skew conformations of propane.

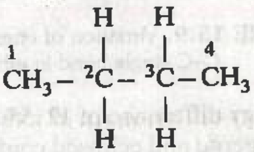
Like ethane, the staggered conformation of propane is more stable than the eclipsed conformation. The energy difference between these two conformations being 14·2 kJ mol^{-1} which is only slightly more than in ethane (12·55 kJ mol^{-1}).

Even then this energy barrier to rotation about C – C bond is so small that it cannot prevent rotation. As a result, *the two conformations are readily interconvertible and thus it is not possible to separate these two conformations.*

Just like in ethane, the two conformations of propane can be interconverted by rotation through an angle of 60°.

15.5.4. Conformations of n-Butane

In order to examine the conformations of *n*-butane, it is considered as a derivative of ethane in which one hydrogen atom of each carbon is replaced by a methyl group. Thus butane is considered as dimethylethane as shown below :



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

Thus, each of the two central carbon atoms (C_2 and C_3) in *n*-butane is linked to one methyl group and two hydrogen atoms. If now one of these carbon atoms (say C_2 or C_3) is fixed and the other is rotated around the central (C_2-C_3) bond through an angle of 360°, an infinite number of conformations are theoretically possible. Out of these, only six conformations are important. Their Newmann projections are given in Fig. 15.11.

In conformation (I), the methyl group and the two hydrogen atoms on C_2 are exactly behind respectively the methyl group and the two hydrogen atoms on C_3. This is called the *fully eclipsed* conformation ; the dihedral angle* for this conformation is 0°.

When conformation (I) is rotated through 60°, the *gauche (or skew or syn)* conformation (II) results. Rotation through another 60° produces *eclipsed conformation* (III) which is different from the fully eclipsed conformation (I). Further rotation through 60° gives rise to the *completely or fully staggered conformation (IV)*. This is called *anti (or trans) conformation.*

Further rotation through 60° gives another eclipsed conformation (V) which is similar to conformation (III). Still further rotation by 60° gives another gauche conformation (VI) similar to II. Finally, if we rotate conformation (VI) by 60°, we

---

*Dihedral angle is the angle between the two planes defined by $\overset{1}{CH_3}-C_2-C_3$ and $C_2-C_3-\overset{4}{CH_3}$.

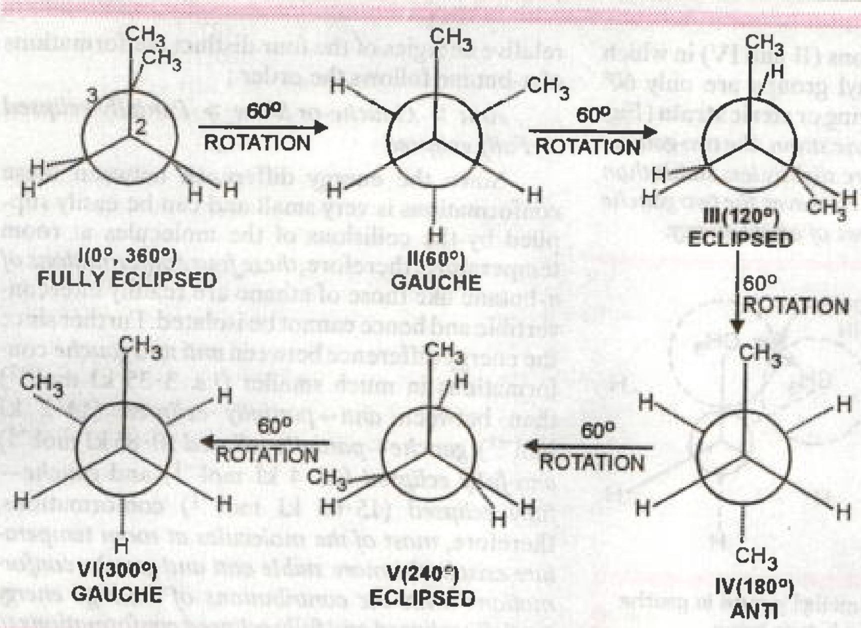


FIGURE 15.11. Newman projections for staggered and eclipsed conformations of *n*-butane.

return to the *fully eclipsed conformation (I)* completing a rotation of 360° around the $C_2 - C_3$ bond.

Thus from the above discussion, it follows that *n*-butane has four distinct conformations, *i.e.*, anti-conformation (IV), gauche conformations (II and IV), eclipsed conformations (III and V) and fully eclipsed conformation (I). There relative potential energies are shown in Fig. 15.12.

Relative Stabilities of the conformations of n-butane.

Out of the four distinct conformations listed above, anti-conformation (IV) is the most stable since in this conformations the two non-bonded methyl groups (dihedral angle 180°) and four non-bonded hydrogen atoms are as far apart as possible. The next in order of higher energy come

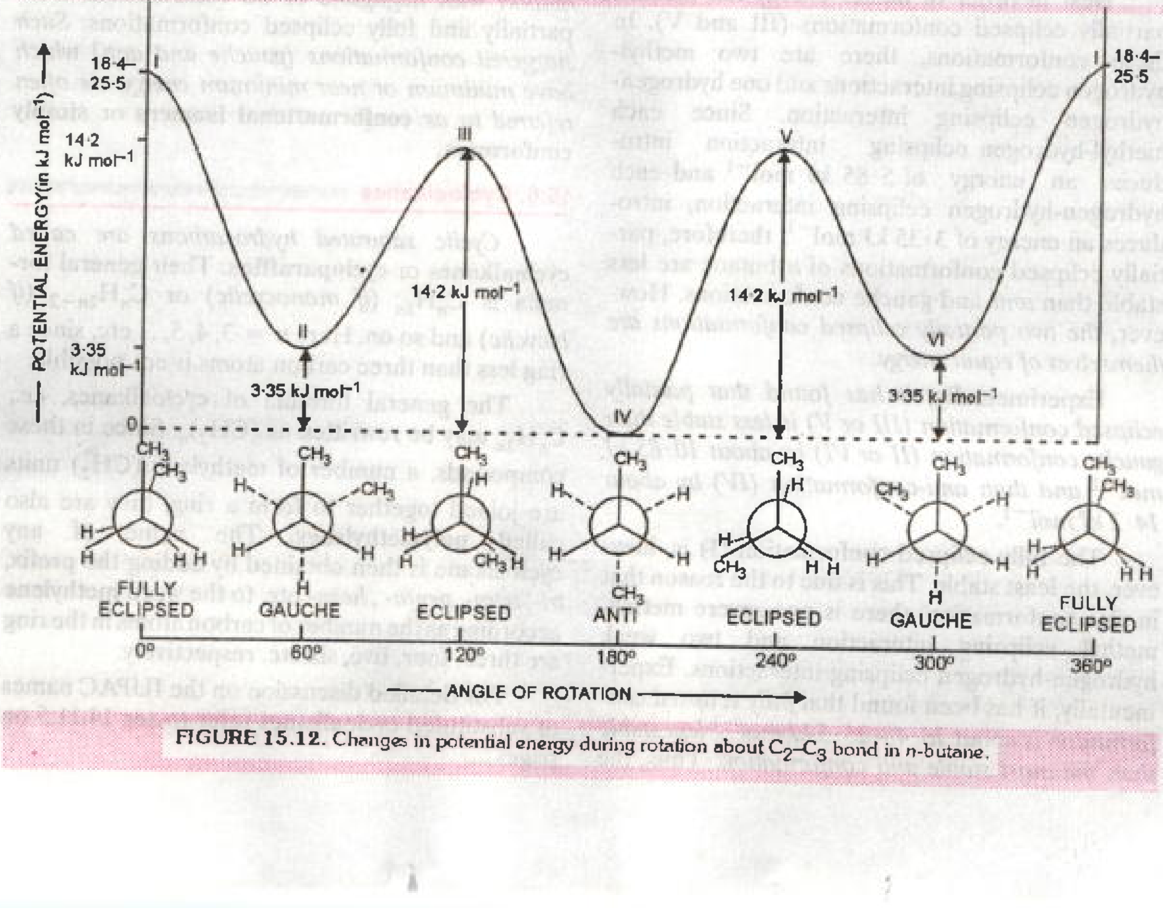


FIGURE 15.12. Changes in potential energy during rotation about C_2–C_3 bond in *n*-butane.

the two gauche conformations (II and IV) in which the two non-bonded methyl groups are only 60° apart and hence cause crowing or **steric strain** (Fig. 15.13). As a result of this *steric strain, the two gauche conformations (II and VI) are slightly less stable than the anti-conformation (IV). However, the two gauche conformations are themselves of equal energy.*

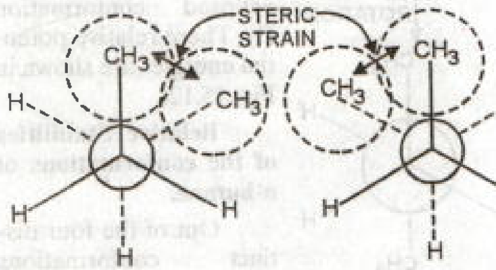


FIGURE 15.13. The two methyl groups in gauche conformations of n-butane being 60° part cause steric strain.

Experimentally, it has been found that the *gauche* conformations are about $3\cdot35$ kJ mol^{-1} less stabe than the *anti* conformation.

Next in order of higher energy fall the two partially eclipsed conformations (III and V). In these conformations, there are two methyl-hydrogen eclipsing interactions and one hydrogen-hydrogen eclipsing interaction. Since each methyl-hydrogen eclipsing interaction introduces an energy of $5\cdot85$ kJ mol^{-1} and each hydrogen-hydrogen eclipsing interaction, introduces an energy of $3\cdot35$ kJ mol^{-1}, therefore, partially eclipsed conformations of *n*-butane are less stable than *anti* and gauche conformations. However, *the two partially eclipsed conformations are themselves of equal energy.*

Experimentally, *it has found that partially eclipsed conformation (III or V) is less stable than gauche conformation (II or VI) by about $10\cdot85$ kJ mol^{-1} and than anti-conformation (IV) by about $14\cdot2$ kJ mol^{-1}.*

The fully eclipsed conformation (I) is, however, the least stable. This is due to the reason that in this conformation, there is one severe methyl-methyl eclipsing interaction and two weak hydrogen-hydrogen eclipsing interactions. Experimentally, it has been found that *fully eclipsed conformation is about $18\cdot4-25\cdot5$ kJ mol^{-1} less stable than the most stable anti conformation.* Thus, the relative energies of the four distinct conformations of *n*-butane follows the order ;

Anti > Gauche or Skew > Partially eclipsed > Fully eclipsed

Since the energy difference between these conformations is very small and can be easily supplied by the collisions of the molecules at room temperature, therefore, *these four conformations of n-butane like those of ethane are readily interconvertible and hence cannot be isolated.* Further since the energy difference between *anti* and *gauche* conformations in much smaller (*i.e.* $3\cdot35$ kJ mol^{-1}) than between *anti – partially eclipsed* ($14\cdot2$ kJ mol^{-1}), *gauche – partially eclipsed* $10\cdot85$ kJ mol^{-1}) *anti-fully eclipsed* ($18\cdot4$ kJ mol^{-1}) and *gauche – fully eclipsed* ($15\cdot05$ kJ mol^{-1}) conformations, therefore, *most of the molecules at room temperature exist in the more stable anti and gauche conformations while the contributions of the high energy partially eclipsed and fully eclipsed conformations to the equilibrium mixture is almost negligible.* Experimentally, it has been found that at room temperature, *2/3 of the molecules of n-butane exist in the more stable anti-conformation while 1/3 of the molecules exist in the little less stable gauche conformation* with negligible or no contributions from partially and fully eclipsed conformations. *Such staggered conformations (gauche and anti) which have minimum or near minimum energy are often referred to as* **conformational isomers** or **simply conformers.**

15.6. Cycloalkanes

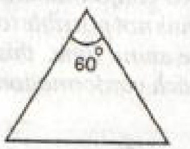
Cyclic saturated hydrocarbons are called **cycloalkanes** or **cycloparaffins.** Their general formula is C_nH_{2n} (*if monocyclic*) or C_nH_{2n-2} (*if bicyclic*) and so on. Here $n = 3, 4, 5, ...$ etc. since a ring less than three carbon atoms is not possible.

The general formula of cycloalkanes, *i.e.*, C_nH_{2n} may be rewritten as $(CH_2)_n$. Since in these compounds, a number of methylene (CH_2) units are joined together to form a ring, they are also called **polymethylenes.** The name of any cycloalkane is then obtained by adding the prefix, *tri-, tetra-, penta- , hexa-* etc. to the word methylene according as the number of carbon atoms in the ring are three, four, five, six etc. respectively.

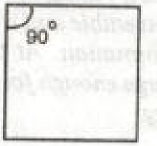
For detailed discussion on the IUPAC names of substituted cycloalkanes refer to **sec** 14.11.5 on pages.....

15.6.1. Conformations in Cycloalkanes

Like alkanes, cycloalkanes also show conformational isomerism. Cyclopropane and cyclobutane are planar molecules with bond angles of 60° and 90° respectively. But the normal tetrahedral angle in saturated compounds of carbon is 109° – 28′. Thus, the bond angles in cyclopropane and cyclobutane are quite different from normal tetrahedral angles. This deviation from normal tetrahedral angle introduces considerable *angle strain* in the molecules of these cycloalkanes. Further, greater the deviation, more strained is the molecule and hence more reactive is the compound. For example, *cyclopropane with a bond angle of 60° is very strained and hence very reactive.*



CYCLOPROPANE



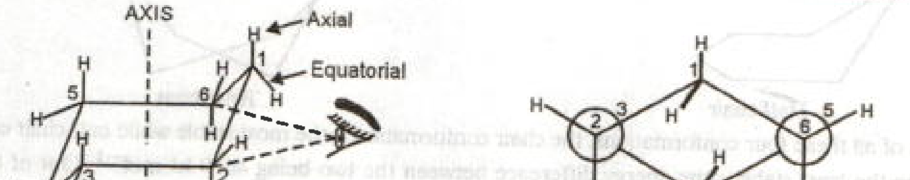
CYCLOBUTANE

CYCLOPENTANE

Cyclobutane with a bond angle of 90° is less strained and hence less reactive than cyclopropane. In cyclopentane, the bond angle is 108° (that of a regular pentagon) which is very close to the tetrahedral angle of 109° – 28′. As a result, it has very *little strain and hence is much less reactive than cyclopropane and cyclobutane.* Further, cyclopentane has been shown to have a *non-planar* conformation, although for all practical purposes, it is considered to be planar. On the other hand, cyclohexane has *non-planar conformations.* This allows all the carbon – carbon bonds in cyclohexane to have tetrahedral bond angles. As a result, *cyclohexane is free from angle strain and hence is quite stable and unreactive.*

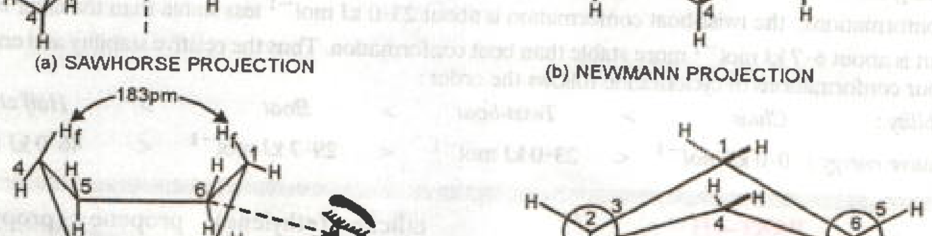
Cyclohexane exists in two *non-planar or puckered conformations* called the **chair** *and the* **boat conformations** (Fig. 15.14). The names chair and boat are used for these conformations because of their resemblance to a lawn chair and a boat respectively.

Although the cyclohexane ring as a whole is puckered (*i.e.* non-planar), the four carbon atoms, *i.e.*, C_2, C_3, C_5 and C_6 lie in the general plane of the molecule. As such we may consider the molecular axis to pass through the centre of the molecule and perpendicular to this general plane. It can be seen from Fig. 15.14 that each carbon in the chair form of cyclohexane has two C – H bonds, one parallel to the molecular axis called the **axial hydrogen** and the other more or less in the plane of the ring called the **equatorial hydrogen.** Thus, in all, *chair form of cyclohexane has six axial and six equatorial hydrogens.*



(a) SAWHORSE PROJECTION

(b) NEWMANN PROJECTION



(c) SAWHOSE PROJECTION

(d) NEWMANN PROJECTION

FIGURE. 15.14. Sawhorse and Newmann Projections of chair and Boat Conformations of Cyclohexane.

Relative stabilities of chair and both conformations of cyclohexane. Although both chair and boat conformations of cyclohexane have no angle strain, yet chair conformation of cyclohexane is more stable than the boat conformation because of the following two reasons.

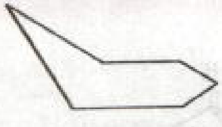
(*i*) In chair conformation, the adjacent hydrogens on C_1-C_2, C_2-C_3, C_3-C_4, C_5-C_6 and C_6-C_1 are all in the more stable *staggered orientations* (Newmann projection '*b*'). As a result, the force of repulsion between these non-bonded H-atoms is minimum. On the other hand, in boat conformation, the adjacent hydrogens on C_2-C_3 and C_5-C_6 are in the less stable *eclipsed orientations* (Newmann Projection '*d*'). As a result, boat conformation has considerable *torsional strain* and hence is less stable than the chair conformation.

(*ii*) The two hydrogen atoms (marked as H_f) called the *flagpole hydrogens* on C_1 and C_4 in the boat conformation are quite close (1·83 Å or 183 pm) as compared to 2·29 Å or 229 pm in the staggered arrangement. As a result, boat conformation has also considerable *van der walls or steric strain*. Thus boat conformation is less stable than chair conformation due to torsional strain as well as steric strain. Conversely *chair form is free from torsional strain and steric strain and hence is more stable than the boat form*. It is because of this reason that 99% of cyclohexane molecules exist in the more stable chair form at room temperature.

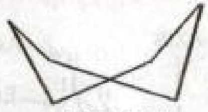
The energy difference between the chair and the boat forms has been found out to be 29·7 kJ mol^{-1}. This difference in energy is so small that even at room temperature, the collisions of molecules supply sufficient energy to overcome this energy barrier. As a result, *the two conformations are readily interconvertible and is thus not possible to isolate each conformation. At the same time, this energy barrier is large enough for each conformation to retain its identity.*

ADD TO YOUR KNOWLEDGE

Conformations of cyclohexane. Besides chair and boat, two other important conformations of cyclohexane are : *half-chair* and *twist boat.*



Half chair



Twist-boat

Out of all these four conformations, the chair conformation is the most stable while half-chair conformation being the least stable ; the energy difference between the two being 46·0 kJ mol^{-1}. Out of the two boat conformations, the twist-boat conformation is about 23·0 kJ mol^{-1} less stable than the chair conformation but is about 6·7 kJ mol^{-1} more stable than boat conformation. Thus the relative stability and energy of these four conformations of cyclohexane follows the order :

Stability :	*Chair*	>	*Twist-boat*	>	*Boat*	>	*Half chair*
Relative energy :	0·0 kJ mol^{-1}	<	23·0 kJ mol^{-1}	<	29·7 kJ mol^{-1}	<	46·0 kJ mol^{-1}

PART—II

ALKENES

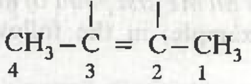
15.7. Alkenes

Acyclic unsaturated hydrocarbons containing a carbon-carbon double bond are called **alkenes**. They are also called **olefins** (Greek : *olefiant* = oil forming) since the lower members of this class such as ethene (ethylene), propene (propylene) etc. produce oily products on reaction with halogens such as chlorine and bromine. Their general formula is C_nH_{2n} where $n = 2, 3, 4$ ... etc.

The first member of the alkene family is ethene, C_2H_4, which contains 5σ-bonds and one π-bond. The bond enthaly of C = C is 610 kJ mol^{-1} while C – C bond enthalpy of ethane is 370 kJ mol^{-1}. As a result, C = C bond length in ethene (134 pm) is shorter than C – C bond length in ethane (154 pm).

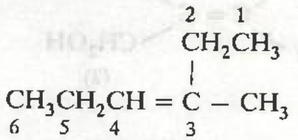
15.7.1. Nomenclature of Alkenes

The nomenclature of alkenes has already been discussed in unit 14. However, for the purpose of recaptulation, the IUPAC names of same alkenes are given below :



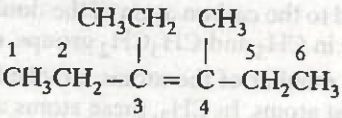
$$\underset{4}{CH_3}-\overset{CH_3}{\underset{3}{C}}=\overset{CH_3}{\underset{2}{C}}-\underset{1}{CH_3}$$

2, 3–Dimethylbut–2–ene



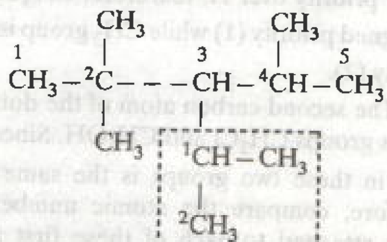
$$\underset{6}{CH_3}\underset{5}{CH_2}\underset{4}{CH}=\overset{\overset{2\quad 1}{CH_2CH_3}}{\underset{3}{C}}-CH_3$$

3–Methylhex–3–ene



$$\overset{1}{CH_3}\overset{2}{CH_2}-\overset{CH_3CH_2}{\underset{3}{C}}=\overset{CH_3}{\underset{4}{C}}-\overset{5}{CH_2}\overset{6}{CH_3}$$

3–Ethyl–4–methylhex–3–ene



$$\overset{1}{CH_3}-{}^2\overset{CH_3}{\underset{CH_3}{C}}-\,-\,-\overset{3}{\underset{{}^1CH-CH_3\,|\,{}^2CH_3}{CH}}-{}^4\overset{CH_3}{CH}-\overset{5}{CH_3}$$

2, 2, 4–Trimethyl–3–(1–methylethyl) pentane

15.7.2. Geometrical isomerism – Hindered rotation around carbon-carbon double bond

We know that a double bond consists of a σ-bond and a π-bond. The π-bond is formed by sideways overlapping of unhybridized *p*-orbitals of two carbon atoms above and below the plane of carbon atoms. If now one of the carbon atoms of the double bond is rotated with respect to the other, the *p*-orbitals will no longer overlap and the π-bond should break (Fig. 15.15). But the breaking of a π-bond requires 251 kJ mol^{-1} of energy which is not provided by the collisions of the molecules at room temperature. Consequently, the rotation about a carbon-carbon double bond is not free but is *strongly hindered or restricted*. In other words, a π-bond prevents free rotation of the carbon atoms of the double bond with respect to each other. Due to this hindered rotation, the relative positions of atoms or groups attached to the carbon atoms of the double bond get fixed. For example, H_a and H_b in Fig. 15.16 cannot exchange their positions by rotation of C_1 with respect to C_2 without breaking the π-bond.

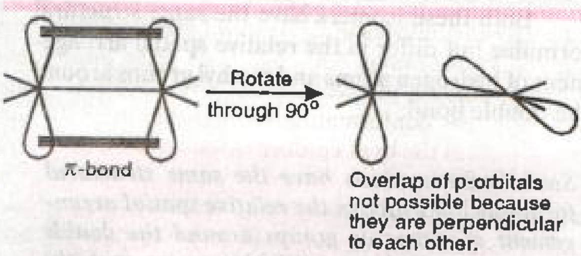


FIGURE 15.15. Rotation about a carbon-carbon double bond.

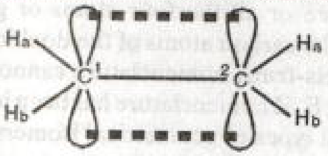
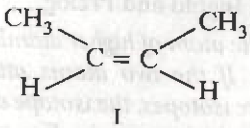


FIGURE 15.16. Restricted rotation about carbon-carbon double bond.

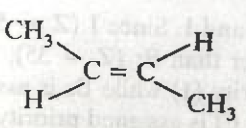
As a result, many substituted alkenes can exist in two distinct isomers which differ from each other only in the relative positions of atoms or groups in space around the double bond. For example, but-2-ene can exist in the following two forms (I and II) :



$$\begin{matrix} CH_3 & & CH_3\\ & C=C & \\ H & & H\end{matrix}$$

I

cis–But–2–ene



$$\begin{matrix} CH_3 & & H\\ & C=C & \\ H & & CH_3\end{matrix}$$

II

trans–But–2–ene

Both these isomers have the same structural formulae but differ in the relative spatial arrangement of hydrogen atoms and methyl groups around the double bond.

Such isomers which have the same structural formulae but differ in the relative spatial arrangement of atoms or groups around the double bond are called geometrical isomers and the phenomenon is called geometrical isomerism. Thus, geometrical isomerism is a type of space or stereoisomerism.

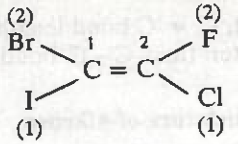
The isomer I, in which the similar atoms or groups lie on the same side of the double bond is called the **cis-isomer** whereas the isomer II, in which the similar atoms or groups lie on the opposite sides of the double bond is called the **trans-isomer**. It is because of this reason that geometrical isomerism is also called **cis-trans isomerism.**

E, Z Nomenclature

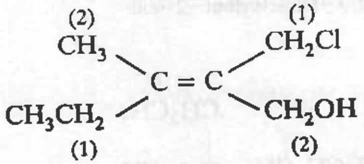
If three or all the four atoms or groups attached to the carbon atoms of the double bond are different, **cis-trans** nomenclature cannot be used. Therefore, E, Z nomenclature has been introduced to name all types of geometrical isomers. According to this nomenclature, *if the atoms or groups of highest priority are on the same side of the double bond, the isomer is designated as* **Z** *(Zusammen in German means together) and if the two atoms or groups of highest priority are on the opposite sides, the isomer is designated as* **E** *(Entegegan in German means opposite)*.

In this system of nomenclature, each of the two atoms or groups on each carbon atom of the double bond are assigned priority number (1) and (2) on the basis of the following sequence rules given by Cahn, Ingold and Prelog.

Rule 1. *The atom of higher atomic number gets higher priority. If the two atoms attached to the double bond are isotopes, the isotope of higher mass number gets the higher priority.* For example, in 1-bromo-2-chloro-2-fluoro-1-iodoethene, C_1 has two atoms *viz.* Br and I. Since I (Z = 53) has higher atomic number than Br (Z = 35), therefore, I is assigned priority (1) while Br is assigned priority (2). Similarly, Cl is assigned priority (1) while F is assigned priority (2).



Rule 2. *If two atoms directly attached to the double bond have the same atomic number, then the relative priority of the groups is determined by a similar comparison of the atomic numbers of the next elements in the groups (and so on, if necessary, working outwards till the first point of difference is reached).* For example, in the following compound,

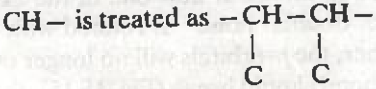


one of the carbon atoms of the double bond carries CH_3 and CH_3CH_2 groups. Since the first atom (*i.e.*, C) attached to the carbon atom of the double bond is the same in CH_3 and CH_3CH_2 groups, compare the atomic number of the atoms attached to each of these first atoms. In CH_3, these atoms are H, H, H while in CH_3CH_2 these are C, H, H. Since C has higher priority over H, therefore, CH_3CH_2 group is assigned priority (1) while CH_3 group is assigned priority (2).

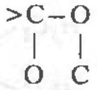
The second carbon atom of the double bond carries groups CH_2Cl and CH_2OH. Since the first atom in these two groups is the same (*i.e.*, C), therefore, compare the atomic numbers of the atoms attached to each of these first atoms. In CH_2Cl, these atoms are Cl, H, H while in CH_2OH, these atoms are O, H, H. Since Cl (Z = 17) has higher priority over O (Z = 8), therefore, CH_2Cl is assigned priority (1) while CH_2OH is assigned priority (2).

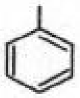
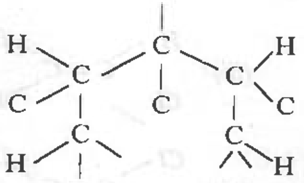
Rule 3. *Double bonds and triple bonds are treated as if they have duplicate or triplicate single bonds.* For example,

$-CH = CH-$ is treated as

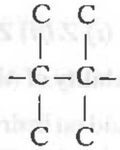


$$-\underset{|\atop C}{CH}-\underset{|\atop C}{CH}-$$

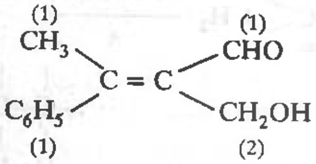
and > C = O is treated as

$>\underset{\displaystyle O}{\underset{|}{C}}-\underset{\displaystyle C}{\underset{|}{O}}$


is treated as


Thus, $C_6H_5 g$ is assigned priority and

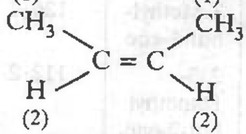
$-C\equiv C-$ is treated as

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

For example, consider the following compound.

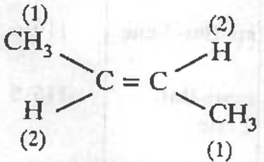


One of the carbon atoms of the double bond carries CH_3 and C_6H_5 groups. Since in C_6H_5 group, the first carbon is attached to two other carbons one by a double bond and the other by a single bond, therefore, C, C, CH of phenyl gets higher priority over H, H, H of CH_3. Thus, C_6H_5 is assigned priority (1) and CH_3 is assigned priority (2). The other carbon atom of the double bond carries CH_2OH and CHO groups. Since in CH = O, C is attached to O by a double bond while in CH_2OH, C is attached to O by a single bond. Therefore, O, O, H of CHO gets higher priority over O, H, H of CH_2OH group. Thus CHO is assigned priority (1) and CH_2OH is assigned priority (2).

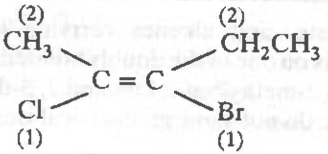
On the basis of relative priorities, E and Z designations are assigned as discussed above. For illustration consider the following examples :



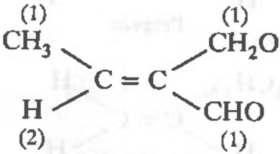
(Z)–But–2–ene



(E)–But–2–ene



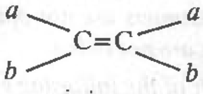
(Z)–isomer
i.e. (Z)–2–Chloro–3–bromopent–2–ene



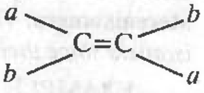
(E)–isomer
i.e. (E)–2–Hydroxymethylbut–2–en–1–al

Necessary and sufficient condition for geometrical isomerism. It may be mentioned here that all compounds containing carbon-carbon double bonds do not show geometrical isomerism. The necessary condition for a molecule to exhibit geometrical isomerism are

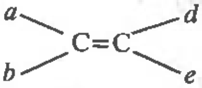
(*i*) *the molecule must contain a double bond*
(*ii*) *each of the two carbon atoms of the double bond must have different substituents which may be same or different.* Thus alkenes of the type abC=Cab and abC=Cde show geometrical isomerism.



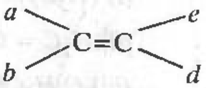
cis–isomer



trans–isomer



(Z)–isomer
(If groups 'a' and 'd' have higher priority)

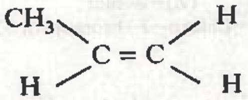


(E)–isomer
(If groups 'a' and 'd' have higher priority)

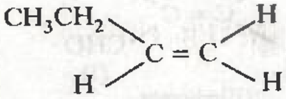
However, geometrical isomers are not possible if one or both the doubly bonded carbon atoms carry two similar substituents. This is because in such cases, the two possible configurations are, in fact, identical as shown below :

It is because of this reason that terminal alkenes such as propene, but-1-ene, 2-methylprop-

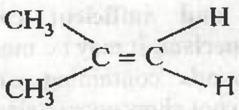
1-ene etc. and alkenes carrying identical substituents on one of the doubly bonded carbon atoms such as 2-methylbut-2-ene and 2, 3-dimethylbut-2-ene etc. do not show geometrical isomerism.



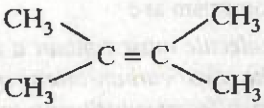
Propene



But-1-ene



2-Methylprop-1-ene



2, 3-Dimethylbut-2-ene

Geometrical isomers have the same molecular structure but differ only in the relative positions of atoms or groups in space, therefore, they are **stereoisomers.** *These stereoisomers are not optical isomers since their molecules are not chiral.*

EXAMPLE 15.3. *Which of the following compounds will show cis- trans isomerism ?*

(*i*) $(H_3C)_2C = CH-CH_3$

(*ii*) $H_2C = CCl_2$

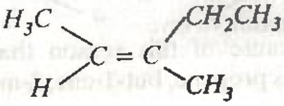
(*iii*) $C_6H_5CH = CHCH_3$

(*iv*) $H_3C-CH = CBr(CH_3)$ **(N.C.E.R.T.)**

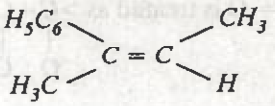
Solution. Alkenes (*i*) and (*ii*) have identical atoms or groups on one of the carbon atoms of the double bond and hence do not show geometrical isomerism. In contrast, alkenes (*iii*) and (*iv*) have different atoms or groups on each carbon atom of the double bond and hence exhibit geometrical isomerism.

EXAMPLE 15.4. *Classify the following as E or Z isomers ?*

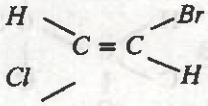
(*i*)



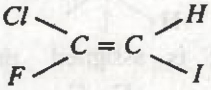
(*ii*)



(*iii*)



(*iv*)

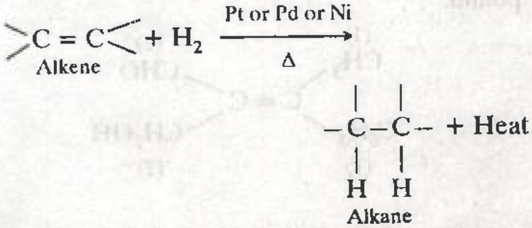


(N.C.E.R.T.)

Solution. (*i*) Z (*ii*) Z (*iii*) E (*iv*) E.

15.7.3. Stability of Alkenes

Alkenes add on hydrogen, in presence of finely divided metals such as platinum, palladium or Raney nickel to form alkanes.



$$>C=C< + H_2 \xrightarrow[\Delta]{\text{Pt or Pd or Ni}} -\underset{H}{\overset{|}{\underset{|}{C}}}-\underset{H}{\overset{|}{\underset{|}{C}}}- + \text{Heat}$$

Alkene Alkane

This reaction is called **hydrogenation.** *It is an exothermic reaction and the amount of heat evolved when one mole of an alkene is hydrogenated is called* ***its heat of hydrogenation.***

The heat of hydrogenation of some alkenes is given in Table 15.2.

TABLE 15.2. Heats of hydrogenation of some alkenes

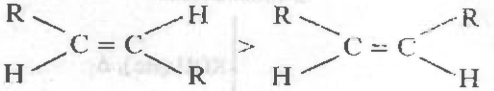
Alkene	Heat of hydrogenation (in kJ mol^{-1})	Alkene	Heat of hydrogenation (in kJ mol^{-1})
Ethene	137·2	2-Methylprop-1-ene	118·8
Propene	125·9	2-Methylbut-1-ene	119·2
But-1-ene	126·7	2-Methylbut-2-ene	112·5
cis-But-2-ene	119·6	3-Methylbut-1-ene	126·7
trans-But-2-ene	115·5	2, 3-Dimethyl but-2-ene	112·2

But-1-ene, *cis*-but-2-ene and *trans*-but-2-ene all on hydrogenation give the same alkane, *i.e.*, *n*-butane but evolve different heats of hydrogenation. This means that these alkenes must have different inherent energies and hence different stabilities. An alkene which has a lower heat of hydrogenation must have less inherent energy and hence will be more stable than its isomers which have higher heats of hydrogenation. Thus, *heat of hydrogenation of an alkene is the index of its stability. The lower the heat of hydrogenation of an alkene more stable it is.* The following conclusions can be drawn from Table 15.2 given above.

(i) An unsubstituted alkene such as ethene has the highest heat of hydrogenation.

(ii) Greater the number of alkyl groups attached to the doubly bonded carbon atoms, more stable is the alkene. In general, alkenes have the following decreasing order of stability :*

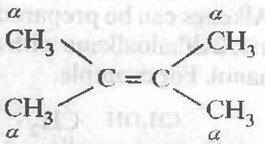
$R_2C = CR_2 > R_2C = CHR > R_2C = CH_2,$



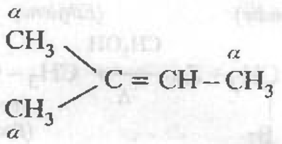
$> RCH = CH_2 > CH_2 = CH_2.$

(iii) Out of geometric isomers, the trans-isomer is slightly more stable than the corresponding cis-isomer.

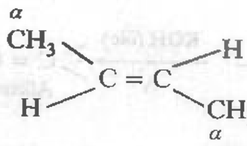
Explanation for relative stabilities of alkenes. The relative stabilities of different alkenes can be explained on the basis of concept of hyperconjugation as discussed in unit 14. Consider, for example, the following alkenes :



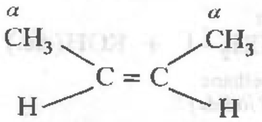
2, 3−Dimethylbut−2−ene (I)
(Twelve α−H ; $\Delta_{H_2} = -\ 112{\cdot}2$ kJ mol^{-1})



2−Methylbut−2−ene (II)
(Nine α−H ; $\Delta_{H_2} = -\ 112{\cdot}5$ kJ mol^{-1})



trans−But−2−ene (III)
(Six α−H, $\Delta_{H_2} = -\ 115{\cdot}5$ kJ mol^{-1})



cis−But−2−ene (IV)
(Six α−H, $\Delta_{H_2} = -\ 119{\cdot}6$ kJ mol^{-1}

$\overset{\alpha}{CH_3} - CH = CH_2$

Propene (V)
(Three α−H ; $\Delta_{H_2} = -\ 125{\cdot}8$ kJ mol^{-1})

$CH_2 = CH_2$

Ethene (VI)
(No α−C, No α−H ; $\Delta_{H_2} = -\ 137{\cdot}2$ kJ mol^{-1})

Alkenes I, II, III (or IV) have *twelve, nine, six, three* and *none* α-hydrogens respectively and hence equal number of hyperconjugation structures can be written for each one of them. Since greater the number of hyperconjugation structures, more stable is the alkene, therefore, relative stability of these alkenes follows the sequence :

I > II > III > IV > V > VI.

Since *trans*-but-2-ene (III) is more stable than the *cis*-but-2-ene (IV) in which the two methylgroups lie on the same side of the double bond and hence cause **steric hendrance**, therefore, heat of hydrogenation of III is less than that of IV.

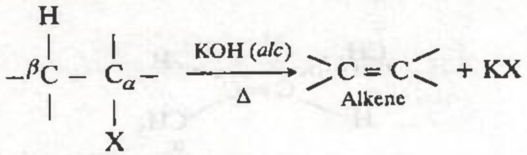
15.7.4. General Methods of Preparation

Alkenes can be prepared in the laboratory by the following general methods of preparation.

✓ **From alkyl halides or haloalkanes.** Alkyl halides on heating with a strong base such as sodium ethoxide or a concentrated alcoholic solution of potassium hydroxide undergo dehydrohalogenation to give alkenes.

---

*This order is given in Organic Chemistry by T.W.G. Solomons and C Fryhle but in Organic Chemistry by R.T. Morrison and R.N. Boyd no distinction has been made on the relative stability of $R_2C = CH_2$ and $RCH = CHR$.



$$-\underset{|}{\overset{\overset{H}{|}}{{}^{\beta}C}}-\underset{\underset{X}{|}}{\overset{|}{C_{\alpha}}}- \xrightarrow[\Delta]{KOH\,(alc)} \;>C=C<\; + KX$$

Alkene

Alkyl halide
(X = Cl, Br or I)

$$e.g., \overset{\beta}{CH_3}\overset{\alpha}{CH_2}-I + KOH(alc.) \xrightarrow{353-363\text{ K}}$$

Iodoethane
(*Ethyl iodide*)

Ae

$$CH_2=CH_2 + KI + H_2O$$

Ethene
(*Ethylene*)

$$CH_3\overset{\beta}{CH_2}\overset{\alpha}{CH_2}-Br + KOH(alc) \xrightarrow{353-363\text{ K}}$$

1-Bromopropane
(*n-Propyl bormide*)

$$CH_3CH=CH_2 + KBr + H_2O$$

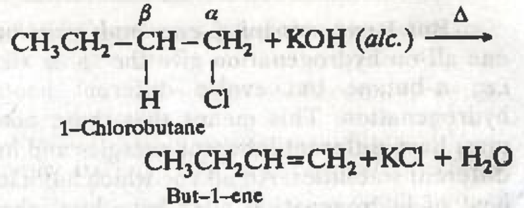
Propene
(*Propylene*)

This process of removal of a molecule of a halogen acid (HCl, HBr or HI) from a haloalkane to form an alkene is called dehydrohalogenation.

Dehydrohalogenation is an example of an **elimination reaction.** Since in this reaction, a hydrogen is removed from a β- carbon and halogen from the α-carbon, therefore, it is called **β-elimination reaction.**

The ease of dehydrohalogenation for different alkyl halides having the same alkyl groups but different halogens is iodides > bromides > chlorides while for different alkyl halides having the same halogen but different alkyl groups is tertiary > secondary > primary. Thus, a tertiary alkyl iodide is most reactive.

Saytzeff rule. Depending upon the structure alkyl halides may give one or more isomeric alkenes. For example, dehydrohalogenation of 1-chlorobutane gives only one alkene, *i.e.*, but-2-ene since only one type of β-hydrogen is available on the left side of the molecule.

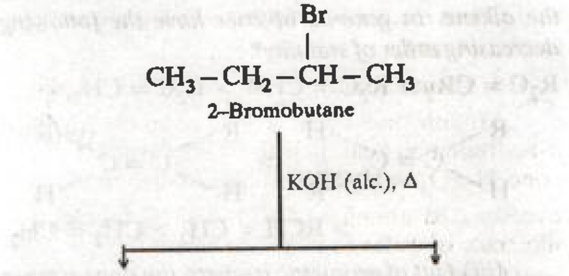


$$CH_3CH_2-\underset{\underset{H}{|}}{\overset{\beta}{CH}}-\underset{\underset{Cl}{|}}{\overset{\alpha}{CH_2}} + KOH\,(alc.) \xrightarrow{\Delta} CH_3CH_2CH=CH_2 + KCl + H_2O$$

1-Chlorobutane

But-1-ene

If, however, the structure of the alkyl halide is such that it has a β-hydrogen on either side of the carbon atom carrying the halogen, it can undergo elimination in two different ways giving two alkenes. The relative amounts of these two alkenes is governed by Saytzeff rule. According to this rule, ***whenever two alkenes are theoretically possible during a dehydrohalogenation reaction, it is always the more highly substituted alkene (i.e.) having lesser number of hydrogen atoms on the double bond) which predominates. For example,***



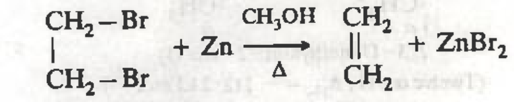
2-Bromobutane

KOH (alc.), Δ

$CH_3-CH=CH-CH_3$
But-2-ene (80%)
(*More highly substituted* **alkene ; more stable)**

$CH_3-CH_2-CH=CH_2$
But-1-ene (20%)
(*Less highly substituted* **alkene ; less stable)**

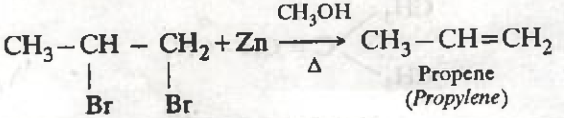
From vicinal dihalides or 1, 2-dihaloalkanes. Dihalogen derivatives of alkanes in which the two halogen atoms are present on adjacent carbon atoms are called ***vicinal or 1, 2-dihaloalkanes*****. Alkenes can be prepared by heating a suitable** ***vic.*** **or 1, 2 dihaloalkane with zinc dust in methanol or ethanol. For example,**



$$\begin{array}{l}CH_2-Br\\ |\\ CH_2-Br\end{array} + Zn \xrightarrow[\Delta]{CH_3OH} \begin{array}{l}CH_2\\ ||\\ CH_2\end{array} + ZnBr_2$$

1, 2,-Dibromoethane
(*Ethylene dibromdie*)

Ethene
(*Ethylene*)



$$CH_3-\underset{\underset{Br}{|}}{CH}-\underset{\underset{Br}{|}}{CH_2} + Zn \xrightarrow[\Delta]{CH_3OH} CH_3-CH=CH_2 + ZnBr_2$$

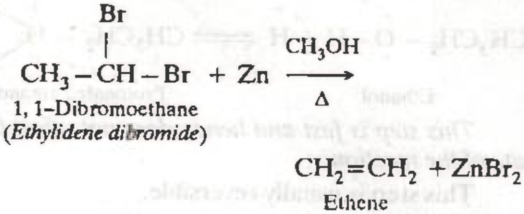
1, 2-Dibromopropane
(*Propylene dibromide*)

Propene
(*Propylene*)

Ae

This process of removal of a molecule of halogen (Cl_2, Br_2 or I_2) from a dihaloalkane to form an alkene is called dehalogenation :

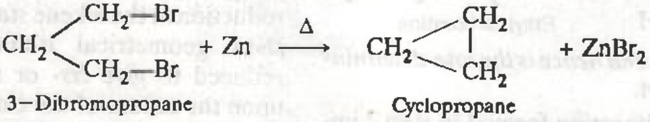
Even 1, 1-dihaloalkanes or *gem*-dihalides also undergo dehalogenation when heated with zinc dust in methanol.



$$\underset{\text{1, 1-Dibromoethane (Ethylidene dibromide)}}{CH_3-\overset{\overset{Br}{|}}{C}H-Br} + Zn \xrightarrow[\Delta]{CH_3OH} \underset{\text{Ethene}}{CH_2=CH_2} + ZnBr_2$$

ADD TO YOUR KNOWLEDGE

α, ω-Dihaloalkanes (*i.e.* alkanes having halogen atoms on terminal carbon atoms) on heating with active metals such as zinc or sodium undergo ring closure to form cycloalkanes. For example,



1, 3–Dibromopropane

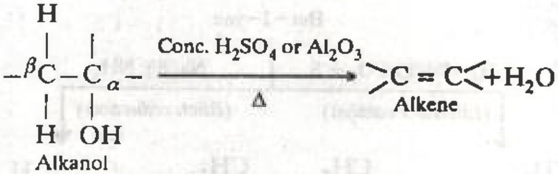
Cyclopropane

This reaction is caled **Freund's method** and gives good yields only for cyclopropane.

3. From monohydric alcohols or alkanols

ae

Monohydric alcohols or alkanols containing a β-hydrogen on heating with a mineral acid such as conc. H_2SO_4 or H_3PO_4 or on passing their vapours over heated alumina at 623–633 K eliminate a molecule of water to form alkenes.



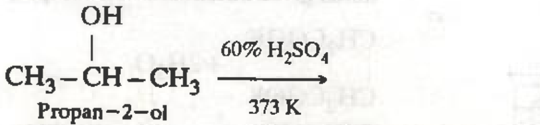
$$-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{{}^{\beta}C}}-\overset{|}{\underset{\underset{OH}{|}}{C_{\alpha}}}- \xrightarrow[\Delta]{\text{Conc. } H_2SO_4 \text{ or } Al_2O_3} \underset{\text{Alkene}}{>C=C<} + H_2O$$

Alkanol

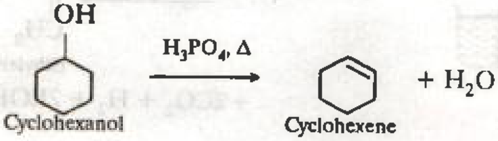
For example,

$$\underset{\substack{\text{Ethanol}\\\text{(Ethyl alcohol)}}}{CH_3CH_2OH} \xrightarrow[623-633\ K]{Al_2O_3} \underset{\substack{\text{Ethene}\\\text{(Ethylene)}}}{CH_2=CH_2} + H_2O$$

$$\underset{\substack{\text{Ethanol}\\\text{(1° Alocohol)}}}{CH_3CH_2OH} \xrightarrow[440\ K]{95\%\ H_2SO_4} \underset{\text{Ethene}}{CH_2=CH_2} + H_2O$$

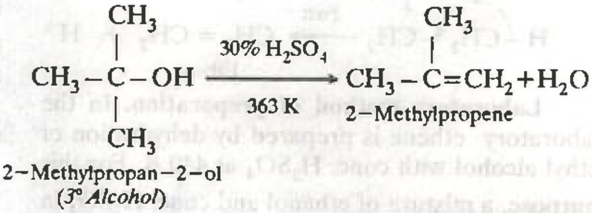


$$\underset{\substack{\text{Propan-2-ol}\\\text{(2° Alcohol)}}}{CH_3-\overset{\overset{OH}{|}}{C}H-CH_3} \xrightarrow[373\ K]{60\%\ H_2SO_4} CH_3-CH=CH_2 + H_2O$$



Cyclohexanol

Cyclohexene

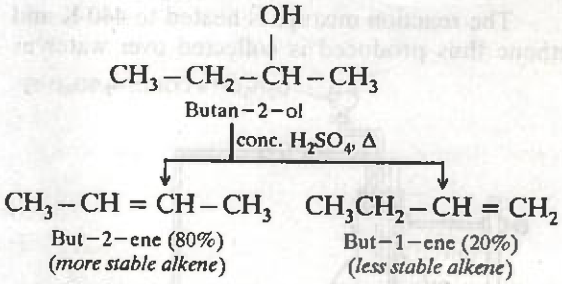


$$\underset{\substack{\text{2-Methylpropan-2-ol}\\\text{(3° Alcohol)}}}{CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-OH} \xrightarrow[363\ K]{30\%\ H_2SO_4} \underset{\text{2-Methylpropene}}{CH_3-\overset{\overset{CH_3}{|}}{C}=CH_2} + H_2O$$

It is evident from the above reactions, that the order of dehydration of different alcohols is : 3° > 2° > 1°.

Like alkyl halides, dehydration of alcohols also follows **Saytzeff rule.**

For example,

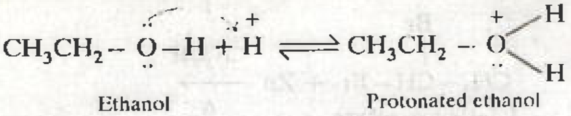


$$\underset{\text{Butan-2-ol}}{CH_3-CH_2-\overset{\overset{OH}{|}}{C}H-CH_3} \xrightarrow{\text{conc. } H_2SO_4,\ \Delta} \underset{\substack{\text{But-2-ene (80\%)}\\\text{(more stable alkene)}}}{CH_3-CH=CH-CH_3} + \underset{\substack{\text{But-1-ene (20\%)}\\\text{(less stable alkene)}}}{CH_3CH_2-CH=CH_2}$$

Mechanism. The dehydration of alcohols does not occur in just one step but occurs in a series of steps. *A knowledge of the series of steps by which the reaction occurs is called the mechanism of the reaction.* The dehydration of alcohols occurs by the following three steps :

Step 1. An alcohol being a *Lewis base* accepts a proton from the strong acid to form a molecule of protonated alcohol.

good

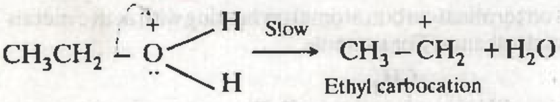


$$CH_3CH_2-\ddot{O}-H + \overset{+}{H} \rightleftharpoons CH_3CH_2-\overset{+}{O}H_2$$

This step is fast and hence does not affect the rate of the reaction.

This step is usually reversible.

Step 2. The presence of a positive charge on the highly electronegative oxygen atom weakens the C – O bond and thus it readily eliminates a molecule of water to form a reactive chemical species called *carbocation*.



$$CH_3CH_2-\overset{+}{O}H_2 \xrightarrow{\text{Slow}} CH_3-\overset{+}{C}H_2 + H_2O$$

This step is slow and hence is the rate-determining step of the reaction.

Step 3. The carbocation formed in step 2 immediately loses a proton to form an alkene.

$$H-CH_2-\overset{+}{C}H_2 \xrightarrow{\text{Fast}} \underset{\text{Ethene}}{CH_2=CH_2} + H^+$$

Laboratory method of preparation. In the laboratory ethene is prepared by dehydration of ethyl alcohol with conc. H_2SO_4 at 440 K. For this purpose, a mixture of ethanol and conc. H_2SO_4 in the ratio of 1 : 2 by volume is added from a dropping funnel into a round bottomed flask containing anhydrous $Al_2(SO_4)_3$ and sand in which $Al_2(SO_4)_3$ catalyses the reaction whereas sand is used to avoid frothing during the process.

The reaction mixture is heated to 440 K and ethene thus produced is collected over water as shown in Fig. 15.17. Ethene produced by the above method contains impurities of SO_2 (formed by the reduction of H_2SO_4) and CO_2 (formed by the oxidation of ethanol). In order to remove these impurities, impure ethene is passed through a solution of caustic soda (NaOH) which absorbs CO_2 and SO_2.

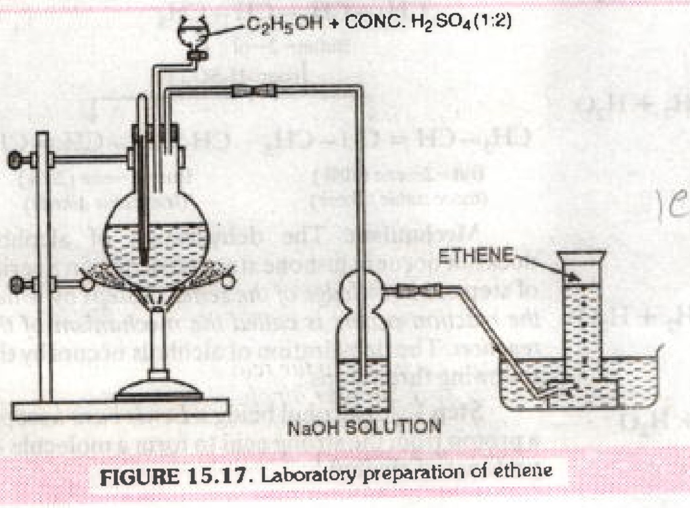


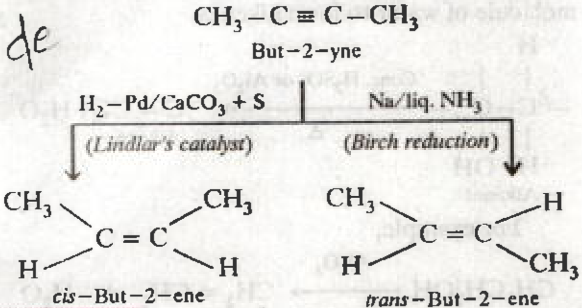
FIGURE 15.17. Laboratory preparation of ethene

$$2\,NaOH + CO_2 \longrightarrow Na_2CO_3 + H_2O$$

$$2\,NaOH + SO_2 \longrightarrow Na_2SO_3 + H_2O$$

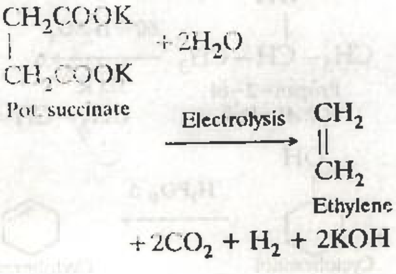
By partial reduction of alkynes. *The catalytic hydrogenation of alkynes to alkenes occurs faster than that of alkenes to alkanes.* Therefore, by using a specific catalyst, it is possible to stop the reduction at the alkene stage. Further since alkynes show geometrical isomerism, alkynes can be reduced to give *cis-* or *trans-*alkenes depending upon the nature of the catalyst used. For example, catalytic reduction of alkynes in presence of palladium supported over $CaCO_3$ or $BaSO_4$ and partially poisoned by addition of $PbCO_3$, S or quinoline **(Lindlar's catalyst)** predominantly gives *cis-*alkenes. However, if alkynes are reduced with sodium in liquid ammonia **(Birch reduction)**, *trans-*alkenes are the major products. Thus,

de



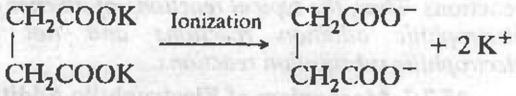
From sodium or potassium salts of saturated dicarboxylic acids *(Kolbe's electrolytic reaction)* Electrolysis of sodium or potassium salts of saturated dicarboxylic acids gives alkenes. For example,

le



$$\underset{\text{Pot. succinate}}{\begin{matrix} CH_2COOK \\ | \\ CH_2COOK \end{matrix}} + 2H_2O \xrightarrow{\text{Electrolysis}} \underset{\text{Ethylene}}{\begin{matrix} CH_2 \\ \| \\ CH_2 \end{matrix}} + 2CO_2 + H_2 + 2KOH$$

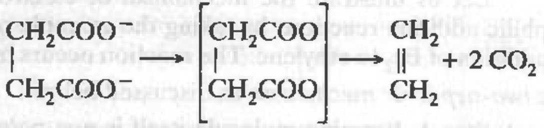
This reaction is called **Kolbe's electrolytic reaction** and is believed to occur by the following steps :



$$\begin{matrix}CH_2COOK\\ |\\ CH_2COOK\end{matrix} \xrightarrow{\text{Ionization}} \begin{matrix}CH_2COO^-\\ |\\ CH_2COO^-\end{matrix} + 2\,K^+$$

$$2\,H_2O \rightleftharpoons 2\,OH^- + 2\,H^+$$

At anode :



$$\begin{matrix}CH_2COO^-\\ |\\ CH_2COO^-\end{matrix} \longrightarrow \left[\begin{matrix}CH_2COO\\ |\\ CH_2COO\end{matrix}\right] \longrightarrow \begin{matrix}CH_2\\ \|\\ CH_2\end{matrix} + 2\,CO_2$$

At cathode. Since the discharge potential of H^+ ions is lower than that of K^+ ions, therefore, H^+ ions are preferentially discharged to produce H_2 while K^+ ions remain in the solution

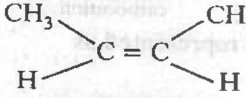
$$2\,H^+ + 2\,e^- \longrightarrow [2\,H] \longrightarrow H_2$$

15.7.5. Physical Properties of Alkenes

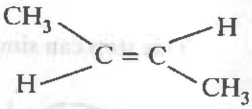
1. Physical state and smell. The first three members of the family, *i.e.*, ethene, propene and butenes are colourless gases ; the next eleven members ($C_5 - C_{15}$) are liquids while the higher ones are solids. Except ethene which has a pleasant smell, all other alkenes are odourless gases.

2. Melting points. The melting points of alkenes do not show a regular gradation. However, *the melting points of alkenes are higher than those of the corresponding alkanes.* This is due to the reason that π-electrons of a double bond are more polarizable than σ-electrons of single bonds. As a result, intermolecular forces of attraction are stronger in alkenes than in alkanes and hence alkenes have higher melting points than the corresponding alkanes.

Amongst isomeric alkenes, *trans-alkenes have higher melting points than their corresponding cis-isomers.* For example,



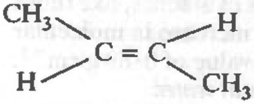
cis−But−2−ene
m.p. 134·1 K



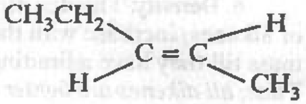
trans−But−2−ene
(m.p. 167·4 K)

This is due to the reason that the molecules of *trans*-alkene being symmetrical pack more closely in the crystal lattice than the molecules of *cis*-alkene which are less symmetrical. As a result, greater amount of energy is required to break the crystal lattice of a *trans*-alkene than the corresponding *cis*-alkene and hence *trans*-alkenes have higher melting points than the corresponding *cis*-isomers.

3. Dipole moments. *Symmetrical trans-alkenes are non-polar and hence have zero dipole moment* since the dipole moments of individual groups being equal and opposite exactly cancel out each other. Unsymmetrical *trans*-alkenes, however, have small but finite dipole moments. The reason being that although the two dipoles oppose each other yet they donot exactly cancel out each other since they are unequal.

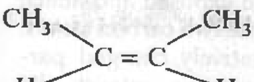


trans−But−2−ene
($\mu = 0$)

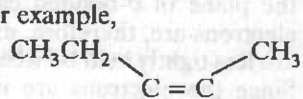


trans−Pent−2−ene
($\mu > 0$)

Both symmetrical and unsymmetrical *cis*-alkenes are polar molecules and hence have finite dipole moments. The reason being that in these cases, the two dipole moments are inclined to each other at an angle of about 60° and hence have a finite dipole moment. For example,

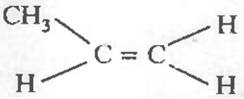


cis−But−2−ene
($\mu = 0·25$ D)

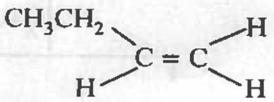


cis−Pent−2−ene
($\mu > 0$)

Similarly, unsymmetrical terminal alkenes such as propene and but-1-ene have finite dipole moments since the polarity due to the alkyl group is not cancelled by corresponding polarity in the opposite direction. Thus,

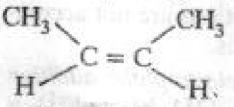


Propene
($\mu = 0·35$ D)

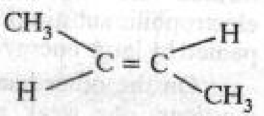


But−1−ene
($\mu = 0·37$ D)

4. Boiling points. The boiling points of alkenes, like alkanes, show a regular gradation with the increase in the number of carbon atoms. Except for the first few members, the boiling points increase by about 20° – 30° for the addition of each carbon. The branched chain alkenes, however, have lower boiling points than the corresponding straight chain alkenes. Amongst the alkenes which show geometrical isomerism, *cis-alkenes have higher boiling points than the* corresponding *trans*- isomers.



trans−But−2−ene
(b.p. 277 K)



cis−But−2−ene
(b.p. 274 K)

This is due to the reason that cis-alkenes being polar have stronger dipole-dipole interactions while trans-alkenes being non-polar (or weakly polar) have weak induced dipole interactions.

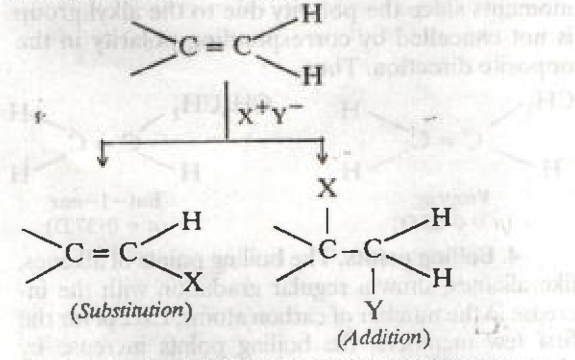
genios

5. Solubility. Alkenes like alkanes being either non-polar or weakly polar molecules are practically insoluble in water and other polar solvents but are quite soluble in non-polar solvents such as benzene, CCl_4, petroleum ether etc. and weakly polar solvents such as ether.

6. Density. The densities of alkenes, like those of alkanes, increase with the increase in molecular mass till they have a limiting value of 0·89 g cm^{-3}. Thus, *all alkenes are lighter than water.*

15.7.6. Why do alkenes undergo Electrophilic Addition Reactions ?

Alkenes are characterized by the presence of a double bond which consists of a strong C–C, σ-bond and a weak C–C, π-bond. The π-electrons form an electron cloud which lies above and below the plane of σ-bonded carbon atoms. These, π-electrons are, therefore, more exposed and hence are less tightly held between the two carbon atoms. Since the electrons are negatively charged particles, therefore, the π-electrons attract the *electrophiles* and repel *nucleophiles*. In other words, alkenes undergo *electrophilic reactions*. Now, in principle electrophilic reactions can be of two types : (*i*) *addition* and (*ii*) *substitution*.



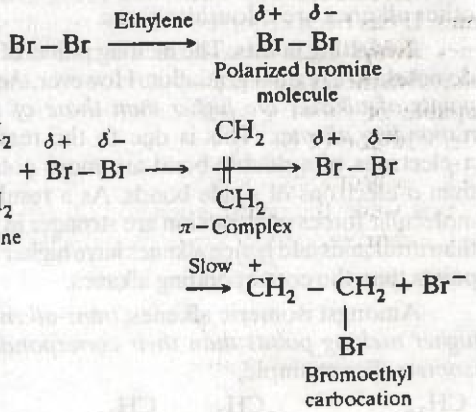
In electrophilic substitution reactions, one σ C–H bond is broken and a new σ-bond between one of the doubly bonded carbon atoms and the electrophile is formed. Since the bond energies of the σ C–H bond broken and the new σ C–X bond formed are not much different, therefore, electrophilic substitution reactions are not accompanied by large energy changes.

On the other hand, *in electrophilic addition reactions*, one weak π-bond (251 kJ mol^{-1}) is broken and two strong σ-bonds (2 × 347 = 694 kJ mol^{-1}) are formed. The overall reaction is accompanied by a release of about 694 – 251 = 443 kJ mol^{-1} of energy. In other words, electrophilic addition reactions are energetically more favourable than electrophilic substitution reactions. *Thus, the typical reactions of alkenes are electrophilic addition reactions and not the electrophilic substitution reactions.*

15.7.7. Mechanism of Electrophilic Addition Reactions

Let us illustrate the mechanism of electrophilic addition reactions by taking the example of addition of Br_2 to ethylene. The reaction occurs by a *two-step ionic mechanism* as discussed below :

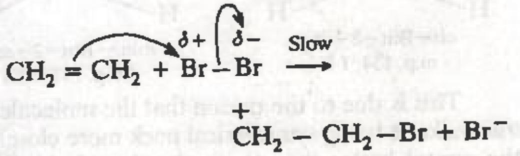
Step 1. Bromine molecule itself is *non-polar* but when it comes close to an ethylene molecule, the π-electrons of the double bond begin to repel the electron pair holding the two bromine atoms in the bromine molecule. As a result, bromine molecule gets *polarized*. The positive end of this bromine dipole behaves as an *electrophile* and is attracted by the π-electrons of the ethylene molecule to form a **π-complex*** which subsequently gives the carbocation and the bromide ion. *This step is slow and hence is the rate-determine step of the reaction.*



$$Br-Br \xrightarrow{\text{Ethylene}} \overset{\delta+}{Br}-\overset{\delta-}{Br}$$

$$\begin{matrix} CH_2 \\ \| \\ CH_2 \end{matrix} + \overset{\delta+}{Br}-\overset{\delta-}{Br} \longrightarrow \begin{matrix} CH_2 \\ \nparallel \\ CH_2 \end{matrix} \longrightarrow \overset{\delta+}{Br}-\overset{\delta-}{Br} \xrightarrow{\text{Slow}} \overset{+}{C}H_2-\underset{\underset{Br}{|}}{C}H_2 + Br^-$$

This step can simply be represented as

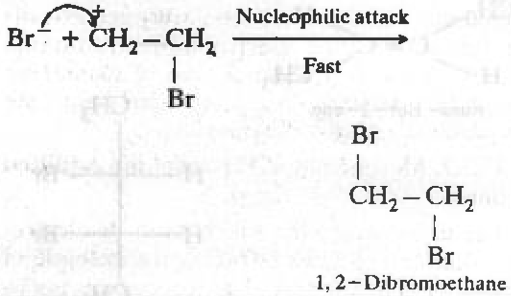


$$CH_2=CH_2 + \overset{\delta+}{Br}-\overset{\delta-}{Br} \xrightarrow{\text{Slow}} \overset{+}{C}H_2-CH_2-Br + Br^-$$

Step 2. The carbocation formed in **step 1** being a reactive chemical species immediately undergoes *nucleophilic attack* by the bromide ion present in the solution forming the addition product. *This step is fast and hence does not affect the rate of the reaction.*

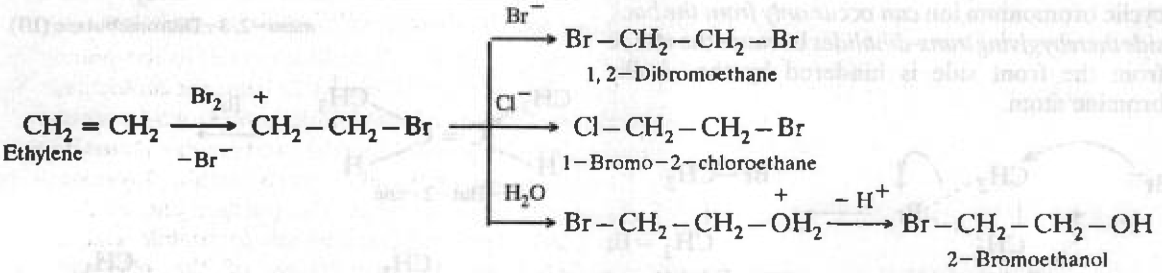
---

*In the π-complex, there is no actual bonding between the ethylene and the polarized bromine molecule. There is only electrostatic attraction.



$$Br^- + \overset{+}{C}H_2-\underset{Br}{\underset{|}{C}H_2} \xrightarrow[\text{Fast}]{\text{Nucleophilic attack}} \underset{\text{1, 2−Dibromoethane}}{\overset{Br}{\overset{|}{C}H_2}-\underset{Br}{\underset{|}{C}H_2}}$$

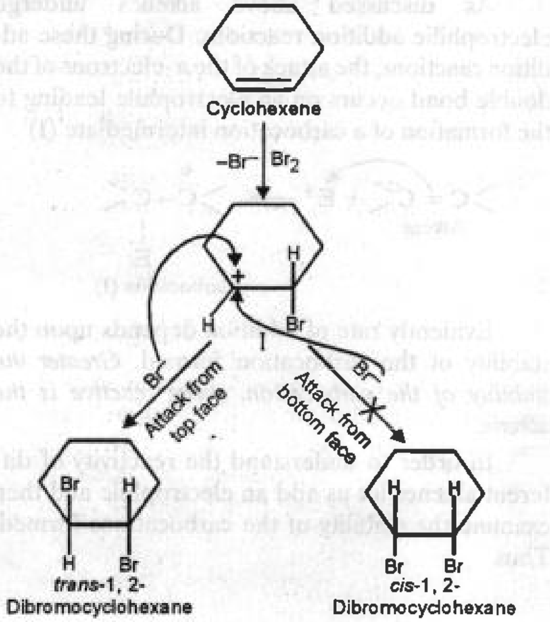
Evidence in support of the above mechanism. If the carbocations are really the intermediates in the above mechanism, then they should also react with other nucleophiles when added to the reaction mixture and hence a mixture of products should be formed. This has indeed been found to be so. For example, when ethylene is bubbled into an aqueous solution of bromine containing sodium chloride, besides 1, 2-dibromoethane ; 1-bromo- 2-chloroethane and 2-bromoethanol are also formed.



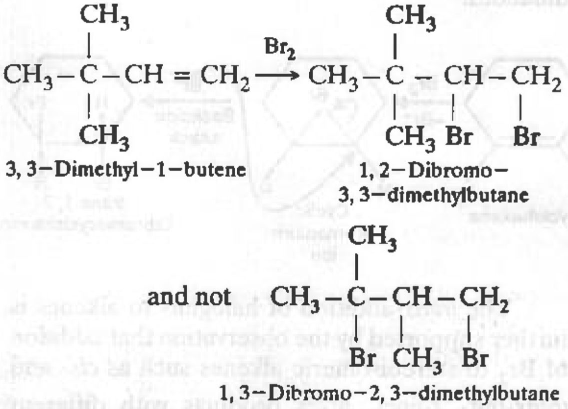
$$\underset{\text{Ethylene}}{CH_2=CH_2} \xrightarrow[-Br^-]{Br_2} \overset{+}{C}H_2-CH_2-Br \begin{cases} \xrightarrow{Br^-} \underset{\text{1, 2−Dibromoethane}}{Br-CH_2-CH_2-Br} \\ \xrightarrow{Cl^-} \underset{\text{1−Bromo−2−chloroethane}}{Cl-CH_2-CH_2-Br} \\ \xrightarrow{H_2O} Br-CH_2-CH_2-\overset{+}{O}H_2 \xrightarrow{-H^+} \underset{\text{2−Bromoethanol}}{Br-CH_2-CH_2-OH} \end{cases}$$

Limitations. The above mechanism involving simple carbocation intermediates does not explain the following two points :

(i) Stereochemistry of addition of halogens to alkenes. It has been observed that halogenation of alkenes always gives *trans*-dihalides and not *cis*-dihalides whenever the product of halogen addition is capable of showing stereoisomerism. For example, addition of Br_2 to cyclohexene gives only *trans*-1, 2-dibromocyclohexane. If the simple carbocations were the intermediates, both *cis* and *trans*-1, 2-dibromocyclohexanes should have been formed. This is due to the reason that carbocations are planar chemical species and hence the attack of the bromide ion on the initially formed carbocation (I) from either side of the molecule is equally probable. Thus,



(ii) Rearrangements of intermediate carbocations are not observed in halogenation of alkenes. The carbocations formed during the halogenation of alkenes do not undergo rearrangement. For example, addition of Br_2 to 3, 3-dimethyl-1- butene gives only the expected 1, 2-dibromo-3, 3-dimethylbutane and not the rearranged 1, 3-dibromo-2, 3-dimethylbutane.

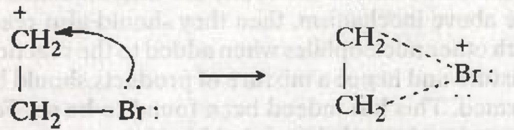


$$\underset{\text{3, 3−Dimethyl−1−butene}}{CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH=CH_2} \xrightarrow{Br_2} \underset{\text{1, 2−Dibromo−3, 3−dimethylbutane}}{CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\underset{Br}{CH}-\underset{Br}{CH_2}}$$

$$\text{and not} \quad \underset{\text{1, 3−Dibromo−2, 3−dimethylbutane}}{CH_3-\underset{Br}{\overset{CH_3}{C}}-\underset{CH_3}{CH}-\underset{Br}{CH_2}}$$

Cyclic Halonium Ion Mechanism

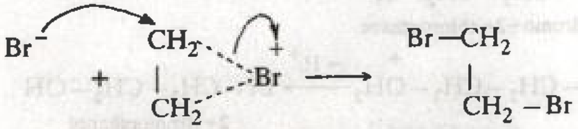
Since the addition of halogens to alkenes *(i) always gives trans-dihalides and (ii) the rearrangement of intermediate carbocations is not observed*, it was suggested that this reaction, in fact, occurs through a cyclic bromonium ion (II) rather than the simple carbocation (I).



Carbocation (I)

Cyclic bromonium ion (II)

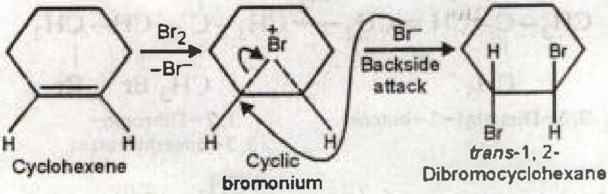
The nucleophilic attack of Br^- ion on this cyclic bromonium ion *can occur only from the back side thereby giving trans-dihalides* because the attack from the front side is hindered by the bulky bromine atom.



Cyclic bromonium ion (II)

trans-Dihalide (*hypothetical*)

Like carbocation, this cyclic bromonium ion is also a very reactive chemical species and hence is readily attacked by bromide ion (*nucleophile*) to complete the addition. *However, unlike simple carbocation on which attack of the bromide ion from either side is equally probable, in cyclic bromonium ion, the attack of the bromide ion can occur only from the backside of the bromine atom (forming the bridge) since the attack from the front side will be hindered by this bulky bromine atom.* This explains why the addition of halogens to alkenes gives *trans*-dihalides.

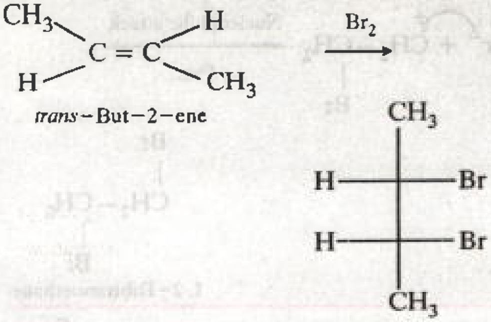


Cyclohexene

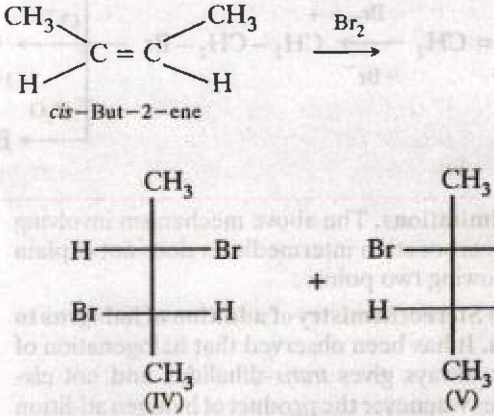
Cyclic bromonium ion

trans-1, 2-Dibromocyclohexane

The *trans*-addition of halogens to alkenes is further supported by the observation that addition of Br_2 to stereoisomeric alkenes such as *cis*- and *trans*-but- 2-enes, gives products with different stereochemistry. For example, addition of Br_2 to *trans*-but-2- ene gives *meso*-2, 3- dibromobutane (III) while that to *cis*-but-2- ene gives a racemic mixture of 2, 3- dibromobutanes (IV and V).



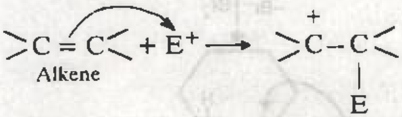
meso-2, 3-Dibromobutane (III)



(±)-2, 3-Dibromobutanes

15.7.8. Reactivity of Alkenes towards Electrophilic Addition Reactions

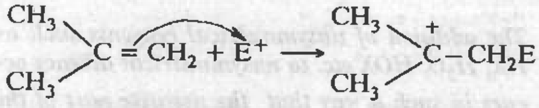
As discussed above alkenes undergo electrophilic addition reactions. During these addition reactions, the attack of the π-electrons of the double bond occurs on an electrophile leading to the formation of a carbocation intermediate (I)



Carbocation (I)

Evidently rate of addition depends upon the stability of the carbocation formed. *Greater the stability of the carbocation, more reactive is the alkene.*

In order to understand the reactivity of different alkenes let us add an electrophile and then examine the stability of the carbocations formed. Thus



$$(CH_3)_2C=CH_2 + E^+ \longrightarrow (CH_3)_2\overset{+}{C}-CH_2E$$

2−Methylpropene 3° Carbocation

$$CH_3CH=CH_2 + E^+ \longrightarrow CH_3-\overset{+}{C}H-CH_2E$$

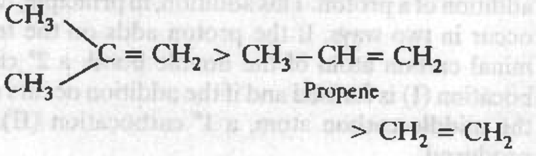
Propene 2° Carbocation

$$CH_2=CH_2 + E^+ \longrightarrow \overset{+}{C}H_2-CH_2E$$

Ethene 1° Carbocation

Since the stability of the carbocations follows the order :

3° > 2° > 1°, therefore, 2-methylpropene which gives a 3° carbocation reacts faster than propene which forms 2° carbocation which, in turn, reacts faster than ethene which forms a 1° carbocation. Thus, the overall reactivity decreases in the following sequence :



$$(CH_3)_2C=CH_2 > CH_3-CH=CH_2 > CH_2=CH_2$$

Propene Ethene

In general, the order of reactivity of alkenes towards electrophilic addition reactions decreases in the order :

$$R_2C=CR'_2 > R_2C=CHR' > R_2C=CH_2 \geq RCH=CHR > RCH=CH_2 > CH_2=CH_2$$

where R and R′ are alkyl groups.

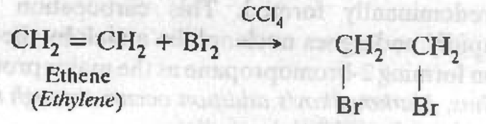
15.7.9. Chemical Reactions of Alkenes

Besides addition reactions, alkenes undergo oxidation, reduction and polymerization reactions. These are briefly described below :

I. Addition Reactions of Alkenes

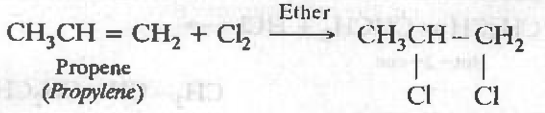
1. Addition of halogens

Halogens such as chlorine and bromine readily add to alkenes to form 1, 2-dihaloalkanes. For example,



$$CH_2=CH_2 + Br_2 \xrightarrow{CCl_4} CH_2Br-CH_2Br$$

Ethene (*Ethylene*) 1, 2−Dibromoethane (*Ethylene bromide*)



$$CH_3CH=CH_2 + Cl_2 \xrightarrow{Ether} CH_3CHCl-CH_2Cl$$

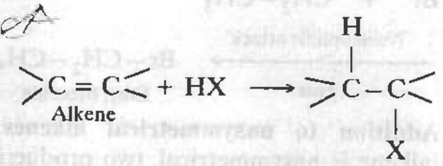
Propene (*Propylene*) 1, 2−Dichloropropane (*Propylene chloride*)

During the addition of bromine to alkenes, *the orange red colour of bromine is discharged since the dibromide formed is colourless.* This reaction is, therefore, used as a **test for unsaturation in organic compounds.**

Fluorine reacts with alkenes too rapidly to be controlled in the laboratory while iodine does not react with alkenes at ordinary temperatures. Thus the order of reactivity of addition of halogens to alkenes is

Fluorine > Chlorine > Bromine > Iodine

2. Addition of halogen acids. Alkenes react with halogen acids (HCl, HBr, HI) to form monohaloalkanes called alkyl halides.



$$>C=C< + HX \longrightarrow >CH-CX<$$

Alkene Alkyl halide

e.g., $CH_2=CH_2 + HBr \longrightarrow CH_3-CH_2Br$

Ethene (*Ethylene*) Bromoethane (*Ethyl bromide*)

The order of reactivity of halogen acids in this reaction is : HI > HBr > HCl. This order of reactivity can be explained on the basis of bond dissociation energies of the halogen acids :

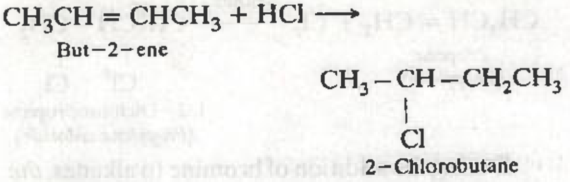
HI (300 kJ mol^{-1}) > HBr (360 kJ mol^{-1}) > HCl (430 kJ mol^{-1})

The actual product formed, however, depends upon whether the alkene is symmetrical or unsymmetrical as discussed below :

(i) Addition to symmetrical alkenes. When the alkene is symmetrical only one product is theoretically possible. For example,

$$CH_2=CH_2 + HBr \longrightarrow CH_3-CH_2-Br$$

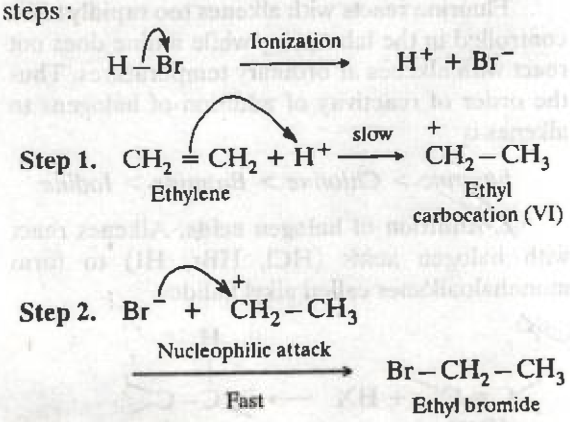
Ethene Bromoethane



$$\underset{\text{But-2-ene}}{CH_3CH=CHCH_3} + HCl \longrightarrow \underset{\text{2-Chlorobutane}}{CH_3-\underset{\underset{Cl}{|}}{CH}-CH_2CH_3}$$

Mechanism.

Like the addition of halogens, additions of halogen acids to alkenes is also an *electrophilic addition reaction* and occurs in the following two steps :

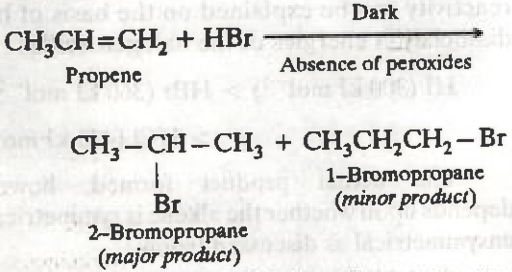


$$H-Br \xrightarrow{\text{Ionization}} H^+ + Br^-$$

Step 1. $$\underset{\text{Ethylene}}{CH_2=CH_2} + H^+ \xrightarrow{\text{slow}} \underset{\substack{\text{Ethyl}\\ \text{carbocation (VI)}}}{\overset{+}{C}H_2-CH_3}$$

Step 2. $$Br^- + \overset{+}{C}H_2-CH_3 \xrightarrow[\text{Fast}]{\text{Nucleophilic attack}} \underset{\text{Ethyl bromide}}{Br-CH_2-CH_3}$$

(ii) Addition to unsymmetrical alkenes. When the alkene is unsymmetrical, two products are theoretically possible. For example, the addition of HBr to propene *in the dark and in the absence of peroxides* can, in principle, give two products. But experimentally, it has been found that under these conditions, the major product is 2-bromopropane and the minor product is 1-bromopropane.

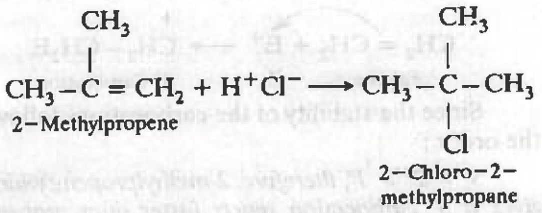


$$\underset{\text{Propene}}{CH_3CH=CH_2} + HBr \xrightarrow[\text{Absence of peroxides}]{\text{Dark}} \underset{\substack{\text{2-Bromopropane}\\ \textit{(major product)}}}{CH_3-\underset{\underset{Br}{|}}{CH}-CH_3} + \underset{\substack{\text{1-Bromopropane}\\ \textit{(minor product)}}}{CH_3CH_2CH_2-Br}$$

Markovnikov's rule. *Markovnikov*, a Russian chemist, studied a large number of such addition reactions and postulated an empirical rule in 1869 which is known after his name as **Markovnikov's rule**. The rule states that

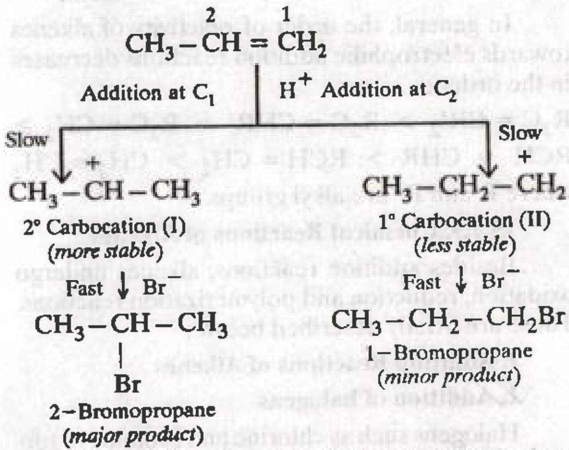
The addition of unsymmetrical reagents such as HX, H_2O, HOX etc. to unsymmetrical alkenes occurs in such a way that the negative part of the addendum (i.e. adding molecule) goes to that carbon atom of the double bond which carries lesser number of hydrogen atoms.

For example,



$$\underset{\text{2-Methylpropene}}{CH_3-\overset{\overset{CH_3}{|}}{C}=CH_2} + H^+Cl^- \longrightarrow \underset{\substack{\text{2-Chloro-2-}\\ \text{methylpropane}}}{CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{Cl}{|}}{C}}-CH_3}$$

Theoretical explanation of Markovnikov's rule. The addition of halogen acids to alkenes is an *electrophilic addition reaction.* Thus, during the addition of HBr to propene, the first step involves the addition of a proton. This addition, in principle, can occur in two ways. If the proton adds on the terminal carbon atom of the double bond, a 2° carbocation (I) is formed and if the addition occurs on the middle carbon atom, a 1° carbocation (II) is produced.



$$CH_3-\overset{2}{C}H=\overset{1}{C}H_2 \xrightarrow{H^+}$$

Addition at C_1: $$\xrightarrow{\text{Slow}} \underset{\substack{\text{2° Carbocation (I)}\\ \textit{(more stable)}}}{CH_3-\overset{+}{C}H-CH_3} \xrightarrow[\text{Fast}]{Br^-} \underset{\substack{\text{2-Bromopropane}\\ \textit{(major product)}}}{CH_3-\underset{\underset{Br}{|}}{CH}-CH_3}$$

Addition at C_2: $$\xrightarrow{\text{Slow}} \underset{\substack{\text{1° Carbocation (II)}\\ \textit{(less stable)}}}{CH_3-CH_2-\overset{+}{C}H_2} \xrightarrow[\text{Fast}]{Br^-} \underset{\substack{\text{1-Bromopropane}\\ \textit{(minor product)}}}{CH_3-CH_2-CH_2Br}$$

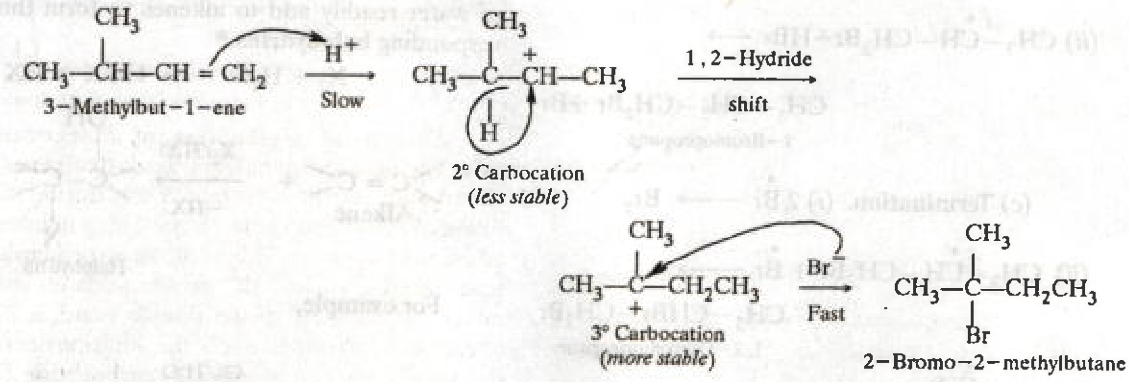
Since a 2° carbocation (I) is more stable than 1° carbocation (II), therefore, carbocation (I) is predominantly formed. This carbocation then rapidly undergoes nucleophilic attack by the Br^- ion forming 2-bromopropane as the major product. *Thus, Markovnikov's addition occurs through more stable carbocation intermediate.*

ADD TO YOUR KNOWLEDGE

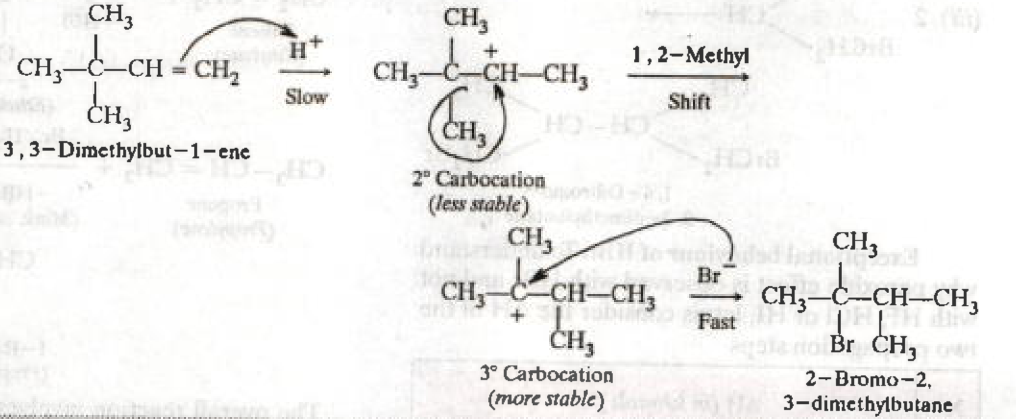
Rearrangements during addition of halogen acids. It may be noted that

However, unlike the addition of Br_2 to alkenes which occurs through a cyclic bromonium ion (II), the addition of HBr occurs through the intermediate formation of simple carbocations (VI).

Since carbocations are prone to rearrangement, therefore, if the structure of the initially formed carbocation permits, it may undergo rearrangement either by a **1, 2-hydride shift** or by a **1, 2- methyl shift** to form the more stable carbocation which then undergoes nucleophilic attack by the Br^- ion to form the rearranged alkyl halide. For example,



Similarly,



Peroxide effect. It may be noted that Markovnikov's rule is not always followed. In presence of peroxides such as benzoyl peroxide ($C_6H_5CO-O-O-COC_6H_5$), the addition of HBr (but not of HCl or HI) to unsymmetrical alkenes takes place contrary to Markovnikov's rule. This is known as **Peroxide effect** or **Kharasch effect.** Thus,

$$\underset{\text{Propene (Propylene)}}{CH_3CH{=}CH_2} + HBr \xrightarrow[\text{Anti-Mark. addn.}]{(C_6H_5COO)_2} \underset{\text{1-Bromopropane (n-Propyl bromide)}}{CH_3CH_2-CH_2Br}$$

Mechanism. The addition of HBr to alkenes in presence of peroxides occurs by a free *radical mechanism*. It consists of the following three steps.

(*a*) **Initiation.**

(*i*) $\underset{\text{Benzoyl peroxide}}{C_6H_5CO-O-O-COC_6H_5} \xrightarrow{\Delta} \underset{\text{Benzoyl free radical}}{2\,C_6H_5CO-\dot{O}}$

(*ii*) $C_6H_5CO-\dot{O} + HBr \longrightarrow C_6H_5COOH + \dot{Br}$

(*b*) **Propagation.** It consists of two steps.

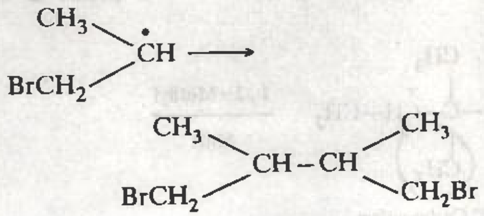
During the first step, a Br• adds to the double bond in such a way to give the more stable free radical. In the second step, the free radical thus produced abstracts a H• from HBr to complete the addition.

(*i*) $\underset{\text{Propene}}{CH_3-CH=CH_2}+\dot{Br}\longrightarrow \underset{\text{2° radical (more stable)}}{CH_3-\dot{C}H-CH_2Br}$

(*ii*) $CH_3-\dot{C}H-CH_2Br+HBr \longrightarrow \underset{\text{1-Bromopropane}}{CH_3-CH_2-CH_2Br} + \dot{Br}$

(*c*) **Termination.** (*i*) $2\dot{Br} \longrightarrow Br_2$

(*ii*) $CH_3-\dot{C}H-CH_2Br + \dot{Br} \longrightarrow \underset{\text{1, 2-Dibromopropane}}{CH_3-CHBr-CH_2Br}$

(*iii*) 2 

1, 4-Dibromo-
2, 3-dimethylbutane

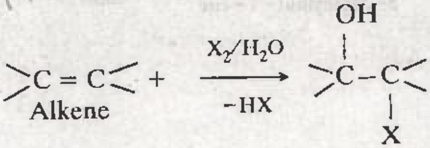
Exceptional behaviour of HBr. To understand why peroxide effect is observed with HBr and not with HF, HCl or HI, let us consider the ΔH of the two propagation steps

X in HX	ΔH (*in kJ/mole*)	
	(*i*) $\dot{X}+CH_2=CHCH_3 \longrightarrow XCH_2-\dot{C}H-CH_3$	(*ii*) $XCH_2-\dot{C}HCH_3+HX \longrightarrow XCH_2-CH_2CH_3+\dot{X}$
F	−209	+159
Cl	−101	+ 27
Br	− 42	−37
I	+12	−104

From the above data, it is clear that only with HBr, both the steps are *exothermic* and hence the peroxide effect is observed. With HCl or HF, the peroxide effect is not observed because the second step involving the reaction of carbon radical with HCl or HF is *endothermic*. Further, the peroxide effect is also not observed with HI because the first step involving the addition of iodine radical to alkenes is *endothermic*.

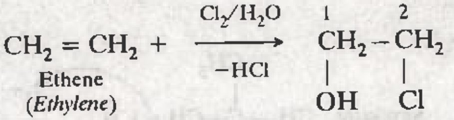
3. Addition of the elements of hypohalous acids (HOX where X = Cl, Br or I) – Halohydrin formation. Chlorine and bromine in the presence of water readily add to alkenes to form the corresponding **halohydrins.***

$$X_2 + H_2O \longrightarrow HOX + HX$$



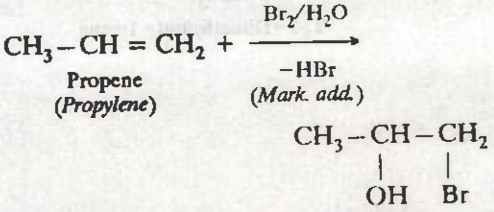
Halohydrin

For example,



$$\underset{\substack{\text{Ethene}\\ \text{(Ethylene)}}}{CH_2 = CH_2} + \xrightarrow[-HCl]{Cl_2/H_2O} \underset{\substack{|\\ OH}}{\overset{1}{CH_2}}-\underset{\substack{|\\ Cl}}{\overset{2}{CH_2}}$$

2-Chloroethanol
(*Ethylene chlorohydrin*)



$$\underset{\substack{\text{Propene}\\ \text{(Propylene)}}}{CH_3-CH = CH_2} + \xrightarrow[\substack{-HBr\\ \text{(Mark. add.)}}]{Br_2/H_2O} CH_3-\underset{\substack{|\\ OH}}{CH}-\underset{\substack{|\\ Br}}{CH_2}$$

1-Bromopropan-2-ol
(*Propylene bromohydrin*)

The overall reaction involves the addition of the elements of hypohalous acid ($HO^{-\delta}-X^{+\delta}$) in accordance with *Markovnikov's rule.*

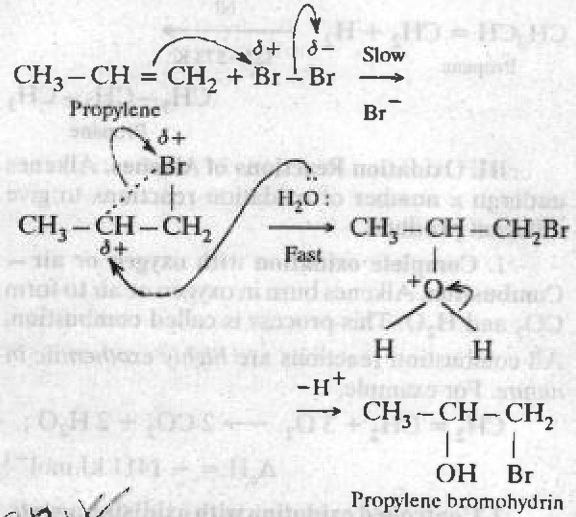
The order of reactivity of different X_2/H_2O (HOX) is

Cl_2/H_2O (HOCl) > Br_2/H_2O (HOBr) > I_2/H_2O (HOI)

Mechanism. The addition of halogens in presence of water occurs by a two step mechanism through cyclic halonium ion intermediate as shown below.

---

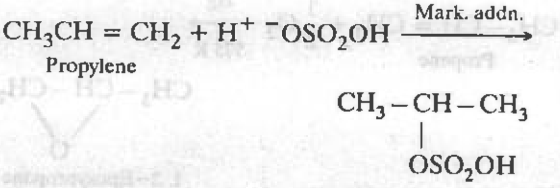
*Compounds containing halogen atom and the hydroxyl group on adjacent carbon atoms are called halohydrins.



$$CH_3-CH=CH_2+\overset{\delta+}{Br}-\overset{\delta-}{Br}\xrightarrow[Br^-]{Slow}CH_3-\overset{\delta+}{C}H-\overset{\delta+}{\underset{Br}{C}}H_2\xrightarrow[Fast]{H_2\ddot{O}:}CH_3-\underset{^+OH_2}{CH}-CH_2Br\xrightarrow{-H^+}\underset{\text{Propylene bromohydrin}}{CH_3-\underset{OH}{CH}-\underset{Br}{CH_2}}$$

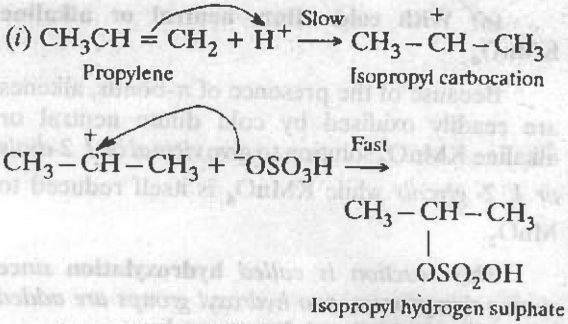
4. Addition of sulphuric acid – Indirect hydration of alkenes. Cold conc. H_2SO_4 adds to alkenes to form alkyl hydrogen sulphates. In case of unsymmetrical alkenes, addition occurs in accordance with *Markovnikov's rule.*

$$\underset{\text{Ethylene}}{CH_2=CH_2}+H^+\,{}^-OSO_2OH\longrightarrow\underset{\text{Ethyl hydrogen sulphate}}{CH_3-CH_2-OSO_2OH}$$



$$\underset{\text{Propylene}}{CH_3CH=CH_2}+H^+\,{}^-OSO_2OH\xrightarrow{\text{Mark. addn.}}\underset{\text{Isopropyl hydrogen sulphate}}{CH_3-\underset{OSO_2OH}{CH}-CH_3}$$

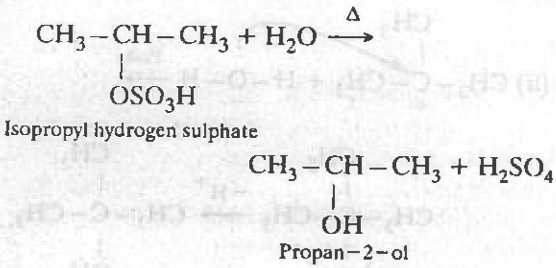
Mechanism. $H_2SO_4\longrightarrow H^+ + {}^-OSO_2OH$



$$(i)\ \underset{\text{Propylene}}{CH_3CH=CH_2}+H^+\xrightarrow{Slow}\underset{\text{Isopropyl carbocation}}{CH_3-\overset{+}{C}H-CH_3}$$

$$(ii)\ CH_3-\overset{+}{C}H-CH_3+{}^-OSO_3H\xrightarrow{Fast}\underset{\text{Isopropyl hydrogen sulphate}}{CH_3-\underset{OSO_2OH}{CH}-CH_3}$$

Importance. Alkyl hydrogen sulphates on boiling with water, undergo hydrolysis to produce alcohols. For example,



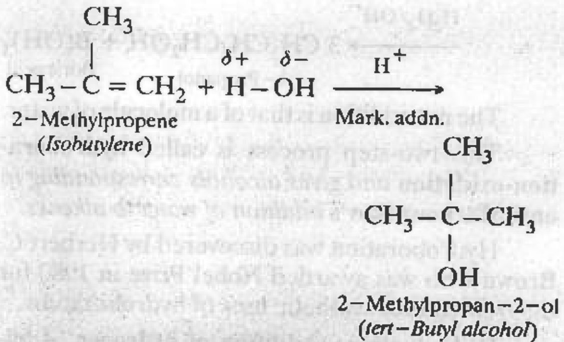
$$\underset{\text{Isopropyl hydrogen sulphate}}{CH_3-\underset{OSO_3H}{CH}-CH_3}+H_2O\xrightarrow{\Delta}\underset{\text{Propan-2-ol}}{CH_3-\underset{OH}{CH}-CH_3}+H_2SO_4$$

Thus, alkenes can be converted into alcohols :

$$\underset{\text{Ethene}}{CH_2=CH_2}\xrightarrow[(ii)\ H_2O,\ \Delta]{(i)\ \text{Conc. } H_2SO_4\ (cold)}\underset{\text{Ethanol}}{CH_3CH_2OH}$$

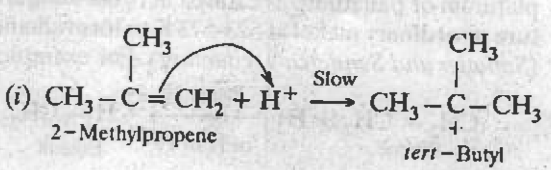
This overall two-step conversion of an alkene first into alkyl hydrogen sulphate followed by hydrolysis with boiling water to form alcohols is called **indirect hydration of alcohols.**

5. Addition of water – Direct hydration of alkenes. By hydration we mean addition of water. Ordinarily, water does not add directly to most of alkenes. However, some reactive alkenes do add water in presence of mineral acids to form alcohols. The addition occurs in accordance with *Markovnikov's rule.* For example,

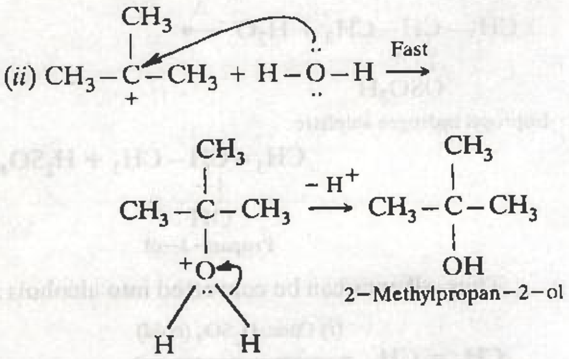


$$\underset{\substack{\text{2-Methylpropene}\\(Isobutylene)}}{CH_3-\overset{CH_3}{C}=CH_2}+\overset{\delta+}{H}-\overset{\delta-}{OH}\xrightarrow[\text{Mark. addn.}]{H^+}\underset{\substack{\text{2-Methylpropan-2-ol}\\(tert\text{-Butyl alcohol})}}{CH_3-\overset{CH_3}{\underset{OH}{C}}-CH_3}$$

Mechanism. It is an *electrophile addition reaction.* In the first step, the π-electrons of the double bond attack the electrophile, *i.e.*, H^+ to form a carbocation which readily reacts with water to form the alcohol :



$$(i)\ \underset{\text{2-Methylpropene}}{CH_3-\overset{CH_3}{C}=CH_2}+H^+\xrightarrow{Slow}\underset{tert\text{-Butyl carbocation}}{CH_3-\overset{CH_3}{\underset{+}{C}}-CH_3}$$



$$(ii)\ CH_3-\overset{CH_3}{\underset{+}{C}}-CH_3 + H-\ddot{O}-H \xrightarrow{Fast} CH_3-\overset{CH_3}{C}-CH_3 \xrightarrow{-H^+} CH_3-\overset{CH_3}{\underset{OH}{C}}-CH_3$$

6. Hydroboration-oxidation. Diborane adds to alkenes to form trialkylboranes which upon subsequent oxidation with alkaline H_2O_2 give alcohols. For example,

$$B_2H_6 \longrightarrow 2\,BH_3$$

$$\underset{\text{Propene}}{CH_3-CH=CH_2} \xrightarrow{BH_3} \underset{n-\text{Propylborane}}{CH_3-CH_2-CH_2BH_2}$$

$$\xrightarrow{CH_3CH=CH_2} \underset{Di-n-\text{Propylborane}}{(CH_3CH_2CH_2)_2B-H}$$

$$\xrightarrow{CH_3CH=CH_2} \underset{\text{Tri}-n-\text{propylborane}}{(CH_3CH_2CH_2)_3B}$$

$$\xrightarrow{H_2O_2/OH^-} 3\,\underset{1-\text{Propanol}}{CH_3CH_2CH_2OH} + \underset{\text{Boric acid}}{B(OH)_3}$$

The net addition is that of a molecule of water.

This two-step process is called **hydroboration-oxidation** *and gives alcohols corresponding to* **anti-Markownikov's** *addition of water to alkenes.*

Hydroboration was discovered by Herbert C. Brown who was awarded Nobel Prize in 1980 for the tremendous synthetic uses of hydroboration.

II. Reduction – Addition of hydrogen. *Addition of hydrogen to unsaturated hydrocarbons (such as alkenes, alkynes, arenes etc.) is called* **catalytic hydrogenation.** Alkenes readily add hydrogen in presence of Raney nickel (an active form of nickel), platinum or palladium as catalyst at room temperature or ordinary nickel at 523-573 K to form alkanes *(Sabatier and Senderen's reduction).* For example,

$$\underset{\text{Ethene}}{CH_2=CH_2} + H_2 \xrightarrow[\text{or Pt or Pd}]{\text{Raney Ni}} \underset{\text{Ethane}}{CH_3-CH_3}$$

$$\underset{\text{Propene}}{CH_3CH=CH_2} + H_2 \xrightarrow[523-573\text{ K}]{\text{Ni}} \underset{\text{Propane}}{CH_3-CH_2-CH_3}$$

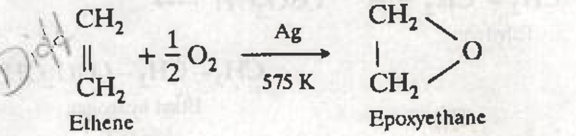
III. Oxidation Reactions of Alkenes. Alkenes undergo a number of oxidation reactions to give different products.

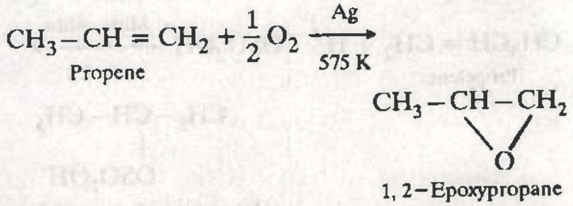
1. Complete oxidation with oxygen or air – Combustion. Alkenes burn in oxygen or air to form CO_2 and H_2O. This process is called combustion. All combustion reactions are *highly exothermic in nature.* For example,

$$CH_2=CH_2 + 3\,O_2 \longrightarrow 2\,CO_2 + 2\,H_2O\,;$$
$$\Delta_cH = -\,1411\text{ kJ mol}^{-1}$$

2. Controlled oxidation with oxidising agents. Alkenes react with a number of oxidising agents to give different products :

(i) Oxidation with oxygen. Alkenes react with O_2 in presence of silver as catalyst to form **epoxyalkanes or epoxides.** For example,





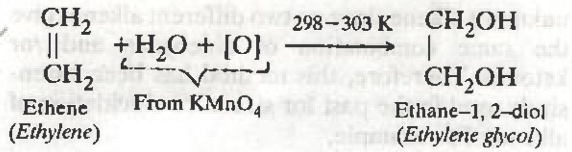
(ii) Oxidation with potassium permanganate. Different products are formed depending upon the reaction conditions.

(a) With cold dilute neutral or alkaline $KMnO_4$

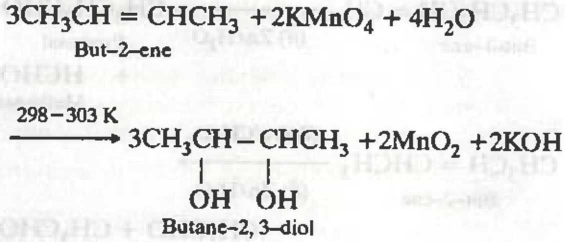
Because of the presence of π-bonds, alkenes are readily oxidised by cold dilute neutral or alkaline $KMnO_4$ solution to give *vicinal or 1, 2-diols or 1, 2- glycols* while $KMnO_4$ is itself reduced to MnO_2.

This reaction is called **hydroxylation** *since during this process, two hydroxyl groups are added across the double bond.* For example,

$$2KMnO_4 + H_2O \longrightarrow 2KOH + 2MnO_2 + 3[O]$$



$$\underset{\substack{\text{Ethene}\\(\textit{Ethylene})}}{\begin{matrix}CH_2\\ \|\\ CH_2\end{matrix}} + \underbrace{H_2O + [O]}_{\text{From } KMnO_4} \xrightarrow{298-303\ K} \underset{\substack{\text{Ethane–1, 2–diol}\\(\textit{Ethylene glycol})}}{\begin{matrix}CH_2OH\\ |\\ CH_2OH\end{matrix}}$$

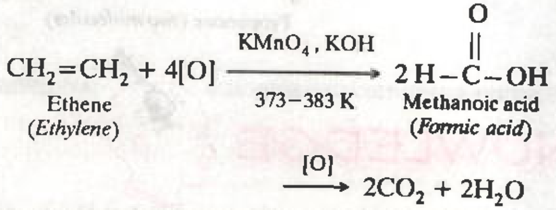


$$\underset{\text{But–2–ene}}{3CH_3CH = CHCH_3} + 2KMnO_4 + 4H_2O \xrightarrow{298-303\ K} \underset{\text{Butane–2, 3–diol}}{3CH_3\underset{OH}{\underset{|}{C}}H-\underset{OH}{\underset{|}{C}}HCH_3} + 2MnO_2 + 2KOH$$

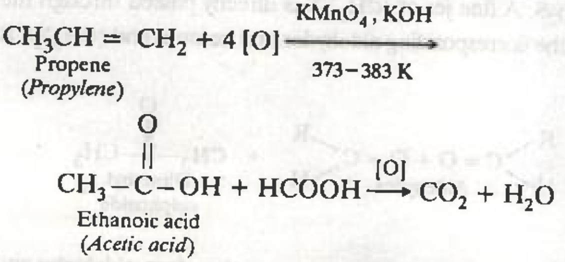
During this reaction, *the pink colour of the $KMnO_4$ solution is discharged and a brown precipitate of manganese dioxide is obtained. The reaction is, therefore, used as a test for unsaturation under the name* **Baeyer's test.**

(ii) Oxidation with hot $KMnO_4$ solution. When an alkene is heated with hot $KMnO_4$ solution, *cleavage of the C = C bond occurs* leading to the formation of carboxylic acids, ketones and carbon dioxide depending upon the nature of the alkene as shown below :

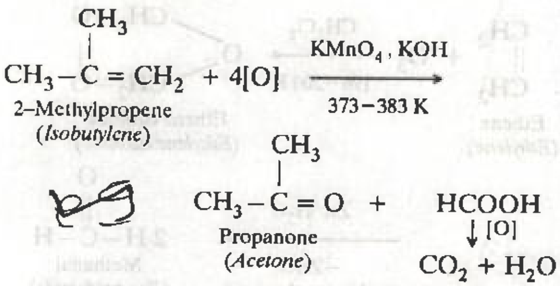
With terminal alkenes*, one of the products is always methanoic acid (formic acid) which on further oxidation gives $CO_2 + H_2O$. For example,



$$\underset{\substack{\text{Ethene}\\(\textit{Ethylene})}}{CH_2{=}CH_2} + 4[O] \xrightarrow[373-383\ K]{KMnO_4,\ KOH} \underset{\substack{\text{Methanoic acid}\\(\textit{Formic acid})}}{2\,H-\overset{\overset{\displaystyle O}{\|}}{C}-OH} \xrightarrow{[O]} 2CO_2 + 2H_2O$$



$$\underset{\substack{\text{Propene}\\(\textit{Propylene})}}{CH_3CH = CH_2} + 4\,[O] \xrightarrow[373-383\ K]{KMnO_4,\ KOH} \underset{\substack{\text{Ethanoic acid}\\(\textit{Acetic acid})}}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-OH} + HCOOH \xrightarrow{[O]} CO_2 + H_2O$$

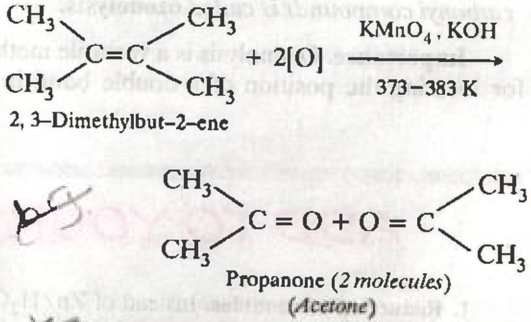


$$\underset{\substack{\text{2–Methylpropene}\\(\textit{Isobutylene})}}{CH_3-\overset{\overset{\displaystyle CH_3}{|}}{C} = CH_2} + 4[O] \xrightarrow[373-383\ K]{KMnO_4,\ KOH} \underset{\substack{\text{Propanone}\\(\textit{Acetone})}}{CH_3-\overset{\overset{\displaystyle CH_3}{|}}{C} = O} + \underset{\substack{\downarrow [O]\\ CO_2 + H_2O}}{HCOOH}$$

With non-terminal alkenes, carboxylic acids or ketones or both of these are obtained depending upon the nature of the alkene. For example,

$$\underset{\text{But–2–ene}}{CH_3CH = CHCH_3} + 4[O] \xrightarrow[373-383\ K]{KMnO_4,\ KOH} \underset{\substack{\text{Ethanoic acid (\textit{2 molecules})}\\(\textit{Acetic acid})}}{CH_3COOH + HOOCCH_3}$$

$$\underset{\text{Pent–2–ene}}{CH_3CH_2CH = CHCH_3} + 4\,[O] \xrightarrow[373-383\ K]{KMnO_4,\ KOH} \underset{\substack{\text{Propanoic acid}\\(\textit{Propionic acid})}}{CH_3CH_2COOH} + \underset{\substack{\text{Ethanoic acid}\\(\textit{Acetic acid})}}{HOOCCH_3}$$

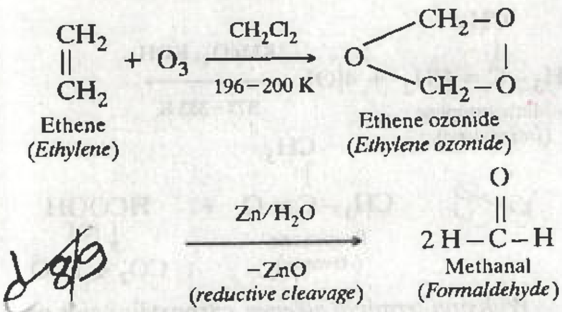


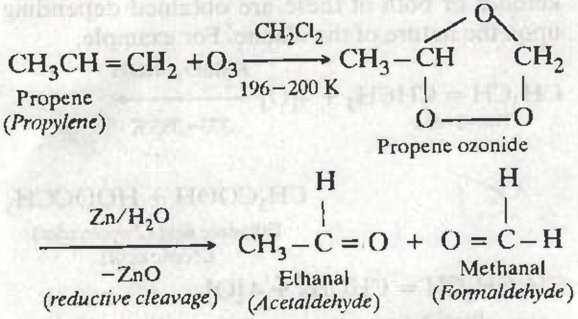
2, 3–Dimethylbut–2–ene + 2[O] $\xrightarrow[373-383\ K]{KMnO_4,\ KOH}$ Propanone (*2 molecules*) (*Acetone*)

(iii) Oxidation with ozone. When ozone is passed through a solution of an alkene in some inert solvent such as CH_2Cl_2, $CHCl_3$ or CCl_4 at a low temperature (196 – 200 K), it oxidises alkenes to *ozonides*. Ozonides are unstable and explosive compounds. Therefore, they are not usually isolated but are reduced, *in situ*, with zinc dust and water or H_2/Pd to give aldehydes or ketones or a mixture of these (*reductive cleavage*) depending upon the structure of the alkene.

---

*Alkenes in which double and triple bond are present at the end of the carbon chains are respectively called **terminal alkenes** and **terminal alkynes.**





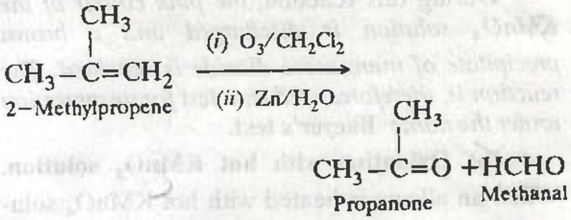
However, if the ozonides are decomposed only with water, the H_2O_2 produced during the reaction oxidises the initially formed aldehydes to the corresponding acids (*oxidative cleavage*).

***This two-step conversion of an alkene into an ozonide followed by its reductive cleavage to yield carbonyl compounds is called* ozonolysis.**

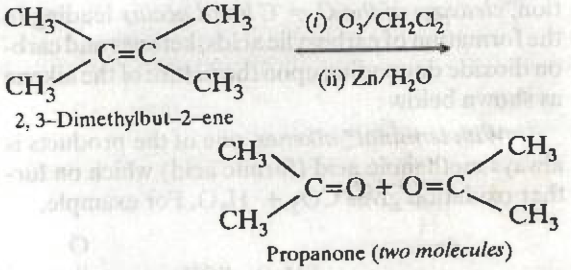
Importance. Ozonolysis is a versatile method for locating the position of a double bond in an unknown alkene since no two different alkenes give the same combination of aldehydes and /or ketones. Therefore, this method has been extensively used in the past for structure elucidation of alkenes. For example,

$$\underset{\text{But-1-ene}}{CH_3CH_2CH=CH_2} \xrightarrow[(ii)\ Zn/H_2O]{(i)\ O_3/CH_2Cl_2} \underset{\text{Propanal}}{CH_3CH_2CHO} + \underset{\text{Methanal}}{HCHO}$$

$$\underset{\text{But-2-ene}}{CH_3CH=CHCH_3} \xrightarrow[(ii)\ Zn/H_2O]{(i)\ O_3/CH_2Cl_2} \underset{\text{Ethanal (two molecules)}}{CH_3CHO + CH_3CHO}$$

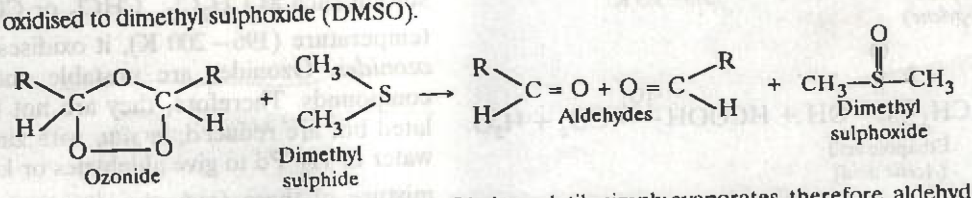


$$\underset{\text{2-Methylpropene}}{CH_3-\overset{\overset{CH_3}{|}}{C}=CH_2} \xrightarrow[(ii)\ Zn/H_2O]{(i)\ O_3/CH_2Cl_2} \underset{\text{Propanone}}{CH_3-\overset{\overset{CH_3}{|}}{C}=O} + \underset{\text{Methanal}}{HCHO}$$



ADD TO YOUR KNOWLEDGE

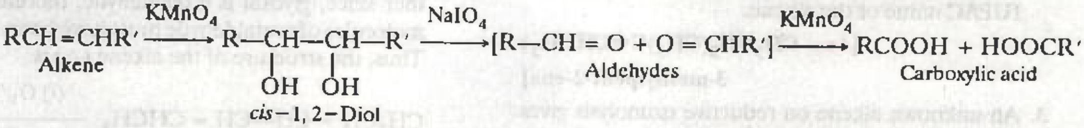
1. **Reduction of ozonides.** Instead of Zn/H_2O or catalytic hydrogenation (H_2/Pd), ozonides can more conveniently be reduced with dimethyl sulphide, $(CH_3)_2S$. A fine jet of $(CH_3)_2S$ is directly passed through the ozonolysis mixture, when the ozonide is reduced to the corresponding aldehydes and ketones and $(CH_3)_2S$ is itself oxidised to dimethyl sulphoxide (DMSO).



Since DMSO is water soluble and excess of $(CH_3)_2S$ being volatile simply evaporates, therefore, aldehydes and ketones are obtained almost in pure state.

ADD TO YOUR KNOWLEDGE CONTD.

2. **Lemieux reagent** is an aqueous solution of sodium periodate ($NaIO_4$) and a trace of $KMnO_4$ and is used for oxidation of alkenes. In fact, it is a better method than ozonolysis for determining the position of double in an alkene and for preparing carbonyl compounds. With this reagent, the alkene is first oxidised to *cis*-1, 2-diol which is then cleaved by periodate to aldehydes and/or ketones. Aldehydes thus produced are further oxidised by $KMnO_4$ to acids. The reaction proceeds at room temperature and the manganese obtained in the lower oxidation state is reoxidised to permanganate and hence only a trace of $KMnO_4$ is needed. Thus,

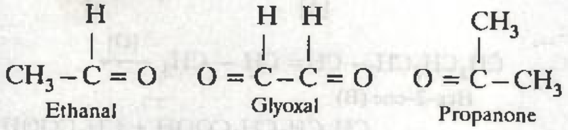


$$\underset{\text{Alkene}}{RCH{=}CHR'} \xrightarrow{KMnO_4} \underset{cis-1,\,2-\text{Diol}}{R{-}\underset{OH}{\underset{|}{C}H}{-}\underset{OH}{\underset{|}{C}H}{-}R'} \xrightarrow{NaIO_4} \underset{\text{Aldehydes}}{[R{-}CH=O+O=CHR']} \xrightarrow{KMnO_4} \underset{\text{Carboxylic acid}}{RCOOH + HOOCR'}$$

PROBLEMS ON OZONOLYSIS

EXAMPLE 15.5. *A hydrocarbon containing two double bonds on reductive ozonolysis gave glyoxal, ethanal and propanone. Give the structure of the hydrocarbon along with its IUPAC name.*

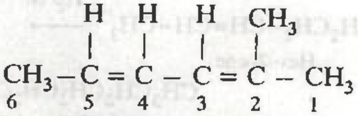
Solution. Step 1. *To write the structure of the products of ozonolysis with their carbonyl groups facing each other.*



$$\underset{\text{Ethanal}}{CH_3-\overset{H}{\overset{|}{C}}=O} \qquad \underset{\text{Glyoxal}}{O=\overset{H}{\overset{|}{C}}-\overset{H}{\overset{|}{C}}=O} \qquad \underset{\text{Propanone}}{O=\overset{CH_3}{\overset{|}{C}}-CH_3}$$

Step 2. *To write the structure of the hydrocarbon.*

Remove oxygen atoms from each of the three carbonyl compounds and connect them by double bonds, we have :—



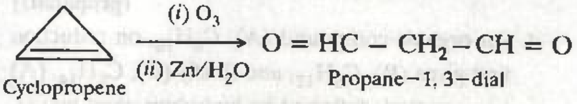
$$\underset{6}{CH_3}-\underset{5}{\overset{H}{\overset{|}{C}}}=\underset{4}{\overset{H}{\overset{|}{C}}}-\underset{3}{\overset{H}{\overset{|}{C}}}=\underset{2}{\overset{CH_3}{\overset{|}{C}}}-\underset{1}{CH_3}$$

2-Methylhexa-2, 4-diene

Thus, the given hydrocarbon is 2-methylhexa-2, 4-diene.

EXAMPLE 15.6. *Give the structures of the compounds which on reductive ozonolysis give :*
(i) propane-1, 3- dial (ii) glyoxal and formaldehyde (iii) acetaldehyde, formaldehyde and carbon dioxide.

Solution. (*i*) Since reductive ozonolysis gives only one product, *i.e.*, propane-1, 3-dial, therefore, the 2compound must be a cyclic alkene, *i.e.*, cyclopropene,



$$\underset{\text{Cyclopropene}}{\triangle} \xrightarrow[(ii)\ Zn/H_2O]{(i)\ O_3} \underset{\text{Propane}-1,\,3-\text{dial}}{O=HC-CH_2-CH=O}$$

(*ii*) Since two products *i.e.*, glyoxal and formaldehyde are obtained, therefore, the compound must be acyclic. Further, since glyoxal (OCH–CHO) contains two aldehyde groups, therefore, on either side, there must a = CH_2 group. Thus, the compound is 1, 3- butadiene.

$$\underset{1,\,3-\text{Butadiene}}{CH_2=CH-CH=CH_2} \xrightarrow[(ii)\ Zn/H_2O]{(i)\ O_3}$$

$$\underset{\text{Formaldehyde}}{HCHO} + \underset{\text{Glyoxal}}{OCH-CHO} + HCHO$$

(*iii*) Formation of CO_2 indicates that on either side of this carbon, there is a double bond. Since CH_3CHO and HCHO are the two aldehydes obtained, therefore, this carbon is attached to $CH_3CH=$ group on one side and $CH_2=$group on the other side. Therefore, the compound is 1, 2-butadiene.

$$\underset{1,\,2-\text{Butadiene}}{CH_3CH=C=CH_2} \xrightarrow[(ii)\ Zn/H_2O]{(i)\ O_3}$$

$$CH_3CHO + O=C=O + HCHO$$

PROBLEMS FOR PRACTICE

1. An alkene with molecular formula C_7H_{14} gives propanone and butanal on ozonolysis. Write down its structural formula. *(N.C.E.R.T.)*

[Hint. The structures of the ozonolysis products are : $\underset{\text{Butanal}}{CH_3CH_2CH_2CH=O}$ $\underset{\text{Propanone}}{O=C(CH_3)_2}$

PRACTICE PROBLEMS CONTD.

Remove the oxygen atoms and connect them by a double bond, the structure of the alkene is

$$\underset{\text{2-Methylhex-2-ene}}{CH_3CH_2CH_2CH = C(CH_3)_2}]$$

2. The reductive ozonolysis of an alkene gave butanone and ethanal. Give the structure and IUPAC name of the alkene.

[Ans. $CH_3CH_2(CH_3)C{=}CHCH_3$, 3-methylpent-2-ene]

3. An unknown alkene on reductive ozonolysis gives two isomeric carbonyl compounds of molecular formula, C_3H_6O. Write the structures of the alkene and the two isomeric carbonyl compounds.

[Ans. $(CH_3)_2C{=}CHCH_2CH_3$ (2-methylpent-2-ene), $(CH_3)_2C{=}O$ (propanone), $CH_3CH_2CH{=}O$ (propanal)]

4. An organic compound (A), C_6H_{10}, on reduction first gives (B), C_6H_{12}, and finally (C), C_6H_{14}. (A) on ozonolysis followed by hydrolysis gives two aldehydes (D), C_2H_4O, and (E), $C_2H_2O_2$. Oxidation of (B) with acidified $KMnO_4$ gives the acid (F), $C_4H_8O_2$. Determine the structure of the compounds (A) to (F) with proper reasoning. *(Roorkee 1993)*

[Ans. (A) = $CH_3CH{=}CH{-}CH{=}CHCH_3$;
(B) = $CH_3CH_2CH_2{-}CH{=}CHCH_3$;
(C) = $CH_3CH_2CH_2CH_2CH_2CH_3$;
(D) = $CH_3CH = O$;
(E) = $O{=}CH{-}CH = O$ and
(F) = $CH_3CH_2CH_2{-}COOH$]

Solution. (*i*) Since the aldehyde (E) contains two O atoms, therefore, it must be a *dialdehyde*. The only dialdehyde having the molecular formula, $C_2H_2O_2$ is glyoxal, *i.e.* $O = CH{-}CH = O$. The other aldehyde (D) having the molecular formula, C_2H_4O must be acetaldehyde, *i.e.*, CH_3CHO. Further since, glyoxal is a dialdehyde, therefore, two molecules of acetaldehyde must have been formed. Thus, the structure of the alkene (A) is

$$\underset{\text{Hexa-2, 4-diene (A)}}{CH_3CH = CH{-}CH = CHCH_3} \xrightarrow[\text{(ii) } Zn/H_2O]{\text{(i) } O_3/CH_2Cl_2}$$

$$\underset{\text{Acetaldehyde}}{CH_3CH = O} + \underset{\text{Glyoxal}}{O{=}CH - CH{=}O} + \underset{\text{Acetaldehyde}}{O = CHCH_3}$$

(*ii*) Since (A) on reduction gives (B) which on oxidation with alk. $KMnO_4$ gives the acid (F), therefore, (B) must be hex-2-ene and (F) must be butanoic acid.

$$\underset{[A]}{CH_3CH{=}CH - CH = CHCH_3} \xrightarrow{H_2/Ni}$$

$$\underset{\text{Hex-2-ene (B)}}{CH_3CH_2CH_2{-}CH{=}CH - CH_3} \xrightarrow{[O]}$$

$$\underset{\text{Butanoic acid (F)}}{CH_3CH_2CH_2COOH} + \underset{\text{Acetic acid}}{CH_3COOH}$$

(*iii*) Since (A) on reduction first gives B(hex-2-ene) and finally (C),therefore, (C) must be *n*- hexane.

$$\underset{\text{Hex-2-ene}}{CH_3CH_2CH_2{-}CH{=}CH{-}CH_3} \xrightarrow{H_2/Ni}$$

$$\underset{n\text{-Hexane (C)}}{CH_3CH_2CH_2CH_2CH_2CH_3}$$

IV. Polymerization Reactions

Polymerization is a process in which a large number of simple molecules combine to form a big molecule. The simple molecules are called monomers while the big molecule is called a macromolecule or a polymer.

Polymers are extremely useful products. These have revolutionized our everyday living. For example, polymers are used as plastic, textile, rubber and in many other industries.

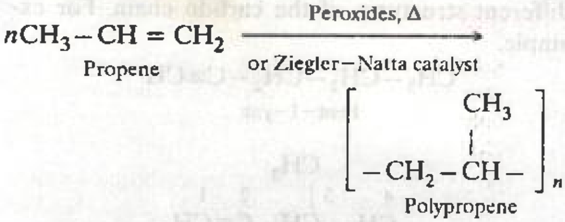
Alkenes readily undergo polymerization in the presence of catalysts.

(i) Polymerization of ethene. When ethene is heated to 473 K under a pressure of 1500 atmospheres and in presence of a trace of oxygen $(0{\cdot}001 - 0{\cdot}1\%)$, it undergoes polymerization to form polythene.

$$nCH_2 = CH_2 \xrightarrow[\text{Traces of oxygen}]{\text{473 K, 1500 atm.}} \underset{\text{Polythene}}{(CH_2 - CH_2)_n}$$

It is widely used as a packaging material (in the form of thin plastic films, bags etc.) and as insulation for electric wires and cables.

(ii) Polymerization of propene. Polypropene or polypropylene is prepared either by heating proplyene in presence of a trace of benzoyl peroxide as radical initiator or by Ziegler-Natta polymerization.

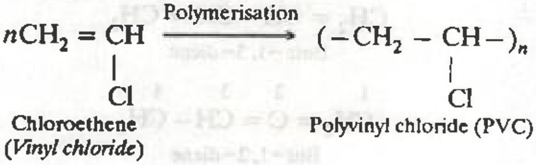


$$n\,CH_3-CH=CH_2 \xrightarrow[\text{or Ziegler–Natta catalyst}]{\text{Peroxides, }\Delta} \left[-CH_2-\underset{}{\overset{CH_3}{\overset{|}{C}H}}-\right]_n$$

Propene   Polypropene

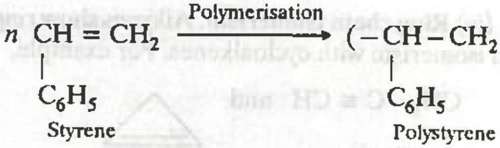
It is a harder and stronger polymer than polythene and is used for making automotive mouldings, seat covers, carpet fibres, ropes etc., containers for oils and gasoline.

(ii) Polymerization of substituted ethenes. A number of polymers can be obtained by using substituted ethenes as monomers in place of ethene. For example,



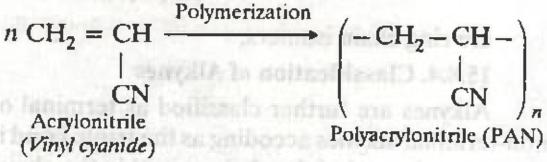
$$n\,CH_2=\underset{Cl}{\underset{|}{CH}} \xrightarrow{\text{Polymerisation}} (-CH_2-\underset{Cl}{\underset{|}{CH}}-)_n$$

Chloroethene (*Vinyl chloride*)   **Polyvinyl chloride (PVC)**



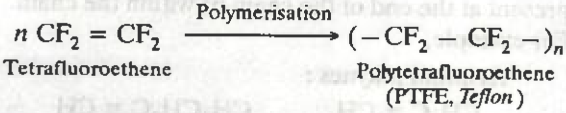
$$n\,\underset{C_6H_5}{\underset{|}{CH}}=CH_2 \xrightarrow{\text{Polymerisation}} (-\underset{C_6H_5}{\underset{|}{CH}}-CH_2-)_n$$

Styrene   **Polystyrene**



$$n\,CH_2=\underset{CN}{\underset{|}{CH}} \xrightarrow{\text{Polymerization}} \left(-CH_2-\underset{CN}{\underset{|}{CH}}-\right)_n$$

Acrylonitrile (*Vinyl cyanide*)   **Polyacrylonitrile (PAN)**



$$n\,CF_2=CF_2 \xrightarrow{\text{Polymerisation}} (-CF_2-CF_2-)_n$$

Tetrafluoroethene   **Polytetrafluoroethene (PTFE, *Teflon*)**

Polyvinyl chloride (PVC) is used for making plastic bottles, syringes, pipes, raincoats, records, etc. Polyacrylonitrile is used for making *Orlon* and *Acrilan* fibres used for making clothes, carpets and blankets. Polystyrene is used for packing and for making toys and household goods. Polytetrafluoroethene or teflon is resistant to the action of acids and other chemicals. It is used in the manufacture of pipes and surgical tubes. Because of its great chemical inertness and high thermal stability, teflon is also used for making non-stick utensils. For this purpose, a thin layer of teflon is coated on the inner side of the vessel.

15.7.10. Uses of Alkenes

(*i*) Lower members of the family are used as fuels and illuminants.

(*ii*) Alkenes and substituted alkenes upon polymerization form a number of useful polymers such as polythene, PVC, teflon, orlon etc.

(*iii*) Ethene is employed for the preparation of ethyl alcohol and ethylene glycol (*anti-freeze*).

(*iv*) Ethylene is used for artificial ripening green fruits.

(*v*) Ethylene is also used in oxygen-ethylene flame for cutting and welding of metals.

PART—III

ALKYNES

15.8. Alkynes

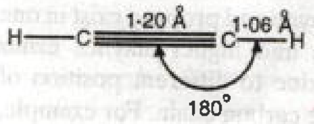
Acyclic unsaturated hydrocarbons containing a carbon-carbon triple bond are called alkynes or acetylenes. Their general formula is C_nH_{2n-2} where $n = 2, 3, 4....$ etc.

15.8.1. Structure of alkynes

In alkynes, the two carbon atoms are linked by a triple bond while the remaining carbons form C–C and C–H, σ bonds. The carbon-carbon triple bond is made up of two weak π-bonds and one strong σ-bond. In all, ethyne has 3σ- and 2π-bonds.

The carbon atoms forming a triple bond are *sp*-hybridized. Therefore, the portion of molecules of all alkynes which is attached to carbon- carbon triple bond is *linear in nature.*

Due to the smaller size of *sp*-orbitals (as compared to sp^2 and sp^3) and sideways overlapping of unhybridized *p*-orbitals, the carbon-carbon bond distance in acetylene is only 1·20 Å (120 pm). Since the acetylene molecule is linear, therefore, H–C–C bond angle is of 180°.

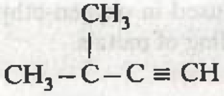


The C ≡ C has a bond strength of 823 kJ mol^{-1} in ethyne. It is stronger than C = C of ethene (610 kJ mol^{-1}) and C–C of ethane (370 kJ mol^{-1}).

In spite of the presence of two *π-bonds, alkynes are less reactive than alkenes towards addition reactions. Further, alkynes unlike alkenes do not exhibit geometrical isomerism due to their linear structure.*

15.8.2. Nomenclature of Alkynes

The IUPAC nomenclature of alkynes has been discussed in detail in unit 14. Even then for the purpose of recaptulation, the IUPAC names of some alkynes are given below :

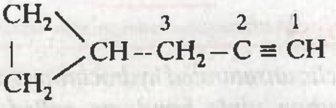


$$\begin{array}{l} \quad\ CH_3 \\ \quad\ \ | \\ CH_3-C-C\equiv CH \end{array}$$

3-Methylbut-1-yne

$C_6H_5-C\equiv CH$

Ethynylbenzene



3-Cyclopropylprop-1-yne

If both double and triple bonds are present and if there is a choice in numbering, the double bond is always given preference. For example,

$$\overset{1}{C}H_2=\overset{2}{C}H-\overset{3}{C}H_2-\overset{4}{C}H_2-\overset{5}{C}\equiv\overset{6}{C}H$$

Hex-1-ene-5-yne

However, if there is no choice in numbering lowest set of locants rule is followed. For example,

$$\overset{5}{C}H_3-\overset{4}{C}H=\overset{3}{C}H-\overset{2}{C}\equiv\overset{1}{C}H$$

Pent-3-en-1-yne (*correct*)

$$\overset{1}{C}H_3-\overset{2}{C}H=\overset{3}{C}H-\overset{4}{C}\equiv\overset{5}{C}H$$

Pent-2-ene-4-yne (*wrong*)

15.8.3. Isomerism in Alkynes

Alkynes show four types of isomerism as discussed below :

(*i*) **Position isomerism.** The first two members, *i.e.* ethyne and propyne exist in one form only. But butyne and higher alkynes exhibit position isomerism due to different position of the triple bond on the carbon chain. For example,

$CH_3-CH_2-C\equiv CH$

But-1-yne

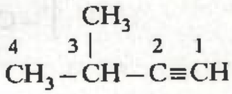
$CH_3-C\equiv C-CH_3$

But-2-yne

(*ii*) **Chain isomerism.** Alkynes having five or more carbon atoms show chain isomerism due to different structures of the carbon chain. For example,

$CH_3-CH_2-CH_2-C\equiv CH$

Pent-1-yne



$$\begin{array}{l} \qquad\quad CH_3 \\ \ \ 4 \qquad 3\,| \qquad 2 \quad 1 \\ CH_3-CH-C\equiv CH \end{array}$$

3-Methylbut-1-yne

(*iii*) **Functional isomerism.** Alkynes are functional isomers of dienes, *i.e.*, compounds containing two double bonds. For example,

$$\overset{4}{C}H_3-\overset{3}{C}H_2-\overset{2}{C}\equiv\overset{1}{C}H$$

But-1-yne

$$\overset{1}{C}H_2=\overset{2}{C}H-\overset{3}{C}H=\overset{4}{C}H_2$$

Buta-1, 3-diene

$$\overset{1}{C}H_2=\overset{2}{C}=\overset{3}{C}H-\overset{4}{C}H_3$$

But-1, 2-diene

(*iv*) **Ring chain isomerism.** Alkynes show ring chain isomerism with cycloalkenes. For example,

$CH_3-C\equiv CH$ and

Propyne

Cyclopropene

are ring chain isomers.

15.8.4. Classification of Alkynes

Alkynes are further classified as terminal or non-terminal alkynes accoding as the triple bond is present at the end of the chain or within the chain. For example,

Terminal alkynes :

$CH_3C\equiv CH$ Propyne

$CH_3CH_2C\equiv CH$ But-1-yne

Non-terminal alkynes :

$CH_3-C\equiv C-CH_3$ But-2-yne

$CH_3-C\equiv C-CH_2CH_3$ Pent-2-yne

15.8.5. Methods of Preparation of Alkynes

Alkynes are prepared by the following general methods.

1. By the action of water on calcium carbide. Ethyne (acetylene) is prepared in the laboratory as well as on commercial scale by the action of water on calcium carbide.

$$\underset{\text{Calcium carbide}}{CaC_2} + 2H_2O \longrightarrow \underset{\substack{\text{Ethyne} \\ (\textit{Acetylene})}}{HC\equiv CH} + Ca(OH)_2$$

Calcium carbide needed for the purpose is manufactured by heating limestone (calcium carbonate) with coke in an electric furnace at 2275 K.

$$CaCO_3 \xrightarrow{2275\text{ K}} CaO + CO_2$$

$$CaO + 3C \xrightarrow{2275\text{ K}} CaC_2 + CO$$

Procedure. Lumps of calcium carbide are placed on a layer of sand in a conical flask fitted with a dropping funnel and a delivery tube (Fig. 15.18). *The air present in the flask is replaced by oil gas since acetylene forms an explosive mixture with air.* Water is now dropped from the dropping funnel and the acetylene gas thus formed is collected over water.

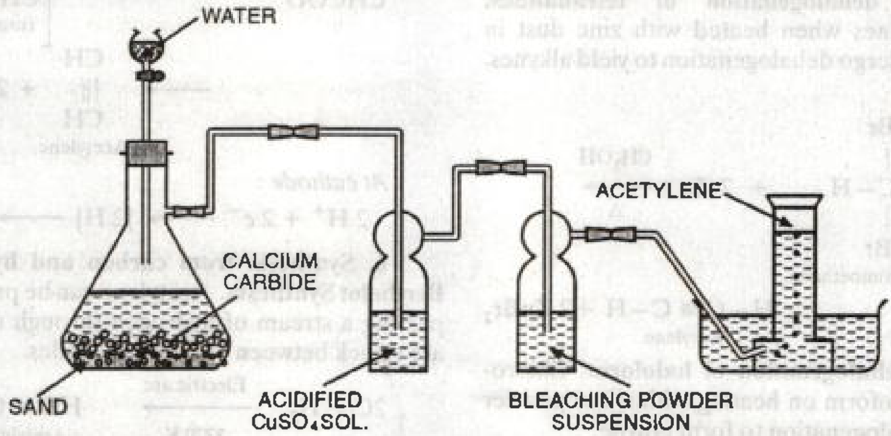


FIGURE 15.18. Laboratory preparation of acetylene.

Purification. Acetylene gas prepared by the above method contains impurities of hydrogen sulphide and phosphine due to the contaminations of calcium sulphide and calcium phosphide in calcium carbide. Hydrogen sulphide is removed by bubbling the gas through an acidified solution of copper sulphate while phosphine is removed by passing the gas through a suspension of bleaching powder. Pure acetylene is finally collected over water.

A4 **2. By dehydrohalogenation of dihaloalkanes.** Alkynes are prepared by dehydrohalogenation of *vicinal*-dihaloalkanes by heating them with an alcoholic solution of potassium hydroxide. For example,

$$\underset{\text{1, 2-Dibromoethane}}{\begin{matrix} CH_2-Br \\ | \\ CH_2-Br \end{matrix}} + 2\,KOH(alc.) \xrightarrow{\Delta} \underset{\text{Acetylene}}{\begin{matrix} CH \\ ||| \\ CH \end{matrix}} + 2KBr + 2H_2O$$

The reaction, in fact, occurs in two steps and under suitable conditions, the intermediate product, vinyl bromide may be isolated.

$$\underset{\text{Ethylene dibromide}}{BrCH_2-CH_2Br} + KOH\,(alc.) \xrightarrow{\Delta} \underset{\text{Vinyl bromide}}{CH_2=CHBr} + KBr + H_2O$$

$$CH_2=CH-Br + KOH\,(alc.) \xrightarrow{\Delta} \underset{\text{Acetylene}}{CH\equiv CH} + KBr + H_2O$$

Instead of alcoholic potassium hydroxide, sodamide in liquid ammonia can also be used. The main advantage is that the yields are better since there is less tendency to form by-products.

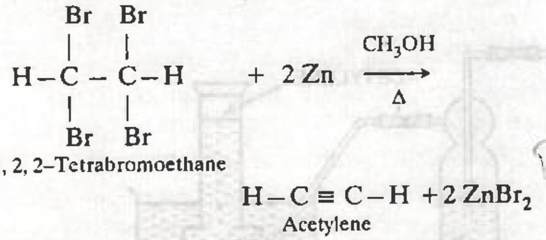
$$\underset{\text{1, 2-Dibromoethane}}{BrCH_2-CH_2Br} + 2NaNH_2 \xrightarrow[196\text{ K}]{\text{Liquid NH}_3} \underset{\text{Acetylene}}{CH\equiv CH} + 2NaBr + 2NH_3$$

$$\underset{\text{1,2-Dibromopropane}}{\begin{matrix} CH_3-CH-CH_2 \\ \quad\;\;| \quad\;\; | \\ \quad\;\; Br \quad Br \end{matrix}} + 2NaNH_2 \xrightarrow[196\text{ K}]{\text{Liquid NH}_3} \underset{\text{Propyne}}{CH_3-C\equiv CH} + 2NaBr + 2NH_3$$

Alkynes can also be prepared by the action of alcoholic potassium hydroxide on *gem*-dihalides. For example,

$$\underset{\text{1, 1-Dibromoethane}}{CH_3-CHBr_2} \xrightarrow[-HBr]{KOH(alc.),\ \Delta} \underset{\text{Vinyl bromide}}{CH_2=CHBr} \xrightarrow[-HBr]{KOH(alc.),\ \Delta} \underset{\text{Acetylene}}{CH\equiv CH}$$

Ad **3. By dehalogenation of tetrahalides.** Tetrahaloalkanes when heated with zinc dust in methanol undergo dehalogenation to yield alkynes. For example,



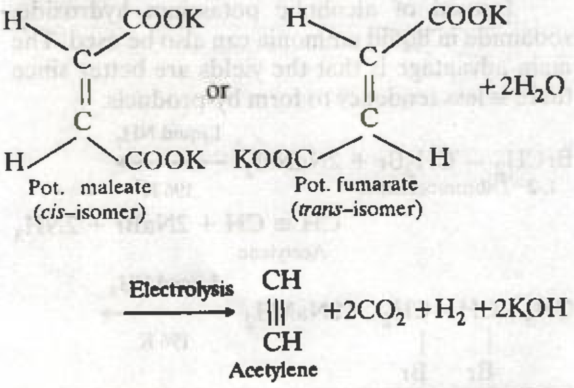
$$\underset{\text{1, 1, 2, 2-Tetrabromoethane}}{HCBr_2-CBr_2H} + 2\,Zn \xrightarrow[\Delta]{CH_3OH} \underset{\text{Acetylene}}{H-C\equiv C-H} + 2\,ZnBr_2$$

Ad **4. By dehalogenation of haloform.** Chloroform and iodoform on heating with silver powder undergo dehalogenation to form ethyne.

$$\underset{\text{Chloroform}}{CH\,Cl_3} + 6\,Ag + Cl_3\,CH \xrightarrow{\Delta} \underset{\text{Ethyne}}{HC\equiv CH} + 6\,AgCl$$

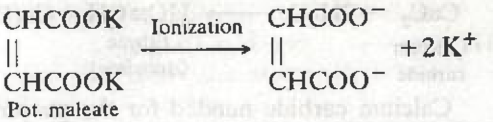
$$\underset{\text{Iodoform}}{CH\,I_3} + 6\,Ag + I_3\,CH \xrightarrow{\Delta} \underset{\text{Ethyne}}{HC\equiv CH} + 6\,AgI$$

1d **5. Kolbe's electrolytic reaction.** Acetylene can be prepared by electrolysis of a concentrated solution of sodium or potassium salt of maleic acid or fumaric acid. Thus,



$$\underset{\substack{\text{Pot. maleate}\\(cis\text{-isomer})}}{KOOC-CH=CH-COOK} \text{ or } \underset{\substack{\text{Pot. fumarate}\\(trans\text{-isomer})}}{KOOC-CH=CH-COOK} + 2H_2O \xrightarrow{\text{Electrolysis}} \underset{\text{Acetylene}}{CH\equiv CH} + 2CO_2 + H_2 + 2KOH$$

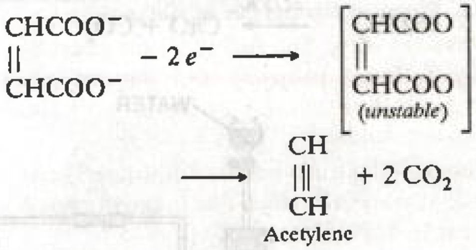
This reaction is called **Kolbe's electrolytic reaction** and is believed to occur by the following steps :



$$\underset{\text{Pot. maleate}}{\begin{matrix}CHCOOK\\ \|\\ CHCOOK\end{matrix}} \xrightarrow{\text{Ionization}} \begin{matrix}CHCOO^-\\ \|\\ CHCOO^-\end{matrix} + 2\,K^+$$

$$2\,H_2O \rightleftharpoons 2\,OH^- + 2H^+$$

At anode :



$$\begin{matrix}CHCOO^-\\ \|\\ CHCOO^-\end{matrix} - 2\,e^- \longrightarrow \left[\begin{matrix}CHCOO\\ \|\\ CHCOO\end{matrix}\right]_{(unstable)} \longrightarrow \underset{\text{Acetylene}}{\begin{matrix}CH\\ |||\\ CH\end{matrix}} + 2\,CO_2$$

At cathode :

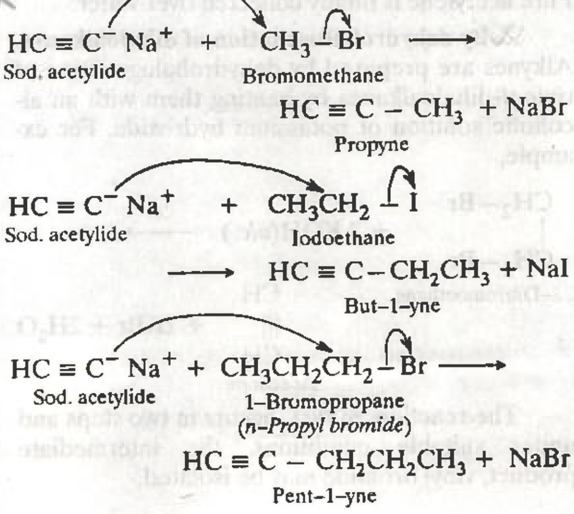
$$2\,H^+ + 2\,e^- \longrightarrow [2\,H] \longrightarrow H_2$$

D **6. Synthesis from carbon and hydrogen – Berthelot Synthesis.** Acetylene can be prepared by passing a stream of hydrogen through an electric arc struck between carbon electrodes.

$$2C + H_2 \xrightarrow[3270\text{ K}]{\text{Electric arc}} \underset{\text{Acetylene}}{HC\equiv CH}$$

A-d **7. Synthesis of higher alkynes from acetylene.** Acetylene is first treated with sodium metal at 475 K or with sodamide in liquid ammonia at 196 K to form sodium acetylide. This upon treatment with alkyl halides gives higher alkynes. For example,

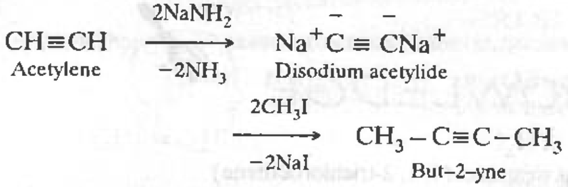
$$\underset{\substack{\text{Ethyne}\\(Acetylene)}}{HC\equiv CH} + NaNH_2 \xrightarrow[196\text{ K}]{\text{Liq. }NH_3} \underset{\text{Sodium acetylide}}{HC\equiv C^-Na^+} + NH_3$$



$$\underset{\text{Sod. acetylide}}{HC\equiv C^-Na^+} + \underset{\text{Bromomethane}}{CH_3-Br} \longrightarrow \underset{\text{Propyne}}{HC\equiv C-CH_3} + NaBr$$

$$\underset{\text{Sod. acetylide}}{HC\equiv C^-\,Na^+} + \underset{\text{Iodoethane}}{CH_3CH_2-I} \longrightarrow \underset{\text{But-1-yne}}{HC\equiv C-CH_2CH_3} + NaI$$

$$\underset{\text{Sod. acetylide}}{HC\equiv C^-\,Na^+} + \underset{\substack{\text{1-Bromopropane}\\(n\text{-Propyl bromide})}}{CH_3CH_2CH_2-Br} \longrightarrow \underset{\text{Pent-1-yne}}{HC\equiv C-CH_2CH_2CH_3} + NaBr$$



$$\underset{\text{Acetylene}}{CH\equiv CH} \xrightarrow[-2NH_3]{2NaNH_2} \underset{\text{Disodium acetylide}}{Na^+\bar{C}\equiv \bar{C}Na^+} \xrightarrow[-2NaI]{2CH_3I} \underset{\text{But-2-yne}}{CH_3-C\equiv C-CH_3}$$

15.8.6. Physical Properties of Alkynes

(*i*) **Physical state.** The first three members of this family (ethyne, propyne and butyne) are colourless gases, the next eight are liquids while the higher ones are solids.

(*ii*) **Smell.** All the alkynes are odourless. However, acetylene has garlic smell due to the presence of phosphine as impurity.

(*iii*) **Melting and boiling points.** The melting points and boiling points of alkynes are slightly higher than those of the corresponding alkenes and alkanes. *This is probably due to the reason that because of the presence of a triple bond, alkynes have linear structures and hence their molecules can be more closely packed in the crystal lattice as compared to those of corresponding alkenes and alkanes.*

Hydrocarbon	Ethane	Ethene	Ethyne
m.p. (K)	101	104	191
b.p. (K)	184·5	171	198

(*iv*) **Solubility.** Alkynes like alkanes and alkenes being non-polar are insoluble in water but readily dissolve in organic solvents such as petroleum ether, benzene, carbon tetrachloride etc.

(*v*) **Density.** Densities of alkynes increase as the molecular size increases. However, they are all ligher than water since their densities lie in the range 0·69 – 0·77 g/cm³.

15.8.7. Reactivity of alkynes versus alkenes

Although alkynes contain two π-bonds, yet they are less reactive than alkenes towards electrophilic addition reactions. This is supported by the observation that a majority of the addition reactions of alkynes are catalysed by heavy metal ions such as Hg^{2+}, Ba^{2+} etc. while no such catalysts are needed in case of electrophilic additions to alkenes. This lower reactivity of alkynes as compared to alkenes towards electrophilic addition reactions is due to the following two reasons :

(*i*) Due to greater electronegativity of *sp*-hybridized carbon atoms of a triple bond than sp^2-hybridized carbon atoms of a double bond, *the π-electrons of alkynes are more tightly held by the carbon atoms than π- electrons of alkenes and hence are less easily available for reaction with electrophiles. As a result, alkynes are less reactive than alkenes towards electrophilic addition reactions.*

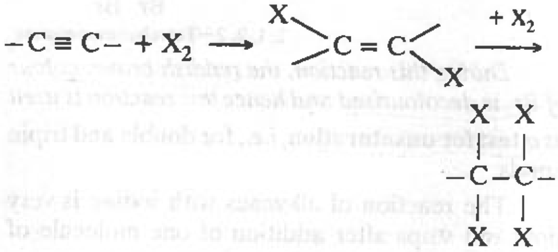
(*ii*) Due to cylindrical nature of the π-electron cloud of alkynes, *the π-electrons of a triple bond are more delocalized that π-electrons of a double bond. In other words, the π-electrons of a triple bond are less readily available for addition reactions than those of the double bond. Consequently alkynes are less reactive than alkenes.*

15.8.8. Chemical Reactions of Alkynes

Some important chemical reactions of alkynes are discussed below :

I. Electrophilic addition reactions

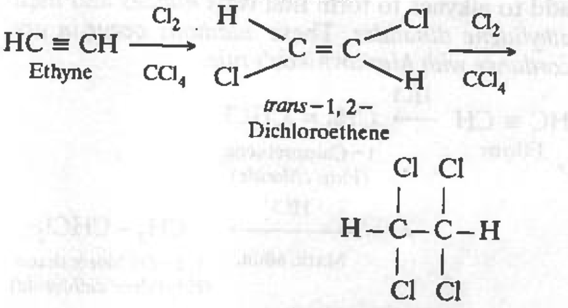
The electrophilic addition reactions of alkynes take place in two stages as shown below :



$$-C\equiv C- + X_2 \longrightarrow XC=CX \xrightarrow{+X_2} -CX_2-CX_2-$$

By a proper choice of reaction conditions, the addition can be stopped after the addition of one mole of the reagent. Some important electrophilic addition reactions are discussed below :

1. Addition of halogens. Chlorine and bromine readily add to alkynes first forming 1, 2-dihaloalkenes and then 1, 1, 2, 2-tetrahaloalkanes. For example,



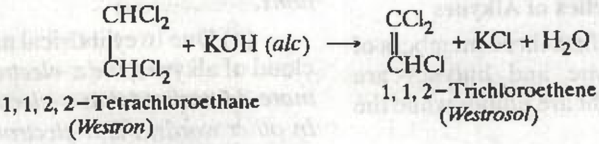
$$\underset{\text{Ethyne}}{HC\equiv CH} \xrightarrow[CCl_4]{Cl_2} \underset{trans\text{-}1,2\text{-Dichloroethene}}{HClC=CClH} \xrightarrow[CCl_4]{Cl_2} \underset{1,1,2,2\text{-Tetrachloroethane (Westron)}}{HCCl_2-CCl_2H}$$

1, 1, 2, 2–Tetrachloroethane

(*Westron*)

ADD TO YOUR KNOWLEDGE

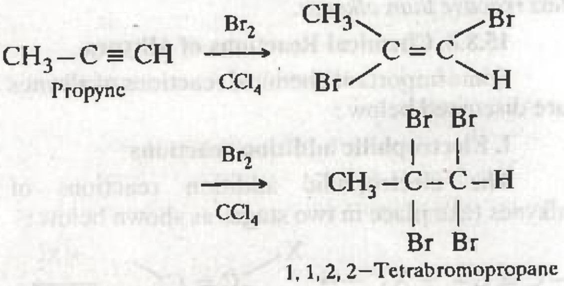
When westron is heated with alcoholic KOH, it forms westrosol (1, 1, 2-trichloroethene)



$$CHCl_2{-}CHCl_2 + KOH\,(alc) \longrightarrow CCl_2{=}CHCl + KCl + H_2O$$

1, 1, 2, 2-Tetrachloroethane (*Westron*) 1, 1, 2-Trichloroethene (*Westrosol*)

Both westron and westrosol are used as solvents.

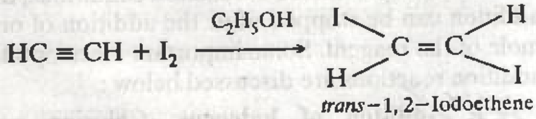


$$\underset{\text{Propyne}}{CH_3{-}C\equiv CH} \xrightarrow[CCl_4]{Br_2} CH_3(Br)C{=}C(Br)H \xrightarrow[CCl_4]{Br_2} CH_3{-}CBr_2{-}CBr_2{-}H$$

1, 1, 2, 2-Tetrabromopropane

During this reaction, the reddish brown colour of Br_2 *is decolourised and hence this reaction is used as a* **test for unsaturation**, *i.e.*, for double and triple bonds.

The reaction of alkyenes with iodine is very slow and stops after addition of one molecule of iodine.

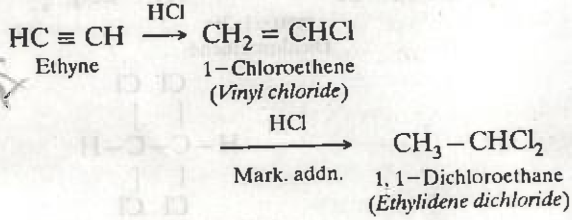


$$HC\equiv CH + I_2 \xrightarrow{C_2H_5OH} I(H)C{=}C(H)I$$

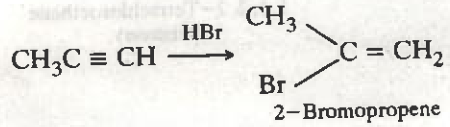
trans-1, 2-Iodoethene

Thus, the order of reactivity of halogens is : $Cl_2 > Br_2 > I_2$.

2. Addition of halogen acids. Halogen acids add to alkynes to form first *vinyl halides* and then *alkylidene dihalides. These additions occur in accordance with Markovnikov's rule.*

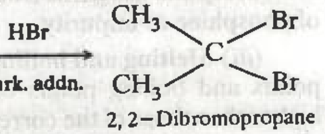


$$\underset{\text{Ethyne}}{HC\equiv CH} \xrightarrow{HCl} \underset{\substack{\text{1-Chloroethene}\\(\textit{Vinyl chloride})}}{CH_2{=}CHCl} \xrightarrow[\text{Mark. addn.}]{HCl} \underset{\substack{\text{1, 1-Dichloroethane}\\(\textit{Ethylidene dichloride})}}{CH_3{-}CHCl_2}$$



$$CH_3C\equiv CH \xrightarrow{HBr} (CH_3)(Br)C{=}CH_2 \xrightarrow[\text{Mark. addn.}]{HBr} (CH_3)_2CBr_2$$

2-Bromopropene

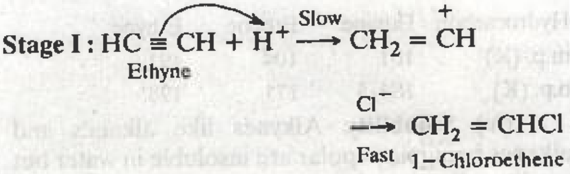


2, 2-Dibromopropane

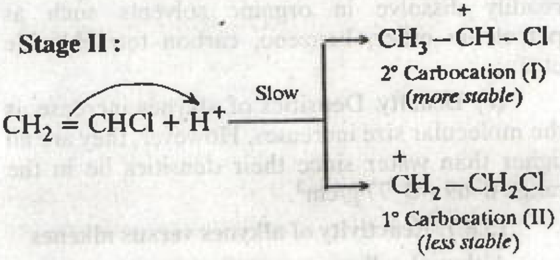
The order of reactivity of halogen acids is :

HI > HBr > HCl

Mechanism. It is an *electrophilic* addition reaction and occurs in two stages as discussed below :

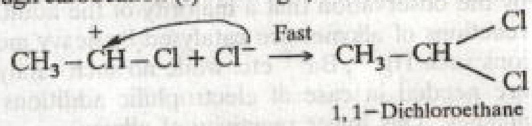


$$\textbf{Stage I : } \underset{\text{Ethyne}}{HC\equiv CH} + H^+ \xrightarrow{\text{Slow}} CH_2{=}\overset{+}{C}H \xrightarrow[\text{Fast}]{Cl^-} \underset{\text{1-Chloroethene}}{CH_2{=}CHCl}$$



$$\textbf{Stage II : } CH_2{=}CHCl + H^+ \xrightarrow{\text{Slow}} \underset{\substack{\text{2° Carbocation (I)}\\(\textit{more stable})}}{CH_3{-}\overset{+}{C}H{-}Cl} \;\text{or}\; \underset{\substack{\text{1° Carbocation (II)}\\(\textit{less stable})}}{\overset{+}{C}H_2{-}CH_2Cl}$$

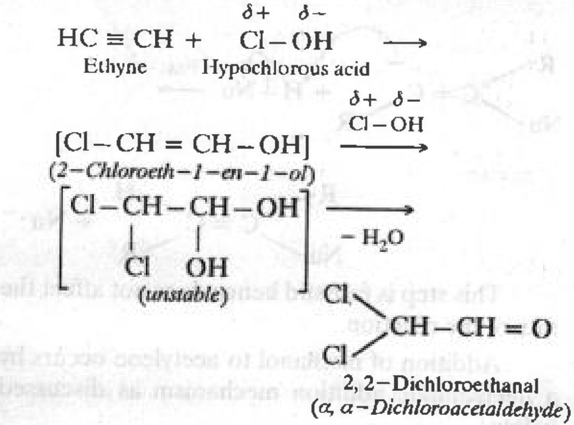
Since carbocation (I) being 2° is more stable than primary carbocation (II), therefore, reaction occurs through carbocation (I) forming 1, 2-dichloroethane.



$$CH_3{-}\overset{+}{C}H{-}Cl + Cl^- \xrightarrow{\text{Fast}} CH_3{-}CHCl_2$$

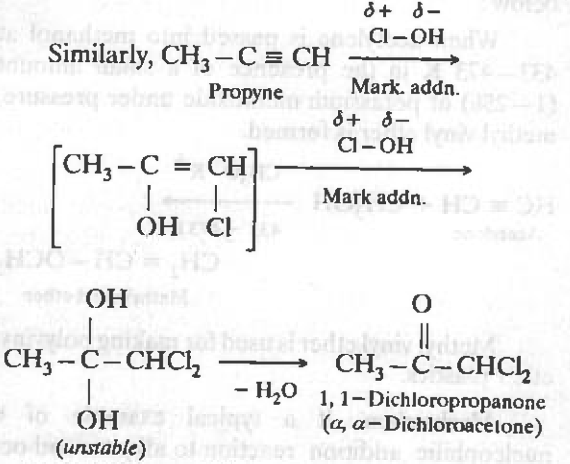
1, 1-Dichloroethane

3. Addition of the elements hypohalous acids. Like alkenes, alkynes also add chlorine or bromine in the presence of water. The overall reaction occurs in two stages, each stage involving the addition of the elements of the hypohalous acid to form dihalo-carbonyl compound as the final product. For example,



$$\underset{\text{Ethyne}}{HC \equiv CH} + \underset{\text{Hypochlorous acid}}{\overset{\delta+\ \ \delta-}{Cl-OH}} \longrightarrow \underset{(2\text{-}Chloroeth\text{-}1\text{-}en\text{-}1\text{-}ol)}{[Cl-CH=CH-OH]} \xrightarrow{\overset{\delta+\ \ \delta-}{Cl-OH}} \underset{(unstable)}{\left[\begin{array}{c} Cl-CH-CH-OH \\ |\qquad\ | \\ Cl\qquad OH \end{array}\right]} \xrightarrow[-H_2O]{} \underset{\substack{2,2\text{-Dichloroethanal}\\(\alpha,\,\alpha\text{-}Dichloroacetaldehyde)}}{\begin{array}{l} Cl \\ \quad \rangle CH-CH=O \\ Cl \end{array}}$$

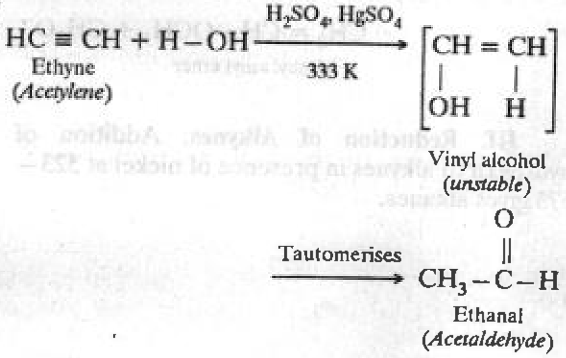
Similarly,



$$\underset{\text{Propyne}}{CH_3-C\equiv CH} \xrightarrow[\text{Mark. addn.}]{\overset{\delta+\ \ \delta-}{Cl-OH}} \left[\begin{array}{c} CH_3-C=CH \\ |\quad\ | \\ OH\ \ Cl\end{array}\right] \xrightarrow[\text{Mark addn.}]{\overset{\delta+\ \ \delta-}{Cl-OH}}$$

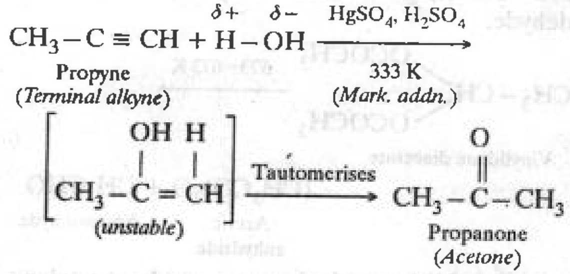
$$\underset{(unstable)}{\begin{array}{c} OH \\ | \\ CH_3-C-CHCl_2 \\ | \\ OH\end{array}} \xrightarrow[-H_2O]{} \underset{\substack{1,1\text{-Dichloropropanone}\\(\alpha,\,\alpha\text{-Dichloroacetone})}}{CH_3-\overset{\overset{O}{\|}}{C}-CHCl_2}$$

4. Addition of H_2O—Hydration of alkynes. Alkynes cannot be hydrated as easily as alkenes because of their lower reactivity towards electrophilic addition reactions. Further dilute H_2SO_4 has no effect on carbon-carbon triple bond. However, in presence of $HgSO_4$ as catalyst, hydration occurs readily. Under these conditions, H_2O adds to the triple bond to form first *an enol which readily tautomerises to the corresponding carbonyl compound.* For example,



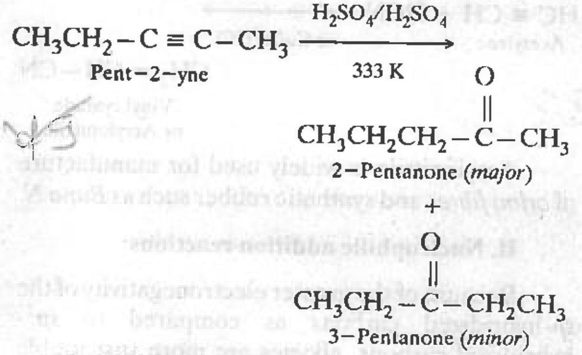
$$\underset{\substack{\text{Ethyne}\\(Acetylene)}}{HC\equiv CH} + H-OH \xrightarrow[333\text{ K}]{H_2SO_4,\ HgSO_4} \underset{\substack{\text{Vinyl alcohol}\\(unstable)}}{\left[\begin{array}{c} CH=CH \\ |\qquad | \\ OH\quad H\end{array}\right]} \xrightarrow{\text{Tautomerises}} \underset{\substack{\text{Ethanal}\\(Acetaldehyde)}}{CH_3-\overset{\overset{O}{\|}}{C}-H}$$

In case of *unsymmetrical terminal* alkynes, *addition occurs in accordance with Markovnikov's rule.* For example,



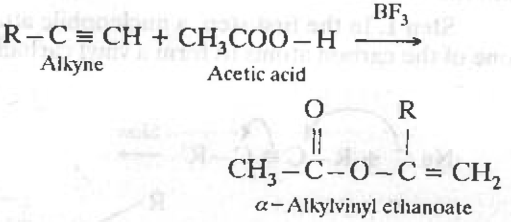
$$\underset{\substack{\text{Propyne}\\(Terminal\ alkyne)}}{CH_3-C\equiv CH} + \overset{\delta+\ \ \delta-}{H-OH} \xrightarrow[\substack{333\text{ K}\\(Mark.\ addn.)}]{HgSO_4,\ H_2SO_4} \underset{(unstable)}{\left[\begin{array}{c} OH\ \ H \\ |\quad\ | \\ CH_3-C=CH\end{array}\right]} \xrightarrow{\text{Tautomerises}} \underset{\substack{\text{Propanone}\\(Acetone)}}{CH_3-\overset{\overset{O}{\|}}{C}-CH_3}$$

However, if the unsymmetrical alkyne is *non-terminal*, a mixture of two isomeric ketones is obtained in which the methyl ketone predominates. For example,



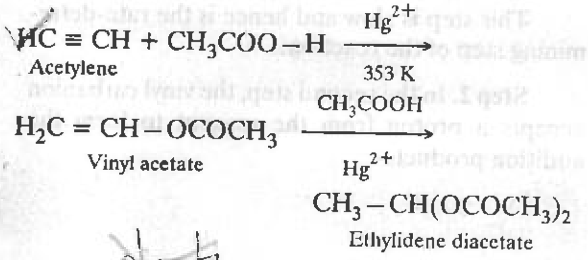
$$\underset{\text{Pent-2-yne}}{CH_3CH_2-C\equiv C-CH_3} \xrightarrow[333\text{ K}]{H_2SO_4/H_2SO_4} \underset{2\text{-Pentanone }(major)}{CH_3CH_2CH_2-\overset{\overset{O}{\|}}{C}-CH_3} + \underset{3\text{-Pentanone }(minor)}{CH_3CH_2-\overset{\overset{O}{\|}}{C}-CH_2CH_3}$$

5. Addition of carboxylic acids. Alkynes add carboxylic acids in presence of Lewis acid catalyst or Hg^{2+} ions to give vinyl esters. For example,



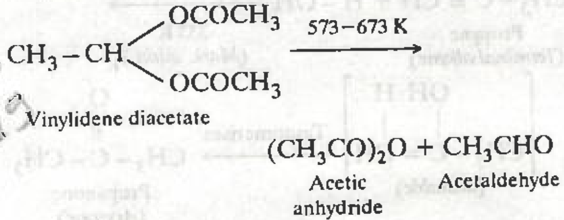
$$\underset{\text{Alkyne}}{R-C\equiv CH} + \underset{\text{Acetic acid}}{CH_3COO-H} \xrightarrow{BF_3} \underset{\alpha\text{-Alkylvinyl ethanoate}}{CH_3-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{R}{|}}{C}=CH_2}$$

When acetylene is passed into warm acetic acid in presence of mercury salts, first vinyl acetate and then vinylidene diacetate is formed.



$$\underset{\text{Acetylene}}{HC\equiv CH} + CH_3COO.H \xrightarrow[353\text{ K}]{Hg^{2+}} \underset{\text{Vinyl acetate}}{H_2C=CH-OCOCH_3} \xrightarrow[Hg^{2+}]{CH_3COOH} \underset{\text{Ethylidene diacetate}}{CH_3-CH(OCOCH_3)_2}$$

Vinyl acetate is used for manufacture of vinyl resin. Vinyidene diacetate, when heated rapidly to 573 – 673 K, gives acetic anhydride and acetaldehyde.



$$CH_3-CH(OCOCH_3)_2 \xrightarrow{573-673\text{ K}} (CH_3CO)_2O + CH_3CHO$$

Vinylidene diacetate; Acetic anhydride; Acetaldehyde

(vi) Addition of hydrogen cyanide. Acetylene adds on hydrogen cyanide in presence of $Ba(CN)_2$ or CuCl in HCl as catalyst to give vinyl cyanide or acrylonitrile.

$$HC \equiv CH + HCN \xrightarrow[\text{or CuCl/HCl}]{Ba(CN)_2} CH_2=CH-CN$$

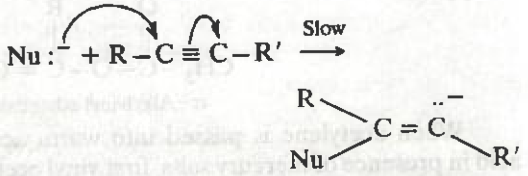
Acetylene; Vinyl cyanide or Acrylonitrile

Acrylonitrile is widely used for manufacture of *orlon fibres* and synthetic rubber such as *Buna N.*

II. Nucleophilic addition reactions

Because of the greater electronegativity of the *sp*-hybridized carbons as compared to *sp*^{2}-hybridized carbons, alkynes are more susceptible to nucleophilic addition reactions than alkenes. Like electrophilic addition reactions, nucleophilic addition reactions also occur in two steps :

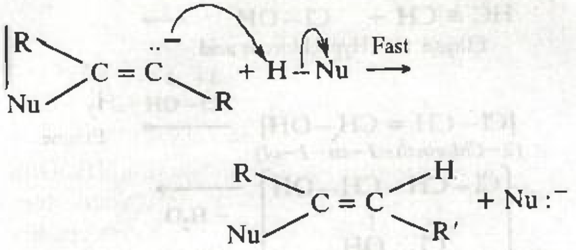
Step 1. In the first step, a nucleophile attacks one of the carbon atoms to form a vinyl carbanion.



(A vinyl carbanion)

This step is slow and hence is the rate-determining step of the reaction.

Step 2. In the second step, the vinyl carbanion accepts a proton from the reagent to form the addition product.



This step is fast and hence does not affect the rate of the reaction.

Addition of methanol to acetylene occurs by a nucleophilic addition mechanism as discussed below :

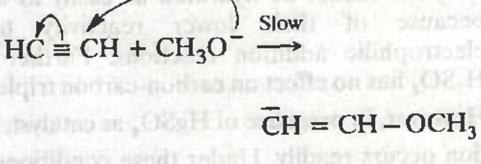
When acetylene is passed into methanol at 433 – 473 K in the presence of a small amount (1 – 2%) of potassium methoxide under pressure, methyl vinyl ether is formed.

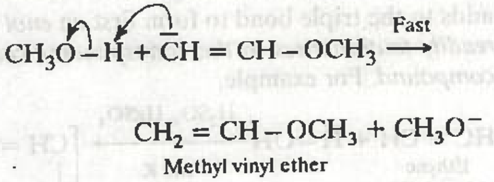
$$HC \equiv CH + CH_3OH \xrightarrow[433-473\text{ K}]{CH_3O^-K^+} CH_2=CH-OCH_3$$

Acetylene; Methyl vinyl ether

Methyl vinyl ether is used for making polyvinyl ether plastics.

Mechanism. It a typical example of a nucleophilic addition reaction to alkynes and occurs through the following two steps :

Step 1. 

Step 2. 

Methyl vinyl ether

III. Reduction of Alkynes. Addition of hydrogen to alkynes in presence of nickel at 523 – 573 gives alkanes.

$$\underset{\text{Ethyne}}{HC \equiv CH} + H_2 \xrightarrow[523-573\text{ K}]{Ni} \underset{\text{Ethene}}{CH_2 = CH_2}$$

$$\xrightarrow[523-573\text{ K}]{Ni} \underset{\text{Ethane}}{CH_3 - CH_3}$$

The heat of hydrogenation data reveal that the first step has larger $\Delta H°$ than the second step, thereby indicating that alkynes are more readily reduced than alkenes. This can be easily explained

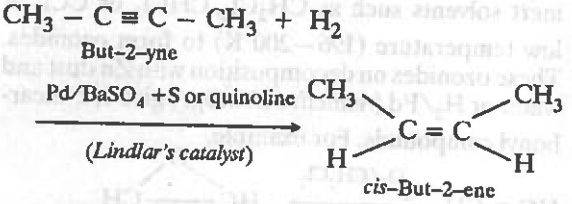
$$HC \equiv CH + H_2 \xrightarrow{\text{Catalyst}} H_2C = CH_2, \quad \Delta H° = -176 \text{ kJ mol}^{-1}$$

$$H_2C = CH_2 + H_2 \xrightarrow{\text{Catalyst}} CH_3 - CH_3; \quad \Delta H° = -138 \text{ kJ mol}^{-1}$$

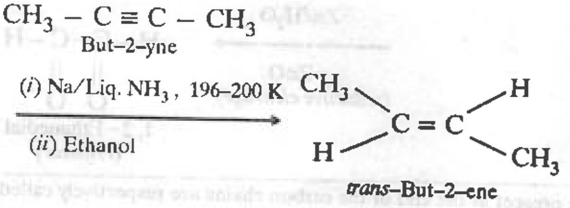
On the basis of *greater reactivity of alkynes towards nucleophiles, electrons being negatively charged are transferred to alkynes more readily than to alkenes.*

Thus, it is possible to stop the reaction at the alkene stage by using specific catalysts such as *Lindlar's catalyst, i.e.*, Pd supported over $CaCO_3$ or $BaSO_4$ and partially poisoned by addition of sulphur or quinoline.

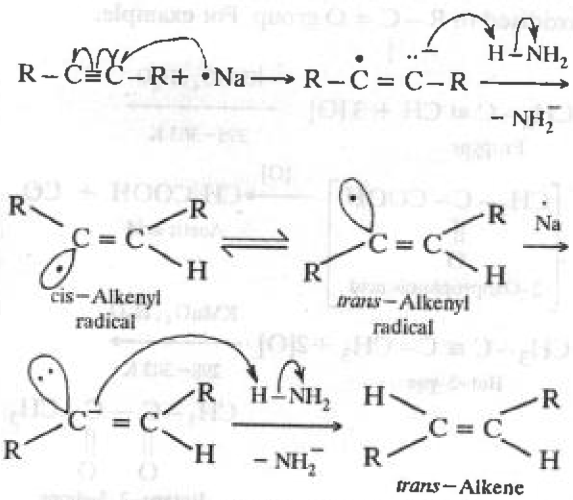
In case of non-terminal alkynes, *catalytic reduction* of alkynes with hydrogen in presence of Lindlar's catalyst always gives *cis*-alkenes since during hydrogenation, the addition of hydrogen occurs on the same face of the alkyne molecule. For example,



In contrast, *chemical reduction i.e.* **Birch reduction of non-terminal alkynes with Na or Li in liquid NH_3 at 196-200 K gives *trans*- alkenes.**



Mechanism. Chemical reduction is believed to occur through two electron transfers and two proton transfers as shown below :



The formation of *trans*-product is due to the rapid equilibrium between the *cis*- and *trans*-alkenyl radicals, in which the *trans*-radical being more stable is readily formed.

IV. Oxidation Reactions of Alkynes

Oxidation of alkynes can be carried out under different conditions to form different products.

1. Oxidation with air – Combustion

When heated in air, alkynes undergo combustion to form CO_2 and H_2O accompanied by release of large amount of heat and light energy.

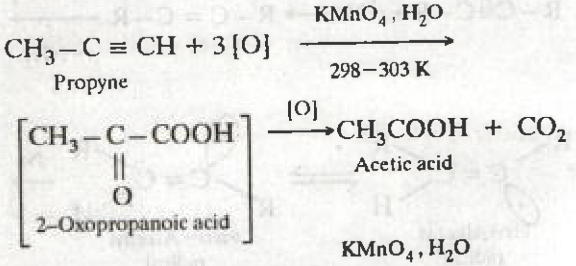
$$2\,\underset{\text{Acetylene}}{CH \equiv CH} + 5\,O_2 \longrightarrow 4\,CO_2 + 2\,H_2O; \quad \Delta H = -1300 \text{ kJ mol}^{-1}$$

Under normal conditions, acetylene burns with *a luminous yellow, sooty flame* due to the presence of higher carbon content than hydrogen. However, with air or oxygen under high pressure, acetylene burns with a *blue flame (oxyacetylene flame)* producing high temperature of the order of 3000 K which is used for cutting and welding of metals.

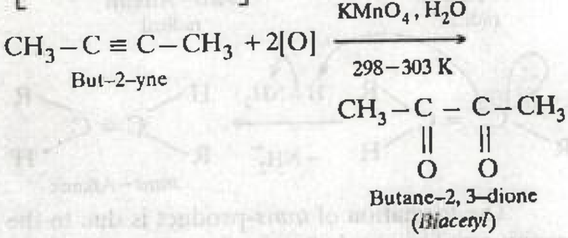
2. Oxidation with cold dilute potassium permanganate

Alkynes are readily oxidised by cold dilute alkaline $KMnO_4$ solution to give α-dicarbonyl compounds, i.e. 1, 2-dialdehydes, 1, 2-diketones 2-oxoacids or 1, 2-dioic acids depending upon the nature of alkyne.

It may be noted here that in case of *terminal** *alkynes*, ≡ CH part is oxidised to − COOH group while in case of *non-terminal alkynes*, ≡ CR part is oxidised to $R-\overset{|}{C}=O$ group. For example.

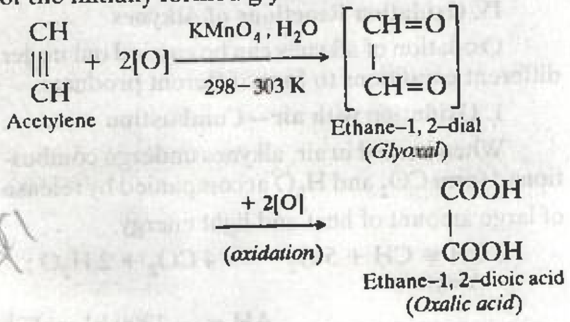


$$\underset{\text{Propyne}}{CH_3-C\equiv CH} + 3[O] \xrightarrow[298-303\,K]{KMnO_4,\,H_2O} \underset{\text{2–Oxopropanoic acid}}{\left[CH_3-\underset{\underset{O}{\|}}{C}-COOH\right]} \xrightarrow{[O]} \underset{\text{Acetic acid}}{CH_3COOH} + CO_2$$



$$\underset{\text{But–2–yne}}{CH_3-C\equiv C-CH_3} + 2[O] \xrightarrow[298-303\,K]{KMnO_4,\,H_2O} \underset{\text{Butane–2, 3–dione (\textit{Biacetyl})}}{CH_3-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{C}-CH_3}$$

Acetylene, however, under these conditions gives oxalic acid probably due to further oxidation of the initially formed glyoxal.



$$\underset{\text{Acetylene}}{\begin{matrix}CH\\ |||\\ CH\end{matrix}} + 2[O] \xrightarrow[298-303\,K]{KMnO_4,\,H_2O} \underset{\text{Ethane-1, 2–dial (\textit{Glyoxal})}}{\left[\begin{matrix}CH=O\\ |\\ CH=O\end{matrix}\right]} \xrightarrow[\text{(oxidation)}]{+2[O]} \underset{\text{Ethane–1, 2–dioic acid (\textit{Oxalic acid})}}{\begin{matrix}COOH\\ |\\ COOH\end{matrix}}$$

During this reaction, *the pink colour of the KMnO$_4$ solution is discharged and a brown precipitate of manganese dioxide is obtained. This reaction is, therefore, used as a test for unsaturation under the name* **Baeyer's test.**

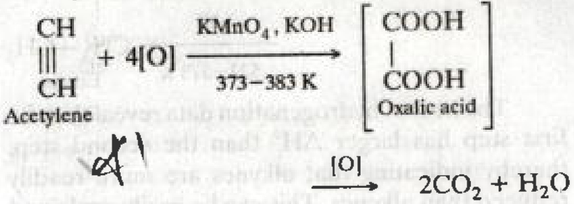
3. Oxidation with hot KMnO$_4$ solution.

Like alkenes, *terminal alkynes* when treated with hot KMnO$_4$ solution, undergo cleavage of the C≡C bond leading to the formation of carboxylic acids and carbon dioxide depending upon the nature of the alkyne. In general,

≡ CH is oxidised to CO$_2$ and H$_2$O and

≡ CR is oxidised to RCOOH

For example, acetylene gives CO$_2$ and H$_2$O while propyne gives acetic acid and CO$_2$.



$$\underset{\text{Acetylene}}{\begin{matrix}CH\\ |||\\ CH\end{matrix}} + 4[O] \xrightarrow[373-383\,K]{KMnO_4,\,KOH} \underset{\text{Oxalic acid}}{\left[\begin{matrix}COOH\\ |\\ COOH\end{matrix}\right]} \xrightarrow{[O]} 2CO_2 + H_2O$$

$$\underset{\text{Propyne}}{CH_3-C\equiv CH} + 4[O] \xrightarrow[373-383\,K]{KMnO_4,\,KOH} \underset{\text{Ethanoic acid}}{CH_3COOH} + CO_2$$

In contrast, *non-terminal alkynes* on oxidation with hot KMnO$_4$ solution give only carboxylic acids. For example,

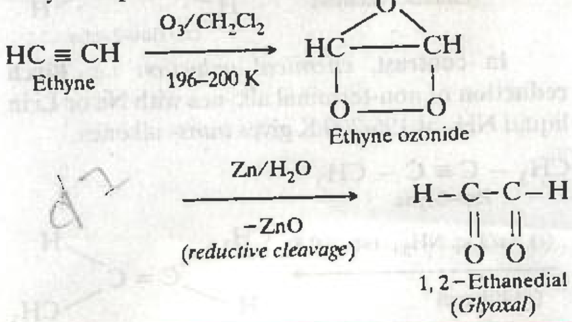
$$\underset{\text{But–2–yne}}{CH_3-C\equiv C-CH_3} + 4[O] \xrightarrow[373-383\,K]{KMnO_4,\,KOH} \underset{\text{Acetic acid (\textit{2 molecules})}}{CH_3COOH + HOOCCH_3}$$

$$\underset{\text{Pent–2–yne}}{CH_3CH_2-C\equiv C-CH_3} + 4[O] \xrightarrow[373-383\,K]{KMnO_4,\,KOH} \underset{\text{Propanoic acid}}{CH_3CH_2COOH} + \underset{\text{Ethanoic acid}}{HOOCCH_3}$$

Thus, *by identifying the products formed during alkaline KMnO$_4$ oxidation, it is possible to determine the position of the triple bond in an alkyne molecule.*

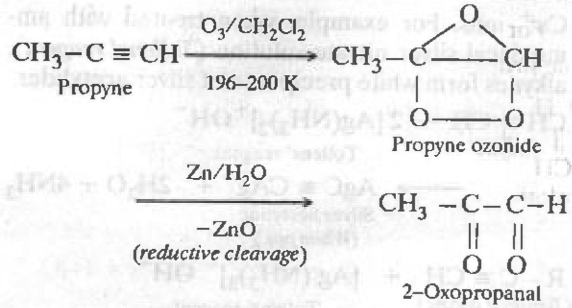
4. Oxidation with ozone.

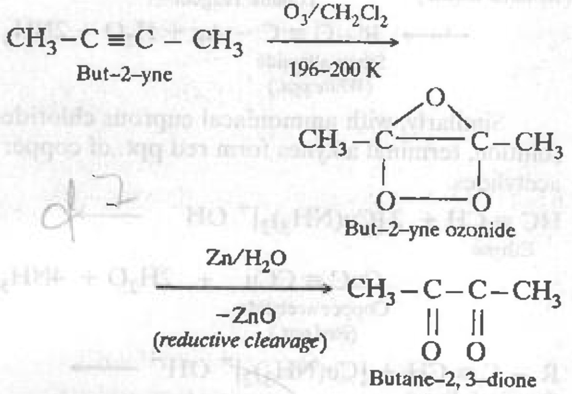
Alkynes react with ozone in presence of some inert solvents such as CH$_2$Cl$_2$, CHCl$_3$ or CCl$_4$ at low temperature (196 − 200 K) to form ozonides. These ozonides on decomposition with Zn dust and water or H$_2$/Pd (*reductive cleavage*) give 1, 2-dicarbonyl compounds. For example,



---

*Alkenes and alkynes in which double and triple bond are present at the end of the carbon chains are respectively called terminal alkenes and terminal alkynes.

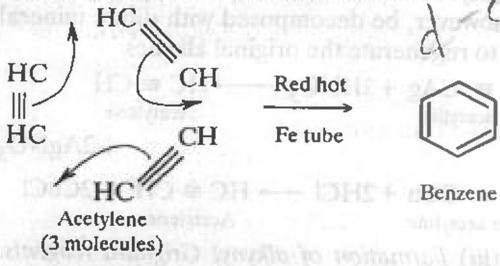




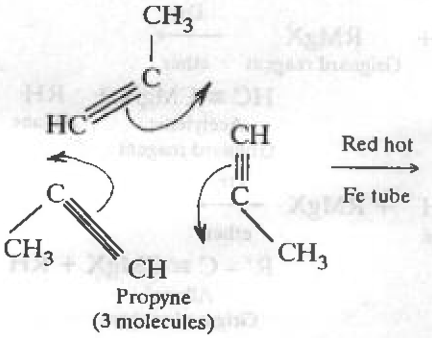
V. Polymerization Reactions of Alkynes

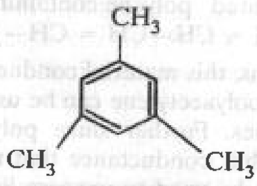
Like alkenes, alkynes also undergo polymerization reactions. For example

(*a*) When *acetylene* is passed through red hot iron tube, it trimerises to give *benzene*.



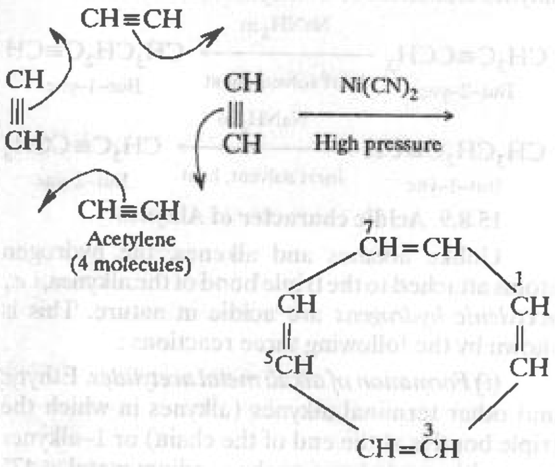
Similarly, *propyne* trimerises under similar conditions to form *mesitylene (1, 3, 5-trimethylbenzene).*





1,3,5–Trimethylbenzene
(*Mesitylene*)

(*b*) In presence of nickel cyanide as catalyst and under high pressure, four molecules of acetylene combine to form a tetramer called *cycloocta-1, 3, 5, 7-tetraene.*



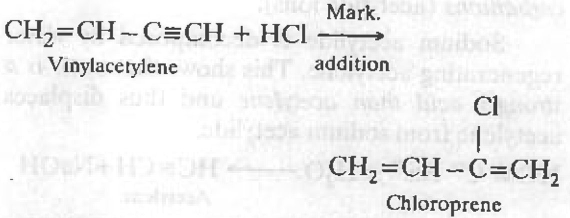
Cycloocta–1,3,5,7–tetraene

(*c*) However, in presence of $CuCl/NH_4Cl$, *acetylene first gives vinylacetylene* and then *divinylacetylene*. Thus,

$$\underset{\text{Acetylene}}{2\,H-C\equiv C-H} \xrightarrow{CuCl/NH_4Cl} \underset{\text{Vinylacetylene}}{H-C\equiv C-CH=CH_2}$$

$$\xrightarrow[CuCl/NH_4Cl]{HC\,\equiv\,CH} \underset{\text{Divinylacetylene}}{H_2C=CH-C\equiv C-CH=CH_2}$$

Vinylacetylene is widely used in the manufacture of chloroprene which is the starting material for the synthetic rubber neoprene.



$$\underset{\text{Vinylacetylene}}{CH_2=CH-C\equiv CH} + HCl \xrightarrow[\text{addition}]{\text{Mark.}} \underset{\text{Chloroprene}}{CH_2=CH-\overset{\overset{\large Cl}{|}}{C}=CH_2}$$

(*d*) Under suitable conditions, polymerization of acetylene produces the linear polymer *polyacetylene*. It is a high molecular weight conjugated polyene containing the repeating unit $(-CH=CH-CH=CH-)_n$. Under proper conditions, this material conducts electricity. Thin films of polyacetylene can be used as electrodes in batteries. Further since polyacetylenes have much higher conductance that metal conductors, these can be used to prepare lighter and cheapter batteries.

VI. Isomerization of alkynes.

When alkynes are heated with $NaNH_2$ in an inert solvent, they undergo isomerization, *i.e.*, 2-alkynes isomerize to 1- alkynes and *vice versa*.

$$\underset{\text{But-2-yne}}{CH_3C\equiv CCH_3} \xrightarrow[\text{inert solvent, heat}]{NaNH_2\text{ in}} \underset{\text{But-1-yne}}{CH_3CH_2C\equiv CH}$$

$$\underset{\text{But-1-yne}}{CH_3CH_2C\equiv CH} \xrightarrow[\text{inert solvent, heat}]{NaNH_2\text{ in}} \underset{\text{But-2-yne}}{CH_3C\equiv CCH_3}$$

15.8.9. Acidic character of Alkynes

Unlike alkanes and alkenes, the hydrogen atoms attached to the triple bond of the alkynes, *i.e.*, *acetylenic hydrogens* are acidic in nature. This is shown by the following three reactions :

(*i*) *Formation of alkali metal acetylides.* Ethyne and other terminal alkynes (alkynes in which the triple bond is at the end of the chain) or 1–alkynes react with strong bases such as sodium metal at 475 K or sodamide in liquid ammonia at 196 K to form sodium acetylides with evolution of H_2 gas.

$$\underset{\substack{\text{Ethyne}\\ (\textit{Acetylene})}}{2HC\equiv CH} + 2Na \xrightarrow{475\text{ K}} \underset{\text{Sodium acetylide}}{2CH\equiv C^-Na^+} + H_2$$

$$\underset{(\textit{A terminal alkyne})}{R-C\equiv CH} + NaNH_2 \xrightarrow[196\text{ K}]{\text{Liq. }NH_3} \underset{(\textit{An acetylide})}{R-C\equiv C^-Na^+} + NH_3$$

During these reactions, the acetylenic hydrogen is removed as a proton to form stable *carbanions* (acetylide ions).

Sodium acetylide is decomposed by water regenerating acetylene. This shows that *water is a stronger acid than acetylene* and thus displaces acetylene from sodium acetylide.

$$HC\equiv C^-Na^+ + H_2O \longrightarrow \underset{\text{Acetylene}}{HC\equiv CH} + NaOH$$

(*ii*) *Formation of heavy metal acetylides.* Acetylenic hydrogens of alkynes can also be replaced by heavy metal ions such as Ag^+ and Cu^+ ions. For example, when treated with ammoniacal silver nitrate solution (*Tollens' reagent*), alkynes form white precipitate of silver acetylides.

$$\underset{\text{Ethyne}}{CH\equiv CH} + \underset{\text{Tollens' reagent}}{2[Ag(NH_3)_2]^+OH^-} \longrightarrow \underset{\substack{\text{Silver acetylide}\\ (\textit{White ppt.})}}{AgC\equiv CAg} + 2H_2O + 4NH_3$$

$$\underset{(\textit{Terminal alkyne})}{R-C\equiv CH} + \underset{\text{Tollens' reagent}}{[Ag(NH_3)_2]^+OH^-} \longrightarrow \underset{\substack{\text{Silver alkynide}\\ (\textit{White ppt.})}}{R-C\equiv C-Ag} + H_2O + 2NH_3$$

Similarly, with ammoniacal cuprous chloride solution, terminal alkynes form red ppt. of copper acetylides.

$$\underset{\text{Ethyne}}{HC\equiv CH} + 2[Cu(NH_3)_2]^+OH^- \longrightarrow \underset{\substack{\text{Copper acetylide}\\ (\textit{Red ppt.})}}{CuC\equiv CCu} + 2H_2O + 4NH_3$$

$$\underset{(\textit{Terminal alkyne})}{R-C\equiv CH} + [Cu(NH_3)_2]^+OH^- \longrightarrow \underset{\substack{\text{Copper alkynide}\\ (\textit{Red ppt.})}}{R-C\equiv C-Cu} + H_2O + 2NH_3$$

Unlike alkali metal acetylides, silver and copper acetylides are not decomposed by water. They can, however, be decomposed with dilute mineral acids to regenerate the original alkynes.

$$\underset{\text{Silver acetylide}}{AgC\equiv CAg} + 2HNO_3 \longrightarrow \underset{\text{Acetylene}}{HC\equiv CH} + 2AgNO_3$$

$$\underset{\text{Copper acetylide}}{CuC\equiv CCu} + 2HCl \longrightarrow \underset{\text{Acetylene}}{HC\equiv CH} + 2CuCl$$

(*iii*) *Formation of alkynyl Grignard reagents.* Acetylene and other terminal alkynes react with Grignard reagents to form the corresponding alkynyl Grignard reagents. For example,

$$\underset{\text{Acetylene}}{HC\equiv CH} + \underset{\text{Grignard reagent}}{RMgX} \xrightarrow[\text{ether}]{\text{Dry}} \underset{\substack{\text{Acetylenic}\\ \text{Grignard reagent}}}{HC\equiv CMgX} + \underset{\text{Alkane}}{RH}$$

$$\underset{\text{Terminal alkyne}}{R'-C\equiv CH} + RMgX \xrightarrow[\text{ether}]{\text{Dry}} \underset{\substack{\text{Alkynyl}\\ \text{Grignard reagent}}}{R'-C\equiv CMgX} + RH$$

Alkynyl Grignard reagents like usual Grignard reagents can be used to prepare a variety of organic compounds.

Importance. The formation of metal acetylides can be used :

(*i*) for separation and purification of terminal alkynes from non-terminal alkynes, alkanes and alkenes.

(*ii*) to distinguish terminal alkynes from non-terminal alkynes or alkenes.

Cause of Acidity of Alkynes. The acidity of alkynes can be explained in terms of the *sp*-hybridization of a triply bonded carbon. We know that an electron in an *s*-orbital is more tightly held than in a *p*-orbital since *s*- electrons are closer to the nucleus. Further, since an *sp*- orbital has more *s*-character than an sp^2-or an sp^3-orbital, therefore, the electrons in an *sp*-orbital are more strongly held by the nucleus than electrons in an sp^2- or a sp^3-orbital. In other words, an *sp*- hybridized carbon is *more electronegative* than sp^2- or sp^3-hybridized carbon atom. Due to this greater electronegativity, the electrons of C – H bond are displaced more towards the carbon than towards the hydrogen atom. In other words, the hydrogen atom is less tightly held by the carbon and hence can be removed as a proton (H^+) by a strong base. Consequently, alkynes behave as acids.

Further, since the *s*-character decreases as we move from *sp*- to sp^2- to sp^3-carbon atoms, the acidic character of hydrocarbons decreases in the following order :

$$\underset{K_a \simeq 10^{-25}}{CH\equiv CH} > \underset{K_a \simeq 10^{-35}}{CH_2 = CH_2} > \underset{K_a \simeq 10^{-40}}{CH_3 - CH_3}$$

It may be noted here that hydrocarbons are very weak acids as compared to H_2O ($K_a \simeq 10^{-14}$), alcohols ($K_a = 10^{-16} - 10^{-18}$) and carboxylic acids ($K_a \simeq 10^{-5}$). For example, ethyne (acetylene) is 10^{20} times and ethane is about 10^{35} times less acidic than ethanoic acid.

ADD TO YOUR KNOWLEDGE

Relative acidities of water, alcohols, acetylene, ammonia and alkanes can be determined as follows :

(*a*) $NaNH_2$ reacts with acetylene to form sodium acetylide and NH_3. Since a stronger acid displaces a weaker acid from its salts, therefore, *acetylene is a stronger and than NH_3*

$$\underset{(stronger\ acid)}{HC\equiv CH} + NaNH_2 \longrightarrow HC\equiv C^-Na^+ + \underset{(weaker\ acid)}{NH_3}$$

(*b*) Since lithium alkyls (RLi) react with ammonia to form alkanes, therefore, *ammonia is a stronger acid than a hydrocarbon (RH)*

$$\underset{(stronger\ acid)}{NH_3} + RLi \longrightarrow \underset{(weaker\ acid)}{R—H} + LiNH_2$$

(*c*) Since H_2O and alcohols decompose sodium acetylide to give back acetylene, therefore, *water and alcohols are stronger acids than acetylene*

$$HC\equiv C^-Na^+ + \underset{(stronger\ acid)}{H_2O} \longrightarrow \underset{(weaker\ acid)}{HC\equiv CH} + NaOH$$

$$HC\equiv C^-Na^+ + \underset{(stronger\ acid)}{ROH} \longrightarrow \underset{(weaker\ acid)}{HC\equiv CH} + RONa$$

(*d*) Since H_2O decomposes sodium alkoxides to form alcohols, therefore, ***water is a stronger acid than alcohols.***

$$RONa + \underset{(stronger\ acid)}{H_2O} \longrightarrow \underset{(weaker\ acid)}{ROH} + NaOH$$

Combining all the facts stated above, the relative acidities of these compounds follow the order:

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

Conversely, the relative basicities follow the order : $R^- > NH_2^- > HC\equiv C^- > RO^- > HO^-$

15.8.10. Uses of Alkynes

(*i*) Acetylene and its derivatives are widely used in synthetic organic chemistry for synthesis of *cis*- and *trans*-alkenes, methyl ketones etc.

(*ii*) Oxyacetylene flame is used for cutting and welding of metals.

(*iii*) Acetylene is used as illuminant in hawker's lamp and in light houses.

(*iv*) Acetylene is used for ripening of fruits and vegetables.

(*v*) Acetylene is used for manufacture of ethyl alcohol, acetaldehyde, acetic acid, vinyl plastics, synthetic rubbers such as *Buna N* and synthetic fibres such as *Orlon*.

PART—IV

DIENES

15.9. Dienes

Unsaturated hydrocarbons containing two double bonds are called **alkadienes or simply dienes.** Their general formula is $C_n H_{2n-2}$ and hence they are isomeric with alkynes. However, their properties are quite different from those of alkynes.

15.9.1. Classification of Dienes

Depending upon the relative positions of the two double-bonds, dienes are classified into three categories :

1. Isolated dienes. *Dienes in which the two double bonds are separated by more than one single bond are called* **isolated dienes.** For example,

$$\underset{\text{penta}-1,\,4-\text{diene}}{\overset{1}{C}H_2=\overset{2}{C}H-\overset{3}{C}H_2-\overset{4}{C}H=\overset{5}{C}H_2}$$

$$\underset{\text{Hexa}-1,\,5-\text{diene}}{\overset{1}{C}H_2=\overset{2}{C}H-\overset{3}{C}H_2-\overset{4}{C}H_2-\overset{5}{C}H=\overset{6}{C}H_2}$$

2. Conjugated dienes. *Dienes in which the two double bonds are separated by one single bond or dienes which contain alternate single and double bonds are called* **conjugated dienes.** For example,

$$\underset{\text{Buta}-1,\,3-\text{diene}}{\overset{1}{C}H_2=\overset{2}{C}H-\overset{3}{C}H=\overset{4}{C}H_2}$$

$$\underset{\text{Penta}-1,\,3-\text{diene}}{\overset{5}{C}H_3-\overset{4}{C}H=\overset{3}{C}H-\overset{2}{C}H=\overset{1}{C}H_2}$$

3. Allenes or cumulenes. *Dienes containing the cumulated system of double bonds, i.e., double bonds between successive carbon atoms are called* **allenes or cumulenes.** For example,

$$\underset{\substack{\text{Propa}-1,\,2-\text{diene}\\(\textit{Allene})}}{CH_2=\overset{2}{C}=\overset{3}{C}H_2}$$

$$\underset{\substack{\text{Penta}-2,\,3-\text{diene}\\(\textit{Dimethylallene})}}{\overset{1}{C}H_3\overset{2}{C}H=\overset{3}{C}=\overset{4}{C}H-\overset{5}{C}H_3}$$

15.9.2. Relative Stabilities of Dienes

Heats of hydrogenation can be used to determine the relative stabilities of dienes. We know that alkenes with similar structures have approx. the same value of heat of hydrogenation. For mono substituted alkenes ($RCH=CH_2$), it is approx. 125·4 kJ/mole, for disubstituted alkenes, ($RCH = CHR$ or $R_2C=CH_2$), it is about 117·1 kJ/mole and for trisubstituted alkenes ($R_2C=CHR$), it is about 112·9 kJ/mole. For a compound having more than one double bond, it is reasonable to expect a heat of hydrogenation which is the sum of the heat of hydrogenation of the individual double bonds. Let us consider, the heats of hydrogenation of 1, 3-pentadiene (*a conjugated diene*) and 1, 4-pentadiene (*an isolated diene*).

$$\underset{\text{Penta}-1,\,3-\text{diene}}{CH_2=CHCH=CHCH_3} + 2\,H_2 \xrightarrow{Ni} \underset{n-\text{Pentane}}{CH_3CH_2CH_2CH_2CH_3}\,;$$

$$\textit{Found} : \Delta H = -\,226{\cdot}2\ \text{kJ mol}^{-1}$$

$$\textit{Calculated} : \Delta H = (117{\cdot}1 + 125{\cdot}4)$$

$$= -\,242{\cdot}5\ \text{kJ mol}^{-1}$$

$$\underset{\text{Penta}-1,\,4-\text{diene}}{CH_2=CH-CH_2CH=CH_2} + 2\,H_2 \xrightarrow{Ni} \underset{n-\text{Pentane}}{CH_3CH_2CH_2CH_2CH_3}$$

Found : $\Delta H = -254{\cdot}2\ \text{kJ mol}^{-1}$

Calculated : $\Delta H = -2 \times 125{\cdot}4$

$= -250{\cdot}8\ \text{kJ mol}^{-1}$

Both these dienes give the same alkane, *i.e.*, *n*-pentane on hydrogenation but their heats of hydrogenation are different, penta-1, 3-diene evolves about 28 kJ per mole of heat less than penta-1, 4-diene. This suggests that the conjugated diene, penta-1, 3-diene contains less energy than the isolated diene, penta-1, 4-diene. In other words, *penta-1, 3-diene is more stable than penta-1, 4-diene by about 28 kJ/mole.* Similarly, the observed heat of hydrogenation of buta-1, 3-diene is about 12·5 kJ/mole less than the calculated value.

Similar studies with other dienes suggest that conjugated dienes are more stable than the isolated dienes.

In contrast, allenes or 1, 2-alkadienes are far less stable than 1, 3 or 1, 4-alkadienes. For example, heat of hydrogenation of 1, 2-propadiene is 298·3 kJ mol^{-1} as compared to 226·2 kJ mol^{-1} for 1, 3-pentadiene and 250·8 kJ mol^{-1} for 1, 4-pentadiene. Thus, in general, the stability of alkadienes follows the order :

Conjugated dienes > Isolated dienes > Cumulated dienes.

Explanation for greater stability of conjugated dienes. The extra stability of conjugated dienes over isolated dienes can be explained in terms of *(i) orbital structure* and *(ii) resonance theory.*

(*i*) Orbital structure. Consider buta-1, 3-diene as a typical example of a conjugated diene.

$$\underset{\text{Buta}-1,\,3-\text{diene}}{\overset{1}{C}H_2=\overset{2}{C}H-\overset{3}{C}H=\overset{4}{C}H_2}$$

Each carbon atom in buta-1, 3-diene is *sp*^{2}-hybridized and forms three σ-bonds. Each terminal

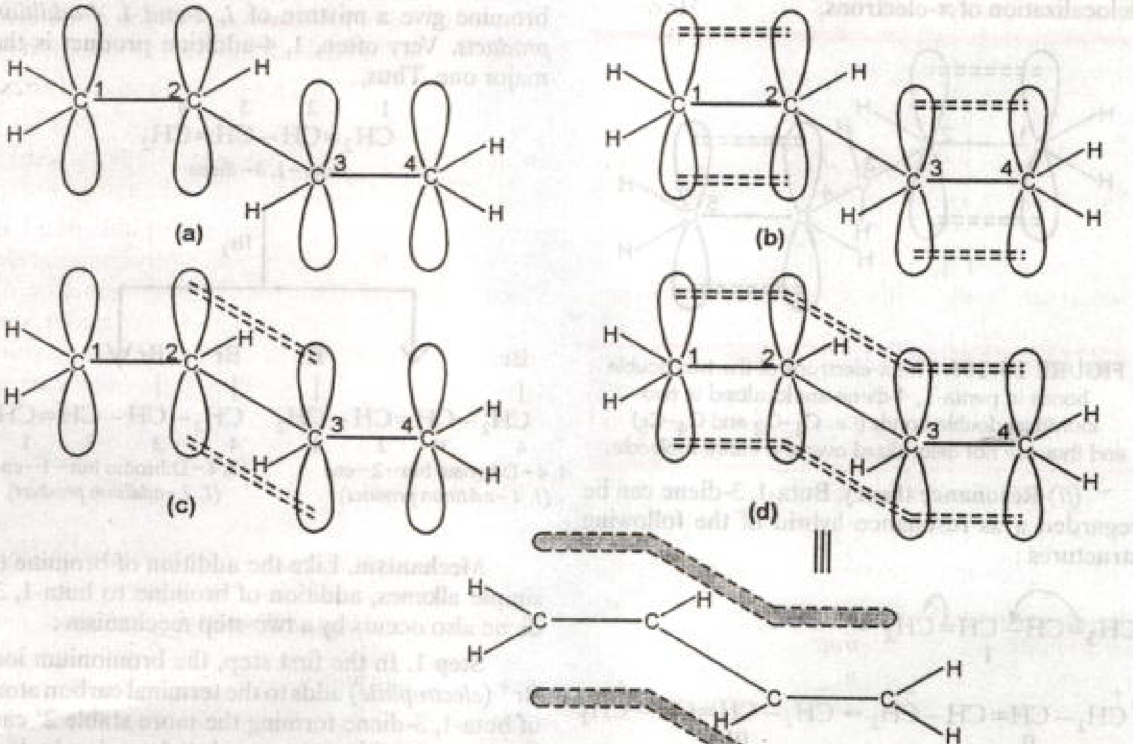


FIGURE 15.19. Orbital picture of buta-1, 3-diene.

carbon atom (C_1 and C_4) forms two sp^2- s, C–H, σ-bonds and one sp^2-sp^2, C–C, σ-bond but each of the middle carbon atoms (C_2 and C_3) forms two sp^2- sp^2, C–C, σ-bonds and one sp^2- s, C–H bond. As a result, each carbon is now left with an unhybridized p-orbital (Fig. 15.19 *a*). The sideways overlapping of the two p-orbitals on C_1 and C_2 and those on C_3 and C_4 form two localized π-orbitals (Fig. 15.19 *b*).

Now if all the four carbon atoms and the six hydrogen atoms lie in the same plane, then there can also be a certain degree of overlap between the p-orbitals on C_2 and C_3 (Fig. 15.19 *c*). Thus, the π-electrons can move to a limited extent over all the four carbon atoms (Fig. 15.19 *d*). In other words, *the π- electrons of buta-1, 3-diene are somewhat delocalized as shown in Fig. 15.19 e. This delocalization of π-electrons imparts extra stability to buta-1, 3-diene and other conjugated dienes since each pair of π-electrons is attracted by four rather than two carbon atoms.* On the other hand, in isolated dienes (Fig. 15.19*f*), each pair of π-electrons is attracted by only two carbon atoms, *i.e.*, there is no delocalization of π-electrons.

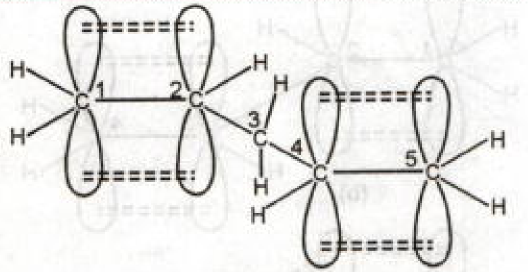
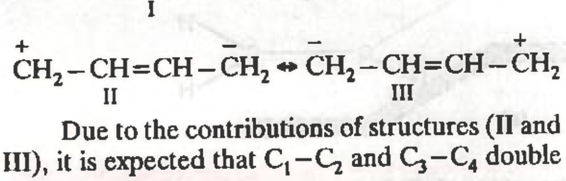


FIGURE 15.19f. The π-electrons of the two double bonds in penta-1, 4-diene are localized in two individual double bonds (*i.e.* C_1–C_2 and C_4–C_5) and thus are not delocalized over the entire molecule.

(*ii*) **Resonance theory.** Buta-1, 3-diene can be regarded a as resonance hybrid of the following structures :



$$\underset{\text{I}}{CH_3=CH-CH=CH_2} \longleftrightarrow$$

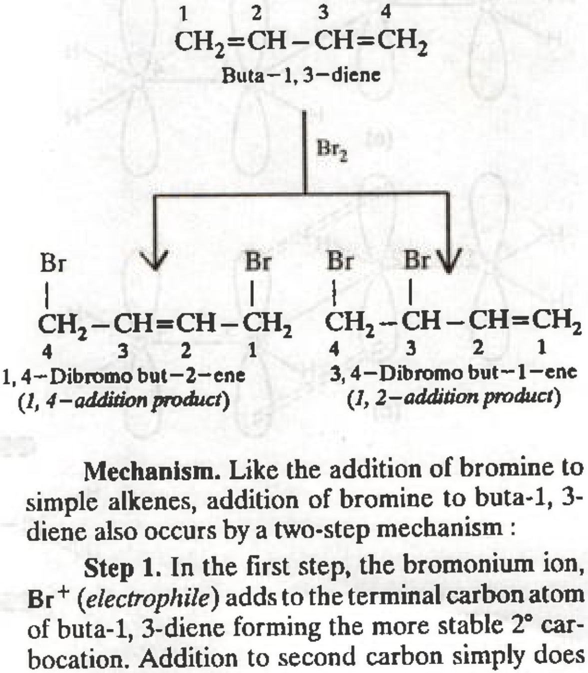
$$\underset{\text{II}}{\overset{+}{C}H_2-CH=CH-\overset{-}{C}H_2} \leftrightarrow \underset{\text{III}}{\overset{-}{C}H_2-CH=CH-\overset{+}{C}H_2}$$

Due to the contributions of structures (II and III), it is expected that C_1-C_2 and C_3-C_4 double bonds of butadiene should have some single bond character and C_2-C_3 single bond should have some double bond character. This has indeed been found to be so. The C_1-C_2 and C_3-C_4 double bonds of butadiene are slightly longer (140 pm) as compared to the typical carbon-carbon double bond length of 134 pm in ethylene. Similarly, C_2-C_3 single bond of butadiene is slightly shorter (146 pm) as compared to the typical carbon-carbon single bond length of 154 pm in ethane.

15.9.3. Chemical Reactions of Dienes

The chemical reactions of isolated dienes are exactly similar to those of simple alkenes since two double bonds react independently as if they were present in different molecules. However, the chemical properties of conjugated dienes are somewhat modified due to the mutual interaction of the two double bonds. Some of the important chemical reactions of conjugated dienes are discussed below with particular reference to 1, 3-butadiene.

1. Electrophile addition to conjugated dienes. (*i*) **Addition of halogens.** Conjugated dienes such as 1, 3-butadiene, when treated with 1 mole of bromine give a mixture of *1, 2-and 1, 4-addition products.* Very often, 1, 4-addition product is the major one. Thus,



$$\overset{1}{C}H_2=\overset{2}{C}H-\overset{3}{C}H=\overset{4}{C}H_2$$

Buta−1, 3−diene

$$\xrightarrow{Br_2}$$

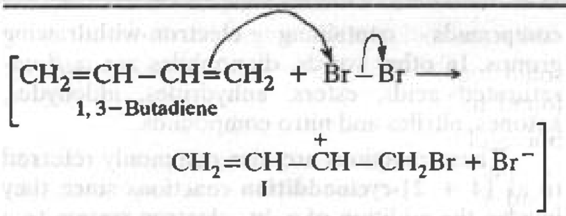
$$\underset{4}{\overset{Br}{C}H_2}-\underset{3}{CH}=\underset{2}{CH}-\underset{1}{\overset{Br}{C}H_2} \qquad \underset{4}{\overset{Br}{C}H_2}-\underset{3}{\overset{Br}{C}H}-\underset{2}{CH}=\underset{1}{CH_2}$$

1, 4−Dibromo but−2−ene (*1, 4−addition product*)

3, 4−Dibromo but−1−ene (*1, 2−addition product*)

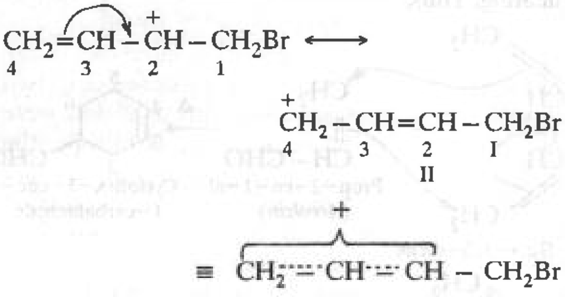
Mechanism. Like the addition of bromine to simple alkenes, addition of bromine to buta-1, 3-diene also occurs by a two-step mechanism :

Step 1. In the first step, the bromonium ion, Br^+ (*electrophile*) adds to the terminal carbon atom of buta-1, 3-diene forming the more stable 2° carbocation. Addition to second carbon simply does not occur since it gives the less stable 1° carbocation.



$$\left[\underset{\text{1, 3-Butadiene}}{CH_2=CH-CH=CH_2} + Br-Br \longrightarrow CH_2=CH-\overset{+}{C}H-CH_2Br + Br^-\right]$$

This intermediate carbocation is *allylic in nature* and hence can be regarded as a resonance hybrid of two equivalent structures (I and II) :

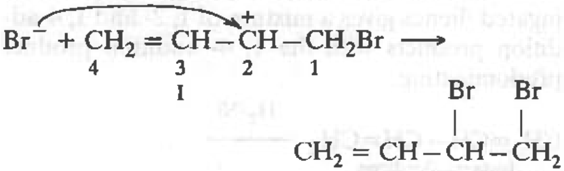


$$\underset{4}{CH_2}=\underset{3}{CH}-\overset{+}{\underset{2}{CH}}-\underset{1}{CH_2Br} \longleftrightarrow \underset{\text{II}}{\overset{+}{\underset{4}{CH_2}}-\underset{3}{CH}=\underset{2}{CH}-\underset{\text{I}}{CH_2Br}}$$

$$\equiv \overbrace{CH_2 \cdots CH \cdots CH}^{+} - CH_2Br$$

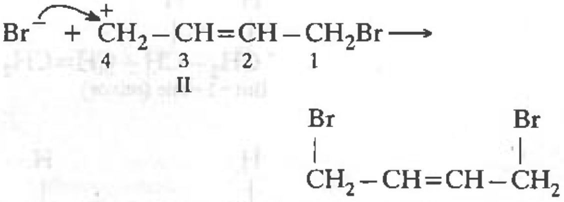
Resonance hybrid

Step 2. Since in the resonance hybrid, the positive charge is almost equally distributed between carbon atoms as indicated in I and II, the attack of bromide ion can occur on either of these. If the attack occurs on C_2, 1, 2-addition product results and if it occurs on C_4, 1, 4-addition product is formed as shown below :



$$Br^- + \underset{\text{I}}{\underset{4}{CH_2}=\underset{3}{CH}-\overset{+}{\underset{2}{CH}}-\underset{1}{CH_2Br}} \longrightarrow CH_2=CH-\overset{\displaystyle Br}{\overset{|}{CH}}-\overset{\displaystyle Br}{\overset{|}{CH_2}}$$

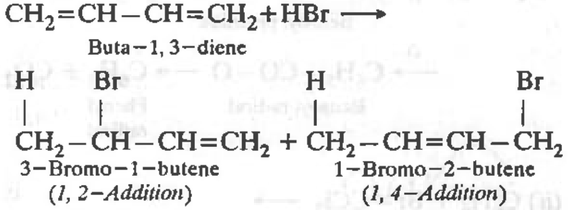
1, 2-Addition product



$$Br^- + \underset{\text{II}}{\overset{+}{\underset{4}{CH_2}}-\underset{3}{CH}=\underset{2}{CH}-\underset{1}{CH_2Br}} \longrightarrow \overset{\displaystyle Br}{\overset{|}{CH_2}}-CH=CH-\overset{\displaystyle Br}{\overset{|}{CH_2}}$$

1, 4-Addition product

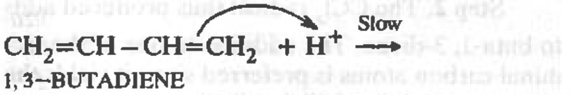
(*ii*) **Addition of halogen acids.** Like halogens, halogen acids (HCl, HBr and HI) also react with buta-1, 3-diene to give a mixture of 1, 2-and 1, 4-addition products :



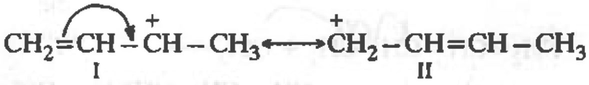
$$\underset{\text{Buta-1, 3-diene}}{CH_2=CH-CH=CH_2} + HBr \longrightarrow \underset{\substack{\text{3-Bromo-1-butene}\\ (1,\,2\text{-Addition})}}{\overset{\displaystyle H}{\overset{|}{CH_2}}-\overset{\displaystyle Br}{\overset{|}{CH}}-CH=CH_2} + \underset{\substack{\text{1-Bromo-2-butene}\\ (1,\,4\text{-Addition})}}{\overset{\displaystyle H}{\overset{|}{CH_2}}-CH=CH-\overset{\displaystyle Br}{\overset{|}{CH_2}}}$$

Mechanism. Mechanism of addition of HBr to 1, 3-butadiene is similar to that of the addition of Br_2 as discussed above.

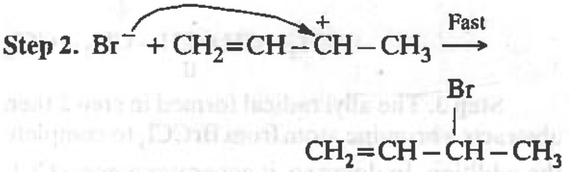
Step 1. $HBr \longrightarrow H^+ + Br^-$



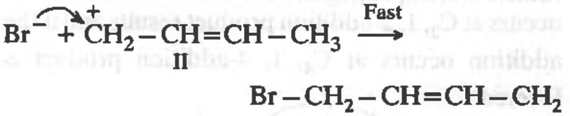
$$\underset{\text{1, 3-BUTADIENE}}{CH_2=CH-CH=CH_2} + H^+ \xrightarrow{\text{Slow}}$$



$$\underset{\text{I}}{CH_2=CH-\overset{+}{C}H-CH_3} \longleftrightarrow \underset{\text{II}}{\overset{+}{C}H_2-CH=CH-CH_3}$$

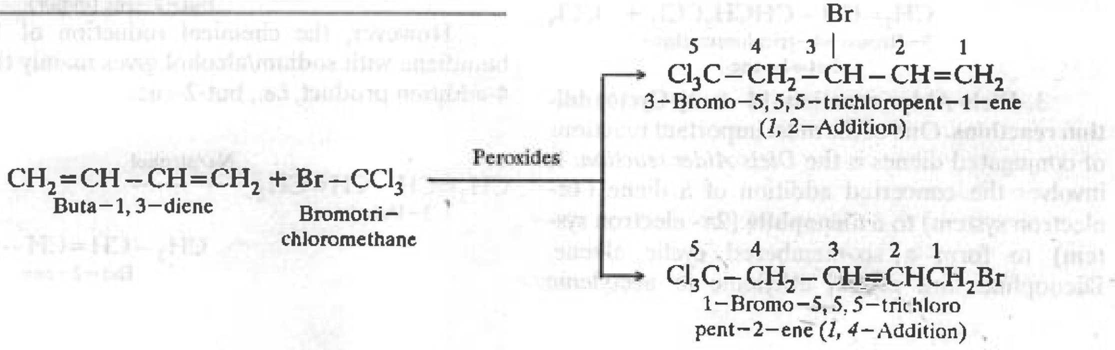


$$\textbf{Step 2. } Br^- + CH_2=CH-\overset{+}{C}H-CH_3 \xrightarrow{\text{Fast}} CH_2=CH-\overset{\displaystyle Br}{\overset{|}{CH}}-CH_3$$



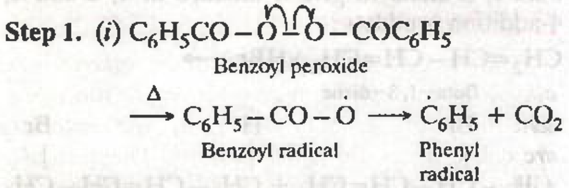
$$Br^- + \underset{\text{II}}{\overset{+}{C}H_2-CH=CH-CH_3} \xrightarrow{\text{Fast}} Br-CH_2-CH=CH-CH_3$$

2. Free radical additions. Like electrophilic additions, conjugated dienes also undergo free radical addition reactions to give a mixture of 1, 2- and 1, 4-addition products. For example,

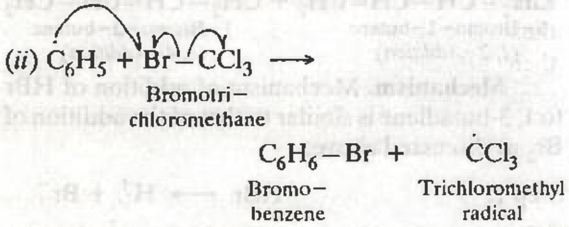


$$\underset{\text{Buta-1, 3-diene}}{CH_2=CH-CH=CH_2} + \underset{\substack{\text{Bromotri-}\\ \text{chloromethane}}}{Br-CCl_3} \xrightarrow{\text{Peroxides}} \begin{cases} \underset{\substack{\text{3-Bromo-5, 5, 5-trichloropent-1-ene}\\ (1,\,2\text{-Addition})}}{\overset{5}{Cl_3C}-\overset{4}{CH_2}-\overset{\displaystyle Br}{\overset{|}{\underset{3}{CH}}}-\overset{2}{CH}=\overset{1}{CH_2}} \\ \underset{\substack{\text{1-Bromo-5, 5, 5-trichloro}\\ \text{pent-2-ene } (1,\,4\text{-Addition})}}{\overset{5}{Cl_3C}-\overset{4}{CH_2}-\overset{3}{CH}=\overset{2}{CH}\overset{1}{CH_2}Br} \end{cases}$$

Mechanism. The reaction is believed to occur by a free radical mechanism by the following steps :

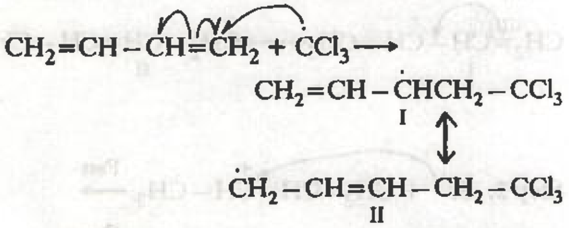


Step 1. (*i*) $\underset{\text{Benzoyl peroxide}}{C_6H_5CO-O-O-COC_6H_5} \xrightarrow{\Delta} \underset{\text{Benzoyl radical}}{C_6H_5-CO-\dot{O}} \longrightarrow \underset{\text{Phenyl radical}}{\dot{C}_6H_5} + CO_2$



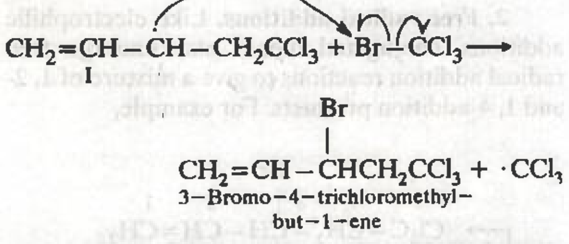
(*ii*) $C_6H_5 + \underset{\text{Bromotri-chloromethane}}{Br-CCl_3} \longrightarrow \underset{\text{Bromo-benzene}}{C_6H_6-Br} + \underset{\text{Trichloromethyl radical}}{\dot{C}Cl_3}$

Step 2. The $\dot{C}Cl_3$ radical thus produced adds to buta-1, 3-diene. The addition to one of the terminal carbon atoms is preferred since it yields the resonance stabilized allyl radical.



$$CH_2=CH-CH=CH_2 + \dot{C}Cl_3 \longrightarrow \underset{\text{I}}{CH_2=CH-\dot{C}HCH_2-CCl_3} \updownarrow \underset{\text{II}}{\dot{C}H_2-CH=CH-CH_2-CCl_3}$$

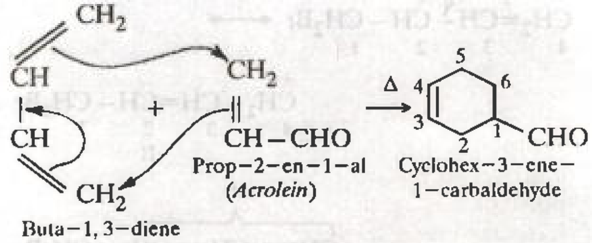
Step 3. The allyl radical formed in **step 2** then abstracts a bromine atom from $BrCCl_3$ to complete the addition. In doing so, it generates a new $\cdot CCl_3$ radical which propagates the chain. If the addition occurs at C_2, 1, 2-addition product results and if the addition occurs at C_4, 1, 4-addition product is formed.

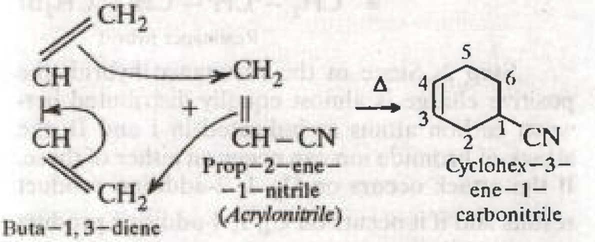


$$\underset{\text{I}}{CH_2=CH-\dot{C}H-CH_2CCl_3} + Br-CCl_3 \longrightarrow \underset{\text{3-Bromo-4-trichloromethyl-but-1-ene}}{CH_2=CH-\overset{\overset{Br}{|}}{C}HCH_2CCl_3} + \cdot CCl_3$$

3. Diels-Alder reaction–[4 + 2]-Cycloaddition reactions. One of the most important reactions of conjugated dienes is the *Diels-Alder reaction.* It involves the concerted addition of a diene (4π-electron system) to a **dienophile** (2π- electron system) to form a six-membered cyclic alkene. Dienophiles are usually ethylenic or acetylenic compounds containing electron-withdrawing groups. In other words, dienophiles are α, β-unsaturated acids, esters, anhydrides, aldehydes, ketones, nitriles and nitro compounds.

These reactions are also commonly referred to as **[4 + 2]-cycloaddition** reactions since they involve the addition of a 4π- electron system to a 2π-electron system. Diels-Alder reactions normally do not require any catalysts and generally occur on heating. Thus,





4. Reduction. Catalytic hydrogenation of conjugated dienes gives a mixture of 1, 2- and 1, 4-addition products with the 1, 4- addition product predominating.

$$\underset{\text{Buta-1, 3-diene}}{CH_2=CH-CH=CH_2} \xrightarrow{H_2/Ni} \underset{\text{But-1-ene (\textit{minor})}}{\overset{H}{\underset{|}{C}}H_2-\overset{H}{\underset{|}{C}}H-CH=CH_2} + \underset{\text{But-2-ene (\textit{major})}}{\overset{H}{\underset{|}{C}}H_2-CH=CH-\overset{H}{\underset{|}{C}}H_2}$$

However, the chemical reduction of 1, 3-butadiene with sodium/alcohol gives mainly the 1, 4-addition product, *i.e.*, but-2-ene.

$$\underset{\text{1, 3-Butadiene}}{CH_2=CH-CH=CH_2} \xrightarrow{\text{Na/alcohol}} \underset{\text{But-2-ene}}{CH_3-CH=CH-CH_3}$$

Under these conditions the isolated double bonds are not reduced. This suggests that dienes are much more reactive than simple alkenes.

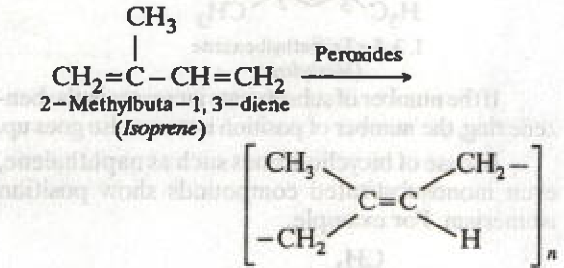
5. Polymerization. Like substituted alkenes, conjugated dienes also undergo free radical polymerization reactions.

It generally occurs by 1, 4-addition and is carried out is presence of peroxides. For example,

$$\underset{\text{Buta-1, 3-diene}}{n\,CH_2{=}CH-CH{=}CH_2} \xrightarrow{\text{Peroxides}} \underset{\text{Polybutadiene}}{(-CH_2-CH{=}CH-CH_2-)_n}$$

Since each repeating unit in polybutadiene contains a double bond, it may have either *cis* or *trans*-configuration. Actually the polybutadiene polymer obtained by free-radical polymerisation has *trans*-configuration.

Similarly substituted dienes also undergo free radical polymerization mostly by 1, 4-addition giving mainly the all *trans*-polymer. For example,

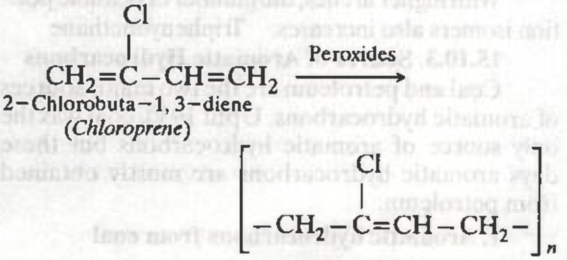


$$\underset{\text{2-Methylbuta-1, 3-diene (Isoprene)}}{CH_2{=}\overset{\overset{\large CH_3}{|}}{C}-CH{=}CH_2} \xrightarrow{\text{Peroxides}}$$

2−Methylbuta−1, 3−diene
(Isoprene)

Major product
All *trans*−polyisoprene
(Gutta percha)

Like isoprene, chloroprene can also be polymerized under free radical conditions to give neoprene.



$$\underset{\text{2-Chlorobuta-1, 3-diene (Chloroprene)}}{CH_2{=}\overset{\overset{\large Cl}{|}}{C}-CH{=}CH_2} \xrightarrow{\text{Peroxides}} \underset{\text{Polychloroprene (Neoprene)}}{\left[-CH_2-\overset{\overset{\large Cl}{|}}{C}{=}CH-CH_2-\right]_n}$$

2−Chlorobuta−1, 3−diene
(Chloroprene)

Polychloroprene
(Neoprene)

Neoprene is an important substitute for natural rubber and is superior to natural rubber in being more resistant to oil, gasoline and other organic solvents.

PART—V

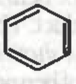
ARENES

15.10. Aromatic Hydrocarbons or Arenes

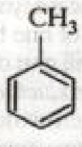
Hydrocarbons and their alkyl, alkenyl and alkynyl derivatives which contain one or more benzene rings either fused or isolated in their molecules are called **aromatic hydrocarbons. They** are also called **arenes (aromatic alkenes). Further,** since these compounds resemble benzene in almost all of their properties, they are also called **benzenoid compounds.**

15.10.1. Classification and Nomenclature of Arenes

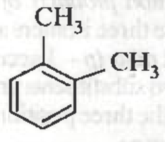
Arenes are further classified into different series depending upon the number of fused benzene rings present in their molecules. Their general formula is $C_n H_{2n-6m}$ where n is the number of carbon atoms and m is the number of rings. For monocyclic arenes, $m = 1$ and $n = 6$, or more. Examples are :



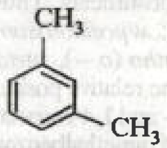
Benzene



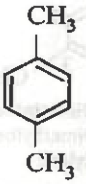
Methylbenzene
(Toluene)



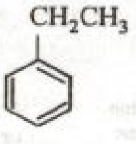
1, 2−Dimethyl− benzene
(o−Xylene)



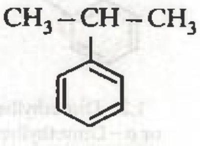
1, 3−Dimethylbenzene
(m−Xylene)



1, 4−Dimethylbenzene
(p−Xylene)



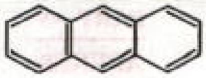
Ethylbenzene



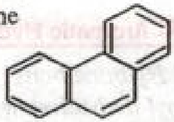
Isopropylbenzene
(Cumene)

For bicyclic arenes, $n = 10$ and $m = 2$. The first member of this series is the well known naphthalene which is used in the form of moth balls as a moth repellent for clothes. For tricyclic arenes, $n = 14$ and $m = 3$. The first member of this series is anthracene or phenanthrene.

Naphthalene

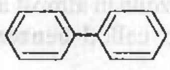


Anthracene

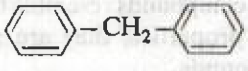


Phenanthrene

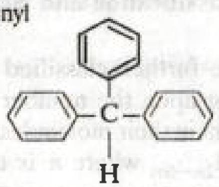
Some arenes may contain two or more isolated rings. For example,



Diphenyl or Biphenyl



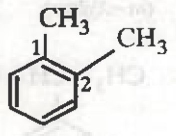
Diphenylmethane



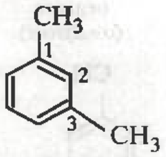
15.10.2. Isomerism in arenes

Arenes show position isomerism as discussed below :

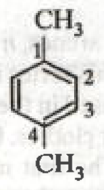
Benzene is a symmetrical molecule. Therefore, the replacement of one hydrogen atom of benzene by any substituent will give only a single product. Thus, *mono-substitution products of benzene do not show isomerism*. However, when two hydrogen atoms of benzene ring are replaced by two same or different substituents, three isomers are possible which differ in the position of substituents. Thus, *di-substitution products of benzene show position isomerism*. These three isomers are called *ortho* (*o*–), *meta* (*m*–) and *para* (*p*–) according as the relative positions of the two substituents are 1, 2 ; 1, 3- and 1, 4-respectively. Thus, the three position isomers of dimethylbenzene or xylene are :



1,2–Dimethylbenzene or *o*–Dimethylbenzene or *o*–Xylene



1,3–Dimethylbenzene or *m*–Dimethylbenzene or *m*–Xylene

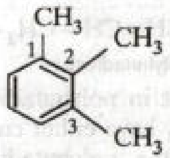


1, 4–Dimethylbenzene or *p*–Dimethylbenzene or *p*–Xylene

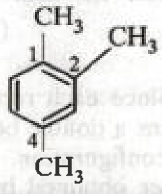
Besides, the three dimethylbenzenes, the fourth isomer, ethylbenzene is also known.

Ethylbenzene

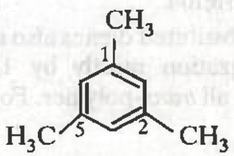
Similarly three position isomers of trimethylbenzene are



1, 2, 3–Trimethylbenzene



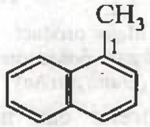
1, 2, 4–Trimethylbenzene



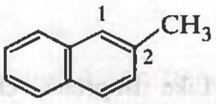
1, 3, 5–Trimethylbenzene (*Mesitylene*)

If the number of substituents increases in the benzene ring, the number of position isomers also goes up.

In case of bicyclic arenes such as naphthalene, even monosubstituted compounds show position isomerism. For example,



1-Methylnaphthalene



2-Methylnaphthalene

With higher arenes, the number of possible position isomers also increases. Triphenylmethane

15.10.3. Source of Aromatic Hydrocarbons

Coal and petroleum are the two major sources of aromatic hydrocarbons. Uptil 1950, coal was the only source of aromatic hydrocarbons but these days aromatic hydrocarbons are mostly obtained from petroleum.

1. Aromatic hydrocarbons from coal

Aromatic hydrocarbons are obtained by destructive distillation of coal.

Destructive distillation of coal. When coal is subjected to destructive distillation, *i.e.*, heated to 1270 – 1675 K in the absence of air, it decomposes to give a number of products as shown in the Flow Chart (Fig. 15.20).

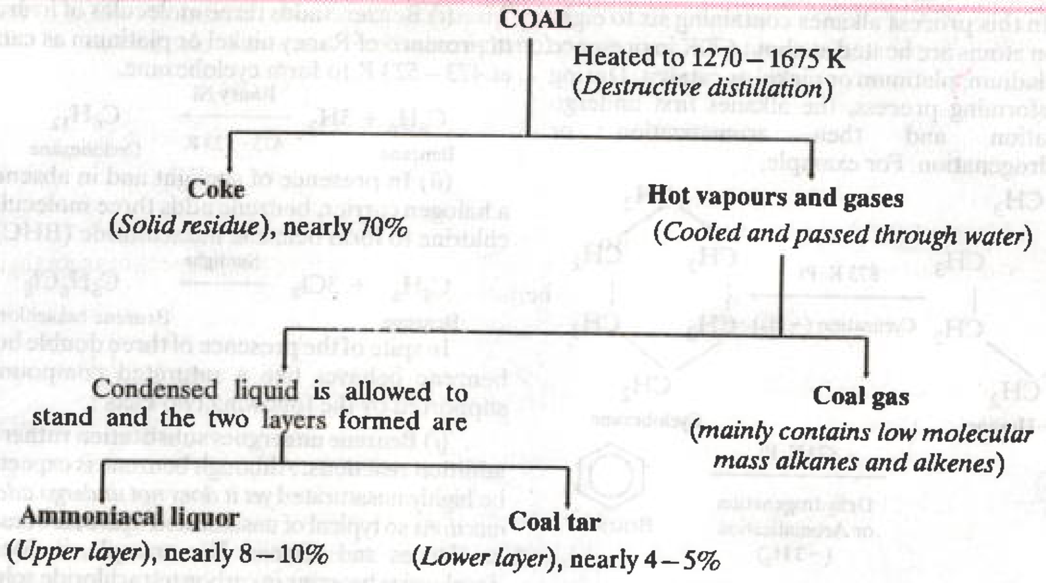


FIGURE 15.20. Flow chart of destructive distillation of coal.

(i) Coke. It is the solid residue left after the distillation. It is mainly used as a fuel and as a reducing agent in metallurgy.

(ii) Coal gas. It mainly consists of low molecular mass alkanes and alkenes. It is used as a *fuel*.

(iii) Ammoniacal liquor. It is a solution of ammonia in water and is removed by absorbing in a suitable mineral acid like dil. H_2SO_4. The ammonium sulphate thus produced is used as a *fertilizer*.

(iv) Coal tar*. It is a thick black viscous liquid with a disagreeable smell. It is a rich source of *aromatic hydrocarbons (arenes)* such as benzene, toluene, 1, 2-, 1, 3- and 1, 4-dimethylbenzenes (xylenes), naphthalene, anthracene and phenanthrene. These are obtained by fractional distillation of coal tar into a number of fractions (Table 15.3) followed by further work up of each fraction.

TABLE 15.3. Fractions of coal tar distillation

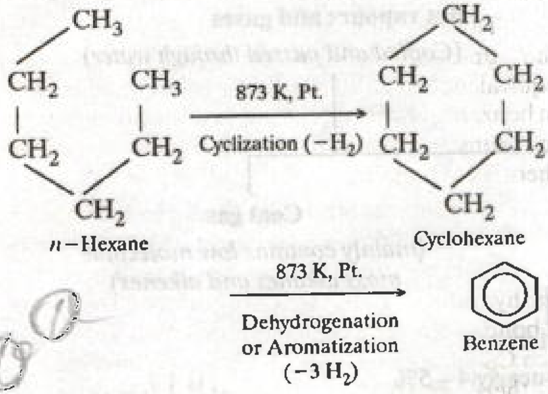
NAME OF THE FRACTION	TEMPERATURE RANGE (IN K)	MAJOR COMPONENTS
1. Light oil	Up to 443	Benzene, toluene, xylenes
2. Middle oil or Carbolic oil	443—503	Phenol, naphthalene, pyridine
3. Heavy oil or Creosote oil	503—543	Methyl and higher alkyl phenols, naphthalene, naphthols, etc.
4. Green oil or Anthracene oil	543—633	Anthracene, phenanthrene
5. Pitch (*Left as residue*)	Non- volatile	92—94% carbon (used for making black paints, varnish for wood and for water-proofing).

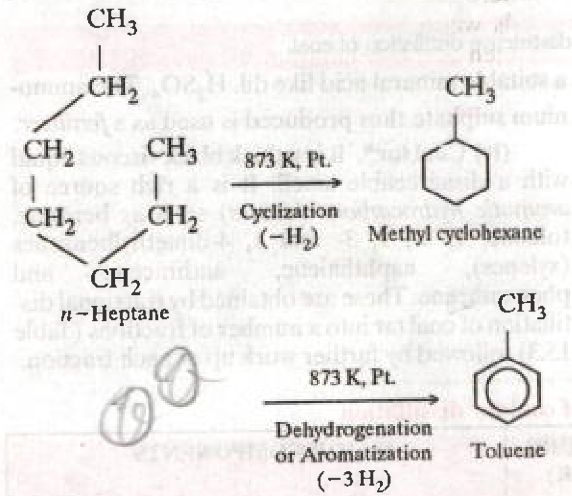
2. Aromatic hydrocarbons from petroleum. Crude naphtha is a fraction of petroleum refining with boiling range 303-343K and contains straight chain alkanes from C_5-C_{11}. This upon further fractionation gives a fraction called petroleum ether which contains straight chain alkanes from six to eight carbon atoms. It is subjected to **reforming** to obtain aromatic hydrocarbons. *Reforming may be defined as a process which converts straight chain alkanes or cycloalkanes into the corresponding aromatic hydrocarbons (arenes) under suitable conditions.*

---

*At one time, coal tar was considered to be a nuisance since it could not be put to any practical use. Further, because of its disagreeable smell, its disposal was a problem. Later on, it was used for metalling of roads.

In this process alkanes containing six to eight carbon atoms are heated at about 670K in presence of palladium, platinum or nickel as catalyst. During the reforming process, the alkanes first undergo cyclisation and then aromatization or dehydrogenation. For example,





In a similar way, *n*-octane gives xylenes.

Platinum is the best catalyst for this process, therefore, reforming is also called **plat forming**.

The main objectives of reforming are : (*i*) to increase the quality of gasoline since aromatic hydrocarbons are better fuels than aliphatic hydrocarbons and (*ii*) for *manufacture of aromatic hydrocarbons such as benzene, toluene, xylenes etc. from alkanes and cycloalkanes.*

15.10.4. Structure of benzene

The molecular formula of benzene is C_6H_6 which implies that it has eight hydrogen atoms less than the corresponding saturated alkane, *i.e.* C_6H_{14} (hexane). Thus, *benzene should be a highly unsaturated compound*. This is supported by the following two observations :

(*i*) Benzene adds three molecules of hydrogen in presence of Raney nickel or platinum as catalyst at 473 – 523 K to form cyclohexane.

$$\underset{\text{Benzene}}{C_6H_6} + 3H_2 \xrightarrow[473-523\text{ K}]{\text{Raney Ni}} \underset{\text{Cyclohexane}}{C_6H_{12}}$$

(*ii*) In presence of sunlight and in absence of a halogen carrier, benzene adds three molecules of chlorine to form benzene hexachloride (BHC).

$$\underset{\text{Benzene}}{C_6H_6} + 3Cl_2 \xrightarrow{\text{Sunlight}} \underset{\text{Benzene hexachloride}}{C_6H_6Cl_6}$$

In spite of the presence of three double bonds, benzene behaves like a saturated compound as supported by the following two facts :

(*i*) **Benzene undergoes substitution rather than addition reactions.** Although benzene is expected to be highly unsaturated *yet it does not undergo addition reactions* so typical of unsaturated hydrocarbons such as alkenes and alkynes. For example, it does not decolourize bromine in carbon tetrachloride solution. Instead, it undergoes *substitution reactions* which are characteristic of saturated compounds. For example, when treated with Br_2 in presence of a trace of $FeBr_3$, benzene forms monobromobenzene.

$$\underset{\text{Benzene}}{C_6H_6} \xrightarrow[CCl_4]{Br_2} \underset{\substack{\text{Not formed}\\ (\textit{Addition product})}}{C_6H_6Br_2}$$

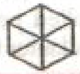
$$\underset{\text{Benzene}}{C_6H_6} \xrightarrow[FeBr_3]{Br_2} \underset{\substack{\text{Bromobenzene}\\ (\textit{Substitution product})}}{C_6H_5Br} + HBr$$

(*ii*) **Benzene is resistant to oxidation.** Unlike alkenes and alkynes, benzene is only slowly oxidised to CO_2 and H_2O even with powerful oxidising agents such as chromic acid, potassium permanganate etc. *Thus, benzene resists oxidation like saturated compounds*.

Kekule structure. The first insight into the structure of benzene was given by Friedrich August Kekule (1865). He proposed that the six carbon atoms of benzene are joined to each other by alternate single and double bonds to form a hexagonal ring as shown in Fig. 15.21. Each carbon is further connected to a hydrogen atom.

Besides Kekule, the following other alternative structures were proposed for benzene from time to time by different scientists, but all these were rejected on one ground or the other.


Dewar (1867)


Claus (1867)


Baeyer (1892)

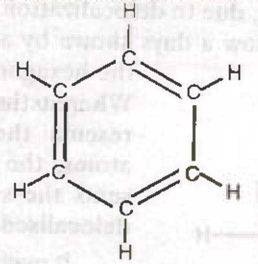


FIGURE 15.21. Kekule structure of benzene.

Objections to Kekule structure. There are three objections to Kekule structure.

(*i*) *Why is it that benzene shows remarkable stability towards oxidising agents like* $KMnO_4$ *and undergoes substitution reactions even though it contains three double bonds ?*

(*ii*) *Kekule formula for benzene contains two kinds of bonds, i.e., single and double bonds. But X-ray diffraction studies have shown that the structure of benzene is a regular hexagon with an angle of 120° and all the carbon-carbon bond lengths are equal, i.e.,* $1 \cdot 39$ *Å or 139 pm which lie in between carbon-carbon single bond length of* $1 \cdot 54$ *Å or 154 pm and carbon-carbon double bond length of* $1 \cdot 34$ *Å or 134 pm.*

(*iii*) *Kekule structure would predict only one monosubstitution product and two o-disubstituted products (a and b) as shown in Fig. 15.22.*

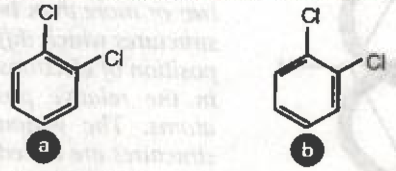


FIGURE 15.22. Kekule isomers of o-dichlorobenzene.

In structure (*a*), there is a double bond between the two carbon atoms carrying chlorine atoms but in structure (*b*) there is a single bond. If Kekule structures were correct, both these isomers should exist and should have different properties. But only one *o*- dichlorobenzene is known. To account for this, Kekule proposed a dynamic equilibrium between the two structures as shown in Fig. 15.23.

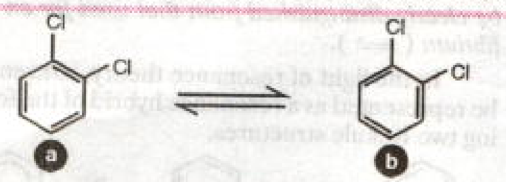


FIGURE 15.23. Dynamic equilibrium between two Kekule isomers of o-dichlorobenzene.

In other words, positions of single and double bonds are not fixed but oscillate back and fourth between adjacent positions.

Thus, Kekule structure failed to account for the unusual stability of benzene and the equivalence of all the carbon-carbon bond lengths in benzene. However, these can be easily explained in terms of molecular orbital and resonance theories of benzene as discussed below :

Molecular orbital structure of benzene. Since all the bond angles in benzene are 120°, therefore, all the carbon atoms of benzene are assumed to be sp^2-hybridized. Each carbon atom forms two C – C, σ-bonds with the neighbouring carbon atoms and one C – H, σ-bond with a hydrogen atom. Thus, in all there are six C – C, σ-bonds and six C – H, σ-bonds which all lie in one plane and the angle between any two adjacent σ-bonds is 120°. (Fig. 15.24)

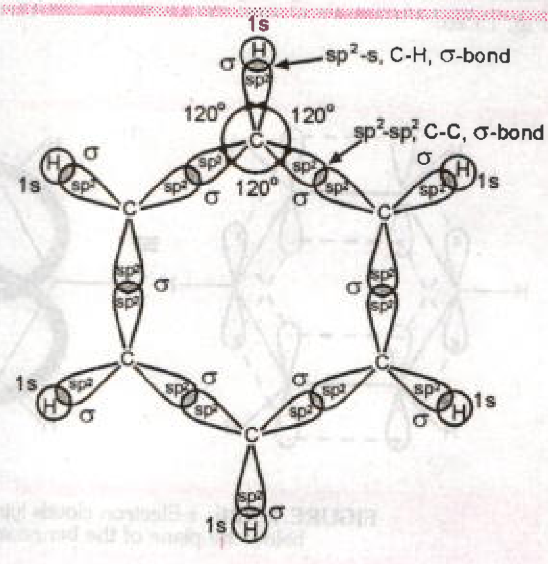


FIGURE 15.24. σ-Bond skeleton of benzene.

Each carbon is now left with an unhybridized *p*-orbital. These six unhybridized *p*-orbitals have one electron each and are not only parallel to one another but are also perpendicular to the plane of σ-bonded carbon skeleton. Further, any two *p*-orbitals on adjacent carbon atoms are close enough for a sideways overlap to form π-bonds.

Now there are two equally good ways in which the *p*- *orbitals on adjacent carbon atoms can overlap* *to form three π-bonds* as shown in Fig. 15.25 (*a*) and 15.25 (*b*).

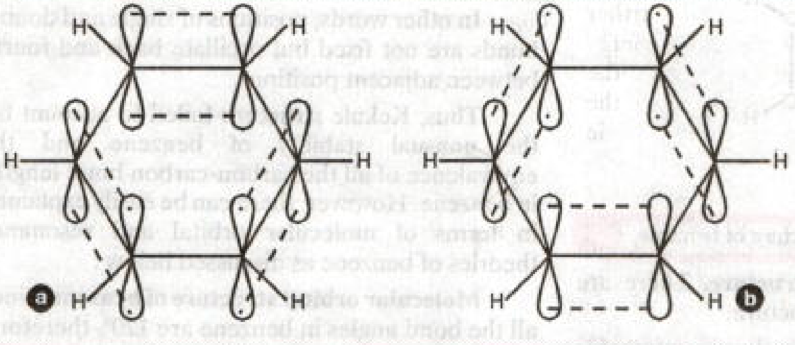


FIGURE 15.25. Two possible sideways overlap of six unhybridized p-orbitals to form three π-bonds.

In fact, each 2*p*-orbital overlaps equally well with 2*p*-orbitals on adjacent carbon atoms on either side to form two doughnut shaped π-electron clouds ; one of which lies above and other below the plane of carbon and hydrogen atoms as shown in Fig. 15.26.

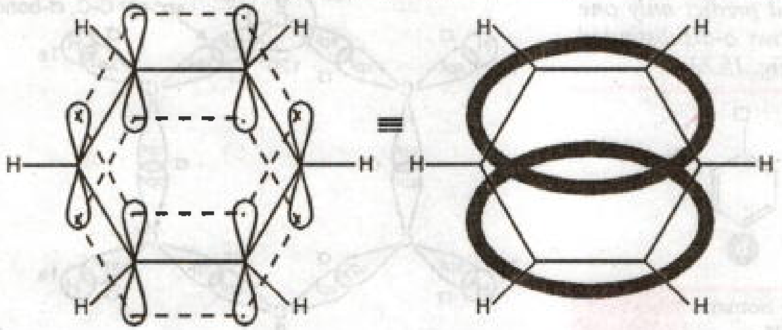


FIGURE 15.26. π-Electron clouds lying above and below the plane of the benzene ring.

Thus, two *p*-orbitals are not confined to a single π-bond between two carbon atoms as was the case with two structures as shown in Fig. 15.25 but are involved in the formation of more than one π-bond. *This participation of π-electrons in more than one bond is called* **delocalization of electrons.** These delocalized electrons are equally attracted by all the six carbon atoms of the benzene ring. As a result, *all the carbon-carbon bond lengths in benzene are equal, all the carbon-hydrogen bonds are equivalent, its dipole moment is zero and does not show the type of isomerism shown in Fig. 15.26.*

Further, due to delocalization of electrons, benzene is now a days shown by a circle within the hexagon (Fig. 15.27). Whereas the hexagon represents the six carbon atoms, the circle represents the six completely delocalised π-electrons.

It may be noted here that it is this delocalization of π- electrons which makes it more stable than the hypothetical cyclohexatriene molecule (*Kekule structure*).

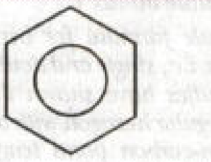
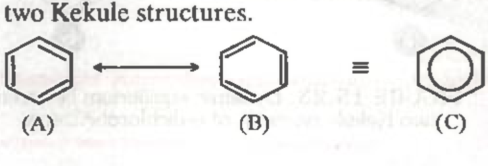


FIGURE 15.27. Modern picture of benzene molecule.

15.10.5. Resonance

The phenomenon of resonance is said to occur if for a molecule, we can write two or more than two Lewis structures which differ in the position of electrons and not in the relative position of atoms. The various Lewis structures are called **canonical structures** *or the* **resonance structures.** *The real structure of the molecule is not represented by any one of the canonical structures but is a resonance hybrid of the various resonance structures. The various resonance structures are separated by a double headed ($\longleftrightarrow$) arrow. This arrow should be clearly distinguished from that used for an equilibrium ($\rightleftharpoons$).*

In the light of resonance theory, benzene can be represented as a resonance hybrid of the following two Kekule structures.



Thus, these two structures are the canonical forms of benzene. The actual structure of benzene is neither represented by 'A' nor by 'B' but *is a resonance hybrid* of these two structures. Further since these two canonical forms are of equal energy so they contribute equally (50%) towards the resonance hybrid. In other words, structure of the resonance hybrid is in between these two Kekule structures. This means that any two adjacent carbon atoms of the benzene molecule are neither joined by a pure single bond nor by a pure double bond. As a result, all the carbon-carbon bond lengths are equal, *i.e.*, 1·39 Å (139 pm) and lie in between C = C bond length of 1·34 Å (134 pm) and C–C bond length of 1·54 Å (154 pm). The resonance hybrid or the actual molecule of benzene is usually represented by the formula 'C'.

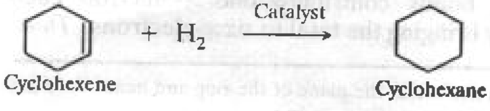
Further, a resonance hybrid is always more stable than any of its canonical structures. Thus, the actual molecule of benzene is more stable than either of the two Kekule structures. The magnitude of stability conferred on a molecule as a result of resonance is expressed in terms of **resonance energy** or **delocalization energy**. *It is defined as the difference in internal energy of the resonance hybrid and that of the most stable canonical form.* In case of benzene, this resonance energy has been determined to be 150·62 kJ (36·0 kcal) mol^{-1}.

15.10.6. Calculation of resonance energy

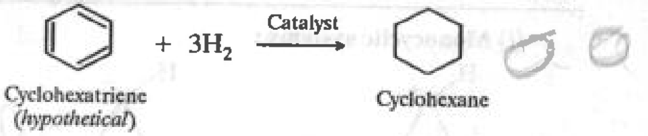
The resonance energy of benzene can be calculated from heat of hydrogenation data.

Heat of hydrogenation *is the amount of heat evolved when one mole of an unsaturated compound is hydrogenated (in presence of a catalyst).*

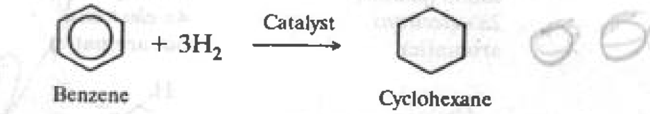
When benzene is fully hydrogenated, it gives cyclohexane and 208·36 kJ (49·8 kcal) mol^{-1} of heat is evolved. On the other hand, cyclohexene having a six- membered ring and one double bond when hydrogenated gives cyclohexane and 119·66 kJ (28·6 kcal) mol^{-1} of heat is evolved. If the three double bonds of benzene did not interact or if there were no resonance (as would be the case in the hypothetical cyclohexatriene molecule with three non-intreacting double bonds in a six-membered ring) then three times the heat of hydrogenation of cyclohexene, *i.e.*, 119·66 × 3 = 358·98 kJ (85·8 kcal) mol^{-1} would have been evolved.



$\Delta H = -119 \cdot 66 \text{ kJ mol}^{-1}$



$\Delta H = -358 \cdot 98 \text{ kJ mol}^{-1}$



$\Delta H = -208 \cdot 36 \text{ kJ mol}^{-1}$

Thus, the actual molecule of benzene is 358·98 – 208·36 = 150·62 kJ (36·0 kcal) mol^{-1} more stable than the hypothetical cyclohexatriene molecule. In other words, 150·62 kJ (36·0 kcal) mol^{-1} is the **resonance energy of benzene.**

15.10.7. Concept of Aromaticity – Huckel Rule.

Huckel, on the basis of molecular orbital theory, has predicted that electrons in cyclic conjugated polyenes (cyclic polyenes having alternate single and double bonds) containing $(4n + 2)$ π-electrons where n = 0, 1, 2, 3...etc. are completely delocalized. This makes these molecules particularly stable. All such compounds are called **aromatic compounds** and have chemical properties altogether different from other cyclic unsaturated compounds which do not contain $(4n + 2)$ π- electrons.

Thus, the necessary and sufficient conditions for a molecule to be aromatic are :

(*i*) *It should have a cyclic cloud of delocalized π-electrons above and below the plane of the molecule.*

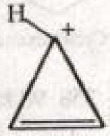
(*ii*) *It should be planar.* This is due to the reason that complete delocalization of π-electrons is possible only if the ring is planar to allow cyclic overlap of *p*-orbitals.

(*iii*) *It should contain $(4n + 2)$ π-electrons where n* = 0,1, 2, 3...etc.

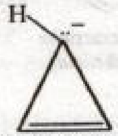
A molecule which does not satisfy any one or more of the above conditions is said to be **non-aromatic.**

Applications of Huckel rule. In the light of the above rules, *any planar cyclic system containing 2, 6, 10, 14, 18...etc. π-electrons and having a single cyclic π-electron cloud encompassing all the carbon atoms in the ring is aromatic.* Let us now test the validity of these rules :

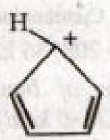
(i) Monocyclic systems :



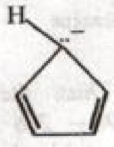
Cyclopropenyl cation (*planar*, 2π-*electrons*, **aromatic)**



Cyclopropenyl anion (*planar*, 4π-*electrons*, **not aromatic)**

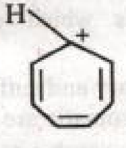


Cyclopentadienyl cation (*planar*, 4π-*electrons*, **non aromatic)**

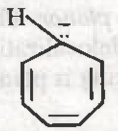


Cyclopentadienyl anion (*planar*, 6π-*electrons*, **aromatic)**

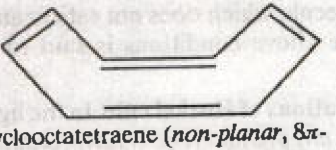
Cycloheptatriene (*non planar*, 6π-*electrons but not spread over the entire ring*, **not aromatic)**



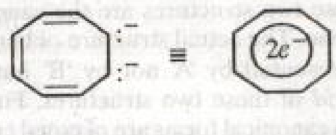
Cycloheptatrienyl cation or Tropylium cation (*planar*, 6π-*electrons spread over the entire ring*, **aromatic)**



Cycloeptatrienyl anion (*non-planar*, 8π-electrons, **not aromatic)**



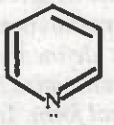
Cyclooctatetraene (*non-planar*, 8π-electrons, **not aromatic)**



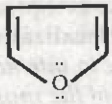
Cyclooctatetraenyl dianion (*planar*, 10π-*electrons spread over the entire ring*, **aromatic**)

(*ii*) **Polycyclic compounds.** Huckel rule can also explain the aromaticity of polycyclic compounds. For example, naphthalene which contains 10 π-electrons ($n = 2$), anthracene and phenanthrene each containing 14 π-electrons ($n = 3$) are all aromatic.

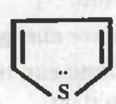
(*iii*) **Heterocyclic compounds.** Heterocyclic compounds such as pyridine, furan, thiophene and pyrrole are all aromatic since each one of them is planar and has a cyclic system of 6 π-electrons which is completely delocalized over the entire ring.



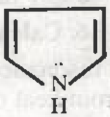
Pyridine



Furan



Thiophene



Pyrrole

In pyridine, each of the five sp^2-hybridized carbon atoms and the sp^2-hybridized nitrogen atom has a *p*-orbital perpendicular to the plane of the ring. Each of these atoms contributes one π-electron thereby producing a single cyclic π-cloud containing 6 π-electrons. The lone pair of electrons on the nitrogen atom is present in a sp^2-orbital which being in the plane of the ring does not contribute towards the aromatic sextet.

In contrast, in case of furan, thiophene and pyrrole, one of the two lone pairs* of electrons on the sp^2-hybridized heteroatom (O, S or N) is present in a *p*-orbital perpendicular to the plane of the ring. Consequently, it contributes two π-electrons while the other four *p*-orbitals of the two double bonds contribute one π-electron each thereby bringing the total to six π-electrons. *Thus,*

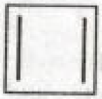
---

*The other lone pair of electrons on the sp^2-hybridized heteroatom lies within the plane of the ring and hence does not contribute towards the aromatic sextet.

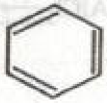
all the three five-membered heterocycles (furan, thiophene and pyrrole) have a single cyclic electronic cloud containing 6π-electrons and hence are **aromatic** *in charactere.*

4. **Annulenes.** *Completely conjugated monocyclic polyenes contianing an even number of carbon atoms are called* **annulenes.** Their general formula is $(CH = CH)_n$, where $n = 2, 3, 4$...etc.

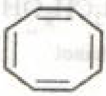
They are named by indicating the number of carbon atoms in the ring enclosed in square brackets before the root word annulene. Thus,



[4]-Annulene
(Cyclobutadiene)

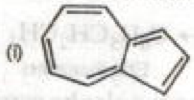


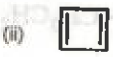
[6]-Annulene
(Benzene)

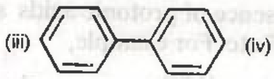


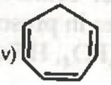
[8]-Annulene
(Cycloctatetraene)

EXAMPLE 15.7. *Predict which of the following systems would be aromatic and why ?* (N.C.E.R.T.)









Ans. Compound (*i*) contains $(4n + 2)\pi$ electrons where $n = 2$, *i.e.*, it contains $5 \times 2 = 10\ \pi$-electrons and hence according to Huckel rule, it is aromatic.

Compound (*iii*) is also aromatic since it contains two benzene rings each one of which contains $(4n + 2)\ \pi$- electrons with $n = 1$, *i.e.*, $3 \times 2 = 6$ electrons.

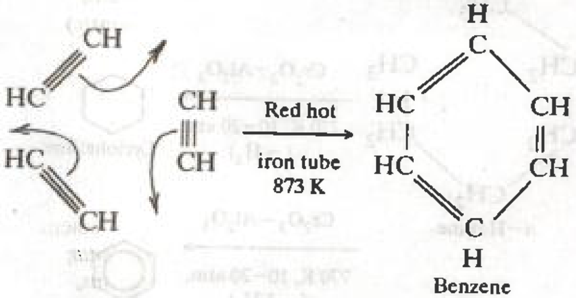
Compound (*ii*) is a $4n\ \pi$ ($n = 1$) electron system and hence is *an antiaromatic compound.*

Although compound (*iv*) contains 6π-electrons, *i.e.* $(4n + 2)\ \pi$ electrons with $n = 1$, yet the system is not completely conjugated due to the presence of a sp^3-hybridized carbon. In other words, this compound is not planar and hence is not aromatic.

15.10.8. Methods of preparation of Arenes

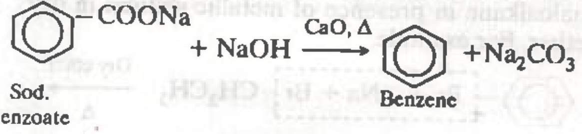
Benzene (*phene*), C_6H_6, was first isolated by *Faraday* (1825) from cylinders of compressed illuminating gas obtained from pyrolysis of whale oil. In 1845, benzene was found in coal-tar by *Hofmann*. Arenes are mainly present in the light oil fraction of coal tar distillation from where they are isolated by suitable methods.

1. From acetylene. Benzene was first synthesized by *Berthelot* by passing acetylene through red-hot iron tube at 873 K. Under similar conditions propyne gives mesitylene (For details refer to page 15/57.



Benzene

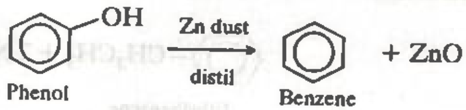
2. From sodium benzoate by decarboxylation with soda-lime (*Laboratory method*)



Sod. benzoate

Benzene

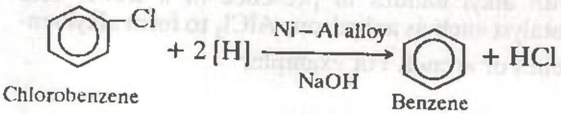
3. From phenol by distillation with zinc dust



Phenol

Benzene

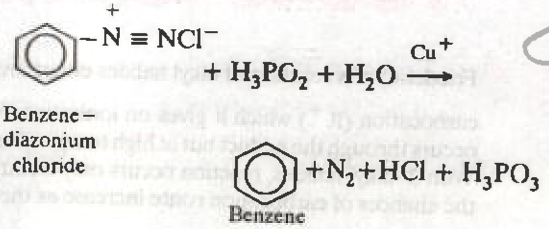
4. From chlorobenzene by reduction with Ni-Al alloy/NaOH



Chlorobenzene

Benzene

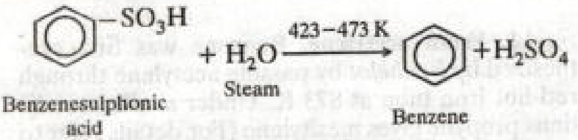
5. From benzenediazonium chloride by reduction with hypophosphorus acid (H_3PO_2) in presence of Cu^+ ions



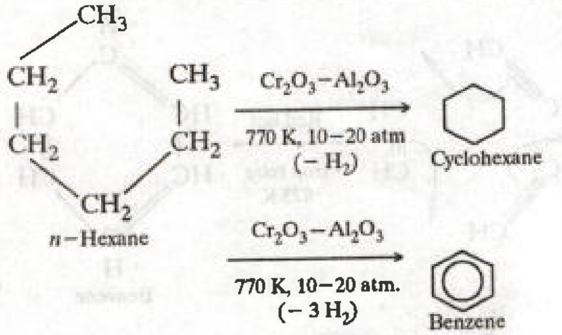
Benzene-diazonium chloride

Benzene

6. From benzenesulphonic acid by heating with superheated steam.

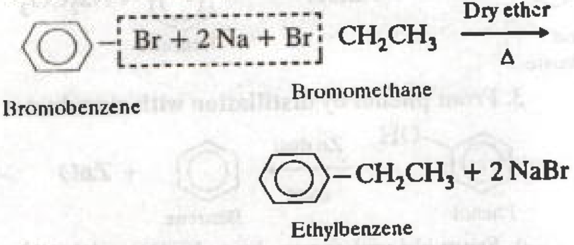


7. From n-hexane and n-heptane

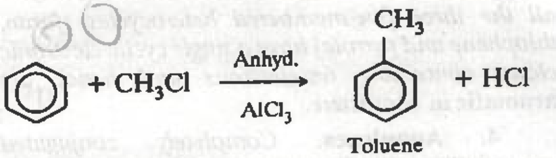


n-Heptane under similar conditions first gives methylcyclohexane and then toluene as shown on page 15/69. The catalyst used mainly consists of oxides of chromium, vanadium and molybdenum supported over alumina.

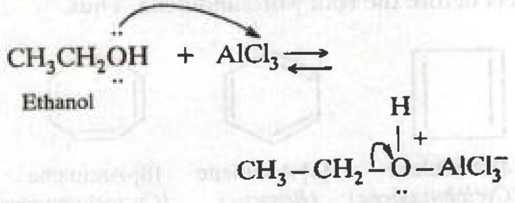
8. By Wurtz-Fittig reaction. It involves the reaction between a suitable haloarene and a haloalkane in presence of metallic sodium in dry ether. For example,



9. Friedel-Crafts reaction. Benzene reacts with alkyl halides in presence of a Lewis acid catalyst such as anhydrous $AlCl_3$ to form alkylbenzenes or arenes. For example,



Instead of alkyl halides, alcohols can also be used in Friedel-Crafts reaction. Here, the Lewis acid helps in the generation of a carbocation which then attacks the benzene ring to form the corresponding alkylbenzene. For example,



$$\rightleftharpoons \underset{\text{Ethyl carbocation}}{CH_3\overset{+}{C}H_2} + HO-AlCl_3^-$$

$$C_6H_6 + CH_3\overset{+}{C}H_2 \longrightarrow \underset{\text{Ethylbenzene}}{C_6H_5CH_2CH_3} + H^+$$

Friedel-Crafts reaction can also be carried out with alkenes in presence of protonic acids such as H_2SO_4, H_3PO_4, HF etc. For example,

$$\underset{\text{2–Methylpropene}}{(CH_3)_2C=CH_2} \xrightarrow[-HSO_4^-]{H_2SO_4} (CH_3)_2\overset{+}{C}-CH_3$$

$$\xrightarrow[-H^+]{C_6H_6} \underset{\textit{tert}\text{–Butylbenzene}}{C_6H_5-C(CH_3)_3}$$

Similarly,

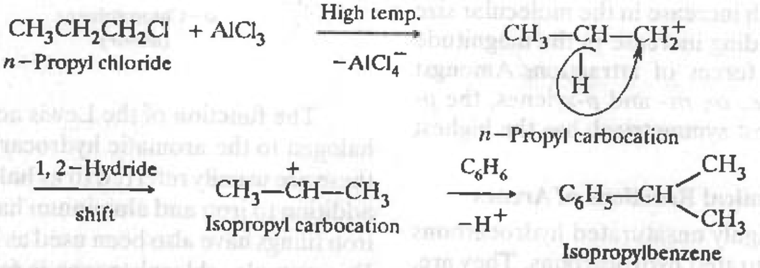
$$C_6H_6 + \underset{\text{Propene}}{CH_3CH=CH_2} \xrightarrow{H_3PO_4} \underset{\text{Cumene}}{C_6H_5-CH(CH_3)_2}$$

ADD TO YOUR KNOWLEDGE

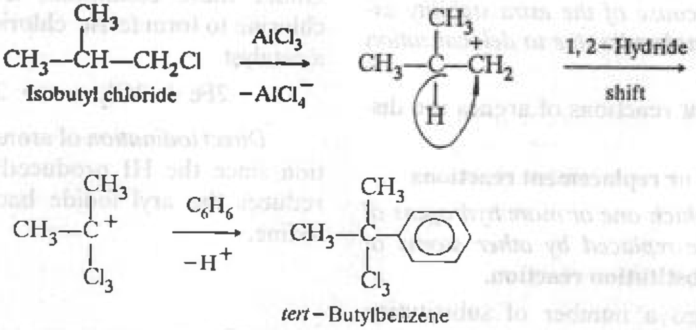
Friedel-Crafts reaction of alkyl halides either involves the adduct $R^{\delta+}$.....$ClAlCl_3^{\delta-}$ as the electrophile or the carbocation (R^+) which it gives on ionization. With *n*-alkyl halides at *low temperatures*, the reaction mainly occurs through the adduct but at high temperatures, the reaction may occur through carbocation intermediate. With 3° alkyl halides, reaction occurs only through the carbocation intermediate. With all other alkyl halides, the chances of carbocation route increase as the branching in the alkyl halide increases.

ADD TO YOUR KNOWLEDGE CONTD.

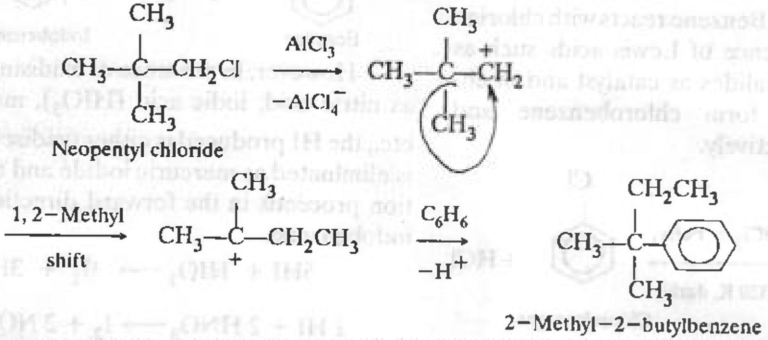
Whenever carbocations are the intermediates, and if the initially formed carbocation is less stable then it always rearranges first to the more stable carbocation either by 1, 2-hydride shift or 1, 2-methyl shift before attacking the benzene ring to give the rearranged product. For example,



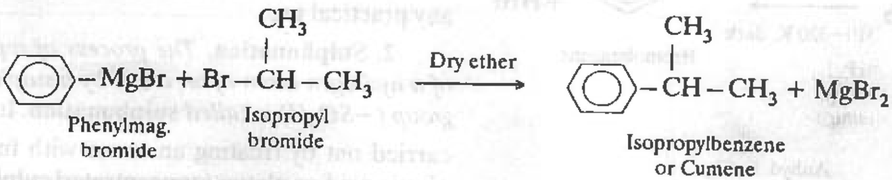
It may be emphasized here that at low temperatures, the major product is *n*-propylbenzene. Similarly, isobutyl chloride gives *tert*-butylbenzene.



With neopentyl chloride, the product is 2-methyl-2-butylbenzene.



10. From Grignard reagents. Grignard reagents react with alkyl halides in presence of dry ether to form arenes. For example,



15.10.9. Physical Properties of Arenes

(*i*) Benzene and its homologues containg upto eight carbon atoms are colourless liquids with characteristic smell.

(*ii*) Due to large hydrophobic hydrocarbon part, arenes are not soluble in water but are soluble in organic solvents.

(*iii*) The melting points and boiling points of arenes increase with increase in the molecular size due to a corresponding increase in the magnitude of *van der Waals'* forces of attraction. Amongst isomeric arenes, *i.e.*, *o*-, *m*- and *p*-xylenes, the *p*-isomer which is most symmetrical, has the highest melting point.

15.10.10. Chemical Reactions of Arenes

Arenes are highly unsaturated hydrocarbons but behave like saturated hydrocarbons. They are, however, *more reactive than alkanes but are less reactive than alkenes and alkynes. This lower reactivity of arenes is because of the extra stability associated with these molecules due to delocalization of π- electrons.*

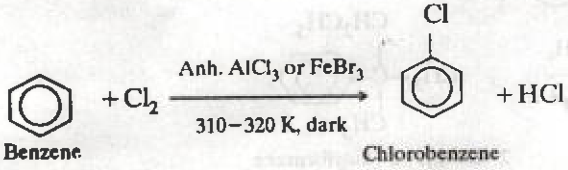
Some important reactions of arenes are discussed below :

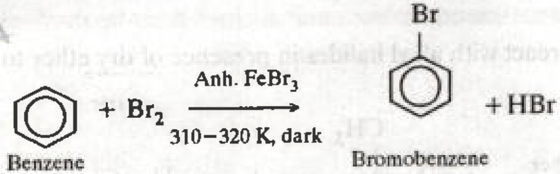
I. Substitution or replacement reactions

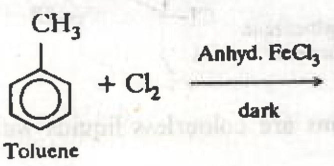
A reaction in which one or more hydrogens of the benzene ring are replaced by other atoms or groups is called a **substitution reaction.**

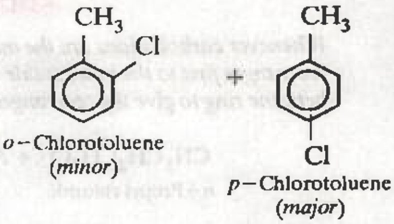
Arenes undergo a number of substitution reactions as discussed below.

1. Halogenation. Benzene reacts with chlorine and bromine in presence of Lewis acids such as ferric or aluminium halides as catalyst and in absence of light to form chlorobenzene and bromobenzene respectively.





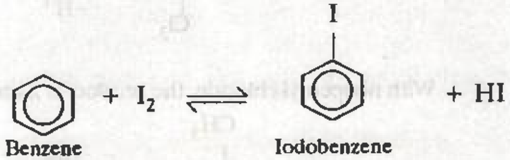




The function of the Lewis acid is to carry the halogen to the aromatic hydrocarbon. That is why these are usually referred to as **halogen carriers.** In addition to iron and aluminium halides, iodine and iron filings have also been used as halogen carriers. For example, chlorobenzene is formed when benzene is treated with chlorine in presence of iron. Under these conditions, iron first reacts with chlorine to form ferric chloride which then acts as a catalyst.

$$2Fe + 3Cl_2 \longrightarrow 2FeCl_3$$

Direct iodination of arenes is not a useful reaction since the HI produced during the reaction reduces the aryl iodide back to the arene and iodine.



However, in presence of oxidising agents such as nitric acid, iodic acid (HIO_3), mercury oxide, etc., the HI produced is either oxidised to iodine or is eliminated as mercuric iodide and thus the reaction proceeds in the forward direction producing iodobenzene.

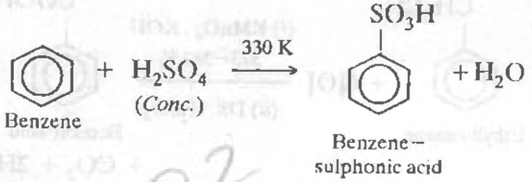
$$5HI + HIO_3 \longrightarrow 3I_2 + 3H_2O$$

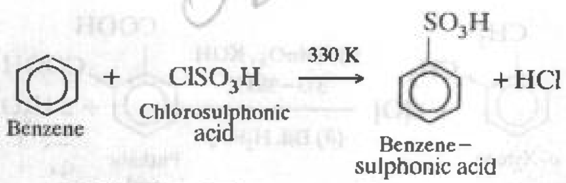
$$2\,HI + 2\,HNO_3 \longrightarrow I_2 + 2\,NO_2 + 2\,H_2O$$

$$2\,HI + HgO \longrightarrow HgI_2 + H_2O$$

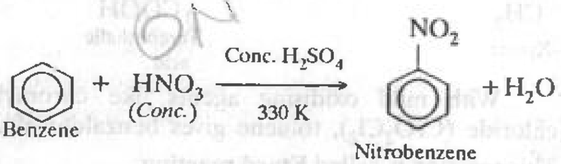
Fluorination of arenes is too vigorous to be of any practical use.

2. Sulphonation. *The process of replacement of a hydrogen atom of an arene by a sulphonic acid group ($-SO_3H$) is called* **sulphonation.** It is usually carried out by treating an arene with fuming sulphuric acid or oleum (concentrated sulphuric acid containing dissolved sulphur trioxide) or chlorosulphonic acid. For example,



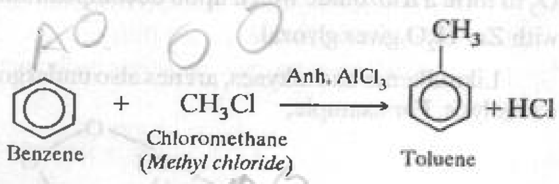


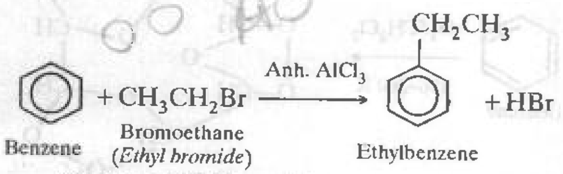
3. Nitration. *The process of replacement of a hydrogen atom of an arene by the nitro group (–NO_2) is called* **nitration.** It is usually carried out by treating an arene with a mixture of conc. HNO_3 and conc. H_2SO_4. (*nitrating mixture*). For example,



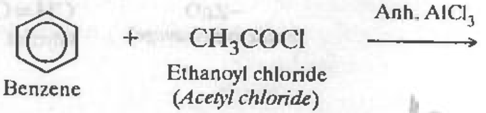
4. Friedel-Crafts reactions. This is a convenient method for the introduction of an alkyl or an acyl (RCO –) group into an arene. It is of two types :

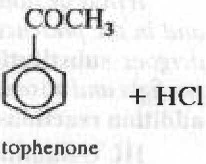
(*i*) *Friedel-Crafts alkylation.* When benzene or its homologue is treated with an alkyl halide, in presence of anhydrous aluminium chloride as catalyst, it forms an alkylbenzene. For example,

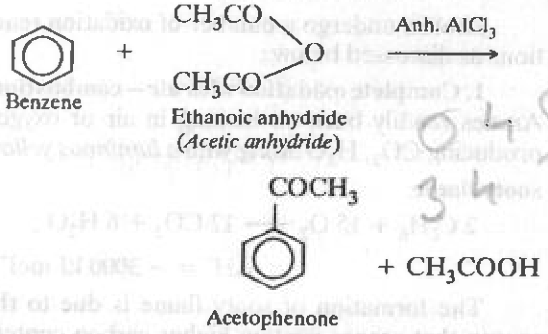




(*ii*) *Friedel-Crafts acylation.* On treatment with a carboxylic acid chloride or the anhydride in presence of anhydrous aluminium chloride, benzene forms an acylbenzene. For example,



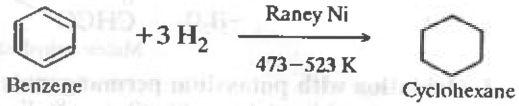




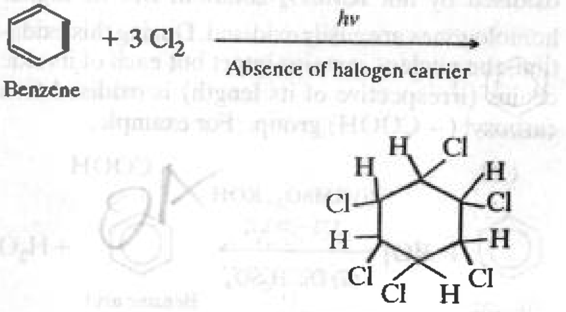
II. Addition reactions.

Benzene and its homologues usually do not undergo addition reactions because of the extra stability of these molecules due to delocalization of π-electrons. However, under drastic conditions, *i.e.*, high temperature and pressure, they do undergo some addition reactions characteristic of alkenes and alkynes. Two such important addition reactions are discussed below :

(*a*) *Addition of hydrogen – Hydrogenation.* Benzene adds three molecules of hydrogen in presence of Raney nickel or platinum as catalyst at 473 – 523 K to form cyclohexane.



(*b*) *Addition of halogens.* In presence of sunlight and in the absence of halogen carriers (such as $AlCl_3$, $FeBr_3$ etc.), benzene adds three molecules of chlorine to form *benzene hexachloride* (BHC) or *Gammexane.*



Benzene hexachloride (BHC)

It may be noted here that in absence of sunlight and in the presence of halogen carriers benzene undergoes **substitution reactions** *but in presence of sunlight and absence of halogen carriers, it undergoes* **addition reactions.**

III. Oxidation reactions

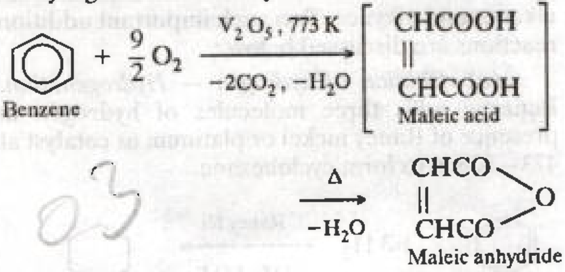
Arenes undergo a number of oxidation reactions as discussed below :

1. Complete oxidation with air – combustion. Arenes readily burn on heating in air or oxygen producing CO_2, H_2O along with *a luminous yellow* **sooty flame.**

$$2\,C_6H_6 + 15\,O_2 \longrightarrow 12\,CO_2 + 6\,H_2O\;;\quad \Delta H° = -3000\ \text{kJ mol}^{-1}$$

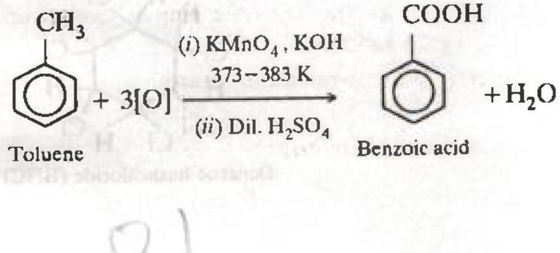
The formation of sooty flame is due to the reason that arenes contain higher carbon content that hydrogen. This sooty flame test is used as a *qualitative test to distinguish aromatic from aliphatic compounds.*

2. Controlled oxidation with air. Benzene on oxidation with air at 773 K in presence of V_2O_5 as catalyst gives *maleic anhydride*.

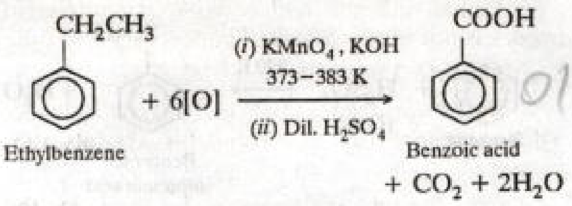


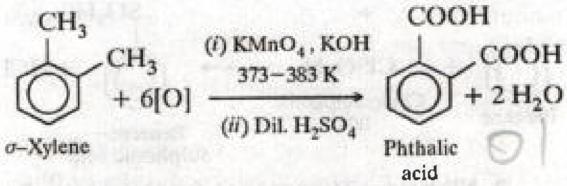
3. Oxidation with potassium permanganate. Arenes are not oxidised by cold dilute alkaline $KMnO_4$ solution (Baeyer's reagent) and hence this reaction is used to distinguish *aromatic compounds from alkenes and alkynes.*

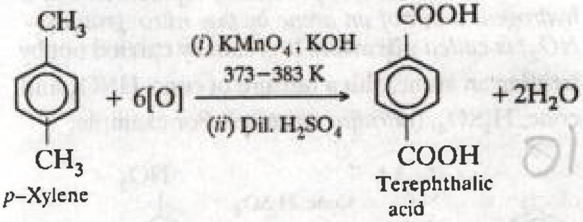
Benzene, the first member of arenes, is not oxidised by hot $KMnO_4$ solution. But its higher homologoues are easily oxidised. During this oxidation, the nucleus remains intact but each of its side chains (irrespective of its length) is oxidised to a carboxyl (–COOH) group. For example,



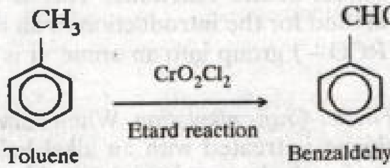
01





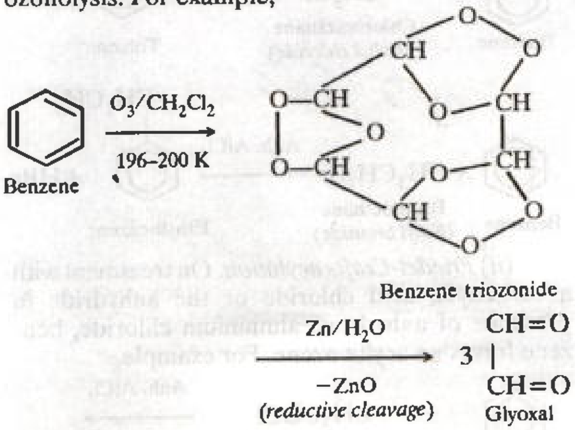


With mild oxidising agents like chromyl chloride (CrO_2Cl_2), toluene gives benzaldehyde. This reaction is called **Etard reaction.**



4. Oxidation with ozone. Benzene reacts with O_3 to form a triozonide which upon decomposition with Zn/H_2O gives glyoxal.

Like alkenes and alkynes, arenes also undergo ozonolysis. For example,



08

Unlike alkenes and alkynes, ozonolysis of arenes is not of any practical importance.

15.10.11. Uses of Arenes

(*i*) Lower arenes such as benzene, toluene, xylenes etc. are used as solvents for oils, fats, rubbers etc.

(*ii*) Arenes are extensively used in the manufacture of dyes, drugs, perfumes, explosives (TNT) and insecticides (DDT, BHC).

(*iii*) Benzene is blended with petrol to improve its octane number.

(*iv*) *p*-Xylene is used to prepare terephthalic acid and its ester for manufacture of synthetic fibre, *terylene*.

15.10.12. Mechanism of Electrophilic Substitution Reactions

Benzene contains two π-electron clouds-one lying above and the other below the plane of the ring. As compared to σ- electrons, these π-electrons are loosely held and hence are easily available to electrophiles. In other words, *benzene ring acts as a source of electrons (i.e., nucleophile) and attracts electrophiles (or repels nucleophiles).* Thus, the reactions of benzene and other arenes are initiated by electrophiles. Now electrophilic substitution reactions can, in principle, be either substitution or addition. *Whereas benzene and other arenes undergo* **electrophilic substitution reactions,** *alkenes undergo* **electrophilic addition** *reactions. In fact, ability of a compound to undergo electrophilic substitution reactions is an excellent test of aromaticity.*

The mechanism of all the electrophilic substitution reactions is basically the same and proceeds through the following steps :

Step 1. *Generation of an electrophile.* First of all, an electrophile is generated as a result of some preliminary reaction.

$$\underset{\text{Reagent}}{E-Nu} \longrightarrow \underset{\text{Electrophile}}{E^+} + \underset{\text{Nucleophile}}{:Nu^-}$$

In some cases, an electrophile is not generated directly but a polarized molecule of the reagent serves as the electrophile. For example, in halogenation and Friedel-Crafts alkylation reactions.

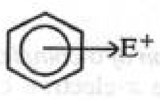
$$Br-Br + FeBr_3 \longrightarrow \overset{\delta+}{Br} \ldots\ldots \overset{\delta-}{BrFeBr_3}$$

Polarized bromine molecule (*electrophile*)

$$CH_3-Cl + AlCl_3 \longrightarrow \overset{\delta+}{CH_3} \ldots\ldots \overset{\delta-}{ClAlCl_3}$$

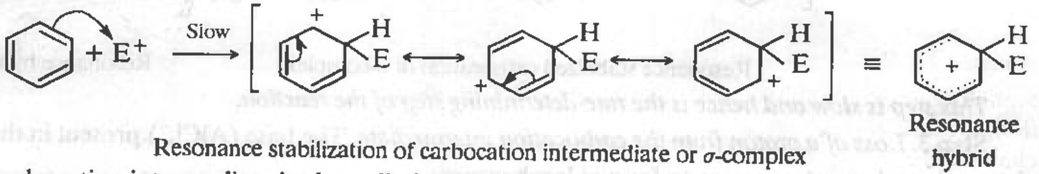
Polarized methyl chloride molecule (*electrophile*)

Step 2. *Formation of carbocation intermediate.* As the electrophile approaches the benzene ring, it is attracted by the π-electrons to form a **π-complex.**



$\pi-$Complex

The π-complex then slowly reorganises or rearranges to form a σ-complex or a carbocation intermediate which is stabilized by resonance



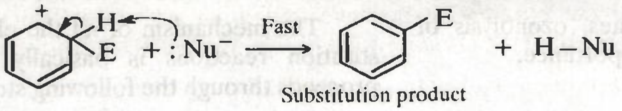
Resonance stabilization of carbocation intermediate or σ-complex

The carbocation intermediate is also called **σ-complex.**

During the formation of σ-complex, the aromatic character of the benzene ring is destroyed. Therefore, *this step is slow and hence is the rate determining ste of the reaction.*

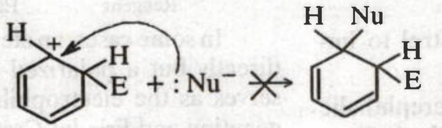
Step 3. *Loss of a proton from the carbocation intermediate.* The carbocation intermediate formed above, in principle, can undergo the following two types of reactions.

(*i*) *It can lose a proton to the nucleophile (Nu$^-$) present in the reaction mixture to form a substitution product*



Since during this step, aromatic character of the benzene ring is restored, therefore, *this step is fast and hence does not affect the rate of the reaction.*

(*ii*) Alternatively, the nucleophile (: Nu^-) may attack the carbocation intermediate to yield the addition product.



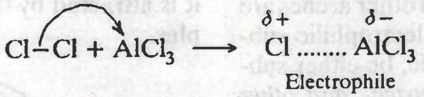
This addition is, however, not observed since during this addition reaction, the aromatic character of the benzene ring is lost.

Let us now discuss the mechanism of some typical electrophilic substitution reactions.

1. Halogenation. The halogenation of benzene and some other arenes is *carried out at low temperatures (310-320 K), in the absence of sunlight and in presence of a Lewis acid such as anhydrous ferric or aluminium chloride as catalyst.*

The halogenation proceeds by the following mechanism :

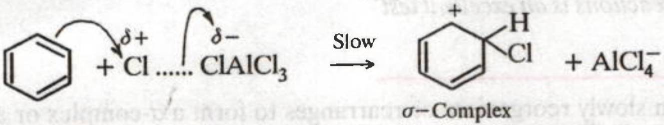
Step 1. *Generation of an electrophile.*

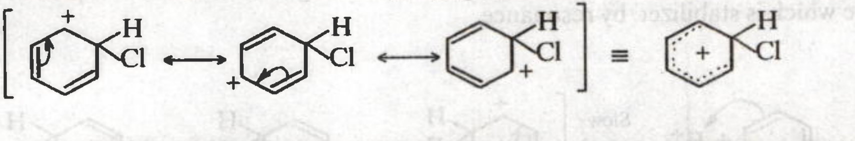


$$Cl{-}Cl + AlCl_3 \longrightarrow \overset{\delta+}{Cl}\ldots\ldots\overset{\delta-}{AlCl_3}$$

Electrophile

Step 2. *Formation of σ-complex or carbocation intermediate.* The +ve end of the polarized chlorine molecule accepts the π-electron cloud of the benzene ring to form a σ-complex or the carbocation intermediate which is stabilized by resonance.



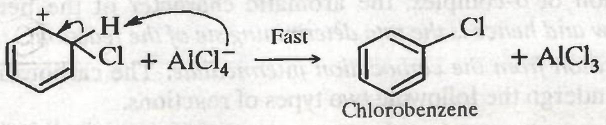


Resonance stabilized carbocation or σ-complex

Resonance hybrid

This step is slow and hence is the rate-determining step of the reaction.

Step 3. *Loss of a proton from the carbocation intermediate.* The base ($AlCl_4^-$) present in the reaction mixture then abstracts a proton to form chlorobenzene



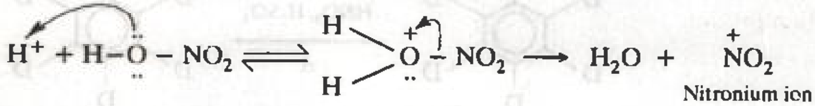
This step is fast and hence does not affect the rate of the reaction.

2. Nitration. It is carried out by treating benzene and other arenes with a mixture of conc. HNO_3 + conc. H_2SO_4 commonly called the *nitrating mixture*. The various steps involved are :

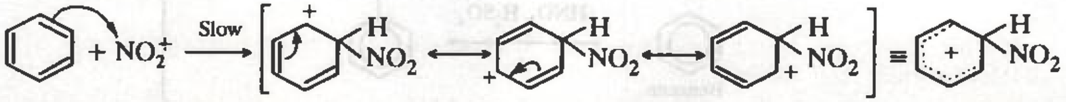
Step 1. *Generation of an electrophile, i.e., NO_2^+ (nitronium ion)*

In presence of conc. H_2SO_4, HNO_3 acts as the base and accepts a proton to form protonated nitric acid which then loses a molecule of H_2O to form nitronium ion.

$$H_2SO_4 \longrightarrow H^+ + HSO_4^-$$



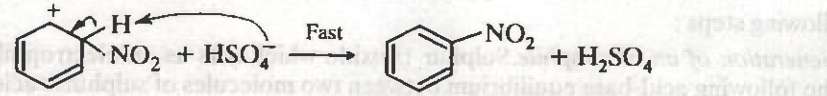
Step 2. *Formation of σ-complex or carbocation intermediate.* **Nitronium ion attacks the benzene ring to form a carbocation which is stabilized by resonance.**



Resonance stabilized carbocation or the σ-complex (I) Resonance hybrid

This step is slow and hence is the rate-determining step of the reaction. (Fig. 15.28)

Step 3. *Loss of a proton from the carbocation intermediate.* **Finally, the carbocation loses a proton to the base (HSO_4^-) to form nitrobenzene.**



(I) Nitrobenzene (II)

This step is fast and hence does not affect the rate of the reaction. (Fig. 15.28)

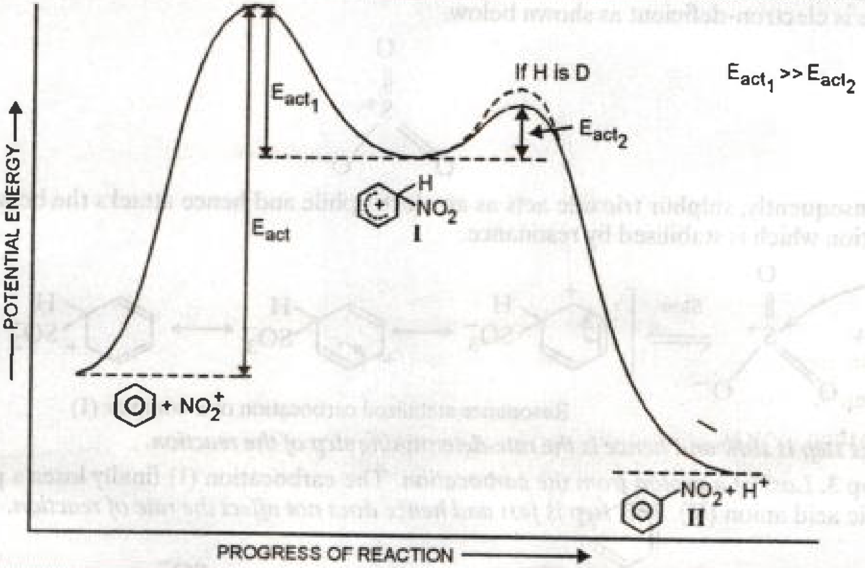
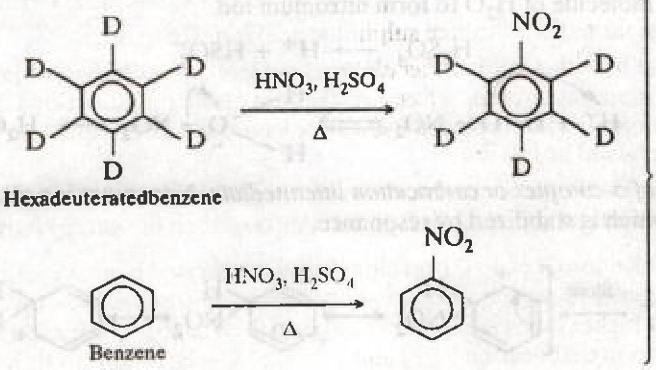


FIGURE 15.28. Formation of carbocation is the rate-determining step ; it occurs equally rapidaly whether C-H or C-D bond is to be broken. All the carbocations (I) go to the product (II). There is no isotope effect and nitration is irreversible.

Evidence in support of the mechanism. This mechanism has been supported by *absence of isotope effect*. It has been found that when hexadeuterobenzene is nitrated, the rate of nitration is exactly the same as that of benzene. Since a C–D bond breaks more slowly than a C–H bond, therefore, the loss of a proton is not the *rate-determining step*. Had it been so, the rates of nitration of benzene and hexadeuterobenzene would have been different ?



Rates are the same

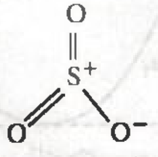
Thus, electrophilic aromatic substitution is a bimolecular reaction in which the attack of the electrophile and loss of proton occur in two different steps and the former is slower and hence is the rate determining step of the reaction.

3. Sulphonation. Sulphonation is carried out by treating benzene or any other arene with concentrated sulphuric acid or oleum (conc. $H_2SO_4 + SO_3 = H_2S_2O_7$). The mechanism for sulphonation involves the following steps :

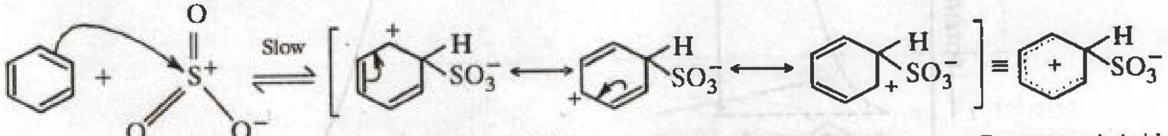
Step 1. *Generation of an electrophile.* Sulphur trioxide which acts as an electrophile is first of all generated by the following acid-base equilibrium between two molecules of sulphuric acid.

$$2H_2SO_4 \rightleftharpoons SO_3 + HSO_4^- + H_3O^+$$

Step 2. *Formation of σ-complex or carbocation intermediate.* Sulphur atom of sulphur trioxide molecule is electron-deficient as shown below.



Consequently, sulphur trioxide acts as an electrophile and hence attacks the benzene ring to give a carbocation which is stabilised by resonance.

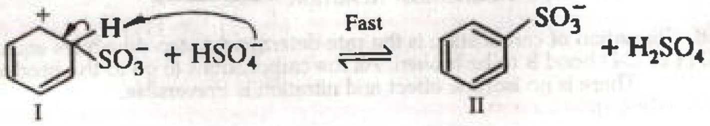


Resonance stabilized carbocation or σ-complex (I)

Resonance hybrid

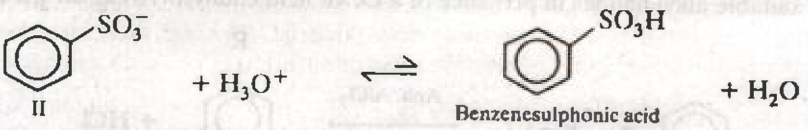
This step is slow and hence is the rate-determining step of the reaction.

Step 3. *Loss of a proton from the carbocation.* The carbocation (I) finally loses a proton to produce sulphonic acid anion (II). *This step is fast and hence does not affect the rate of reaction.*



I II

Step 4. *Addition of proton to the benzenesulphonic acid anion (II) gives the final product.*



This equilibrium lies far to the left since sulphonic acid is a strong acid.

It may be pointed out here that *unlike other electrophilic aromatic substitution reactions,* sulphonation is *reversible* and shows a moderate *isotope effect, i.e.,* the rate of the reaction slows down when hydrogen atoms of the aromatic compound are replaced by heavier isotopes – deuterium or tritium. The moderate isotope effect may be explained as follows :

In sulphonation (Fig. 15.29), the energy barriers on either side of the resonance stabilized carbocation (I) are roughly of the same height (*i.e.* $E_{act_1} \sim E_{act_2}$). If this is so then the energy barrier for the *backward reaction* for both the carbocations, *i.e.,* I (D)-resulting from deuterated benzene and I (H) resulting from ordinary benzene, is the same. However, energy barrier for the *forward reaction* (*i.e.,* conversion of I into II) for carbocation I (D) is higher (shown by dotted line) than that for the carbocation I (H) since a stronger C – D bond is to be broken in carbocation I (D) and a weaker C – H bond is to be broken in carbocation I (H). In other words, more deuterated carbocations I (D) than carbocations I (H) revert to the starting material and hence overall sulphonation is slower for deuterated benzene. This explains the moderate isotope effect.

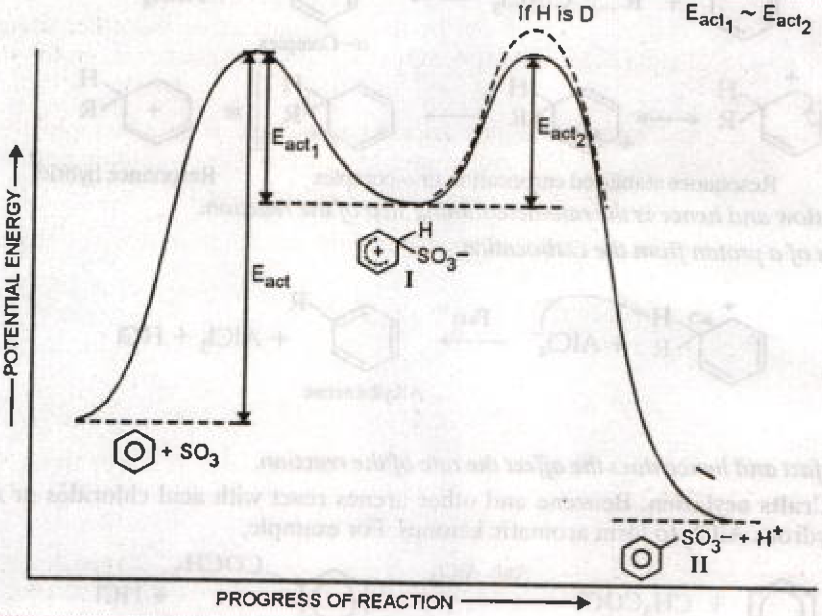
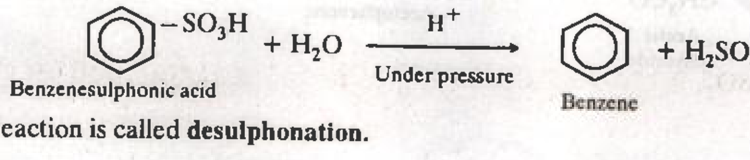


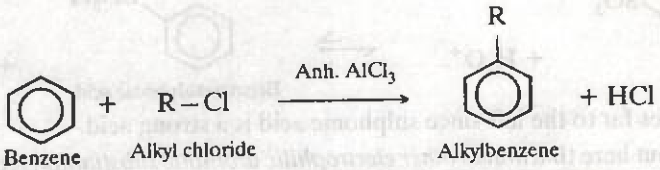
FIGURE 15.29. Some carbocations (I) go to the product, some revert to the starting material. There is some isotope ffect, and sulphonation is reversible.

Because of the reversibility of this reaction, sulphonic acid group can be easily removed by heating a sulphonic acid with steam under pressure or by hot dilute mineral acids.



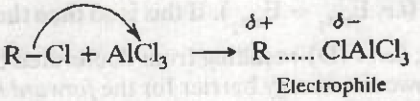
This reaction is called **desulphonation.**

4. Friedel-Crafts alkylation. Alkyl substituted benzenes may be prepared by the reaction between benzene and a suitable alkyl halides in presence of a Lewis acid catalyst ($AlCl_3$, BF_3, $FeCl_3$, etc).

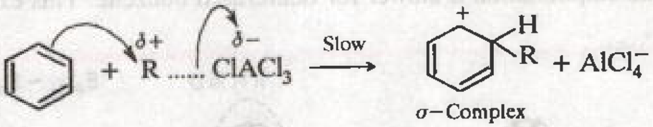


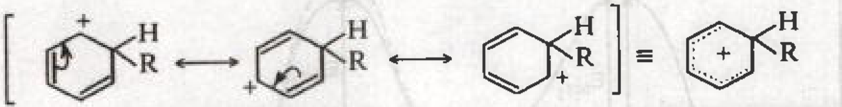
The reaction is believed to proceed through the following mechanism.

Step 1. *Generation of an electrophile.* The alkyl halide first reacts with anhydrous $AlCl_3$ to form polarized alkyl halide molecule which acts as the electrophile



Step 2. *Formation of σ-complex or carbocation intermediate.* The +ve end of the polarized alkyl halide molecule attacks the π-electron cloud of the benzene ring to form a σ-complex or the carbocation intermediate which is stabilized by resonance.

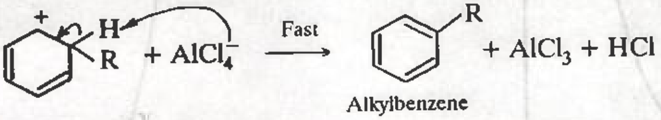




Resonance stabilized carbocation or σ-complex

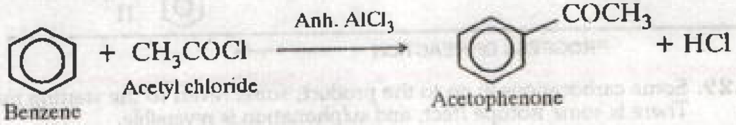
This step is slow and hence is the rate-determining step of the reaction.

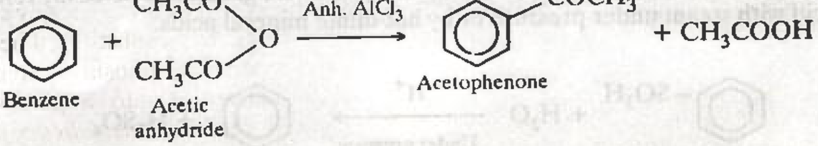
Step 3. *Loss of a proton from the carbocation.*

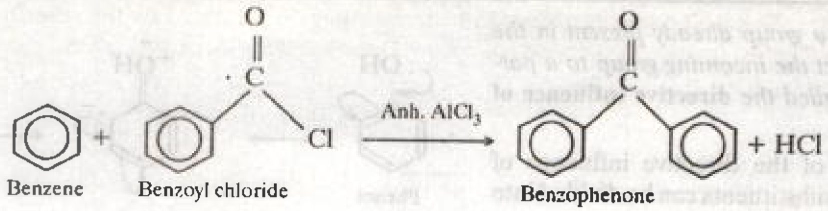


This step is fast and hence does the affect the rate of the reaction.

5. Friedel-Crafts acylation. Benzene and other arenes react with acid chlorides or anhydrides in presence of anhydrous $AlCl_3$ to form aromatic ketones. For example,

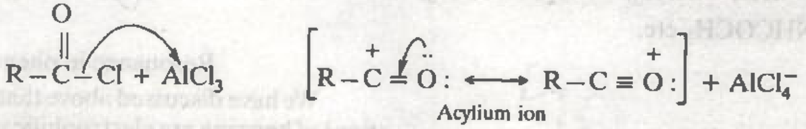


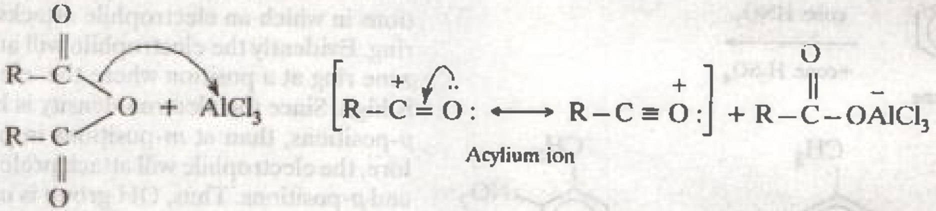




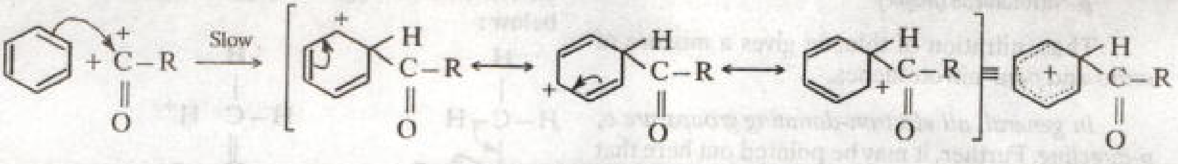
Mechanism. The reaction involves the following steps :

Step 1. *Generation of an electrophile.* **The acid chloride or anhydride reacts with anhydrous aluminium chloride to form *acylium ion*, ($R\overset{+}{C}=O$) which serves as an electrophile.**





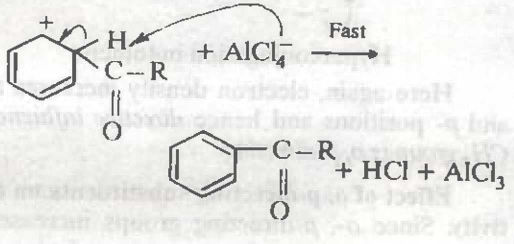
Step 2. *Formation of σ-complex or carbocation intermediate.* The acylium ion attacks the benzene ring resulting in the formation of a carbocation which is stabilised by resonance.



Resonance stabilized carbocation or σ-complex Resonance hybrid

This step is slow and hence is the rate-determining step of the reaction.

Step 3. *Loss of a proton.* The carbocation loses a proton to the base ($\overset{-}{AlCl_4}$ or $R-COO\overset{-}{AlCl_3}$) present in the reaction mixture to form the final product.



This step is fast and hence does not affect the rate of the reaction.

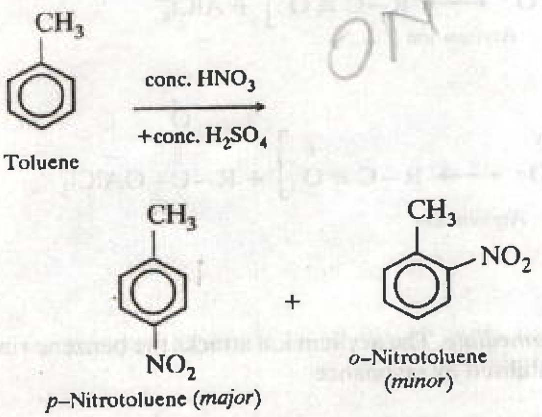
15.10.13. Directive influence of substituents and their effect on reactivity

All the six hydrogen atoms of benzene ring are equivalent. Therefore, replacement of any one of these six hydrogen atoms by any substituent always gives a single monosubstituted benzene derivative. However, when a monosubstituted benzene derivative is converted into a disubstituted benzene derivative, *the substituent already present in the benzene ring determines the position of the incoming group.*

This ability of a group already present in the benzene ring to direct the incoming group to a particular position is called the **directive influence of groups.**

On the basis of the directive influence of groups, the various substituents can be divided into the following two categories :

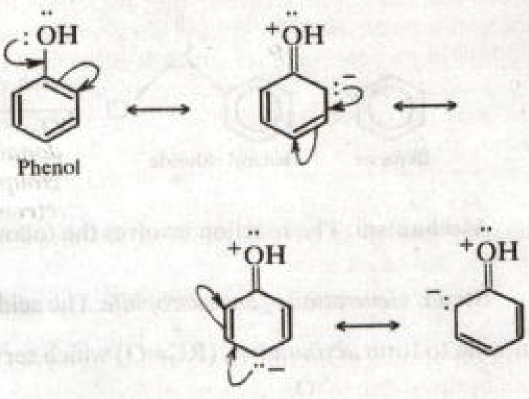
1. o, p-Directing groups. *The substituents or groups which direct the incoming group to ortho and para positions are called* **ortho, para-directing groups.** For example, $-CH_3$, $-CH_2CH_3$, $-C_6H_5$, $-Cl$, $-Br$, $-I$, $-OH$, $-OCH_3$, $-NH_2$, $-NHCH_3$, $-N(CH_3)_2-$, $NHCOCH_3$ etc.



Thus, nitration of toluene gives a mixture of *ortho* and *para*-nitrotoluenes.

In general, all electron-donating groups are o, p-directing. Further, it may be pointed out here that although two *o*- and one *p*-positions are available for disubstitution yet due to *steric hindrance* with the incoming group at *o*-position, *it is usually the p-isomer which predominates* in these substitution reactions.

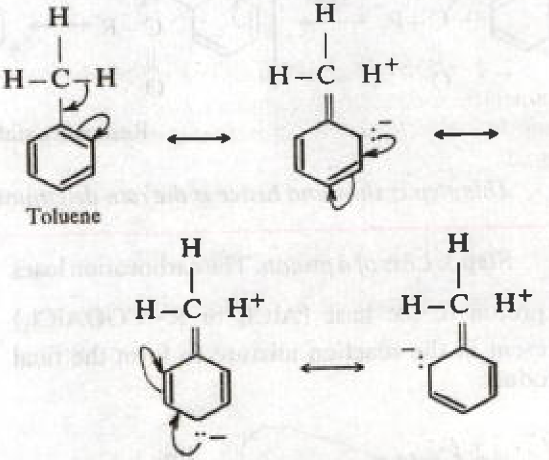
Explanation for directive influence of o, p-directing groups. With the exception of alkyl and phenyl groups all other groups have atleast one lone pair of electrons on the atom directly attached to the benzene ring. This lone pair of electrons is involved in resonance with the π- electrons of the benzene ring. As a result of resonance, the electron density increases at all the nuclear positions of the benzene ring but the increase in electron density is much more at *o*- and *p*-positions than at *m*-position as shown below :



Resonance in phenol

We have discussed above that the typical reactions of benzene are electrophilic substitution reactions in which an electrophile attacks the benzene ring. Evidently the electrophile will attack the benzene ring at a position where the electron density is high. Since the electron density is high at *o*- and *p*-positions, than at *m*-positions in phenol, therefore, the electrophile will attack preferentially at *o*- and *p*-positions. Thus, OH group is **o, p-directing.**

Directive influence of the alkyl group. The alkyl group (R) does not have a lone pair of electrons. Its directive influence can be explained on the basis of hyperconjugation effect as shown below :



Hyperconjugation in toluene

Here again, electron density increases at *o*- and *p*- positions and hence *directive influence of* CH_3 *group is o, p-directing.*

Effect of o, p-directing substituents on reactivity. Since *o*-, *p*-directing groups increase the electron density in the benzene ring, therefore, the ring gets *activated and the further electrophilic substitution in the ring becomes easier.* It is because of this reason that all *o, p*-directing groups except halogens are called *activating groups.* Further, because of the *ability of these groups to donate electrons to the benzene ring, o-, p- directing groups are also called* **electron-repelling** or **electron-donating groups (EDG).** In the light of above discussion, two cases arise :

(*i*) *o, p-Directing groups facilitate further electrophilic substitution reaction.* For example, nitration of toluene occurs faster than that of benzene because due to hyperconjugation effect of the CH_3 group, electron density in toluene ring is higher than that in benzene ring.

(*ii*) *Higher the electron-donating ability of the substituent, more facile is the reaction.* For example, bromination of aniline occurs faster than that of phenol because due to lower electronegativity of N over O, the electron-donating ability of $-NH_2$ group is much higher than that of OH group. As a result, *electron density in the aniline ring is much higher than that in phenol and hence bromination of aniline occurs faster than that of phenol.*

The electron-donating ability of some substituents follows the order :

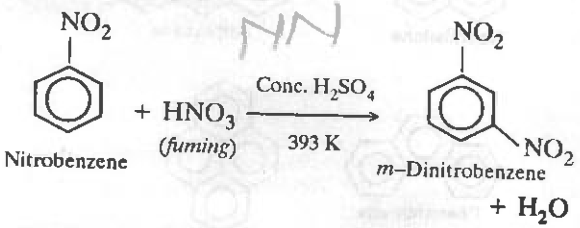
$$-O^- > -NH_2 > -NR_2 > -OH > -OCH_3,$$
$$-NHCOCH_3 > -CH_3 > -X$$
$$(-F > -Cl > -Br > -I)$$

2. 2-m-Directing groups. *The substituents or groups which direct the incoming group to the meta-position are called* **meta- directing groups.** For example,

$-NO_2, -CN, -CF_3, -CHO, -COR,$

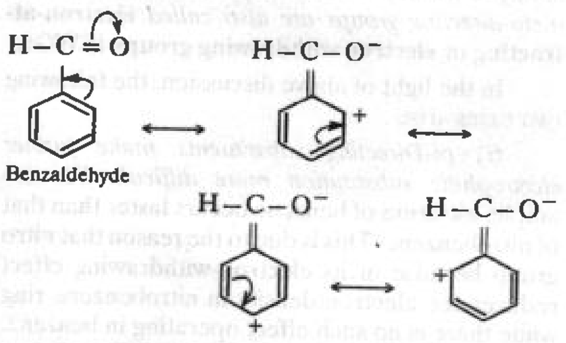
$-COOH, -COOR, -SO_3H$ etc.

Thus, nitration of nitrobenzene mainly gives *m*- dinitrobenzene.



In general, all electron-withdrawing groups are m- directing.

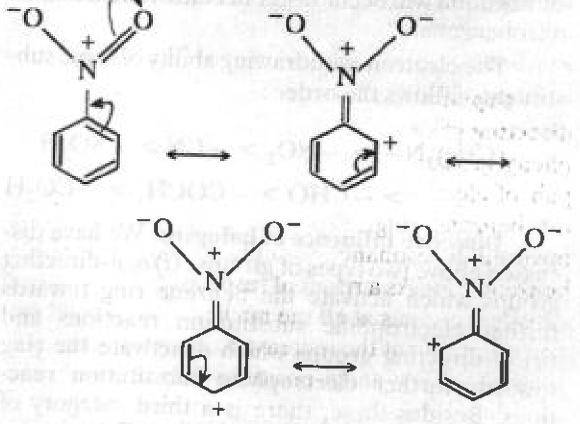
Explanation for the directive influence of m-directing groups. With the exception of trifluoromethyl (*i.e.* CF_3) group, in all other groups the atom directly attached to benzene ring has one more electronegative atom linked to it by a multiple bond. This more electronegative atom pulls the electrons of the multiple bond towards it which, in turn, withdraws electrons from all the nuclear positions. As a result, electron density falls at all the nuclear positions but the decrease is much more at *o*- and *p*-positions than at *m*-positions as shown below :



Resonance in benzaldehyde

In other words, the electron density is comparatively higher at *m*-positions than at *o*- and *p*-positions and hence the electrophile will attack preferentially at the *m*- position in benzaldehyde. Thus, – *CHO group is* **m- directing.**

Similarly, we can explain the *meta*-directing influence of the $-NO_2$ group. Due to electron-withdrawing resonance effect (*i.e.,* $-R$-effect) of the $-NO_2$ group, electron density falls more at the *o*- and *p*-positions that at *m*-positions as shown below :



Resonance in nitrobenzene

In other words, *electron-density is comparatively more at m-positions than at o- and p-positions, therefore, further substitution in nitrobenzene will occur at m-position.*

Effect of m-directing substituents on reactivity. Since *m*- directing groups decrease the electron-density in the benzene ring, therefore, *the ring gets deactivated and hence further electrophilic substitution becomes difficult.* It is because of this reason that *meta-directing groups are also called* **deactivating groups.** Further, because of *their ability to withdraw electrons from the benzene ring, meta-directing groups are also called* **electron-attracting** or **electron withdrawing groups (EWG).**

In the light of above discussion, the following two cases arise :

(*i*) *m-Directing substituents make further electrophilic substitution more difficult.* For example, nitration of benzene occurs faster than that of nitrobenzene. This is due to the reason that nitro group because of its electron-withdrawing effect reduces the electron density in nitrobenzene ring while there is no such effect operating in benzene. As a result, electron density in benzene ring is higher than that in nitrobenzene ring and hence the electrophile (*i.e.* NO_2^+) will attack benzene faster than nitrobenzene.

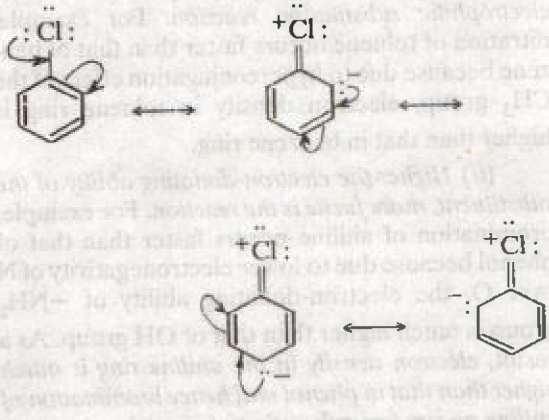
(*ii*) *Higher the electron-withdrawing ability of the substituent, more difficult is the reaction.* Nitration of nitrobenzene occurs much slower than that of benzoic acid since NO_2 group is a much more powerful electron- withdrawing group than carboxylic acid group. As a result, electron density in benzoic acid ring is much higher than that in nitrobenzene ring and hence further electrophilic substitution will occur faster in benzoic acid than in nitrobenzene.

The electron-withdrawing ability of some substituents follows the order :

$$(CH_3)_3\overset{+}{N}- > -NO_2 > -CN > -SO_3H$$
$$> -CHO > -COCH_3 > -CO_2H$$

Directive influence of halogens. We have discussed above two types of groups : (*i*) *o, p*-directing groups which activate the benzene ring towards further electrophilic substitution reactions and (*ii*) *m*-directing groups which deactivate the ring towards further electrophilic substitution reactions. Besides these, there is a third category of groups, *i.e.*, halogens which though *deactivating are o, p-directing.* This is explained as follows :

In case of ary halides, halogens are highly deactivating because of their strong $-$I-effect. Therefore, overall electron density on the benzene ring decreases. *In other words, halogens are deactivatng due to $-$I-effect.* However, because of the $+$R$-$effect, *i.e.*, participation of lone pairs of electrons on the halogen atom with the π-electrons of the benzene ring as shown below, the electron density increases more at *o*- and *p*-positions than at *m*-positions.

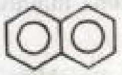


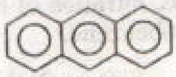
Resonance in chlorobenzene

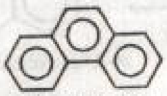
As a result, *halogens are o, p-directing.* The combined result of $+$R-effect and $-$I-effect of halogens is that, *halogens are deactivating but o, p-directing.*

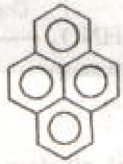
15.10.14. Polynuclear Hydrocarbons

We have already discussed in this unit that hydrocarbons containing two or more fused or isolated benzene rings are called polynuclear hydrocarbons. These may either be linear (naphthalene, anthracene etc.) or angular (phenanthrene, pyrene etc.)


Naphthalene


Anthracene


Phenanthrene

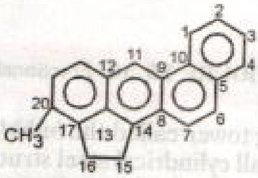

Pyrene

The main source of polynuclear aromatic hydrocarbons is coal tar. Naphthalene is the largest single constituent (6–10%) of coal tar. It is obtained by cooling the middle oil fraction (b.p. 443–503 K) of coal tar distillation. Anthracene is obtained from green oil fraction (b.p. 543–633 K) of coar tar distillation in about 1% yield.

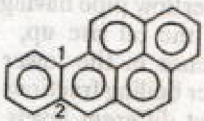
Carcinogenicity and Toxicity

Most of the polynuclear hydrocarbons are cancer-producing, *i.e.*, are carcinogenic. Notable among these are 1, 2- benzanthracene, 20-methylcholanthrene, 1, 2-benzpyrene, 9, 10- dimethyl-1, 2-benzathracene and 1, 2, 5, 6-Dibenzanthracene.

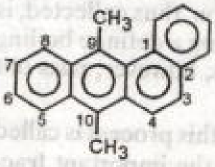
1,2-Benzanthracene



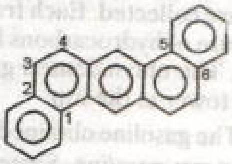
20-Methycholanthene



1,2-Benzpyrene



9,10-Dimethyl
1,2-benzanthraene



1,2,5,6-Dibenzanthracene

There is no general rule by which one can predict the carcinogenic activity of a polynuclear hydrocarbon or its derivative. However, the number and position of certain groups such as $-CH_3$, $-OH$, $-CN$, $-OCH_3$ etc. have been found to influence carcinogenic activity.

Cancer is primarily an environmental disease. Just as draining of swamps and elimination of mosquitoes can be used to control malaria and yellow fever, in the same way, elimination of carcinogens from the environment can reduce the incidence of cancer to a great extent.

In fact, polynuclear hydrocarbons are the products of incomplete combustion of organic matter such as coal, petroleum, tobacco etc. They are widely present in the environment and thus are the major cause of human cancer.

It is believed that when these polynuclear hydrocarbons enter the body of a human being, they are first converted into their oxides called *epoxides* and then into *dihydroxy epoxides*. The dihydroxy epoxides thus produced react with the purine bases such as guanine present in DNA and RNA of the human cells. The attachment of this big hydrocarbon part to purine prevents it from fitting into the double helix of DNA. This damage causes mutations and ultimately leads to cancer.

A simplified view of carcinogenic effect of polynuclear hydrocarbons (PNH) is shown below :

$$\text{PNH} \xrightarrow{O_2} \text{PNH epoxide} \longrightarrow \text{PNH dihydroxy epoxide} \xrightarrow{\text{DNA or RNA}} \text{Mutations} \longrightarrow \text{Cancer}$$

PART VI

PERLOLEUM AND PETROCHEMICALS

15.11. Petroleum

Coal and petroleum or rock oil (Latin : *petra* = rock and *oleum* = oil) both are considered to be of *biological origin*. Millions of years ago, as a result of earthquakes, upheavels and other natural calamities, plants and animals got buried under the surface of the earth. Under the influence of high pressure, temperature and absence of air, the buried plants and animals got converted into coal and petroleum. Further, it is believed that coal is derived from plants while petroleum is derived from marine animals.

Like any other mineral, coal is mined from the earth while petroleum is obtained by drilling wells.

Petroleum occurs underground deep below the earth's crust trapped within rock or much below the sea bed. It usually occurs underground deep below earth's crust trapped within rock structure or much below the sea bed covered with a gaseous mixture known as **natural gas.** It mainly consists of methane (90%) alongwith decreasing quantities of ethane, propane, butanes and the vapours of low boiling pentanes and hexanes.

The chief oil producing countries in the world are Saudi Arabia, Iran, Iraq, Russia., U.S.A., U.K., Mexico, China, and to a lesser extent India. The leading oil producing centres in India are located in Gujrat, Assam and Bombary High (off shore).

15.11.1. Composition of Crude oil

Petroleum or crude oil is a dark coloured viscous fluorescent liquid. *It consists essentially of a* *mixture of aliphatic hydrocarbons particularly alkanes* ($C_1 - C_{40}$) *with much lesser amounts of cycloparaffins (naphthenes) and aromatic hydrocarbons*. Small amounts of organic compounds of sulphur and nitrogen are also present.

With this brief introduction about coal and petroleum, let us now briefly discuss the industrial methods of preparation of aromatic and aliphatic compounds.

15.11.2. Fractionation of Crude oil—Petroleum refining

Crude oil is obtained by drilling holes in the earth's crust. Due to the pressure exerted by the natural gas, the oil rushes out through the pipes. When the pressure of the gas decreases, two coaxial pipes are lowered into the bore. When compressed air is passed through one pipe, the crude oil rushes out of the other pipe. From the oil fields, the crude oil is taken to the refineries through pipelines.

The crude oil is purified by subjecting it to fractional distillation. During this process, the impurities are removed and the crude oil is separated into different useful fractions.

The process of separating petroleum into different useful fractions having different boiling ranges with the simultaneous removal of undesirable impurities is called refining.

Refining of petroleum. The crude oil is first of all neutralised by washing it with an acidic or basic solution depending upon whether the impurities are basic or acidic in nature. This is then subjected to fractional distillation. For this purpose, the crude oil is heated to 723 K in coiled pipes in a furnace and the pressure reduced. The vapours, thus obtained, are admitted into the bottom of a fractionating tower called the *bubble tower* (Fig. 15.30). It is a tall cylindrical steel structure fitted with horizontal trays. Each tray is provided with a number of holes and an overflow pipe having a *bubble cap*. As the vapours of the oil rise up, the high boiling fractions condense in the lower portions of the tower. The lower boiling fractions rise up the tower and condense at different levels depending upon their boiling ranges. In this way, a number of fractions are collected. Each fraction, thus collected, is a mixture of hydrocarbons having a definite boiling range. The uncondensed gases, however, pass out of the tower at the top.

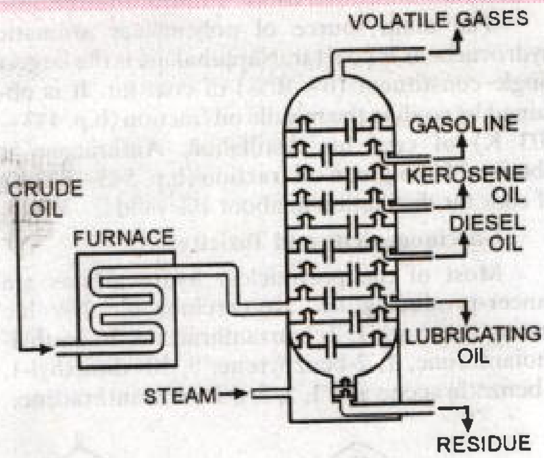


FIGURE 15.30. Fractional distillation of crude oil.

The gasoline obtained by this process is called *straight run gasoline*. Some of the important fractions along with their approximate composition, boiling ranges and important uses are given in Table 15.4.

TABLE 15.4. Some important fractions of petroleum refining

FRACTION	APPROXIMATE COMPOSITION	BOILING RANGE (K)	USES
1. Gaseous hydrocarbons	$C_1 - C_4$	113—303	As a fuel, production of carbon black, H_2 and CO, used to make NH_3, methanol and gasoline.
2. Crude naphtha	$C_5 - C_{10}$		
(*i*) Petroleum ether	$C_5 - C_7$	303—363	As solvent in varnish and rubber industries, for dry cleaning.
(*ii*) Petrol or gasoline	$C_7 - C_9$	363—393	As motor fuel, dry cleaning
(*iii*) Benzine	$C_9 - C_{10}$	393—423	For dry cleaning

3. Kerosene oil	$C_{10} - C_{13}$	423—573	Fuel for stoves, manufacture of oil gas, as an illuminant fuel
4. Fuel oil	$C_{13} - C_{18}$	513—623	Fuel for diesel engine and tractors, cracking stock for gasoline
(*i*) Gas oil			
(*ii*) Diesel oil			
(*iii*) Furnace oil			
5. Lubricating oil	$C_{15} - C_{18}$	Above 543	Paint oil, transformer oil, lubrication, sizing paper
(*i*) Medicinal oil			
(*ii*) Motor oil			
(*iii*) Grease			
6. Paraffin wax	$C_{18} - C_{30}$	673 upward	Ointments, candles, paraffin wax for matches, paints, water proofing, solid fuel, protecting paints
(*i*) Petroleum jelly			
(*ii*) Petroleum wax			
(*iii*) Petroleum coke			
7. Heavy oil and Bitumen	C_{30} onwards	Forms residue	Paints, road surfacing.

15.11.3. LPG and CNG

LPG stands for liquefied petroleum gas. It is a mixture of hydrocarbons containing 3-4 carbon atoms. These include propane (C_3H_8), propene (C_3H_6), *n*-butane* (C_4H_{10}), isobutane* (2-methylpropane) and various butenes with small amount of ethane (C_2H_6) It is compressed under pressure as liquid and stored in iron cylinders. The major source of LPG is natural gas and from refining and cracking of petroleum. Alkenes are mainly produced during cracking. LPG is mainly used for manufacture of chemicals, as a pollution free house-hold fuel because the combustion of constituents of LPG is complete and no unburnt carbon is released into the atmosphere.

As stated earlier in this unit, natural gas mainly consists of methane (90%) alongwith decreasing quantities of ethane, propane, butanes and vapours of low boiling pentanes and hexanes. Earlier it used to be carried by pipelines from the oil fields to the houses for cooking in our kitchens. Now cheap techniques have been developed to compress natural gas under high pressure as a liquid and stored in steel cylinders. The compressed natural gas is called CNG and is now being used as a fuel for running buses, cars and three-wheelers in metropolitan cities like Delhi, Mumbai, Chennai, Kolkata etc. Recently a plant for **LNG** (*liquid natural gas*) has been established in Gujarat.

15.11.4. Cracking and reforming

Out of all the fractions obtained by fractional distillation of crude oil, only gasoline (petrol), kerosene oil and diesel oil are the most important. But the demand for these products has further increased in the recent times due to rapid industrialization and growth in automoible industry. In order to meet the ever-increasing demand for these fractions, the following two methods have been developed :

(i) Cracking and
(ii) Reforming.

(i) Cracking. Decomposition of a compound by the application of heat is called *pyrolysis*. Pyrolysis of higher boiling petroleum fractions such as fuel oil and lubricating oil is called cracking.

Cracking may be defined as a process in which high boiling hydrocarbons are converted into a mixture of low boiling hydrocarbons by the action of heat alone or heat in presence of a catalyst.

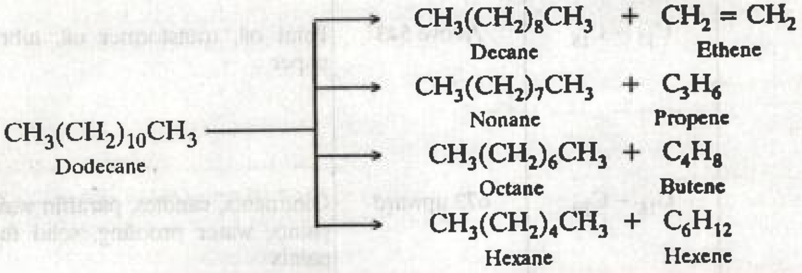
Cracking involves breaking of carbon – carbon and carbon – hydrogen bonds resulting in the formation of a mixture of lower hydrocarbons. For example,

---

*Butane and isobutane are the main constituents.

$$\underset{\text{Dodecane}}{CH_3(CH_2)_{10}CH_3} \xrightarrow[\text{Catalyst}]{973\text{ K}} \underset{\substack{\text{Heptane}\\ \text{b.p. 371 K}}}{C_7H_{16}} + \underset{\substack{\text{Pentene}\\ \text{b.p. 309 K}}}{C_5H_{10}}$$

Thermal cracking. *It is cracking by action of heat alone.* Since during thermal cracking, *random cleavage of carbon – carbon bond occurs*, therefore, cracking of dodecane can also give a number of other hydrocarbons such as heptane, hexane, pentane, butane, propene, butene, pentene, hexene, etc. as shown below :

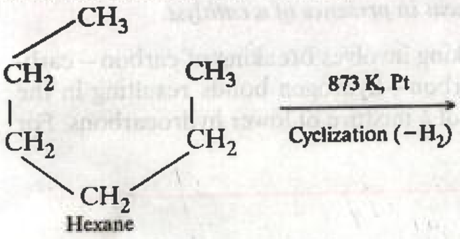


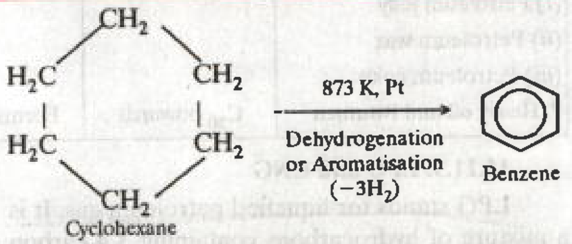
Thus, from the above discussion, we conclude that thermal cracking is difficult to control and hence a complex mixture of products is always obtained. It is because of this limitation that now-a-days, catalytic cracking is used instead of thermal cracking.

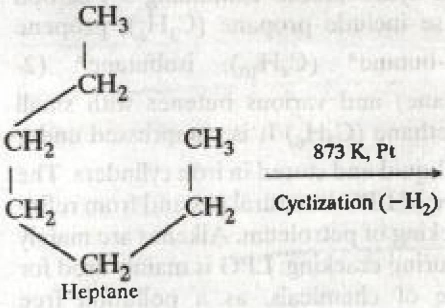
Catalytic cracking. *Catalytic cracking is, in fact, thermal cracking in presence of a catalyst.* The most commonly used catalyst is a mixture of silica and aluminia (4 : 1). Catalytic cracking is generally carried out at lower temperatures (600 – 650 K) than thermal cracking.

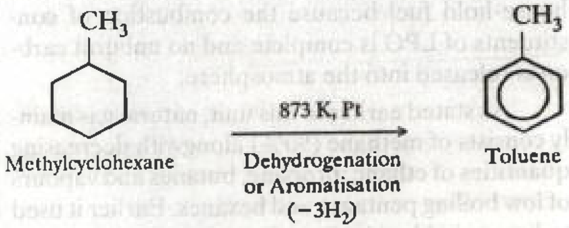
This is the most widely used method in petroleum industry and at present about 85% of the total world production of gasoline is obtained by this method. Further, this is the most important method for the manufacture of alkenes such as ethene, propene and butenes which are widely used in industry.

(ii) Reforming. This process is used to (*i*) *increase the quality of the gasoline, and* (*ii*) *for the manufacture of aromatic hydrocarbons such as benzene, toluene, xylenes, etc. from alkanes and cycloalkanes.* In this process, alkanes containing six to eight carbon atoms are heated at about 873 K in presence of palladium, platinum or nickel as catalyst. During the reforming process, alkanes first undergo cyclization and then aromatization or dehydrogenation. For example,









Further, it has been found that platinum is the best catalyst and that is why reforming is sometimes referred to as *platforming*.

15.11.5. Synthetic Petrol or Gasoline

During World War II, Germany was cut off from the petroleum producing countries. In order to meet the shortage of petroleum products, German chemists and engineers developed the following two methods for converting coal into petroleum like fuels :

(i) Fischer-Tropsch process. In this process, a mixture of water gas ($CO + H_2$) and excess of hydrogen is heated to 473-523 K under a pressure of 1 – 10 bar in presence of cobalt or nickel as catalyst. Under these conditions, a mixture of hydrocarbons is produced which can be refined as discussed above.

$$\underset{\text{(Excess)}}{CO + H_2} \xrightarrow[\text{Co or Ni}]{473-523\text{ K},\ 1-10\text{ bar}} \underset{\text{hydrocarbons}}{\text{Mixture of}} + H_2O$$

The overall yield of petroleum produced by this method is higher than that obtained from the *Bergius process* (discussed below) but the quality is poor.

(ii) Bergius process – Hydrogenation of Coal. In this process, coal is finely powdered and made into a paste with heavy oil. The paste is then heated in a current of hydrogen at 773-873 K at 200-250 bar pressure using iron oxide as a catalyst.

$$C + H_2 \xrightarrow[\text{Iron oxide}]{773-873\text{ K},\ 200-250\text{ bar}} \underset{\text{hydrocarbons}}{\text{Mixture of}}$$

The overall yield of petroleum by this method is lower than that obtained from Fischer-Tropsch process but the quality is better.

Due to depleting petroleum reserves in the world, these synthetic methods have received considerable interest particularly in countries which are rich in coal but poor in oil.

15.11.6. Quality of gasoline – Octane number

Gasoline is mainly used as a fuel in internal combustion engines of scooters, cars, aeroplanes etc. In the operation of such an engine, during the downstroke of the piston, a mixture of gasoline and air is drawn into the cylinder. During the upstroke, the mixture is compressed to a small volume and is instantaneously ignited by a spark from the spark plug to produce CO_2 and H_2O. As a result of combustion, considerable expansion occurs and the hot gases push the piston downward thereby making the wheels move forward.

The efficiency of such an engine depends upon the extent to which a gasoline-air mixture is compressed at the time of ignition ; *greater the compression, greater is the efficiency.* But increase in compression beyond a certain limit results in *pre-ignition* of the fuel-air mixture before the spark is actually passed. This results in irregular combustion which gives violent jerks to the piston. These violent jerks produce a rattling metallic noise known as **knocking**. Thus,

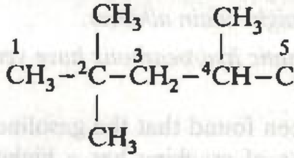
Knocking may be defined as pre-ignition of the fuel-air mixture in the cylinder ahead of the flame. Knocking reduces efficiency of the engine and also causes damage to the cylinder and the piston of the engine.

Thus, the extent of knocking depends upon the quality of the fuel used. In other words, a fuel which produces minimum knocking is considered as a good quality fuel. The anti-knocking property or the quality of a fuel is usually expressed in terms of *octane number*.

Octane number. Octane number is a scale which is used to determine the quality of a fuel in an internal combustion engine. It has been found that straight chain aliphatic hydrocarbons have a higher tendency to *knock* than branched chain hydrocarbons. Two pure hydrocarbons have been selected as standards. **n-Heptane**, a straight chain hydrocarbon, knocks very badly when used as a fuel. Due to its poor anti-knocking properties, it has been arbitrarily assigned an octane number of zero. On the other hand, **2, 2, 4-trimethylpentane** or **iso-octane**, a branched chain hydrocarbon, has the highest antiknocking properties. Thus, it has been given an octane number of 100.

$$CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3$$

n–Heptane
(Octane number taken as zero)



$$\overset{1}{C}H_3-\overset{2}{C}(CH_3)_2-\overset{3}{C}H_2-\overset{4}{C}H(CH_3)-\overset{5}{C}H_3$$

2, 2, 4–Trimethylpentane or Iso–octane
(Octane number taken as 100)

All the fuels are then graded on the basis of their octane number ranging from 0 to 100. In order to do so, various mixtures of these two hydrocarbons are tried in a test engine till a mixture is formed which produces the same knocking as the fuel being tested. The percentage of iso-octane in this mixture is then taken as the *octane number*. Thus,

Octane number may then be defined as the percentage of iso-octane by volume in a mixture of iso-octane and n-heptane which has the same anti-knocking properties as the fuel under examination.

For example, a fuel is assigned an octane number of 90 if it has the same anti-knocking properties as a mixture of 90 percent iso- octane and 10 percent *n*-heptane.

All good quality gasolines used in motor cars have an octane number of 80 or higher, while gasoline used in aeroplanes has an octane number of 100 or even higher. Recently, it has been found that certain hydrocarbons are even worse than *n*-heptane and are assigned octane numbers of less than zero while certain others are even better than iso-octane and hence are given octane numbers of greater than 100 . For example, *n-nonane* has an octane number of – 45 while 2, 2, 3- *trimethylbutane* or *triptane* has an octane number of 125.

The determination of octane numbers of various hydrocarbons has revealed the following facts:

(*i*) *Straight chain alkanes have very low octane numbers. As the length of the chain increases, the octane number further decreases.* For example, octane number of methane is 122, that of ethane is 101, of propane is 96 and of butane is 89.

(*ii*) *Branched chain alkanes have high octane numbers. As the extent of branching increases, octane number further increases.*

(*iii*) *Cycloalkanes have higher octane number than the corresponding straight chain alkanes.*

(*iv*) *Unsaturated hydrocarbons i.e., alkenes and alkynes have higher octane numbers than the corresponding straight chain alkanes*.

(*v*) *Aromatic hydrocarbons have very high octane numbers.*

It has been found that the gasoline obtained by the process of cracking has a higher octane number than gasoline obtained by direct distillation. This is due to the reason that the *cracked gasoline contains a higher percentage of alkenes, branched chain aliphatic hydrocarbons and aromatic hydrocarbons.* The octane number of a fuel can be further increased by the process of reforming which involves a number of processes such as *isomerization, dehydrogenation and cyclization of acyclic hydrocarbons*.

15.11.7. Anti-knocking agents or gasoline additives

The problem of knocking in internal combustion engines can be checked in two ways :

(*i*) *By using fuels of higher octane number as discussed above.*

(*ii*) *By the addition of certain compounds to the gasoline which reduce knocking. These are called* **anti- knocking agents.**

The overall order of decreasing octane number for various hydrocarbons containing the same carbon content is : *aromatic hydrocarbons > cycloalkanes > alkenes > branched chain alkanes > straight chain alkanes.*

The best known anti-knocking agent is *tetraethyl lead* (TEL), $Pb(C_2H_5)_4$ which is added to the extent of 0·01% in the gasoline. Such a gasoline is called *ethyl gasoline or leaded gasoline. In the cylinder of internal combustion engine, tetraethyl lead decomposes to produce ethyl radicals.* These free radicals combine with straight chain alkanes and convert them into branched chain alkanes. As a result, *octane number increases and the knocking decreases.*

$$Pb(C_2H_5)_4 \xrightarrow{\text{Heat}} Pb + \underbrace{4CH_3\dot{C}H_2}_{\text{Ethyl radicals}}$$

The lead deposited in the cylinder is removed by adding 1, 2- dibromoethane (ethylene bromide) whch decomposes into ethene (ethylene) and bromine. The bromine thus obtained combines with lead to form lead bromide which being volatile is carried off from the engine by exhaust gases.

$$BrCH_2CH_2Br \longrightarrow CH_2 = CH_2 + Br_2$$

$$Pb + Br_2 \longrightarrow PbBr_2 \ (\textit{volatile})$$

Pollution problem. An internal combustion engine discharges many gaseous products into the atmosphere. These include CO_2, H_2O, CO, oxides of nitrogen, unburnt hydrocarbons from gasoline and certain compounds of lead. Some of these products are highly poisonous and thus pose a pollution problem for the mankind. The gravity of pollution problem has further aggravated due to the increasing use of automobiles in the recent past. To check this problem, the following measures are being undertaken :

(*i*) In order to oxidise unburnt hydrocarbons and CO to CO_2 and to decompose oxides of nitrogen to nitrogen and oxygen, the use of *catalytic converter* in internal combustion engines is increasingly being used. In this regard, Goverment of India has ordered that all the new cars meant for use in metropolitan cities of the country must be fitted with catalytic converters.

(*ii*) As far as possible, the use of tetraethyl lead is being avoided by increasing the octane number of the fuel by adding more aromatic and branched chain aliphatic hydrocarbons to it.

Instead of using petrol or diesel, CNG is now being used as a fuel for running buses, cars and three-wheelers in metropolitan cities like Delhi, Mumbai, Kolkata, Chennai etc. Its octane number is 130. Since the combustion of CNG is complete without any unburnt carbon being released into the atmosphere, the use of CNG has reduced pollution to a considerable extent.

15.11.8. Quality of diesel – Cetane number

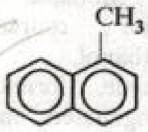
The quality of diesel fuel is expressed in terms of cetane number. It is defined as follows :–

Cetane number of a sample of diesel is the percentage of cetane by volume in a mixture of cetane and α-methylnaphthalene which has the same ignition properties as the diesel under examination in a test engine.

Cetane (*n*-hexadecane, $C_{16}H_{34}$) ignites rapidly and is given a cetane number of 100 whereas α-methylnaphthalene ignites slowly and is given a cetane number of zero.

$CH_3-(CH_2)_{14}-CH_3$

Cetane (*n*–Hexadecane)
Cetane No. = 100
(*Ignites spontaneously*)



α–Methylnaphthalene
Cetane No. = 0
(*Ignites slowly*)

For example, a diesel oil having a cetane number of 80 would have the same ignition properties as a mixture of 80% cetane and 20% α-methylnaphthalene.

A sample of diesel has the same knocking characteristics as a 60 ml mixture of cetane and α-methylnaphthalene mixed in 2 : 1 ratio (v/v). What is the cetane number of the diesel sample ? **(N.C.E.R.T.)**

Solution. Vol. of cetane $= 60 \times \frac{2}{3} = 40$ ml

Vol. of α-methylnaphthalene $= 60 \times \frac{1}{3} = 20$ ml

∴ Cetaine number of diesel sample

$$= \frac{40}{60} \times 100 = 66\cdot6.$$

15.12. Petrochemicals

Organic compounds obtained directly or indirectly from natural gas or petroleum are called petrochemicals. The major hydrocarbons obtained from petroleum refining are given in the flow-sheet chart given in Fig. 15.31.

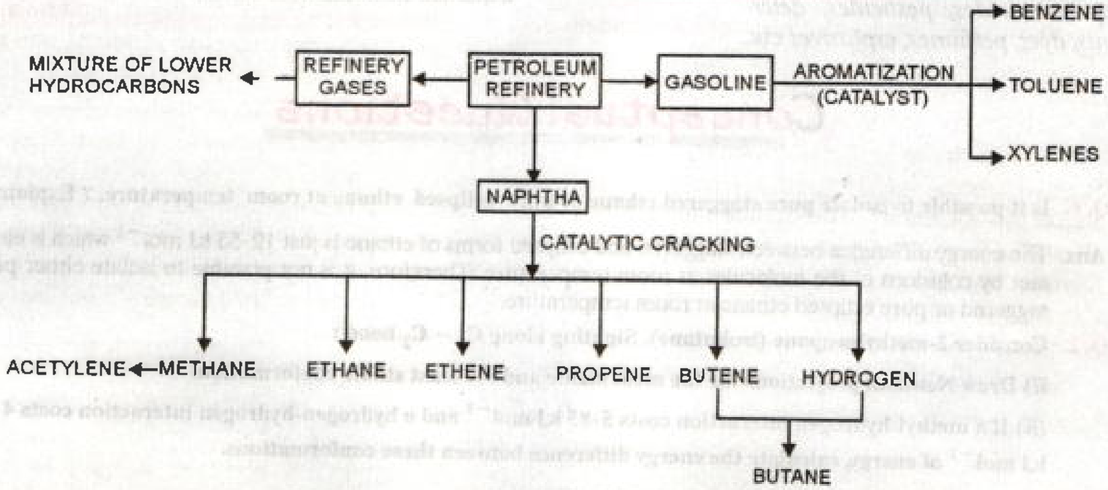


FIGURE 15.31. Hydrocarbons from petroleum refining.

Methane is the major source for methanol, formaldehyde, formic acid, halogenated methanes such as methyl halides, dichloromethane, chloroform, carbon tetrachloride and mixed halides like freon (Fig. 15.32). It is also used for making carbon black, acetylene and synthesis gas or water gas ($CO + H_2$). Hydrogen from synthesis gas is used for hydrogenation and nitrogen fixation.

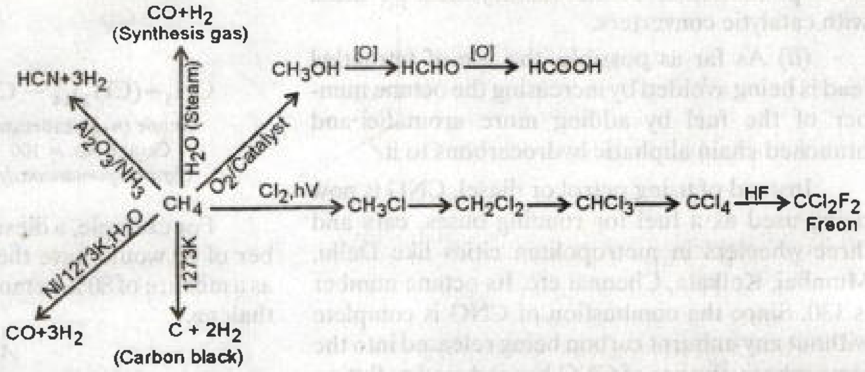


FIGURE 15.32. Industrial preparation of some important chemicals from methane

Ethylene oxide prepared from ethane can be converted into a large number of organic chemicals such as ethyl alcohol, acetone, acetic acid, acetaldehyde, ethylene glycol and its monomethyl derivative, ethylene chlorohydrin and ethylene cyanohydrin as shown in Fig. 15.33.

These petrochemicals are widely used in the manufacture of iso-octane (aviation fuel), plastics (polythene, polyvinyl chloride (PVC) etc.), *synthetic fibres* (nylon, terylene, dacron etc.), *synthetic rubber, insecticides, pesticides, detergents, dyes, perfumes, explosives* etc.

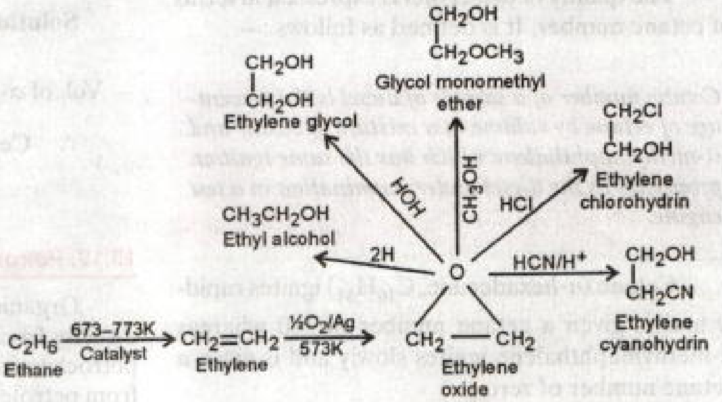


FIGURE 15.33. Industrial preparation of some important chemicals from ethane.

Conceptual Questions

Q. 1. **Is it possible to isolate pure staggered ethane or pure eclipsed ethane at room temperature. ? Explain.**

Ans. The energy difference between staggered and eclipsed forms of ethane is just 12·55 kJ mol^{-1} which is easily met by collisions of the molecules at room temperature. Therefore, it is not possible to isolate either pure saggered or pure eclipsed ethane at room temperature.

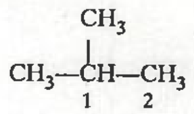
Q. 2. **Consider 2-methylpropane (isobutane). Sighting along $C_1 - C_2$ bond :**

(*i*) Draw Newman projections for the most stable and the least stable conformation.

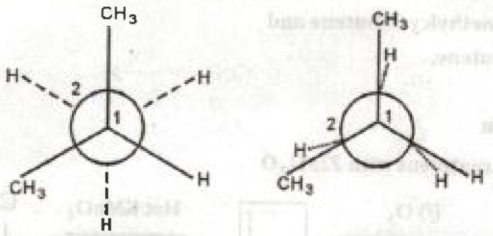
(*ii*) If a methyl-hydrogen interaction costs 5·85 kJ mol^{-1} and a hydrogen-hydrogen interaction costs 4·18 kJ mol^{-1} of energy, calculate the energy difference between these conformations.

Ans. 2-Methylpropane may be regarded as 1, 1-dimethylethane.

Sighting along $C_1 - C_2$ bond, the Newman projections for the most stable and least stable conformations are :



$$\underset{1}{CH_3}-\overset{\overset{\displaystyle CH_3}{|}}{CH}-\underset{2}{CH_3}$$



STAGGERED
(most stable)

ECLIPSED
(least stable)

Now eclipsed conformation has two methyl-hydrogen and one hydrogen-hydrogen interactions, therefore, the energy of eclipsed conformation is expected to be more than that of staggered conformation by $2 \times 5{\cdot}85 + 1 \times 4{\cdot}18 = 15{\cdot}88$ kJ mol^{-1}.

Q. 3. Why propane has only one eclipsed conformation while butane has two ? Explain. *(N.C.E.R.T.)*

Ans. For purpose of writing conformations, propane may be regarded as 1-methylethane while butane may be regarded has 1, 2- dimethylethane. Since propane has only one methyl group, therefore it has only one eclipsed conformation in which there is one strong methyl- hydrogen interaction and two weak hydrogen-hydrogen interactions. (For Newman projection of this conformation refer to Fig. 15.10).

However, in case of butane, there are two methyl groups, one each on each carbon and hence has two eclipsed conformations.

(*i*) *fully eclipsed conformation* in which there are one severe methyl-methyl interaction and two weak hydrogen-hydrogen interactions.

(*ii*) *partially eclipsed conformation* in which there are two strong methyl-hydrogen interactions and one weak hydrogen-hydrogen interaction. For Newman projections of these conformations refer to Fig. 15.11

Q. 4. Which of the following has the highest boiling point ?

(*i*) 2-methylpentane (*ii*) 2, 3-dimethylbutane (*iii*) 2, 2-dimethylbutane. *(N.C.E.R.T.)*

Ans. As the branching increases, surface area decreases. As a result, magnitude of *van der Waal's forces* of attraction decreases and hence the boiling point decreases. Now 2- methylpentane has the largest surface area and hence has the highest boiling point. Further because of two branches on the same carbon, 2, 2-dimethylbutane has lower surface area and hence lower boiling point that 2, 3-dimethylbutane. Thus, the overall order of decreasing boiling points is

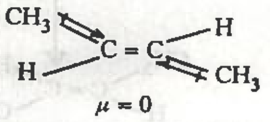
2-methylpentane (333 K) > 2, 3-dimethylbutane (331 K) > 2, 2- dimethylbutane (323 K).

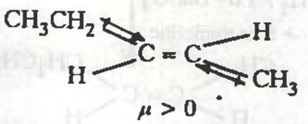
Q. 5. What effect the branching of an alkane has on its melting point ? *(N.C.E.R.T.)*

Ans. In general, as the branching increases, the packing of the molecules in the crystal lattice becomes less close and hence the m.p. decreases accordingly. However, if the branching makes the molecule symmetrical, the packing of the molecules in the crystal lattice becomes close and hence the m.p. increases. For example, the m.p. of isopentane (113 K) is lower than of *n*- pentane (143 K) but the m.p. of neopentane (256 K) is much higher than that of isopentane and *n*-pentane.

Q. 6. *trans*-Pent-2-ene is polar while *trans*- but-2-ene is non-polar. Explain.

Ans. In *trans*-but-2-ene, the dipole moments of the two C—CH_3 bonds are equal and opposite and hence they exactly cancel out each other. Thus, *trans*-but- 2-ene is non-polar





However, in *trans*-pent-2-ene, the dipole moments of C—CH_3 and C—CH_2CH_3 bonds are unequal. Although these two dipoles oppose each other, yet they do not exactly cancel out each other and hence *trans*-pent-2-ene has a small but finite dipole moment and thus is polar.

Q. 7. **Predict the products when each one of the following :**

(a) Cyclobutene (b) 1-methylcyclobutene and

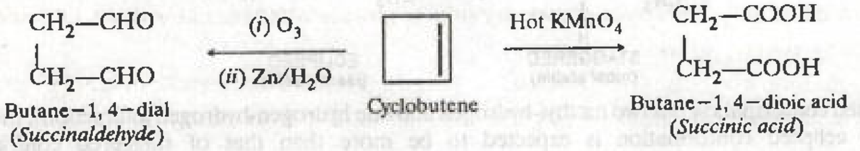
(c) 1, 2-dimethylcyclobutene,

is subjected to

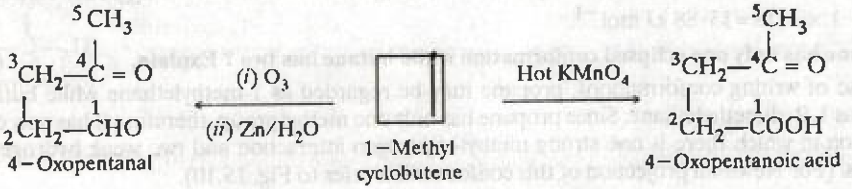
(i) hot $KMnO_4$ solution

(ii) ozone followed by treatment with Zn/H_2O

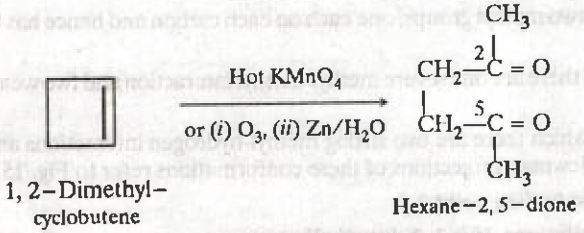
Ans. (a)



(b)

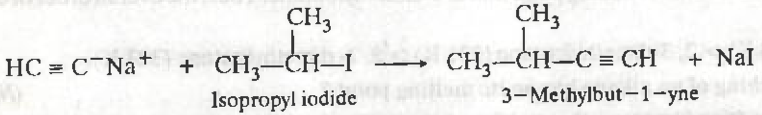


(c)



Q. 8. **How will you prepare 3-methylbut-1-yne by starting with ethyne ?**

Ans. $\underset{\text{Ethyne}}{HC \equiv CH} \xrightarrow[196\text{ K}]{Na,\ NH_3(l)} \underset{\text{Sod. acetylide}}{HC \equiv C^-Na^+}$

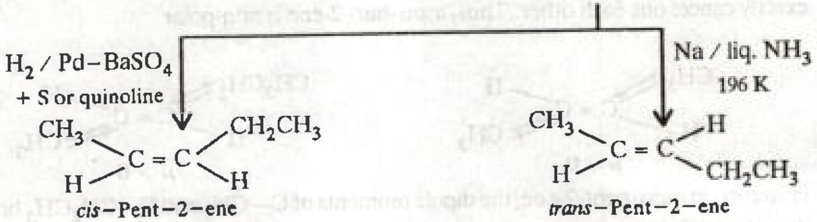


$$HC \equiv C^-Na^+ + \underset{\text{Isopropyl iodide}}{CH_3-\overset{\overset{CH_3}{|}}{C}H-I} \longrightarrow \underset{\text{3-Methylbut-1-yne}}{CH_3-\overset{\overset{CH_3}{|}}{C}H-C \equiv CH} + NaI$$

Q. 9. **How will you prepare (i) *cis*-pent-2-ene and *trans*-pent-2-ene by starting with ethyne.**

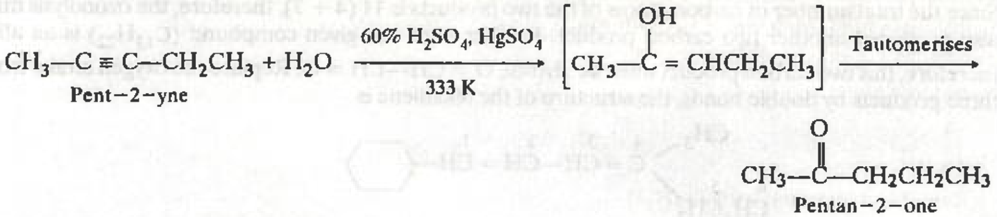
Ans. $\underset{\text{Ethyne}}{HC \equiv CH} \xrightarrow[196\text{ K}]{Na,\ NH_3(l)} HC \equiv C^-Na^+ \xrightarrow[-\ NaI]{CH_3I}$

$\underset{\text{Propyne}}{CH_3-C \equiv CH} \xrightarrow[196\text{ K}]{Na,\ NH_3(l)} CH_3-C \equiv C^-Na^+ \xrightarrow[-\ NaI]{CH_3CH_2I} \underset{\text{Pent-2-yne}}{CH_3-C \equiv C-CH_2CH_3}$



Q. 10. **Starting with acetylene, how will you prepare pentan-2-one ?**

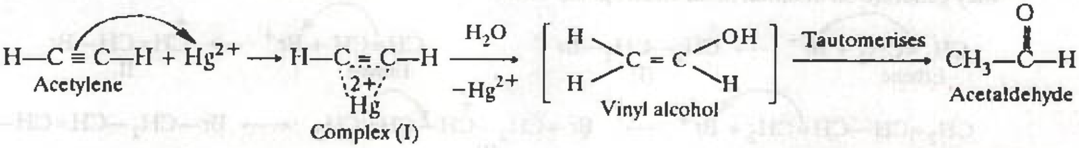
Ans. Prepare pent-2-yne as discussed in Q. 6 and then convert it to pentan-2-one by hydration.



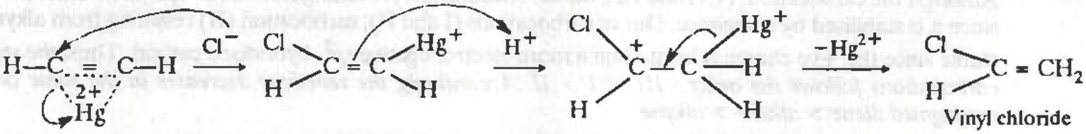
$$CH_3{-}C\equiv C{-}CH_2CH_3 + H_2O \xrightarrow[333\ K]{60\%\ H_2SO_4,\ HgSO_4} \left[CH_3{-}\overset{OH}{\overset{|}{C}}=CHCH_2CH_3\right] \xrightarrow{\text{Tautomerises}} CH_3{-}\overset{O}{\overset{\|}{C}}{-}CH_2CH_2CH_3$$

Q. 11. Acetylene reacts with dil. H_2SO_4 in presence of mercury salts to give acetaldehyde but with dil. HCl under similar conditions, it gives vinyl chloride. Explain why ?

Ans. First of all mercury ions form a complex (I) with acetylene. Since H_2O is more nucleophilic than SO_4^{2-} ion, it attacks the complex to form first vinyl alcohol which then tautomerises to give acetaldehyde



In case of dil. HCl, since Cl^- ion is more nucleophilic than H_2O, it reacts with complex (I) to form vinyl chloride.



Q. 12. How will you separate a mixture of ethane, ethylene and acetylene ?

Ans. This mixture can be separated into its constituents by the following steps :

Step 1. Pass the mixture of gases through Tollens' reagent when acetylene will form white precipitate of disilver acetylide while ethane and ethylene will pass through.

$$\underset{\text{Acetylene}}{HC\equiv CH} + \underset{\text{Tollens' reagent}}{2\,[Ag(NH_3)_2]^+OH^-} \longrightarrow \underset{\text{Disilver acetylide}}{Ag{-}C\equiv C{-}Ag} + 4\,NH_3 + 2\,H_2O$$

Separate the white ppt. by filtration and treat it with dil. HNO_3 to regenerate acetylene. Collect it in a separate container.

$$Ag{-}C\equiv C{-}Ag + 2\,HNO_3 \longrightarrow HC\equiv CH + 2\,AgNO_3$$

Step 2. Pass the mixture of ethane and ethylene through cold conc. H_2SO_4 when ethylene will be absorbed as ethyl hydrogen sulphate while ethane escapes. The ethane thus obtained is collected in a separate container.

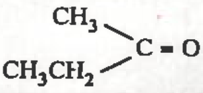
$$\underset{\text{Ethylene}}{CH_2=CH_2} + H_2SO_4\,(conc.) \longrightarrow \underset{\text{Ethyl hydrogen sulphate}}{CH_3CH_2OSO_2OH}$$

The ethyl hydrogen sulphate thus obtained is heated to 433—443 K when ethylene is obtained which is collected in a separate container

$$CH_3CH_2OSO_3H \xrightarrow{433-443\ K} CH_2=CH_2 + H_2SO_4$$

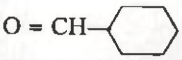
Q. 13. A conjugated alkadiene having molecular formula $C_{13}H_{22}$ on ozonolysis yielded ethyl methyl ketone and cyclohexanecarbaldehyde. Identify the diene, write its structural formula and give its IUPAC name.
(N.C.E.R.T.)

Ans. The structures of the products of ozonolysis are :



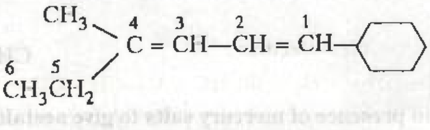
Ethyl methyl ketone (C_4H_8O)

and



Cyclohexanecarbaldehyde ($C_7H_{12}O$)

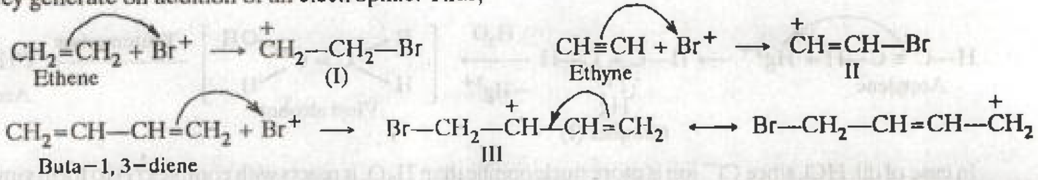
Since the total number of carbon atoms of the two products is 11 (4 + 7), therefore, the ozonolysis must have also produced another two carbon product. Further since the given compound ($C_{13}H_{22}$) is an alkadiene, therefore, this two carbon product must be glyoxal, $O = CH—CH = O$. Replace the oxygen atoms from these three products by double bonds, the structure of the alkadiene is



1-Cyclohexyl-4-methylhexa-1, 3-diene

Q. 14. Why are conjugated dienes more reactive than alkenes or alkynes towards electrophilic addition reactions ?

Ans. The relative reactivity of alkenes, alkynes and conjugated dienes depends upon the stability of the carbocations they generate on addition of an electrophile. Thus,



Amongst the carbocations (I, II and III), the carbocation (III) resulting from buta-1, 3-diene is the most stable since it is stabilised by resonance. Out of carbocations (I and II), carbocation (II) resulting from alkyne is less stable since the +ve charge is located on a more electronegative sp^2- hybridised carbon. Thus, *the stability of carbocations follows the order : III > I > II. Accordingly, the reactivity decreases in the same order, i.e., conjugated diene > alkene > alkyne.*

Q. 15. How will you distinguish between buta-1, 3-diene and but-1-yne ?

Ans. But-1-yne is a *terminal alkyne* and hence can be distinguished from buta-1, 3-diene by *Tollens' reagent* which forms a white ppt. with but-1-yne and but not with buta-1, 3-diene.

$$\underset{\text{But-1-yne}}{CH_3CH_2—C \equiv CH} + \underset{\text{Tollens' reagent}}{[Ag(NH_3)_2]^+OH^-} \longrightarrow \underset{\substack{\text{Silver but-1-ynide}\\ \textit{(white ppt.)}}}{CH_3CH_2—C \equiv C\,Ag} + 2\,NH_3 + H_2O$$

$$\underset{\text{Buta-1, 3-diene}}{CH_2=CH—CH=CH_2} + [Ag\,(NH_3)_2]^+\,OH^- \longrightarrow \text{No reaction.}$$

Q. 16. What are the main constituents of LPG ?

Ans. The main constituents of LPG are butane and isobutane. Both these isomers can be easily liquefied and hence can be conveniently transported in iron cylinders.

Q. 17. Out of 2, 2, 3-trimethylbutane, 2, 2, 4- trimethylpentane and 2, 2, 3, 3-tetramethylbutane which has the highest octane number. Explain.

Ans. Since the octane number increases as the branching increases. Therefore, 2, 2, 3, 3-tetramethylbutane having four branches has the highest octane number.

Q. 18. Why do the C—C bonds rather than C—H bonds break during cracking of alkanes ?

Ans. Since the bond dissociation energy of C—C bonds (355 kJ mol^{-1}) is lower than bond dissociation energy of C—H bonds (414 kJ mol^{-1}), therefore, during cracking of alkanes, C—C bonds break more easily than C—H bonds.

Q. 19. What is solvent naphtha ? What is its use ?

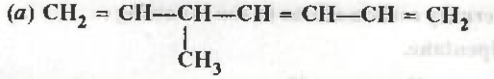
Ans. During coal-tar distillation, various fractions can be collected. The fraction distilling between 413-433 K is called *solvent naphtha*. It mainly contains xylenes and cumenes and is used as a solvent for resins, rubbers, paints etc.

Very Short Answer Questions CARRYING 1 MARK

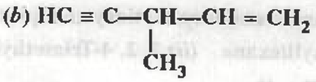
Q. 1. Give the IUPAC name of the lowest molecular weight alkane that contains a quaternary carbon.

Ans. 2,2-Dimethylpropane.

Q. 2. Write the IUPAC names of the following molecules :



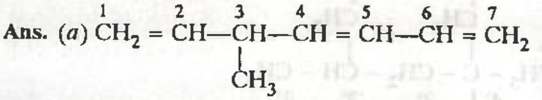
$$(a)\ CH_2=CH-\underset{\underset{CH_3}{|}}{CH}-CH=CH-CH=CH_2$$



$$(b)\ HC\equiv C-\underset{\underset{CH_3}{|}}{CH}-CH=CH_2$$

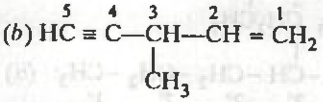
(*N.C.E.R.T.*)

Ans.



$$(a)\ \overset{1}{CH_2}=\overset{2}{CH}-\underset{\underset{CH_3}{|}}{\overset{3}{CH}}-\overset{4}{CH}=\overset{5}{CH}-\overset{6}{CH}=\overset{7}{CH_2}$$

3−Methylhepta−1, 4, 6−triene



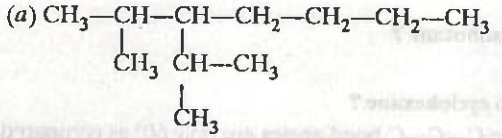
$$(b)\ \overset{5}{HC}\equiv\overset{4}{C}-\underset{\underset{CH_3}{|}}{\overset{3}{CH}}-\overset{2}{CH}=\overset{1}{CH_2}$$

3−Methylpent−1−en−5−yne

Q. 3. Draw the structures of the following showing all C and H atoms.

(*a*) 2-Methyl-3-isopropylheptane (*b*) Dicyclopropylmethane. (*N.C.E.R.T.*)

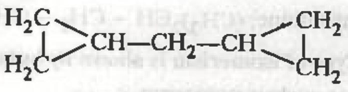
Ans.



$$(a)\ CH_3-\underset{\underset{CH_3}{|}}{CH}-\underset{\underset{\underset{\underset{CH_3}{|}}{CH-CH_3}}{|}}{CH}-CH_2-CH_2-CH_2-CH_3$$

2−Methyl−3−isopropylheptane

(*b*)

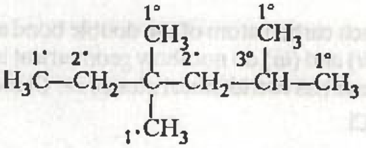


Dicyclopropylmethane

Q. 4. In the alkane,

$H_3C-CH_2-C(CH_3)_2-CH_2-CH(CH_3)_2$, identify 1°, 2°, 3° carbon atoms and give the total number of H-atoms bonded to each of these. (*N.C.E.R.T.*)

Ans.



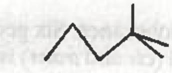
$$\overset{1^\circ}{H_3C}-\overset{2^\circ}{CH_2}-\underset{\underset{1^\circ CH_3}{|}}{\overset{\overset{1^\circ}{CH_3}}{\overset{|}{C}}}-\overset{2^\circ}{CH_2}-\overset{\overset{1^\circ}{CH_3}}{\overset{3^\circ\ |}{CH}}-\overset{1^\circ}{CH_3}$$

$1^\circ H = 3+3+3+3+3 = 15,$

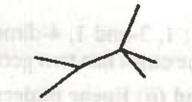
$2^\circ H = 2+2 = 4\ ;\ 3^\circ H = 1$

Q. 5. Arrange the following in increasing order of their release of energy on combustion.

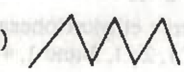
(i)



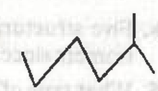
(ii)



(iii)



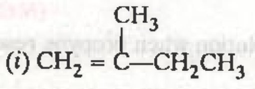
(iv)



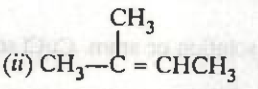
Ans. More the number of C-atoms having maximum hydrogens, *i.e.*, CH_3 groups, greater is the heat of combustion. Thus the increasing order of heat of combustion is (*iii*) < (*iv*) < (*i*) < (*ii*).

Q. 6. Write the structure of all alkenes which on hydrogenation give 2- methylbutane. (*N.C.E.R.T.*)

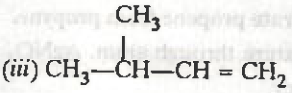
Ans.



$$(i)\ CH_2=\overset{\overset{CH_3}{|}}{C}-CH_2CH_3$$



$$(ii)\ CH_3-\overset{\overset{CH_3}{|}}{C}=CHCH_3$$



$$(iii)\ CH_3-\overset{\overset{CH_3}{|}}{CH}-CH=CH_2$$

Q. 7. Which of the following polymerises most readily ?

(*i*) Acetylene (*ii*) Ethene (*iii*) Buta-1, 3- diene. (*N.C.E.R.T.*)

Ans. Buta-1, 3-diene being more reactive undergoes polymerization readily. The actual order is : buta-1, 3-diene > ethene > acetylene.

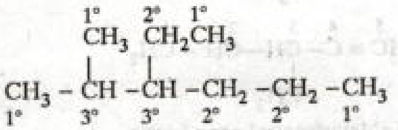
Q. 8. Arrange the following set of compounds in order of their decreasing relative reactivity with an electrophile, E^+.

(*i*) Chlorobenzene, 2, 4-dinitrochlorobenzene, *p*- nitrochlorobenzene
(*ii*) toluene, *p*-$H_3C—C_6H_4—CH_3$, *p*-$H_3C—C_6H_4—NO_2$, *p*-$O_2N—C_6H_4—NO_2$ *(N.C.E.R.T.)*

Ans. Electron-donating groups increase the reactivity while electron- withdrawing groups decrease the reactivity. Thus, (*i*) chlorobenzene > *p*-nitrochlorobenzene > 2, 4- dinitrochlorobenzene.
(*ii*) *p*-$CH_3—C_6H_4—CH_3$ > toluene > *p*-$H_3C—C_6H_4—NO_2$ > *p*-$NO_2—C_6H_4—NO_2$

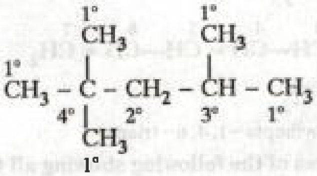
Q. 9. Indicate the primary, secondary, tertiary and quaternary carbon atoms in the following :
(*i*) 3-Ethyl-2-methylhexane (*ii*) 2, 2, 4-Trimethylpentane.

Ans. (*i*)



$$\underset{1^\circ}{CH_3} - \underset{3^\circ}{\overset{\overset{1^\circ}{CH_3}}{\overset{|}{CH}}} - \underset{3^\circ}{\overset{\overset{2^\circ\ \ 1^\circ}{CH_2CH_3}}{\overset{|}{CH}}} - \underset{2^\circ}{CH_2} - \underset{2^\circ}{CH_2} - \underset{1^\circ}{CH_3}$$

(*ii*)



$$\overset{1^\circ}{CH_3} - \underset{\underset{\underset{1^\circ}{CH_3}}{|}}{\overset{\overset{1^\circ}{CH_3}}{\overset{|}{\underset{4^\circ}{C}}}} - \underset{2^\circ}{CH_2} - \underset{3^\circ}{\overset{\overset{1^\circ}{CH_3}}{\overset{|}{CH}}} - \underset{1^\circ}{CH_3}$$

Q. 10. Name the chain isomer of C_5H_{12} which has a tertiary hydrogen atom.

Ans. 2-Methylbutane, $(CH_3)_2CH - CH_2 - CH_3$.

Q. 11. What type of isomerism is shown by butane and isobutane ?

Ans. Chain or nuclear isomerism.

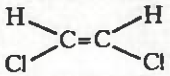
Q. 12. Why is cyclopropane very reactive as compared to cyclohexane ?

Ans. In cyclopropane, the ring is quite strained since the C—C—C bond angles are only 60° as compared to 109° 28′ in cyclohexane.

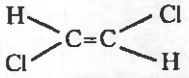
Q. 13. Which of the following shows geometrical isomerism ?
(*i*) $CHCl=CHCl$ (*ii*) $CH_2=CCl_2$ (*iii*) $CCl_2=CHCl$

Give the structures of its *cis* and *trans* forms.

Ans. Only (*i*) *i.e.* $ClCH = CHCl$ has two different substituents on each carbon atom of the double bond and hence shows geometrical isomerism. The other two compounds, *i.e.* (*ii*) and (*iii*) do not show geometrical isomerism because one of the carbon atoms of the double bond in each case has two identical atoms, *i.e.* Cl atoms.



cis−1, 2−Dichloroethene



trans−1,2−Dichloroethene

Q. 14. How many structural and geometrical isomers are possible for a cyclohexane derivative having the molecular formula, C_8H_{16} ?

Ans. Five structural isomers : ethylcyclohexane, 1, 1 ; 1, 2 ; 1, 3-and 1, 4-dimethylcyclohexanes. Six geometrical isomers since each of 1, 2 ; 1, 3-and 1, 4-dimethylcyclohexanes has two geometrical (*cis* and *trans*) isomers.

Q. 15. What type of hybridization is involved in (*i*) planar and (*ii*) linear molecules ?

Ans. (*i*) sp^2 and (*ii*) *sp*.

Q. 16. Write all the possible isomers for a benzene derivative having the molecular formula C_8H_{10}.

Ans. Four isomers ; ethylbenzene, *o*-xylene, *m*-xylene and *p*-xylene. For structures refer to the text.

Q. 17. How will you separate propene from propyne. *(N.C.E.R.T.)*

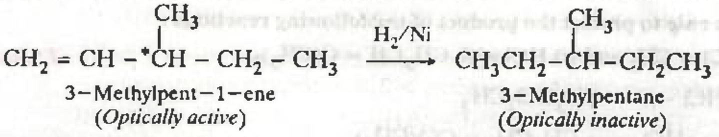
Ans. By passing the mixture through amm. $AgNO_3$ solution or amm. CuCl solution when propyne reacts while propene passes over.

Q. 18. A compound is formed by the substitution of two chlorine atoms for two hydrogen atoms in propane. What is the number of structural isomers possible? *(B.I.T. Ranchi, 1992)*

Ans. Four : 1, 1-dichloropropane ($CH_3CH_2CHCl_2$), 2, 2- dichloropropane ($CH_3CCl_2CH_3$), 1, 2-dichloropropane ($CH_3CHClCH_2Cl$) and 1, 3-dichloropropane ($ClCH_2CH_2CH_2Cl$).

Q. 19. Give the structure of an optically active hydrocarbon (C_6H_{12}) which on catalytic hydrogenation gives an optically inactive compound (C_6H_{14}). *(I.I.T. 1993)*

Ans. 3-Methylpent-1-ene



$$CH_2 = CH - \overset{CH_3}{\overset{|}{^{*}CH}} - CH_2 - CH_3 \xrightarrow{H_2/Ni} CH_3CH_2-\overset{CH_3}{\overset{|}{CH}}-CH_2CH_3$$

3-Methylpent-1-ene *(Optically active)* 3-Methylpentane *(Optically inactive)*

Q. 20. Arrange the following in the increasing order of C—C bond length C_2H_6, C_2H_4, C_2H_2

(B.I.T. Ranchi 1994)

Ans. $C_2H_2 < C_2H_4 < C_2H_6$.

Q. 21. Name two industrial sources of hydrocarbons.

Ans. Coal and petroleum.

Q. 22. What does LPG stand for ?

Ans. Liquefied petroleum gas.

Q. 23. What type of hydrocarbons are present in high octane gasoline ?

Ans. Branched chain aliphatic and/ or aromatic hydrocarbons.

Q. 24. What are the chief constituents of light oil fraction?

Ans. Benzene, toluene and xylenes.

Q. 25. Name the products formed when an ethereal solution containing ethyl iodide and methyl iodide is heated with sodium metal.

Ans. A mixture of ethane, propane and butane is formed.

Q. 26. Out of ethylene and acetylene which is more acidic and why ?

Ans. Acetylene, due to greater electronegativity of the *sp*- hybridized carbon.

Q. 27. What is Lindlar's catalyst ? What is it used for ?

Ans. Pd deposited over $CaCO_3$ or $BaSO_4$ and partially poisoned by addition of lead acetate or sulphur or quinoline. It is used for partial reduction of alkynes to *cis*-alkenes.

Q. 28. Define cracking ?

Ans. The thermal decomposition of higher hydrocarbons into lower hydrocarbons in presence or absence of a catalyst is called cracking.

Q. 29. What scale is used for measuring the quality of gasoline ?

Ans. Octane number.

Q. 30. Write the structure of the alkene which on reductive ozonolysis gives butanone and ethanal.

Ans. $CH_3CH_2C(CH_3) = CHCH_3$ (3-methyl-2-pentene).

Q. 31. What is teflon ? What is it used for ?

Ans. Poly (tetrafluoroethylene) is called teflon. It is used for making non-stick utensils.

Q. 32. Name two reagents which can be used to distinguish between ethene and ethyne.

Ans. Tollens' reagent and ammoniacal CuCl solution.

Q. 33. How can ethylene be converted into ethane ? *(B.I.T. Ranchi 1990)*

Ans. By catalytic reduction with H_2 in presence of nickel at 523—573 K.

Q. 34. How will you detect the presence of unsaturation in an organic compound ? *(M.L.N.R. Allahabad 1990)*

Ans. Either by Baeyer's reagent or by Br_2 in CCl_4.

Q. 35. Explain the term knocking. A sample of petrol produces the same knocking properties as the mixture containing 30% *n*-heptane and 70% iso-octane. What is the octane number of the sample ?

(I.S.M. Dhanbad 1990)

Ans. 70.

Q. 36. Write the structural formulae of all the possible isomers of $C_2H_2Cl_2$ and indicate which of them is non-polar ?

(M.L.N.R. Allahabad 1992)

Ans (*i*) *cis* -1, 2-dichloroethene (*ii*) *trans*-1, 2-dichloroethene and (*iii*) 1, 1- dichloroethene (*ii*) is non-polar]

Q. 37. Use Markownikov's rule to predict the product of the following reactions :

(*i*) HCl with $CH_3CCl = CH_2$ and (*i*) HCl with $CH_3CH = C(CH_3)_2$. *(I.S.M. Dhanbad 1992)*

Ans. $CH_3CCl = CH_2 + HCl \longrightarrow CH_3CCl_2CH_3$

$CH_3CH{=}C(CH_3)_2 + HCl \longrightarrow CH_3CH_2 - CCl(CH_3)_2$

Q. 38. Arrange the following in order of increasing volatility : gasoline, kerosene and diesel. *(B.I.T. Ranchi 1992)*

Ans. Diesel, kerosene, gasoline.

Q. 39. Arrange the following : HCl, HBr, HI, HF in order of decreasing reactivity towards alkenes. *(M.L.N.R. Allahabad 1993)*

Ans. HI > HBr > HCl > HF.

Q. 40. Give the structure of the alkene (C_4H_8) which adds on HBr in the presence and in the absence of peroxide to give the same product, C_4H_9Br. *(I.I.T. 1991)*

Ans. 2-Butene (being symmetrical gives the same product *i.e.,* 2-bromobutane).

Q. 41. Give the structure of an alkene (C_4H_8) which when treated with H_2O / H_2SO_4 gives $C_4H_{10}O$ which cannot be resolved into optical isomers.

Ans. 2-Methylpropene or isobutylene on hydration gives *t*-butyl alcohol which is optically inactive. The other two butenes, *i.e.*, 1-butene and 2-butene will give 2-butanol which can be resolved.

Q. 42. Although benzene is highly unsaturated, it does not undergo addition reactions. *(M.L.N.R. Allahaband 1995)*

Ans. Because of extra stability due to delocalization of π-electrons, the double bonds of benzene usually do not undergo addition reactions.

Q. 43. How will you demonstrate that double bonds of benzene are somewhat different from that of olefines ? *(West Bengal J.E.E. 2004)*

Ans. The double bonds of olefines decolourize Br_2 in CCl_4 and discharge the pink colour of Baeyer's reagent with simultaneous formation of a brown ppt. of MnO_2 while those of benzene do not.

Q. 44. Which one of the following has the maximum number of π-bonds — propyne, butadiene, benzene ? *(West Bengal J.E.E. 2004)*

Ans. Benzene has three π-bonds while propyne and butadiene both have two π-bonds each.

Short Answer Questions CARRYING 2 or 3 MARKS

Sec. 15.1. to 15.3.

1. What are alkanes ? Why are they called paraffins ?
2. Draw the structure of 2, 2, 4-trimethylhexane and indicate how many each of the 1°, 2°, 3° and 4° carbons does it contain ?
3. Comment upon three dimensional structures of alkanes and their planar representations.
4. Write the structural isomers of C_5H_{12} and their IUPAC names.
5. How can alkanes be prepared from (*i*) an alkene, (*ii*) an alkyl halide, and (*iii*) a carboxylic acid ?
6. How can the following reactions be used to prepare alkanes.
   (*i*) Wurtz reaction, (*ii*) Kolbe's electrolytic method, and (*iii*) Sabatier and Senderen's reaction ?
7. Give reasons for the following :
   (*i*) The boiling points of alkanes decrease with branching.
   (*ii*) The melting points of alkanes with odd number of carbon atoms are lower than those with even number of carbon atoms.
   (*iii*) Straight chain alkanes possess higher boiling points than the corresponding branched chain isomers.

8. What effect does branching of an alkane have on its melting point. *(N.C.E.R.T.)*

9. Give two methods for the preparation of alkanes from carboxylic acids.

10. Starting from ethanoic acid, how will you prepare (*i*) methane (*ii*) ethane ?

11. What is Wurtz reaction ? How can it be used to prepare butane ?

12. Wurtz reaction is a good method for the preparation of alkanes containing even number of carbon atoms but not for alkanes containing odd number of carbon atoms. Comment.

13. Grignard reagent on hydrolysis gives a hydrocarbon. Give equation suggesting another method by which the hydrocarbon obtained in the above reaction can be prepared.

14. What is a Grignard reagent ? How is propane prepared from a Grignard reagent ?

[**Ans.** $CH_3CH_2CH_2Br + Mg \longrightarrow CH_3CH_2CH_2MgBr$ *(Grignard reagent)*

$CH_3CH_2CH_2MgBr + H_2O \longrightarrow CH_3CH_2CH_3 + Mg(OH)Br$]

15. *n*-Propylmagnesium bromide on hydrolysis gives propane. Is there another Grignard reagent which also gives propane ? It so, give its name, structure and equation for the reaction.

[**Ans.** Isopropylmagnesium bromide, $(CH_3)_2CHMgBr$, $(CH_3)_2CHMgBr + H_2O \longrightarrow CH_3CH_2CH_3 + Mg(OH)Br$]

16. Discuss briefly the mechanism of halogenation of methane.

17. What is Wurtz reaction ? What are its liminations ? How have these liminations been overcome ?

18. What is Corey-House reaction ? In what way, it is superior to Wurtz reaction ?

19. Write short notes on : (*i*) Oxidation reactions of alkanes. (*ii*) Isomerization of alkanes.

Sec. 15.3. to 15.6.

20. Why is rotation about carbon-carbon single bond free ? What type of isomerism does it lead to ? [**Ans.** Conformational isomerism]

21. Draw the Sawhorse and Newman projections for the staggered and eclipsed conformations of ethane. Discuss their relative stability. Can these conformations be separated ? If not, then why ?

22. Write the gauche, staggered, eclipsed and partially eclipsed conformations of *n*-butane. Comment upon their relative stability.

23. Draw Newman projection formulae of *n*-butane. *(N.C.E.R.T.)*

24. Why propane has only one eclipsed conformation while butane has two ? Explain and give diagrams. *(N.C.E.R.T.)*

25. Draw the structures of three cycloalkane isomers with molecular formula C_5H_{10} each with a different ring size. *(N.C.E.R.T.)*

26. Between the two conformational isomers of cyclohexane, *i.e.*, chair and boat forms, which one is more stable and why ? *(N.C.E.R.T.)*

Sec. 15.7

27. How can alkenes be prepared from (*i*) alcohol, and (*ii*) an alkyl halide ?

28. How can ethene be prepared from (*i*) ethanol and (*ii*) ethyl iodide ?

29. Give the mechanism of dehydration of alcohols.

30. Chloroethane is treated with alcoholic caustic potash ? Give another method by which the hydrocarbon obtained in the above reaction be prepared.

31. Explain the following with one example :

(*a*) Dehydrohalogenation (*b*) Dehydration.

32. Discuss briefly the mechanism of addition of Br_2 to alkenes.

33. How will you test the presence of double bond in an alkene ? Give chemical equations for the reactions involved.

34. Explain why rotation about carbon-carbon double bond is hindered ?

35. What is the origin of geometrical isomerism in alkenes ?

36. Which of the following alkenes will show geometrical isomerism ?

(*i*) Propene (*ii*) But-2-ene (*iii*) But-1-ene (*iv*) 2, 3-Dimethylbut-2-ene. [**Ans.** (*ii*) but-2-ene]

37. Draw structures of six isomeric pentenes, C_5H_{10}. Specify as E and Z to each geometric isomer. *(N.C.E.R.T.)*

38. Addition of HBr to propene yields 2-bromopropane while in presence of benzoyl peroxide, the same reaction yields 1- bromopropane. Explain and give mechanism. *(N.C.E.R.T.)*

39. What is peroxide effect ? Why is it applicable only in case of HBr and not in case of HCl or HI ?

40. (*a*) What is ozonolysis ? How can ozonolysis be used to determine the position of a double bond in an unknown alkene ?

(*b*) Give the name of the alkene which on ozonolysis gives only propanone.

41. Give reasons for the following :

(*i*) The melting point of *cis*-2-butene is lower than that of *trans*-2-butene.

(*ii*) Addition of Br_2 to cyclohexene gives only *trans*-addition product.

42. Write notes on : (*i*) Markovnikov's rule (*ii*) Polymerization of ethene and substituted ethenes.

Sec.15.8 **43.** How is acetylene prepared by (*i*) Kolbe's electrolysis (*ii*) Dehydrohalogenation of 1, 2-dihaloalkanes ?

44. What happens when calcium carbide is treated with water ? Give chemical equation for the reaction.

45. Describe with a labelled diagram the laboratory method of preparation of acetylene. How can it be converted to 1-butyne and 2-butyne ?

[Hint.
$$\underset{\text{Sod. acetylide}}{HC \equiv C^-Na^+} + \underset{\text{Ethyl iodide}}{CH_3CH_2I} \longrightarrow \underset{\text{1−Butyne}}{HC \equiv CCH_2CH_3} + NaI$$
$$\underset{\text{Disodium acetylide}}{Na^{+\,-}C{\equiv}C^-Na^+} + \underset{\text{Methyl iodide}}{2\,CH_3I} \longrightarrow \underset{\text{2−Butyne}}{CH_3C \equiv CCH_3} + 2\,NaI]$$

46. Write the equation for preparation of propyne.

47. Alkynes contain two π-bonds but still do not show geometrical isomerism whereas alkenes contain only one π- bond but show geometrical isomerism. Comment.

48. Comment upon acidic character of terminal alkynes.

49. Account for the order of acidity : acetylene > benzene > hexane. *(N.C.E.R.T.)*

50. Explain why are alkynes less reactive than alkenes towards electrophilic addition reactions ?

51. Explain why alkynes undergo nucleophilic addition reactions while simple alkenes do not ? *(N.C.E.R.T.)*

52. Discuss the stereochemistry of the reduction products obtained when but-2-yne is reduced with (*i*) Lindlar's catalyst (*ii*) Na in liquid NH_3.

53. Sketch the mechanism of addition of water to alkynes.

54. Discuss the polymerization reactions of alkynes.

55. Write short notes on : (*i*) Oxidation of alkynes (*ii*) Isomerization of alkynes.

56. How will you carry out the following conversions ?

(*i*) $H_3C{-}CH_2{-}CH = CH_2 \longrightarrow H_3C{-}CH_2{-}CH_2{-}CH_2OH$

(*ii*) $H_3C{-}CH_2{-}CH = CH_2 \longrightarrow H_3C{-}CH_2{-}CH(OH){-}CH_2OH$

(*iii*) $Br_2CH{-}CHBr_2 \longrightarrow HC \equiv CH$

(*iv*) $H_3CC \equiv CH \longrightarrow H_3C{-}COCH_3$ *(N.C.E.R.T.)*

Sec.15.9 **57.** Give one example of each of (*i*) a conjugated diene (*ii*) an isolated diene (*iii*) a cummulene.

58. Draw orbital diagram for 1, 3-pentadiene and 1, 4-pentadiene and explain which of the two is more stable.

59. Explain why addition of Br_2 to 1, 3-butadiene predominantly gives 1, 4-addition product when 1, 2-addition product is formed faster.

60. Discuss briefly the mechanism of addition of Br_2 to 1, 3-butadiene.

61. Write short notes on :
(*i*) Diels Alder reaction. (*ii*) Polymerization of conjugated dienes.

62. Why conjugated dienes undergo 1, 4-additions ? Explain. *(N.C.E.R.T.)*

63. If one mole of HBr is added to the following compounds, write down the structures of the products expected to be formed : (*i*) buta-1, 3-diene
(*ii*) penta-1, 3-diene (*iii*) penta-1, 4-diene (*iv*) but-1-ene. *(N.C.E.R.T.)*

Sec.15.10 **64.** Discuss the orbital structure of benzene.

65. Benzene contains three double bonds yet it behaves like a saturated compound. Explain.

66. Why is that the carbon-carbon bond distance in benzene is intermediate between carbon-carbon single bond and a carbon- carbon double bond.

67. What is meant by (*i*) delocalization (*ii*) resonance energy ?

68. Draw structures to show position isomerism in arenes.

69. How is resonance energy of benzene calculated ? Explain.

70. Write down the products of ozonolysis of 1, 2-dimethylbenzene (*o*-xylene). How does the result support Kekule structure of benzene ?

71. (*a*) Define substitution reactions. Why do arenes undergo substitution reactions even though they contain double bonds ?

(*b*) What happens when benzene is treated with :

(*i*) Br_2 in presence of anh. $AlCl_3$

(*ii*) Conc. H_2SO_4 at 330 K

(*iii*) Mixture of conc. H_2SO_4 and conc. HNO_3 at 330 K

(*iv*) Chloroethane and anhydrous $AlCl_3$ and

(*v*) Ethanoyl chloride in presence of anhydrous $AlCl_3$.

72. Why does benzene undergo electrophilic substitution reactions easily and nucleophilic substitution reactions with difficulty. *(N.C.E.R.T.)*

73. Discuss the mechanism of nuclear halogenation of arenes ?

74. Discuss the role of catalyst in the electrophilic substitution reactions in benzene.

75. Explain the term aromaticity ? How can Huckel rule be used to determine the aromaticity of a compound.

76. What are the necessary conditions for any compound to show aromaticity ? *(N.C.E.R.T.)*

77. Discuss the directive influence of nitro group and its effect on the reactivity of the compound.

78. How will you explain that methyl group is *o, p*- directing ?

79. Predict the products of the following reactions :

(*i*) Toluene $\xrightarrow[(ii)\ H^+/H_2O]{(i)\ \text{Alk. } KMnO_4,\ \Delta}$ (*ii*) Nitrobenzene $\xrightarrow[+\ \text{Conc. } H_2SO_4]{\text{Conc. } HNO_3}$

(*iii*) Ethylbenzene + acetic anhydride $\xrightarrow{\text{Anhyd. } AlCl_3}$

80. Write down the products and give the mechanism of the following reactions.
(*i*) $C_6H_5OH + H_2SO_4$ (conc.) (*ii*) $C_6H_5CH_3 + HNO_3$ and H_2SO_4 (conc.) *(N.C.E.R.T.)*

81. How will you convert the following compounds into benzene ?
(*i*) Acetylene (*ii*) Benzoic acid (*iii*) Hexane. *(N.C.E.R.T.)*

82. Comment upon the toxicity of polynuclear hydrocarbons.

Sec.15.11. to 15.12. **83.** What is straight run gasoline ? Describe the principle of obtaining straight run gasoline from petroleum.

84. Explain the term 'knocking'. What is the relationship between the structure of a hydrocarbon and knocking ?

85. (*i*) Describe a scale for measuring the quality of gasoline.

(*ii*) A sample of gasoline produces the same knocking as a mixture containing 35% *n*-heptane and 65% iso-octane. What is the octane number of the sample ? **[Ans. 65]**

86. Some fuels have octane number higher than 100. Explain. *(N.C.E.R.T.)*

87. Name three major products obtained by fractional distillation of petroleum and state one major use of each.

88. Name one anti-knocking agent ? What are its merits and demerits ?

89. Discuss the principle of petroleum refining.

90. What do the abbreviations LPG and CNG stand for ? Discuss their uses.

91. Explain the term 'octane number'. How can octane number of a fuel be increased ?

92. Describe two methods to improve the quality of a fuel used in an internal combustion engine.

93. Explain the following processes : (*i*) Cracking (*ii*) Reforming.

94. What are petrochemicals. Discuss their utility.

Long Answer Questions CARRYING 5 or more MARKS

Sec.15.1. to 15.3.

1. What are hydrocarbons ? How are they classified ?

2. Discuss briefly the structure of alkanes. What are the various methods used for their representation.

3. Draw all the structural isomers with the molecular formula, C_6H_{14}. Name each one of them by the IUPAC system. Also indicate primary, secondary, tertiary and quaternary carbons in each one of them.

4. Give the various methods used for the preparation of alkanes. Describe with labelled diagram the laboratory preparation of methane from sodium acetate and soda lime.

5. Discuss briefly the various physical properties and chemical reactions of alkanes.

Sec.15.4. to 15.6.

6. What do you understand by the term conformation ? Discuss briefly the various methods used for the representation of conformations of an alkane ?

7. Why does a planar structure for cyclohexane fail to account for its characteristics ? Draw the chair and the boat conformations of cyclohexane and explain their relative stability.

8. Draw the various conformations of *n*-butane and comment upon their relative stability.

Sec. 15.7

9. What are alkenes ? Discuss briefly the various methods used for the preparation of alkenes. Describe with a labelled diagram the laboratory preparation of ethene from ethanol.

10. Give an account of physical and chemical reactions of alkenes.

Sec.15.8. to 15.9.

11. What are alkynes ? How are they prepared in the laboratory ?

12. Give an account of physical properties and chemical reactions of alkynes.

13. What are alkadienes ? How are they classified ? Discuss their relative stabilities.

14. Discuss briefly the chemical reactions of dienes.

Sec.15.10

15. What are arenes ? How are they classified ? Discuss briefly the isomerism and nomenclature of arenes.

16. Discuss the structure of benzene laying emphasis on resonance and orbital structure.

17. Justify the statement : Benzene is a highly unsaturated compound but behaves like a saturated compound.

18. Discuss briefly the mechanism of electrophilic substitution reactions in benzene.

19. Explain the directive influence of various substituents and their effect on reactivity of arenes.

Sec.15.11. to 15.12.

20. What is petroleum ? How does it occur in nature ? Give its chemical composition. Describe the most accepted theory about its origin.

21. How is petroleum refined ? Give the composition, boiling ranges and uses of various fractions obtained from petroleum refining.

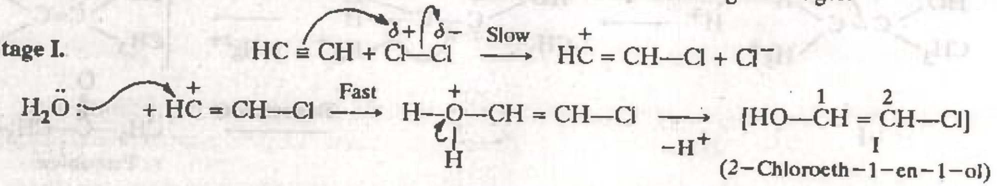
22. What are petrochemicals. Write the names and uses of some of them.

COMPETITION FOCUS

ADDITIONAL USEFUL INFORMATION

1. Mechanism of addition of elements of hypohalous acids to alkynes. Addition of Cl_2 or Br_2 in presence of H_2O to alkynes is an *electrophilic addition* reaction and occurs in the following two stages.

Stage I.

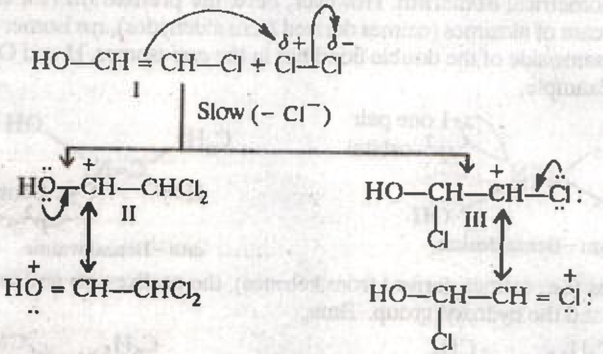


$$HC \equiv CH + \overset{\delta+}{Cl}-\overset{\delta-}{Cl} \xrightarrow{\text{Slow}} \overset{+}{H}C = CH-Cl + Cl^-$$

$$H_2\ddot{O}: + \overset{+}{H}C = CH-Cl \xrightarrow{\text{Fast}} H-\underset{H}{\overset{+}{O}}-CH = CH-Cl \xrightarrow[-H^+]{} \underset{\text{I}}{[HO-\overset{1}{C}H = \overset{2}{C}H-Cl]}$$

(2−Chloroeth−1−en−1−ol)

Stage II. The addition of Cl^+ to (I) can occur to give either carbocation (II or III) both of which are stabilized by resonance.

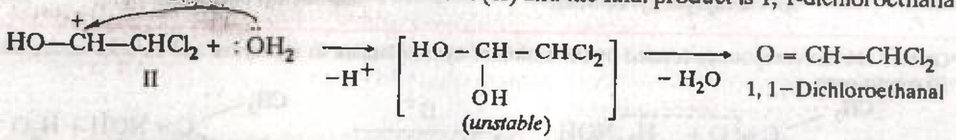


$$\underset{\text{I}}{HO-CH = CH-Cl} + \overset{\delta+}{Cl}-\overset{\delta-}{Cl} \xrightarrow{\text{Slow }(-\,Cl^-)}$$

$$\underset{\text{II}}{H\ddot{O}-\overset{+}{C}H-CHCl_2} \longleftrightarrow H\overset{+}{\ddot{O}} = CH-CHCl_2$$

$$\underset{\text{III}}{HO-\underset{Cl}{CH}-\overset{+}{C}H-\ddot{Cl}:} \longleftrightarrow HO-\underset{Cl}{CH}-CH = \overset{+}{Cl}:$$

In carbocation (II), the lone pair of electrons on O are present in a 2*p*-orbital and the carbon atom having +ve charge has an empty 2*p*-orbital. Therefore, carbocation (II) is stabilized by 2*p*-2*p* stabilization. In contrast in carbocation (III), the lone pair of electrons on Cl are in a 3*p*-orbital while the carbon atom having +ve charge like that of carbocation (II) has 2*p*-empty orbital. Since 2*p*-orbitals of O and C are almost of equal size, therefore, *carbocation (II) is better resonance stabilized than carbocation (III) in which orbitals of unequal sizes interact.* As a result, reaction occurs through the more stable carbocation (II) and the final product is 1, 1-dichloroethanal :

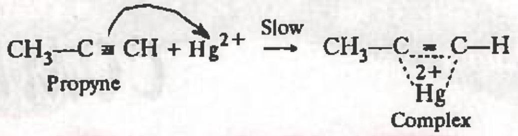


$$\underset{\text{II}}{HO-\overset{+}{C}H-CHCl_2} + :\ddot{O}H_2 \xrightarrow{-H^+} \underset{(\textit{unstable})}{\left[HO-\underset{OH}{CH}-CHCl_2\right]} \xrightarrow{-\,H_2O} \underset{\text{1, 1−Dichloroethanal}}{O = CH-CHCl_2}$$

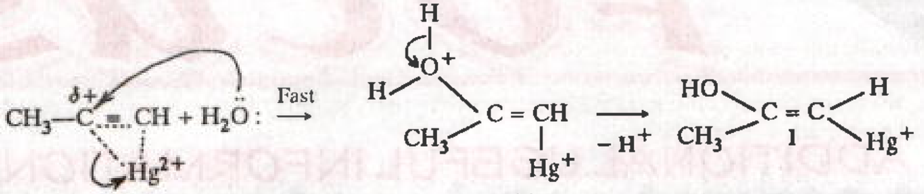
2. Mechanism of hydration of alkynes. Hydration of alkynes is an *electrophilic addition reaction* and is believed to occur in two steps. In the first step, the Hg^{2+} forms a complex with the triple bond which is then attacked by water to form an intermediate (I)

ADDITIONAL USEFUL INFORMATION contd.

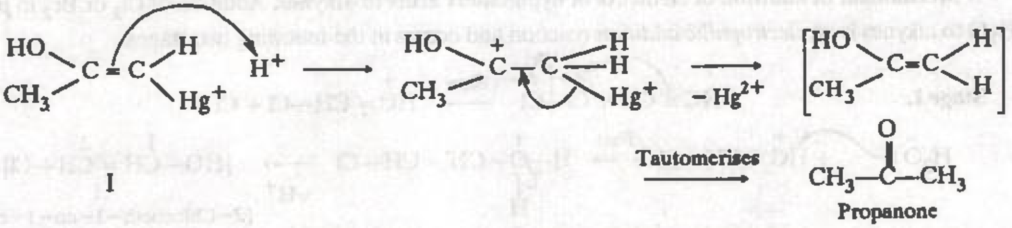
Step 1.



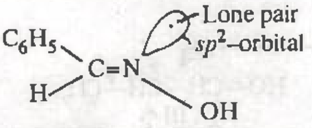
Step 2.



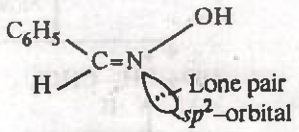
Protonation of intermediate (I) followed by loss of Hg^{2+} gives the enol (II) which subsequently readily tautomerises to give the corresponding carbonyl compound



3. Geometrical isomerism in oximes and azo-compounds. Due to restricted rotation around C = N, oximes* like alkenes also show geometrical isomerism. However, here, the prefixes *syn* (for cis) and *anti* (for trans) are more commonly used. In case of aloximes (oximes derived from aldehydes), *syn* isomer is the one in which H atom and OH group lie on the same side of the double bond but in the *anti*-isomer, H and OH lie on the opposite sides of the double bond. For example,

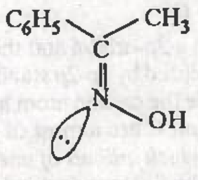


syn–Benzaldoxime

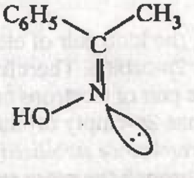


anti–Benzaldoxime

In case of ketoximes (*i.e.*, oximes derived from ketones), the prefixes *syn* and *anti* indicate the relationship of the *first* group named and the hydroxyl group. Thus,



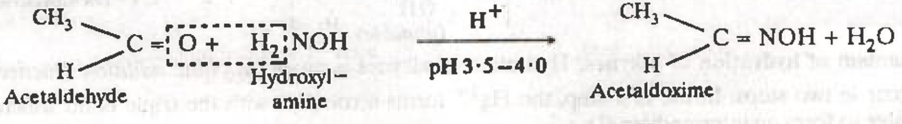
syn-Methyl phenyl ketoxime



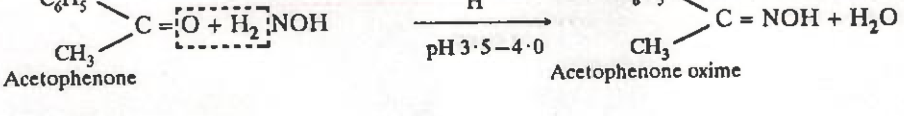
anti-Methyl phenyl ketoxime

---

*Oximes are the compounds formed by the action of hydroxylamine to aldehydes and ketones under weakly acidic (pH 3·5 – 4·0) conditions :



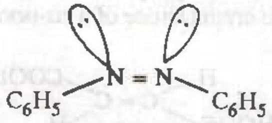
$$CH_3CH{=}O + H_2NOH \xrightarrow[\text{pH } 3\cdot5-4\cdot0]{H^+} CH_3CH{=}NOH + H_2O$$



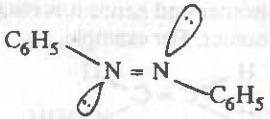
$$(C_6H_5)(CH_3)C{=}O + H_2NOH \xrightarrow[\text{pH } 3\cdot5-4\cdot0]{H^+} (C_6H_5)(CH_3)C{=}NOH + H_2O$$

ADDITIONAL USEFUL INFORMATION contd.

Similarly, due to restricted rotation around N = N, azo* compounds also show geometrical isomerism. For example,

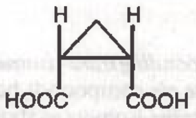


syn – Azobenzene

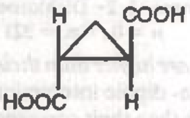


anti – Azobenzene

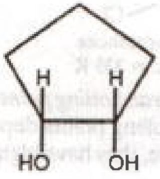
4. Geometrical isomerism in cyclic compounds. Disubstituted cyclic compounds also show geometrical isomerism even though they do not contain a double bond. This is due to the reason that because of rigid ring structures, these compounds have hindered rotation even around carbon-carbon single bonds and hence show geometrical isomerism. For example,



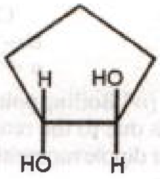
cis-Cyclopropane-1, 2-dicarboxylic acid



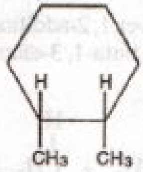
trans-Cyclopropane 1, 2-dicarboxylic acid



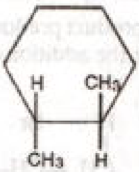
cis-Cyclopentane-1, 2-diol



trans-Cyclopentane-1, 2-diol



cis-1, 2,-Dimethylcyclohexane

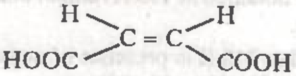


trans-1, 2, Dimethylcyclohexane

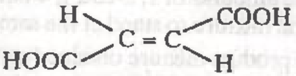
Geometrical isomerism plays an important role in the chemistry of vision. For example, when light falls on the retina of the eye, the first step in the visual process is the conversion of one geometrical isomer (*cis*-retinal) to another (*trans*- retinal).

5. Distinction between cis- and trans-isomers. The distinction between *cis*- and *trans*-isomers of a compound can be made on the basis of their physical properties such as melting point, boiling point, solubility, dipole moment etc. For example,

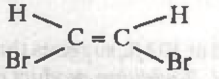
(i) Melting points. *In general, the melting point of a trans- isomer is higher than that of the corresponding cis-isomer.* This is due to the reason that the molecules of a *trans*- isomer are more symmetrical and hence fit more closely in the crystal lattice as compared to the molecules of a *cis*- isomer. For example,



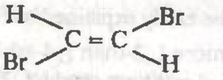
Maleic acid (*cis*–isomer)
m.p. 403 K



Fumaric acid (*trans*–isomer)
m.p. 575 K



cis–1, 2–Dibromoethene
m.p. 220 K



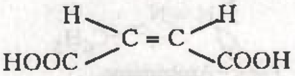
trans–1, 2–Dibromoethene
m.p. 260 K

---

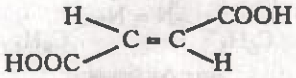
*Compounds containing N = N are called **azo compounds.**

ADDITIONAL USEFUL INFORMATION contd.

(ii) Solubility. *In general, solubility of a cis- isomer is higher than that of the corresponding trans-isomer.* This is due to the reason that the molecules of a *cis-* isomer are less tightly held in the crystal lattice than the corresponding trans-isomer and hence it is easier to break the crystal lattice of a *cis*-isomer as compared to the corresponding *trans*-isomer. For example,

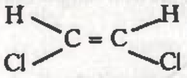


Maleic acid
(Solubility : 79 g/100 ml H_2O)

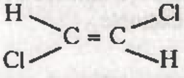


Fumaric acid
(Solubility : 0·7 g/100 ml H_2O)

(iii) Dipole moments. *In general, cis-isomers have higher dipole moments than the corresponding trans-isomers which may even be zero when the two atoms or groups on each carbon of the double bond are the same.* For example,



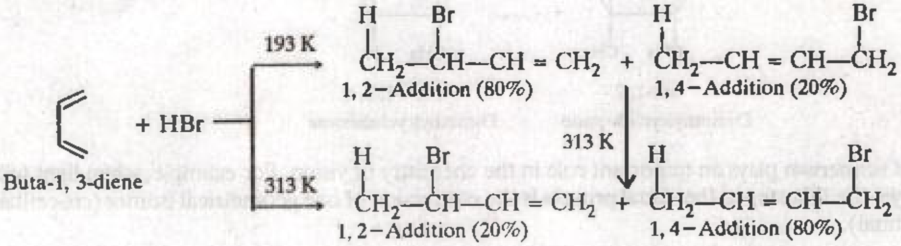
cis−1, 2−Dichloroethene
μ = 1·85 D ; b.p. = 333 K



trans−1, 2−Dichloroethene
μ = 0 ; b.p. = 321 K

(iv) **Boiling points.** *In general, boiling points of cis- isomers are higher than their corresponding trans- isomers.* This is due to the reason that boiling points depend upon dipole- dipole interactions. Since *cis*-compounds have higher dipole moments, therefore, they have higher boiling points than their corresponding *trans*-isomers as shown above.

6. 1, 2-versus 1, 4-addition to conjugated dienes—Rate *versus* Equilibrium. We have explained above that why the addition of Br_2 and HBr to buta-1, 3-diene gives a mixture of 1, 2-and 1, 4-addition products. Now the question arises as to why 1, 4-addition product predominates over 1, 2-addition product at ordinary temperatures. To answer this question, let us consider the addition of HBr to buta-1, 3-diene at different temperatures :



The following are some of the salient features of this reaction :

(*i*) At 193 K, the addition of HBr to 1, 3-butadiene gives a mixture of 80% of the 1, 2-addition product and 20% of the 1, 4- addition product whereas at 313K, a mixture of 20% of 1, 2-and 80% of 1, 4-addition product is obtained.

(*ii*) The relative amounts of 1, 2-and 1, 4-addition products obtained at 193 K remain unchanged no matter how long we allow the mixture to stand at the same temperature.

(*iii*) When the product mixture obtained at 193 K is heated to 313 K in presence of more HBr, the relative amounts of the 1, 2 and 1, 4-addition products slowly change from 80 : 20 to 20 : 80.

(*iv*) Although each product (1, 2-or, 1, 4-) is stable at low temperatures, prolonged heating of either the 1, 2- or 1, 4- addition product gives the same mixture.

These facts can be easily explained as follows :

(*i*) The fact that more 1, 2-than 1, 4-addition product is obtained at 193 K, suggests that *1, 2-addition product is formed faster than 1, 4-addition product. This means that E_{act} for 1, 2-addition product is lower than that for 1, 4- addition product.*

ADDITIONAL USEFUL INFORMATION contd.

(*ii*) The fact that each product remains unchanged at 193 K, suggests that *the proportion in which they are isolated is the same in which they are initially formed. In other words, at 193 K, the relative amounts of the two products are governed by their relative rates. Thus, the addition of HBr to buta-1, 3-diene at 193 K, is* **kinetically controlled.**

(*iii*) The fact that at higher temperature (313 K), the 1, 4-addition product predominates over 1, 2-addition product, *suggests that 1, 4-addition product is thermodynamically more stable than the 1, 2-addition product.*

(*iv*) The fact that each product (1, 2- or 1, 4-) is converted into the same mixture on heating suggests that this mixture is obtained as a result of equilibrium between the two products. Since 1, 2-addition product is thermodynamically less stable than 1, 4-addition product, therefore, 1, 2-addition product is converted into 1, 4-addition product at a faster rate than the rate at which 1, 4-addition product is converted back to 1, 2-addition product. In other words, the relative amounts of the products isolated at 313K are governed by their relative stability. Thus, *the addition of HBr to buta-1, 3-diene at 313 K is* **thermodynamically controlled.**

With these points in mind, let us examine the addition of HBr to buta-1, 3-diene in little more detail by drawing potential energy diagram for this reaction (Fig. 15.34).

As stated above, the first step in the addition of HBr to buta-1, 3-diene is the addition of a proton to give the allylic carbocation (I) which then gives both 1, 2-and 1, 4-addition products. Since E_{act} is less for 1, 2- addition than for 1, 4-addition, the 1, 2-addition product is *initially* formed faster than the 1, 4-addition product.

Now, in principle, each product can undergo ionization to give back the same allylic carbocation (I). But the E_{act} for the ionization for 1, 4-addition product to allylic carbocation (I) is much higher than for 1, 2-addition product. As a result, 1, 4-addition product will ionize much more slowly than 1, 2-addition product. Equilibrium is finally reached when the rates of the two opposing reactions (formation and ionization of each product) are equal. Thus, 1, 2-addition product is formed rapidly but also ionizes rapidly but the 1, 4- addition product is formed slowly but ionizes even more slowly. In other words, 1,4-addition product once formed tends to stay and hence constitutes the major product of the reaction at temperatures high enough for equilibrium to be reached.

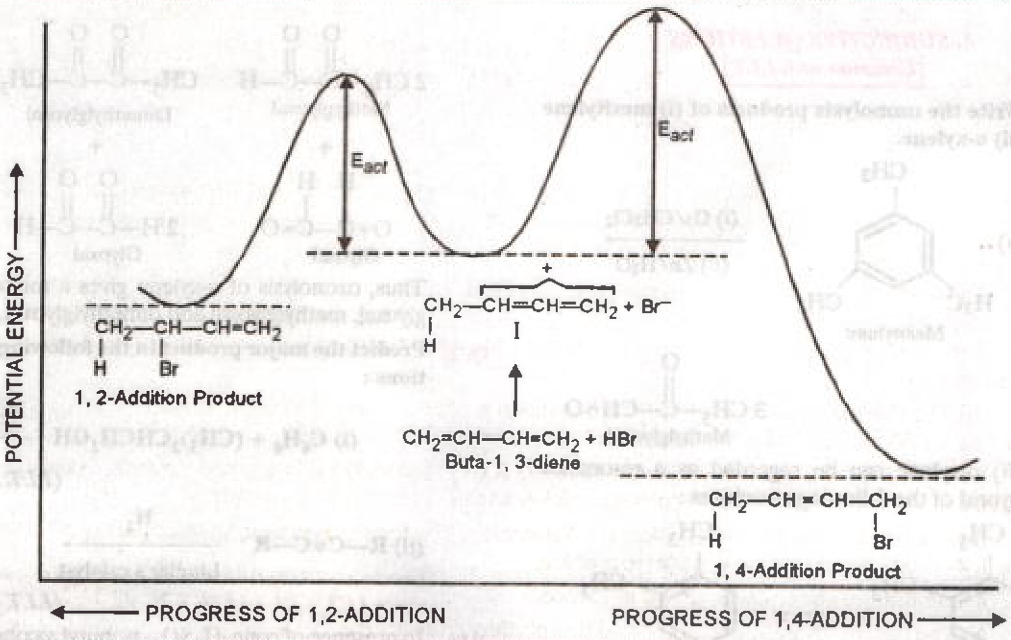
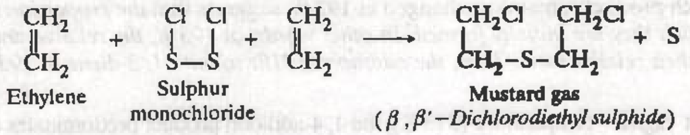


FIGURE 15.34. Potential energy changes during the progress of the reaction : 1, 2-*vs*.-1, 4-addition.

7. War Gases. Two important war gases are : (*i*) *mustard gas* and (*ii*) *lewisite*

Mustard gas is obtained by the reaction of ethylene with sulphur monochloride.

ADDITIONAL USEFUL INFORMATION contd.

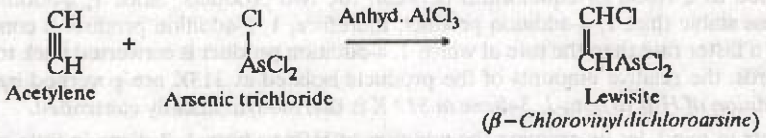


$$CH_2{=}CH_2 + Cl{-}S{-}S{-}Cl + CH_2{=}CH_2 \longrightarrow ClCH_2{-}CH_2{-}S{-}CH_2{-}CH_2Cl + S$$

Ethylene   Sulphur monochloride   Mustard gas (β, β′–*Dichlorodiethyl sulphide*)

It was used as a war gas in World war I.

Lewisite is obtained by the action of arsenic trichloride with acetylene in presence of anhydrous $AlCl_3$.

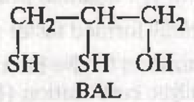


$$HC{\equiv}CH + AsCl_3 \xrightarrow{\text{Anhyd. } AlCl_3} ClCH{=}CHAsCl_2$$

Acetylene   Arsenic trichloride   Lewisite (*β–Chlorovinyldichloroarsine*)

It is more poisonous than mustard gas and was used in World war—II.

Lewisite is more poisonous than mustard gas. The British chemists developed an antidote for Lewisite and named it as **BAL** (British Anti Lewisite).



$$\underset{SH}{CH_2}{-}\underset{SH}{CH}{-}\underset{OH}{CH_2}$$

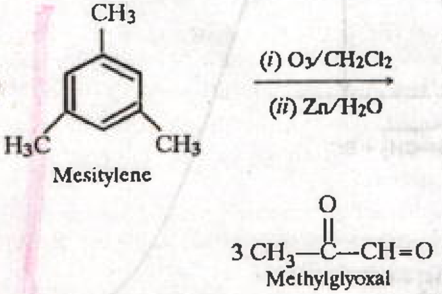
BAL

C.B.S.E.-P.M.T. (MAINS) SPECIAL

A. SUBJECTIVE QUESTIONS
(Common with I.I.T.)

Q. 1. Write the ozonolysis products of (i) mesitylene (ii) o-xylene.

Ans. (*i*)

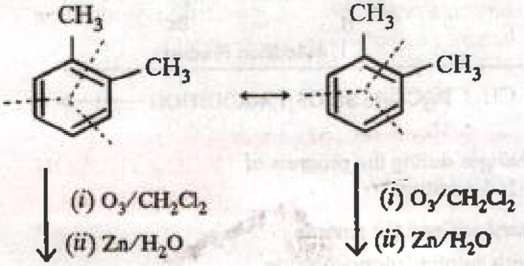


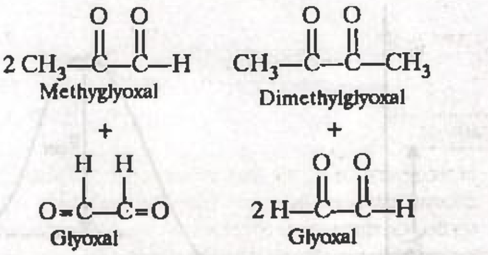
Mesitylene

$$3\,CH_3{-}\overset{O}{\overset{\|}{C}}{-}CH{=}O$$

Methylglyoxal

(*ii*) *o*-xylene can be regarded as a resonance hybrid of the following structures :





$$2\,CH_3{-}\overset{O}{\overset{\|}{C}}{-}\overset{O}{\overset{\|}{C}}{-}H \qquad CH_3{-}\overset{O}{\overset{\|}{C}}{-}\overset{O}{\overset{\|}{C}}{-}CH_3$$

Methylglyoxal   Dimethylglyoxal

$$+ \qquad\qquad +$$

$$O{=}\underset{}{\overset{H}{\overset{|}{C}}}{-}\overset{H}{\overset{|}{C}}{=}O \qquad 2\,H{-}\overset{O}{\overset{\|}{C}}{-}\overset{O}{\overset{\|}{C}}{-}H$$

Glyoxal   Glyoxal

Thus, ozonolysis of *o*-xylene gives a mixture of glyoxal, methylglyoxal and dimethylglyoxal.

Q. 2. Predict the major product in the following reactions :

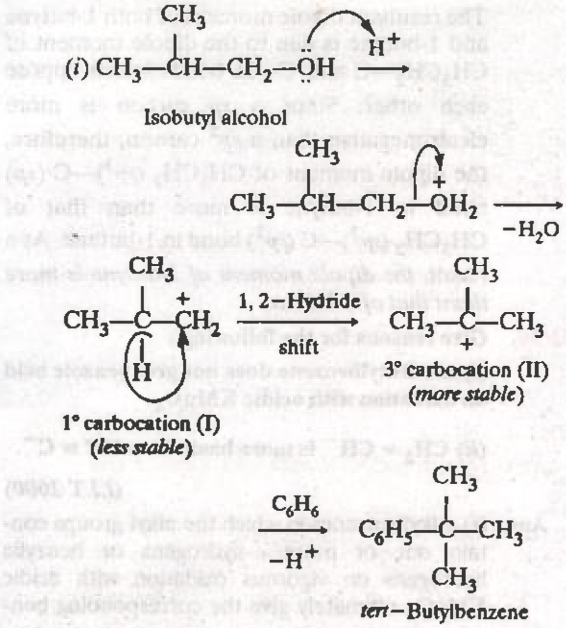
(i) $C_6H_6 + (CH_3)_2CHCH_2OH \xrightarrow{H_2SO_4}$

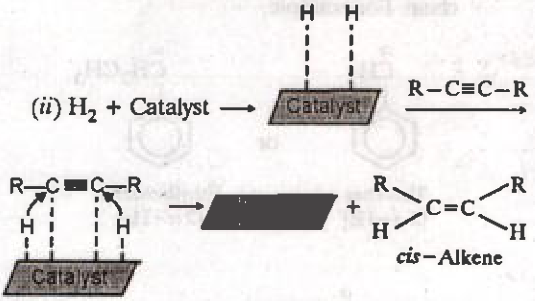
(I.I.T. 1994)

(ii) $R{-}C{\equiv}C{-}R \xrightarrow[\text{Lindlar's catalyst}]{H_2}$

(I.I.T. 1994)

Ans. In presence of conc. H_2SO_4, isobutyl alcohol first gives 1° carbocation (I) which then rearranges to the more stable 3° carbocation (II) by 1, 2-hydride shift. Carbocation (II) then reacts with benzene to form *tert*-butylbenzene.





Hydrogenation of alkynes in presence of Lindlar's catalyst gives *cis*-alkenes since the hydrogen absorbed on the surface of the catalyst gets transferred to the alkyne molecule from the same face.

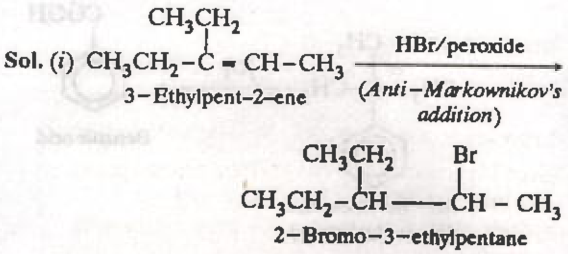
Q. 3. Give the structures of the major products from 3- ethylpent-2-ene under each of the following reaction conditions.

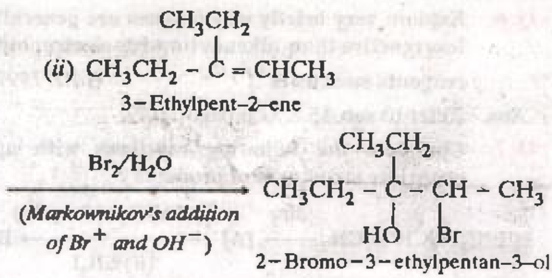
***(a)* HBr in the presence of peroxide**

***(b)* Br_2 / H_2O**

(I.I.T. 1996)

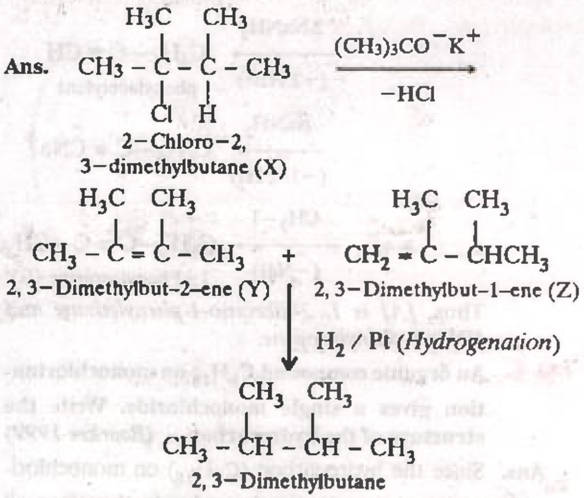
Sol. *(i)*





Q. 4. An alkyl halide, X, of formula $C_6H_{13}Cl$ on treatment with potassium tertiary butoxide gives two isomeric alkenes Y and Z (C_6H_{12}). Both alkenes on hydrogenation give 2, 3-dimethylbutane. Predict the structures of X, Y and Z. *(I.I.T. 1996)*

Ans.



Q. 5. A hydrocarbon A, adds one mole of hydrogen in presence of platinum catalyst to form n-hexane. When A is oxidised vigorously with $KMnO_4$, a single carboxylic acid containing three carbon atoms is isolated. Give the structure of A and explain. *(I.I.T. 1997)*

Sol. *(i)* Since the hydrocarbon A adds one molecule of H_2 in presence of Pt to form *n*-hexane, therefore, A *must be an hexene.*

(ii) Since A on vigorous oxidation with $KMnO_4$ gives a single carboxylic acid containing three carbon atoms, therefore, A *must be a symmetrical hexene, i.e., hex-3-ene.*

$$\underset{\text{Hex-3-ene (A)}}{CH_3CH_2CH{=}CHCH_2CH_3} \xrightarrow[KMnO_4]{[O]} \underset{\text{Propionic acid}}{2\,CH_3CH_2COOH}$$

Thus, the given hydrocarbon A is hex-3-ene.

Q. 6. **Explain very briefly why alkynes are generally less reactive than alkenes towards electrophilic reagents such as H^+** *(I.I.T. 1997)*

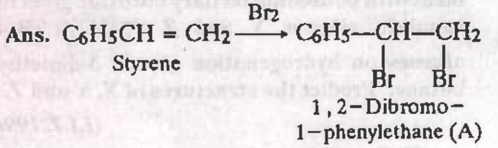
Ans. Refer to sec. 15.8.7 on page 15/49.

Q. 7. **Complete the following reactions with appropriate structures of products ?**

$$C_6H_5CH = CH_2 \xrightarrow{Br_2} [A] \xrightarrow[(ii)\ CH_3I]{(i)\ NaNH_2\ (3.0\ equiv.)} B$$

(I.I.T. 1998)

Ans.



$$\underset{\text{Styrene}}{C_6H_5CH = CH_2} \xrightarrow{Br_2} \underset{\substack{\text{1, 2-Dibromo-}\\ \text{1-phenylethane (A)}}}{C_6H_5-\underset{Br}{CH}-\underset{Br}{CH_2}}$$

$$\xrightarrow[(-2\,HBr)]{2\,NaNH_2} \underset{\text{phenylacetylene}}{C_6H_5—C \equiv CH}$$

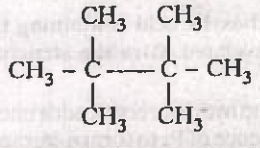
$$\xrightarrow[(-1/2\,H_2)]{NaNH_2} C_6H_5—C \equiv \bar{C}Na^+$$

$$\xrightarrow[(-NaI)]{CH_3-I} \underset{\text{1-Phenylpropyne (B)}}{C_6H_5—C \equiv C—CH_3}$$

Thus, *[A] is 1, 2-dibromo-1-phenylethane and [B] is 1-phenylpropyne.*

Q. 8. **An organic compound C_8H_{18} on monochlorination gives a single monochloride. Write the structure of the hydrocarbon.** *(Roorkee 1999)*

Ans. Since the hydrocarbon (C_8H_{18}) on monochlorination gives a single monochloride, therefore, all the 18 H-atoms are equivalent. The only such hydrocarbon is 2, 2, 3, 3-tetramethylbutane, *i.e.*

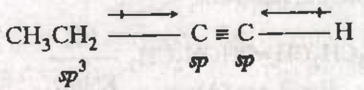


$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\underset{CH_3}{\overset{CH_3}{C}}-CH_3$$

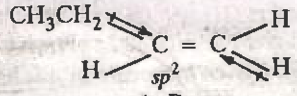
Q. 9. **Which of the following has larger dipole moment? Explain.**

1-Butyne or 1-Butene *(Roorkee 1999)*

Ans. The direction of dipole moments of individual bonds in 1-butyne and 1-butene are shown below:



1-Butyne



1-Butene

The resultant dipole moment of both 1-butyne and 1-butene is due to the dipole moment of CH_3CH_2—C and C—H bonds which oppose each other. Since a *sp* carbon is more electronegative than a sp^2 carbon, therefore, the dipole moment of CH_3CH_2 (sp^3)—C (sp) bond in 1-butyne is more than that of CH_3CH_2 (sp^3)—C (sp^2) bond in 1-butene. As a result, *the dipole moment of 1-butyne is more thant that of 1-butene.*

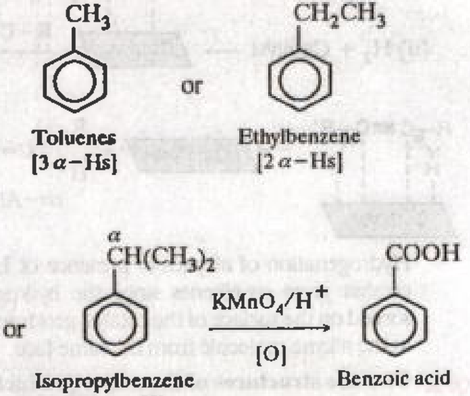
Q. 10. **Give reasons for the following :**

(*i*) *tert*-Butylbenzene does not give benzoic acid on oxidation with acidic $KMnO_4$.

(*ii*) $CH_2 = CH^-$ is more basic than $HC \equiv C^-$.

(I.I.T. 2000)

Ans. (*i*) Alkylbenzenes in which the alkyl groups contain one or more α-hydrogens or benzylic hydrogens on vigorous oxidation with acidic $KMnO_4$ ultimately give the corresponding benzoic acids irrespective of the length of the carbon chain. For example,



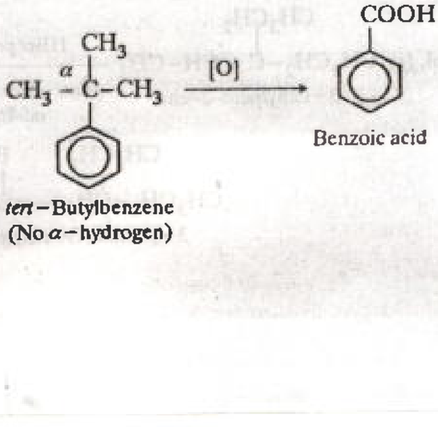
Toluenes [3 α–Hs]

Ethylbenzene [2 α–Hs]

Isopropylbenzene [one α–H]

Benzoic acid

tert-Butylbenzene, on the other hand, does not contain any α-hydrogen or benzylic hydrogen and hence does not undergo oxidation to give benzoic acid.

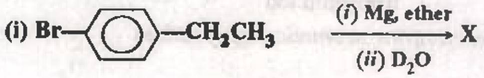


tert–Butylbenzene (No α–hydrogen)

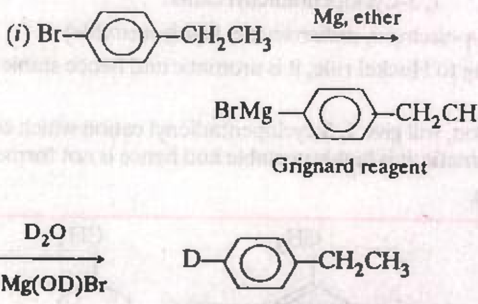
Benzoic acid

(*ii*) $CH_2 = CH^-$ is the conjugate base of the acid $H_2C = CH_2$ and $HC \equiv C^-$ is the conjugate base of the acid $HC \equiv CH$. We know that stronger the acid, weaker is the conjugate base. Since $HC \equiv CH$ is stronger acid than $CH_2 = CH_2$, therefore, $CH_2 = CH^-$ is a stronger base than $HC \equiv C^-$.

Q. 11. Give structure of the products (X) and Y in the following reactions :



$$\text{(ii) } 2\,HC \equiv C{-}H \xrightarrow[O_2]{Cu^{2+}} Y$$ *(Roorkee 2001)*

Ans. 

p−Deuteratedethylbenzene

$$(ii)\ 2\,HC \equiv CH + \frac{1}{2}O_2 \xrightarrow[\textit{(Erlington coupling)}]{Cu^{2+}} \underset{\text{Buta−1, 3−diyne}}{HC{\equiv}C{-}C{\equiv}CH} + H_2O$$

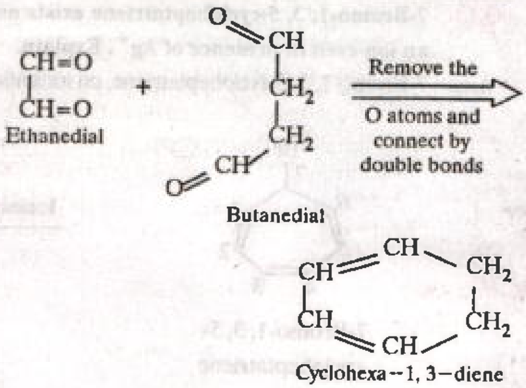
Q. 12. (*a*) Find the structure of a hydrocarbon that produces one mole each of ethanedial and butanedial on ozonolysis.

(*b*) Devise a scheme for the synthesis of *n*-butane using CH_3I as the only carbon source. Can you employ the reactions in your scheme to synthesize propane in fairly pure state ? Explain.

(*c*) How many monochloro products would you expect when 2-methylbutane is chlorinated ? Write their structures and IUPAC names. One of them may have stereoisomer. Indicate it.

(*d*) Which of the isomers will not give one product only on dehydrohalogenation with alcoholic KOH ? *(West Bengal J.E.E. 2003)*

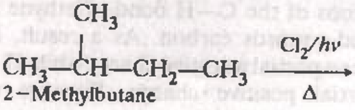
Ans. (*a*) The structures of the ozonolysis products are :



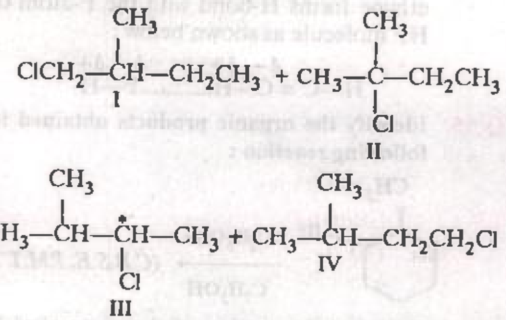
(*b*)
$$\underset{\text{Methyl iodide}}{2\,CH_3I} \xrightarrow[\text{Wurtz reaction}]{\text{Na, dry ether}} \underset{\text{Ethane}}{CH_3{-}CH_3} \xrightarrow[\text{or } SO_2Cl_2/RCOOR]{(i)\ Cl_2/h\nu} \underset{\text{Ethyl chloride}}{CH_3CH_2Cl} \xrightarrow[\text{Wurtz reaction}]{\text{Na, dry ether}} CH_3CH_2{-}CH_2CH_3$$

Propane cannot be synthesized by the above scheme in fairly pure state because Wurtz reaction between CH_3I and C_2H_5I will give three products, *i.e.*, ethane, propane and butane.

(*c*) Chlorination of 2-methylbutane gives a mixture of four isomeric monochloro products (I-IV) :



$$\underset{\text{2−Methylbutane}}{CH_3{-}\overset{CH_3}{\overset{|}{C}H}{-}CH_2{-}CH_3} \xrightarrow[\Delta]{Cl_2/h\nu}$$



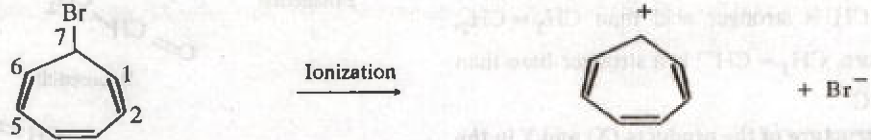
$$\underset{\text{I}}{ClCH_2{-}\overset{CH_3}{\overset{|}{C}H}{-}CH_2CH_3} + \underset{\text{II}}{CH_3{-}\overset{CH_3}{\overset{|}{C}}(Cl){-}CH_2CH_3} + \underset{\text{III}}{CH_3{-}\overset{CH_3}{\overset{|}{C}H}{-}\overset{*}{C}H(Cl){-}CH_3} + \underset{\text{IV}}{CH_3{-}\overset{CH_3}{\overset{|}{C}H}{-}CH_2CH_2Cl}$$

Product (III) has a chiral carbon and hence exists in two stereoisomeric forms which are optically active.

(*d*) Isomers (II) and (III) on dehydrohalogenation will give two products each while isomers (I) and (IV) will give one product each. Write the products yourself.

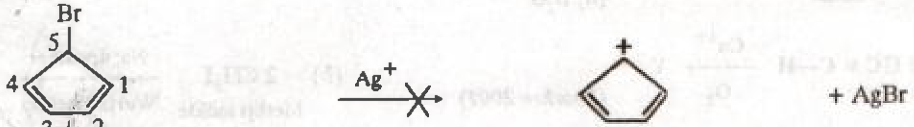
Q.13. 7-Bromo-1, 3, 5-cycloheptatriene exists as an ion whereas 5-bromo- 1, 3-cyclopentadiene does not form an ion even in presence of Ag^+. Explain.

Ans. 7-Bromo-1, 3, 5-cycloheptatriene, on ionization, gives tropylium ion. Since tropylium ion contains 6π-electrons which are completely delocalized. Therefore, according to Huckel rule, it is aromatic and hence stable. Being highly stable, it is easily formed.



7-Bromo-1, 3, 5-cycloheptatriene

Tropylium ion (*6π-electrons, aromatic, highly stable*)



5-Bromo-1, 3, cyclopentadiene

1, 3-Cyclopentadienyl cation (*4π-electrons, antiaromatic, highly unstable*)

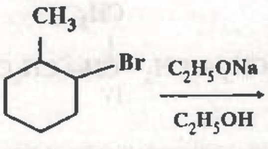
In contrast, 5-bromo-1, 3-cyclopentadiene, on ionization, will give 1, 3-cyclopentadienyl cation which contains 4 π-electrons and hence is *antiaromatic*. Being antiaromatic, it is highly unstable and hence is not formed even in the presence of Ag^+ ion which facilitates ionization.

Q. 14. Why HF forms H-bonding with ethyne even though it is non-polar in nature ? *(C.B.S.E. P.M.T. 2004)*

Ans. Due to *sp*-hybridization of carbon, the electrons of the C—H bond of ethyne are attracted towards carbon. As a result, carbon carries a partial negative charge while H carries a partial positive charge. Because of the presence of partial positive charge on H, ethyne forms H-bond with the F-atom of the HF molecule as shown below :

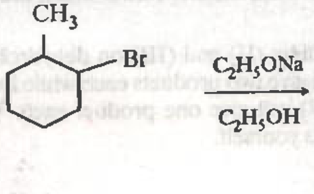
$$H—\overset{\delta-}{C} \equiv \overset{\delta+}{C}—H..........\overset{\delta-}{F}—\overset{\delta+}{H}$$

Q. 15. Identify the organic products obtained in the following reaction :



(C.B.S.E. P.M.T. 2004)

Ans. Dehydrohalogenation of the given alkyl halide can, in principle, yield alkenes (I) and (II)



I (*major*) II (*minor*)

But according to Saytzeff rule, more highly substituted alkene, *i.e.*, I being more stable is the major product of dehydrohalogenation. Therefore, in the above reaction, alkene (I) alongwith a small amount of alkene (II) is produced.

Q. 16. Write all the important conformations of n-butane. *(C.B.S.E. P.M.T. 2004)*

Ans. Refer to Fig. 15.11 on page 15/19.

Q. 17. Give the Newman configuration of the least staggered form of n-butane. Due to which of the following strain it is destabilized ?

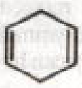
(i) torsional strain (ii) van der Waal's strain (iii) combination of the two.

Ans. Least stable staggered form of *n*-butane is *gauche* form. Since in this conformation, all the tetrahedral carbons attached to one another have staggered bonds, therefore, it is free from torsional strain. Further, in *anti*-form, the two CH_3 groups are 180° apart but in gauche form they are only 60° apart. Therefore, *gauche* form is less stable than *anti*-form due to *van der Waal's* strain.

B. PROBLEMS

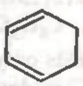
Problem 1. **Two isomeric cyclic dienes X and Y having molecular formula C_6H_8 on hydrogenation give cyclohexane as the only product. A mixture of these two dienes on reductive ozonolysis gives succinaldehyde, propanal, 3-dial and glyoxal. Deduce the structures of dienes X and Y.**

Solution. Since X and Y on hydrogenation give cyclohexane as the only product, therefore, X and Y *must be cyclohexadienes.* The two possible cyclohexadienes are



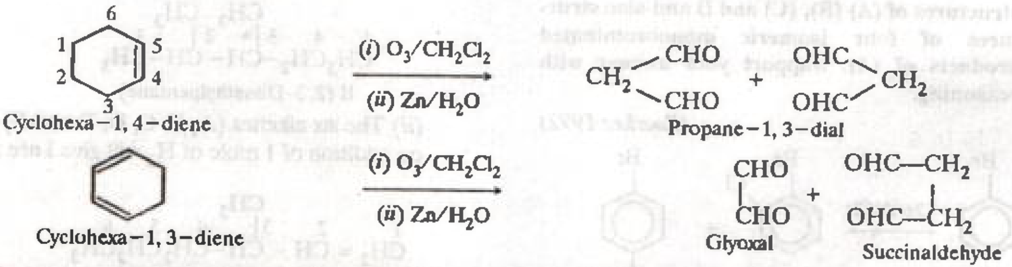
and

Cyclohexa-1, 4-diene, X



Cyclohexa-1, diene, Y

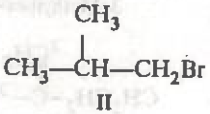
Whereas reductive ozonolysis of X will two molecules of propane-1, 3-dial, reductive ozonolysis of Y will give succinaldehyde and glyoxal as shown below :



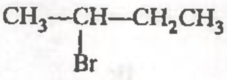
Problem 2. **An alkyl halide A with molecular formula, C_4H_9Br on dehydrobromination with alcoholic KOH gave a single alkene, C_4H_8. Photochemical bromination of A gave a single dibromo compound B, $C_4H_8Br_2$. A reacts with Mg in ether to form a Grignard reagent which on treatment with water gave an alkane C. Identify A, B and C.**

Solution. (*i*) Possible structures of alkyl halide A are :

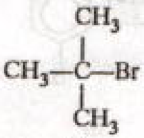
(*i*) $CH_3CH_2CH_2Br$
I



$CH_3-\overset{CH_3}{\overset{|}{C}}H-CH_2Br$
II



$CH_3-\underset{Br}{\underset{|}{C}}H-CH_2CH_3$
III

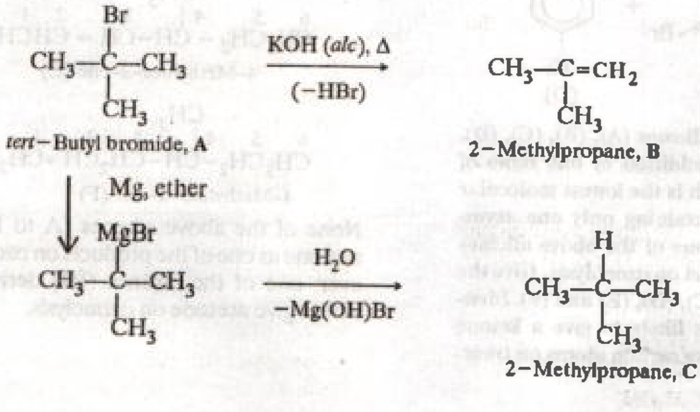


$CH_3-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-Br$
IV

(*ii*) Since dehydrobromination of A with *alc.* KOH gave a single alkene, *therefore,* A *could be* **I, II** or **IV.**

(*iii*) Since photobromination of A gave a single dibromo compound, therefore, all the H-atoms in the alkyl halide are similar. If this is so then the alkyl halide A must *tert*-butyl bromide (IV).

(*iv*) If A is *tert*-butyl bromide, then **B** must 1, 2- dibromo-2-methylpropane and **C** must be 2-methylpropane as shown below :

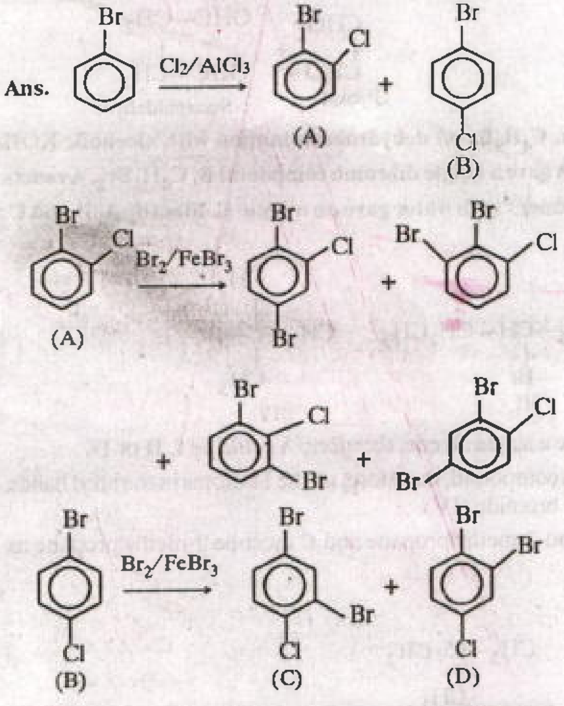


I.I.T. (MAINS) SPECIAL

Q. 1. When bromobenzene is monochlorinated, two isomeric compounds (A) and (B) are obtained. Monobromination of (A) gives several isomeric products of molecular formula, $C_6H_3ClBr_2$ while monobromination of (B) yields only two isomers (C) and (D). Compound (C) is identical with one of the compounds obtained from bromination of (A), however, (D) is totally different from any of the isomeric compounds obtained from the bromination of (A). Give structures of (A) (B), (C) and D and also structures of four isomeric monobrominated products of (A). Support your answer with reasoning.

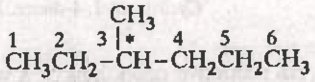
(Roorkee 1992)

Ans.



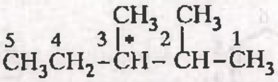
Q. 2. There are six different alkenes (A), (B), (C), (D), (E) and (F). Each on addition of one mole of hydrogen gives (G) which is the lowest molecular weight hydrocarbon containing only one asymmetric carbon atom. None of the above alkenes gives acetone as a product on ozonolysis. Give the structures of (A), (B), (C), (D), (E) and (F). Identify the alkene which is likely to give a ketone containing more than five carbon atoms on treatment with a warm concentrated solution of alkaline $KMnO_4$. *(Roorkee 1992)*

Ans. (*i*) Lowest molecular weight hydrocarbon (G) having an asymmetric carbon atom (marked by an asterisk) can have two structures, *i.e.*, I and II



$$\overset{1}{C}H_3\overset{2}{C}H_2-\overset{\overset{CH_3}{|*}}{\overset{3}{C}}H-\overset{4}{C}H_2\overset{5}{C}H_2\overset{6}{C}H_3$$

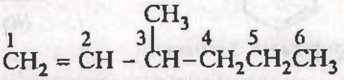
I (3–Methylhexane)



$$\overset{5}{C}H_3\overset{4}{C}H_2-\overset{\overset{CH_3}{|*}}{\overset{3}{C}}H-\overset{\overset{CH_3}{|}}{\overset{2}{C}}H-\overset{1}{C}H_3$$

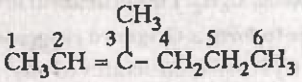
II (2, 3–Dimethylpentane)

(*ii*) The six alkenes (A, B, C, D, E and F) which on addition of 1 mole of H_2 will give I are :



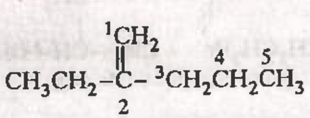
$$\overset{1}{C}H_2=\overset{2}{C}H-\overset{\overset{CH_3}{|}}{\overset{3}{C}}H-\overset{4}{C}H_2\overset{5}{C}H_2\overset{6}{C}H_3$$

3–Methylhex–1–ene (A)



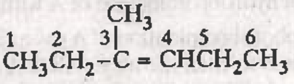
$$\overset{1}{C}H_3\overset{2}{C}H=\overset{\overset{CH_3}{|}}{\overset{3}{C}}-\overset{4}{C}H_2\overset{5}{C}H_2\overset{6}{C}H_3$$

3–Methylhex–2–ene (B)



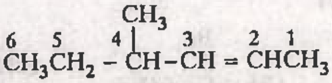
$$CH_3CH_2-\underset{2}{\overset{\overset{^1CH_2}{\|}}{C}}-{}^3CH_2\overset{4}{C}H_2\overset{5}{C}H_3$$

2–Ethylpent–1–ene (C)



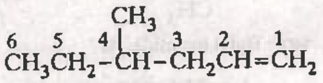
$$\overset{1}{C}H_3\overset{2}{C}H_2-\overset{\overset{CH_3}{|}}{\overset{3}{C}}=\overset{4}{C}H\overset{5}{C}H_2\overset{6}{C}H_3$$

3–Methylhex–3–ene (D)



$$\overset{6}{C}H_3\overset{5}{C}H_2-\overset{\overset{CH_3}{|}}{\overset{4}{C}}H-\overset{3}{C}H=\overset{2}{C}H\overset{1}{C}H_3$$

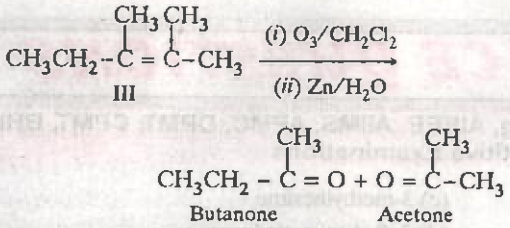
4–Methylhex–2–ene (E)



$$\overset{6}{C}H_3\overset{5}{C}H_2-\overset{\overset{CH_3}{|}}{\overset{4}{C}}H-\overset{3}{C}H_2\overset{2}{C}H=\overset{1}{C}H_2$$

4–Methylhex–1–ene (F)

None of the above alkenes (A to F) would give acetone as one of the products on ozonolysis. However, one of the alkenes (III) derived from (II) would give acetone on ozonolysis.



$$CH_3CH_2-\overset{CH_3}{\overset{|}{C}}=\overset{CH_3}{\overset{|}{C}}-CH_3 \xrightarrow[(ii)\ Zn/H_2O]{(i)\ O_3/CH_2Cl_2}$$

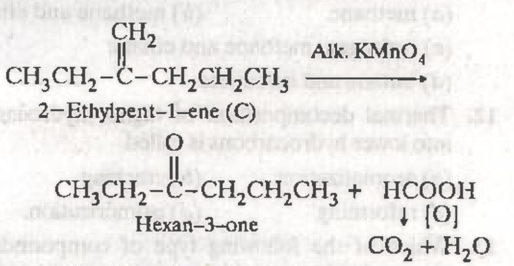
III

$$CH_3CH_2-\overset{CH_3}{\overset{|}{C}}=O+O=\overset{CH_3}{\overset{|}{C}}-CH_3$$

Butanone Acetone

Thus, the correct structure for the lowest molecular weight hydrocarbon (G) is I and not II.

(*iii*) Only alkene (C) on oxidation with a hot solution of alkaline $KMnO_4$ will give a ketone with more than five carbon atoms, *i.e.*, hexan-3-one



$$CH_3CH_2-\overset{CH_2}{\overset{||}{C}}-CH_2CH_2CH_3 \xrightarrow{Alk.\ KMnO_4}$$

2-Ethylpent-1-ene (C)

$$CH_3CH_2-\overset{O}{\overset{||}{C}}-CH_2CH_2CH_3 + HCOOH \xrightarrow{[O]} CO_2+H_2O$$

Hexan-3-one

Q. 3. **An alkene (A), C_5H_{12} on chlorination at 300°C gives a mixture of four different monochloro-derivations, (B), (C), (D) and (E). Two of these derivatives give the same stable alkene (F) on dehydrohalogenation. On oxidation with hot alkaline $KMnO_4$, followed by acidification, (F) gives two products (G) and (H). Give structures of (A) to (H) with proper reasoning.** ***(Roorkee 1995)***

Ans. (A) = 2-Methylbutane, (B) = 1-chloro-2-methylbutane, (C) = 2-chloro-2-methylbutane, (D) = 2-chloro-3-methylbutane, (E) = 1-chloro-3-methylbutane, (F) = 2-methylbut-2-ene, (G) = acetone and (H) = acetic acid

[Hint. Refer to Q. 12 on page 15/115]

Q. 4. **Hydrocarbon (A) C_6H_{10} on treatment with H_2/Ni, H_2/Lindlar's catalyst and Na/NH_3 (*l*) forms three different reduction products (B), (C) and (D) respectively. (A) forms salt (E) on heating with $NaNH_2$ in an inert solvent but it does not form salt with ammoniacal $AgNO_3$ solution. Compound (E) further reacts with CH_3I to form (F). Compound (D) on oxidative ozonolysis gave n-butyric acid along with other products. Give structures from (A) to (F) with proper reasoning.** ***(Roorkee 1998)***

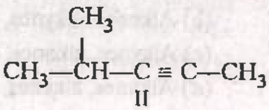
Ans. (*i*) The M.F. C_6H_{10} corresponds to C_nH_{2n-2} therefore, A *is an alkyne.*

(*ii*) Since (A) does not form a salt with ammoniacal $AgNO_3$ solution, therefore, *(A) is not a terminal alkyne.* Further, since (A) on heating with $NaNH_2$ in an inert solvent forms a salt (E), therefore, *(A) must be some 2-alkyne.*

(*iii*) The two possible structures for 2-alkyne having M.F. C_6H_{10} are

$$CH_3CH_2CH_2-C\equiv C-CH_3$$

I

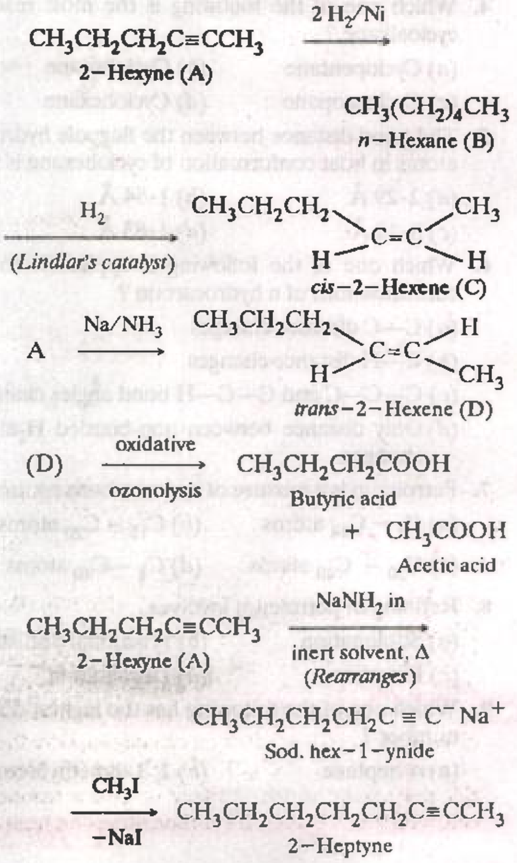


$$CH_3-\overset{CH_3}{\overset{|}{C}H}-C\equiv C-CH_3$$

II

(*iv*) Since (D) the reduction product of (A) with Na/NH_3 (*l*) on ozonolysis gives *n*-butyric acid as one of the products, therefore, one of the carbon atoms of the triple bond must be attached to *n*-propyl group. If this is so, then the structure of the alkyne (A) is I, *i.e.*, 2-hexyne.

If (A) is 2-hexyne, then the structures of the products (B), (C), (D), (E) and (F) can be deduced as follows :



$$\underset{\text{2-Hexyne (A)}}{CH_3CH_2CH_2C\equiv CCH_3} \xrightarrow{2\,H_2/Ni} \underset{n\text{-Hexane (B)}}{CH_3(CH_2)_4CH_3}$$

$$A \xrightarrow[\text{(Lindlar's catalyst)}]{H_2}$$ cis-2-Hexene (C)

$$A \xrightarrow{Na/NH_3}$$ *trans*-2-Hexene (D)

$$(D) \xrightarrow[\text{ozonolysis}]{\text{oxidative}} \underset{\text{Butyric acid}}{CH_3CH_2CH_2COOH} + \underset{\text{Acetic acid}}{CH_3COOH}$$

$$\underset{\text{2-Hexyne (A)}}{CH_3CH_2CH_2C\equiv CCH_3} \xrightarrow[\text{inert solvent, }\Delta]{NaNH_2\text{ in}}$$ *(Rearranges)*

$$\underset{\text{Sod. hex-1-ynide}}{CH_3CH_2CH_2CH_2C\equiv C^-Na^+}$$

$$\xrightarrow[-NaI]{CH_3I} \underset{\text{2-Heptyne}}{CH_3CH_2CH_2CH_2CH_2C\equiv CCH_3}$$

MULTIPLE CHOICE QUESTIONS

For CBSE– PMT (Preliminary), IIT Screening, AIEEE, AIIMS, AFMC, DPMT, CPMT, BHU and All Other Competitive Examinations

1. Which one of the following is the correct order of unsaturation ?
   (*a*) Alkanes, alkynes, alkenes
   (*b*) Alkenes, alkynes, alkanes
   (*c*) Alkynes, alkanes, alkenes
   (*d*) Alkanes, alkenes, alkynes.

2. Staggered conformation of ethane is :
   (*a*) more stable than eclipsed conformation
   (*b*) less stable than eclipsed conformation
   (*c*) equally stable as eclipsed conformation
   (*d*) impossible to exist.

3. Cycloalkanes are isomeric with :
   (*a*) alkanes (*b*) alkenes
   (*c*) alkynes (*d*) arenes.

4. Which one of the following is the most reactive cycloalkane ?
   (*a*) Cyclopentane (*b*) Cyclobutane
   (*c*) Cyclopropane (*d*) Cyclohexane.

5. The bond distance between the flagpole hydrogen atoms in boat conformation of cyclohexane is :
   (*a*) 2·29 Å (*b*) 1·54 Å
   (*c*) 3·10 Å (*d*) 1·83 Å.

6. Which one of the following is applicable to the conformations of a hydrocarbon ?
   (*a*) C—C distance changes
   (*b*) C—H distance changes
   (*c*) C—C—C and C—C—H bond angles change.
   (*d*) Only distance between non-bonded H-atoms changes.

7. Petroleum is a mixture of hydrocarbons containing
   (*a*) $C_1 - C_{14}$ atoms (*b*) $C_{15} - C_{20}$ atoms
   (*c*) $C_{20} - C_{40}$ atoms (*d*) $C_1 - C_{40}$ atoms.

8. Refining of petroleum involves
   (*a*) Sublimation (*b*) Fractional distillation
   (*c*) Filtration (*d*) Decantation.

9. Which one of the following has the highest octane number ?
   (*a*) *n*-heptane (*b*) 2, 3-dimethylhexane
   (*c*) 3-methylhexane
   (*d*) 2, 2, 4-trimethylpentane.

10. Which of the following is not a product of petroleum refining ?
    (*a*) Toluene (*b*) Gasoline
    (*c*) Kerosene oil (*d*) Diesel oil.

11. LPG mainly contains :—
    (*a*) methane (*b*) methane and ethane
    (*c*) hydrogen, methane and ethane
    (*d*) butane and isobutane

12. Thermal decomposition of higher hydrocarbons into lower hydrocarbons is called
    (*a*) aromatization (*b*) cracking
    (*c*) reforming (*d*) isomerization.

13. Which of the following type of compounds are expected to have the highest octane number ?
    (*a*) Straight chain alkanes
    (*b*) Cycloalkanes
    (*c*) Branched chain alkanes
    (*d*) Aromatic hydrocarbons.

14. Which of the following has the highest boiling point?
    (*a*) $(CH_3)_4C$ (*b*) $(CH_3)_2CHCH_3$
    (*c*) $CH_3CH_2CH_2CH_2CH_3$
    (*d*) $CH_3CH_2CH_2CH_3$.

15. Which of the following has the highest melting point ?
    (*a*) *o*-xylene (*b*) *m*- xylene
    (*c*) *p*-xylene (*d*) toluene.

16. Which of the following reagents can be used to distinguish ethene from ethyne ?
    (*a*) Br_2 / CCl_4
    (*b*) ammoniacal CuCl solution
    (*c*) cold aqueous or alkaline $KMnO_4$ solution
    (*d*) none of the above.

17. Benzene is less reactive than ethene and ethyne towards addition reactions due to
    (*a*) the presence of 3 π-bonds

ANSWERS

1. *d* **2.** *a* **3.** *b* **4.** *c* **5.** *d* **6.** *d* **7.** *d* **8.** *b* **9.** *d* **10.** *a*
11. *d* **12.** *b* **13.** *d* **14.** *c* **15.** *c* **16.** *b*

(*b*) cyclic nature

(*c*) sp^2-hybridization of carbon atoms

(*d*) delocalization of π-electrons.

18. Which of the following compounds reacts with sodamide in liquid NH_3 at 196 K to form an alkynide

(*a*) $CH_2=CH_2$ (*b*) C_6H_6

(*c*) $CH_3-C\equiv CH$ (*d*) $CH_3C\equiv CCH_3$.

19. When 1-butyne reacts with excess of HBr, the final product is

(*a*) 1, 1-Dibromobutane (*b*) 2, 2-Dibromobutane

(*c*) 1, 2-Dibromobutane

(*d*) 1, 1, 2, 2-Tetrabromobutane.

20. The heat of hydrogenation of benzene is 49·8 kcal mol^{-1} while its resonance energy is 36·0 kcal mol^{-1}. Then, the heat of hydrogenation of cyclohexene is

(*a*) 28·6 kcal mol^{-1} (*b*) 13·8 kcal mol^{-1}

(*c*) 85·8 kcal mol^{-1} (*d*) 36·0 kcal mol^{-1}

21. Anti-Markownikov's addition of HBr is not observed in

(*a*) Propene (*b*) But-1-ene

(*c*) But-2-ene (*d*) Pent-2-ene.

(I.I.T. 1985)

22. The highest boiling point is expected for

(*a*) Isooctane (*b*) *n*-octane

(*c*) 2, 2, 3, 3-Tetramethylbutane

(*d*) *n*-Butane. *(I.I.T. 1986)*

23. *n*-Propyl bromide on treatment with ethanolic potassium hydroxide produces

(*a*) Propane (*b*) Propene

(*c*) Propyne (*d*) Propanol.

(I.I.T. 1987)

24. Out of the following compounds, which one would have a zero dipole moment ?

(*a*) 1, 1-Dichloroethylene

(*b*) *cis*-1, 2-Dichloroethylene

(*c*) *trans*-1, 2-Dichloroethylene

(*d*) None of these compounds. *(I.I.T. 1987)*

25. Which of the following has least hindered rotation about carbon- carbon bond ?

(*a*) Ethane (*b*) Ethylene

(*c*) Acetylene (*d*) Hexachloroethane

(I.I.T. 1988)

26. The number of structural and configuration isomers of a bromo compound, C_5H_9Br formed by the addition of HBr to 2-pentyne respectively are :

(*a*) 1 and 2 (*b*) 2 and 4

(*c*) 4 and 2 (*d*) 2 and 1. *(I.I.T. 1988)*

27. Natural gas is composed primarily of

(*a*) methane (*b*) *n*-butane

(*c*) *n*-octane (*d*) a mixture of octanes

(M.L.M.R. Allahabad 1990)

28. Aromatic compounds burn with a sooty flame because ?

(*a*) they have a ring structure of carbon atoms

(*b*) they have a relatively high percentage of hydrogen

(*c*) they have a relatively high percentage of carbon

(*d*) they resist reaction with oxygen of air.

(B.I.T. Ranchi 1991)

29. 1-Chlorobutane on reaction with alcoholic potash gives

(*a*) 1-Butene (*b*) 1-Butanol

(*c*) 2-Butene (*d*) 2-Butanol.

(I.I.T. 1991)

30. Which of the following is not a mixture of hydrocarbons ?

(*a*) candle wax (*b*) kerosene

(*c*) vegetable oil (*d*) paraffin oil.

(B.I.T. Ranchi 1992)

31. Isomers which can be interconverted through rotation around a single bond are :

(*a*) conformers (*b*) diastereomers

(*c*) enantiomers (*d*) positional isomers

(I.I.T, 1992)

32. Ozonolysis of 2, 3-dimethyl-1-butene followed by reduction with zinc and water gives

(*a*) methanoic acid and 3-methyl-2-butanone

(*b*) methanal and 3-methyl-2-butanone

(*c*) methanal and 2-methyl-3-butanone

(*d*) methanoic acid and 2-methyl-3-butanone.

(I.I.T. 1992)

33. Which is the decreasing order of strength of bases: OH^-, NH_2^-, $HC\equiv C^-$ and $CH_3CH_2^-$?

(*a*) $CH_3CH_2^- > NH_2^- > HC\equiv C^- > OH^-$

(*b*) $HC\equiv C^- > CH_3CH_2^- > NH_2^- > OH^-$

ANSWERS

17. *d* **18.** *c* **19.** *b* **20.** *a* **21.** *c* **22.** *b* **23.** *b* **24.** *c* **25.** *a* **26.** *b*
27. *a* **28.** *c* **29.** *a* **30.** *c* **31.** *a* **32.** *b*

(*c*) $OH^- > NH_2^- > HC \equiv C^- > CH_3CH_2^-$

(*d*) $NH_2^- > HC \equiv C^- > OH^- > CH_3CH_2^-$.

(I.I.T. 1993 ; J & K C.E.T. 2004)

34. Which of the following reactions will yield 2, 2-dibromopropane ?

(*a*) $HC \equiv CH + 2HBr$

(*b*) $CH_3CH = CH_2 + HBr$

(*c*) $CH_3C \equiv CH + 2HBr$

(*d*) $CH_3CH = CHBr + HBr$.

(M.L.N.R. Allahabad 1993)

35. The order of appearance of the following with rising temperature during the refining of crude oil is

(*a*) kerosene oil, gasoline, diesel

(*b*) diesel, gasoline, kerosene oil

(*c*) gasoline, diesel, kerosene oil

(*d*) gasoline, kerosene oil, diesel.

(M.L.N.R. Allahabad 1993)

36. Indicate the expected structure of the organic product when ethylmagnesium bromide is treated with heavy water (D_2O).

(*a*) $C_2H_5-C_2H_5$ (*b*) C_2H_5OD

(*c*) C_2H_6 (*d*) C_2H_5D.

(D.C.E. 1994)

37. Isopropyl bromide on Wurtz reaction gives

(*a*) Hexane (*b*) Propane

(*c*) 2, 3-Dimethylbutane (*d*) Neohexane.

(B.H.U. 1994)

38. In the reaction,

$$C_6H_5CH_3 \xrightarrow{\text{Oxidation}} A \xrightarrow{\text{NaOH}} B \xrightarrow{\text{Sodalime}} C,$$

the product C is

(*a*) C_6H_5OH (*b*) C_6H_6

(*c*) C_6H_5COONa (*d*) C_6H_5ONa.

(B.H.U. 1994)

39. A compound X (C_5H_8) reacts with ammoniacal $AgNO_3$ to give a white precipitate, and on oxidation with hot alkaline $KMnO_4$ gives the acid, $(CH_3)_2CHCOOH$. Therefore, X is

(*a*) $CH_2=CHCH=CHCH_3$

(*b*) $CH_3(CH_2)_2C \equiv CH$

(*c*) $(CH_3)_2CH-C \equiv CH$

(*d*) $(CH_3)_2C=C=CH_2$.

(A.I.I.M.S. 1994)

40. Which of the following compounds has the lowest boiling point ?

(*a*) $CH_3CH_2CH_2CH_2CH_3$

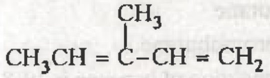
(*b*) $CH_3CH = CHCH_2CH_3$

(*c*) $CH_3CH = CH-CH = CH_2$

(*d*) $CH_3CH_2CH_2CH_3$.

(C.B.S.E. P.M.T. 1994)

41. Which set of products is expected on reductive ozonolysis of the following diolefin ?



$$CH_3CH = \overset{\overset{\displaystyle CH_3}{|}}{C}-CH = CH_2$$

(*a*) $CH_3CHO\ ;\ CH_3COCH = CH_2$

(*b*) $CH_3CH = C(CH_3)\,CHO\ ;\ CH_2O$

(*c*) $CH_3CHO\ ;\ CH_3COCHO\ ;\ CH_2O$

(*d*) $CH_3CHO\ ;\ CH_3COCH_3\ ;\ CH_2O$

(D.C.E. 1994)

42. Which of the following does not give a white precipitate with $AgNO_3$ solution ?

(*a*) Propyne (*b*) 1-Butyne

(*c*) 2-Butyne (*d*) 1-Pentyne.

(Haryana C.E.E.T. 1994)

43. Toluene reacts with methyl choride in presence of anhydrous aluminium chloride to give mainly *m*-xylene. This is because

(*a*) CH_3-group is *m*- directing

(*b*) CH_3-group has +I-effect

(*c*) because of hyperconjugation effect of the CH_3-group

(*d*) *m*-xylene is thermodynamically more stable.

(Haryana C.E.E.T. 1994)

44. Which of the following compounds exhibits geometrical isomerism ?

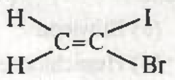
(*a*) C_2H_5Br (*b*) $(CH)_2(COOH)_2$

(*c*) CH_3CHO (*d*) $(CH_2)_2(COOH)_2$.

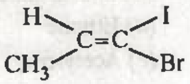
(B.H.U. 1994)

45. Geometrical isomerism is shown by

(*a*)

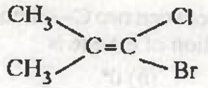


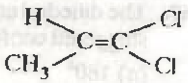
(*b*)



A N S W E R S

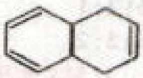
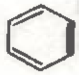
33. *a* **34.** *c* **35.** *d* **36.** *d* **37.** *c* **38.** *b* **39.** *c* **40.** *d* **41.** *c* **42.** *c*
43. *d* **44.** *b*

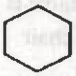
(c) 

(d) 

(M.L.N.R. Allahabad 1994)

46. Which of the following will show aromatic behaviour?

(a) 
(b) 

(c) 
(d) 

(Haryana C.E.E.T. 1996)

47. Which of the following is used as an antiknocking material ?

(a) T.E.L. (b) C_2H_5OH

(c) Glyoxal (d) Freon.

(C.B.S.E. P.M.T. 1996)

48. $(CH_3)_3CMgCl$ on reaction with D_2O produces

(a) $(CH_3)_3CD$ (b) $(CH_3)_3OD$

(c) $(CD_3)_3CD$ (d) $(CD_3)_3OD$.

(I.I.T. 1997)

49. When cyclohexane is poured on water, it floats because

(a) Cyclohexane is in 'boat' form

(b) Cyclohexane is in 'chair' form

(c) Cyclohexane is in 'crown' form

(d) Cyclohexane is less dense than water.

(I.I.T. 1997)

50. In the reaction of C_6H_5Y, the major product (> 60%) is *m*-isomer, so the group Y is

(a) —COOH (b) —Cl

(c) —OH (d) $-NH_2$

(A.I.I.M.S. 1997)

51. 1-Butyne reacts with cold alkaline $KMnO_4$ to produce

(a) $CH_3CH_2CH_2COOH$

(b) CH_3CH_2COOH

(c) $CH_3CH_2COOH + CO_2$

(d) $CH_3CH_2COOH + HCOOH$

(A.I.I.M.S. 1997)

52. In commercial gasolines, the type of hydrocarbons which are more desirable is

(a) branched chain hydrocarbons

(b) straight chain hydrocarbons

(c) linear unsaturated hydrocarbons

(d) toluene *(C.B.S.E. P.M.T. 1997)*

53. The most stable conformation of *n*-butane is

(a) skew boat (b) eclipsed

(c) gauche (d) staggered-anti

(C.B.S.E. P.M.T. 1997)

54. Which of the following is *not* aromatic ?

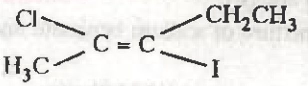
(a) Benzene

(b) Cyclooctatetraenyl dianion

(c) Tropylium cation

(d) Cyclopentadienyl cation *(A.I.I.M.S. 1997)*

55. The IUPAC name of the compound



is

(a) *trans*-3-iodo-4-chloro-3-pentene

(b) *cis*-2-chloro-3-iodo-2-pentene

(c) *trans*-2-chloro-3-iodo-2-pentene

(d) *cis*-3-iodo-4-chloro-3-pentene.

(C.B.S.E. P.M.T. 1998)

56. Which one of the following is not compatible with arenes ?

(a) Greater stability

(b) Delocalization of π-electrons

(c) Electrophilic addition

(d) Resonance. *(C.B.S.E. P.M.T. 1998)*

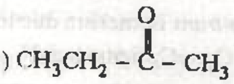
57. Among the following compounds, the strongest acid is

(a) $HC \equiv CH$ (b) C_6H_6

(c) C_2H_6 (d) CH_3OH.

(I.I.T. 1998)

58. The product(*s*) obtained *via* oxymercuration ($HgSO_4 + H_2SO_4$) of 1-butyne would give

(a) 
$CH_3CH_2-\overset{O}{\overset{\|}{C}}-CH_3$

(b) $CH_3CH_2CH_2-CHO$

(c) $CH_3CH_2CHO + HCHO$

(d) $CH_3CH_2COOH + HCOOH$. *(I.I.T. 1999)*

ANSWERS

45. *b* 46. *b* 47. *a* 48. *a* 49. *d* 50. *a* 51. *c* 52. *a* 53. *d* 54. *d*
55. *c* 56. *c* 57. *d* 58. *a*

59. A gas decolourises alkaline $KMnO_4$ solution but does not give precipitate with $AgNO_3$, it is

(*a*) CH_4 (*b*) C_2H_4

(*c*) C_2H_2 (*d*) C_2H_6.

(M.P.C.E.E. 1999)

60. In the reaction with silver nitrate, acetylene shows

(*a*) Oxidising property (*b*) Reducing property

(*c*) Basic property (*d*) Acidic property.

(M.P.C.E.E. 1999)

61. When acetylene reacts with arsenic trichloride in presence of anhydrous aluminium chloride, it produces

(*a*) β-Chlorovinyldichloroarsine

(*b*) Lewisite

(*c*) Nitrobenzene

(*d*) Both (*a*) and (*b*). *(A.F.M.C. 1999)*

62. Heating a mixture of sodium benzoate and soda-lime gives

(*a*) Benzene (*b*) Methane

(*c*) Sodium benzoate (*d*) Calcium benzoate.

(M.P.C.E.E. 1999 ; A.F.M.C. 1999)

63. When acetylene is passed through dil. H_2SO_4 in the presence of $HgSO_4$, the compound formed is

(*a*) ether (*b*) ketone

(*c*) acetic acid (*d*) acetaldehyde.

(C.B.S.E. P.M.T. 1999)

64. In Friedel-Crafts alkylation, besides $AlCl_3$, the other reactants are :

(*a*) $C_6H_6 + NH_3$ (*b*) $C_6H_6 + CH_4$

(*c*) $C_6H_6 + CH_3Cl$ (*d*) $C_6H_6 + CH_3COCl$.

(C.B.S.E. P.M.T. 1999)

65. Benzene reacts with chlorine to form benzene hexachloride in presence of

(*a*) Nickel (*b*) $AlCl_3$

(*c*) Bright sunlight (*d*) Zinc.

(M.P.C.E.E. 1999)

66. But-2-ene exhibit *cis-trans* isomerism due to

(*a*) rotation around $C_3 - C_4$ sigma bond

(*b*) restricted rotation around C = C bond

(*c*) rotation around $C_1 - C_2$ bond

(*d*) rotation around $C_2 - C_3$ double bond.

(C.B.S.E. P.M.T. 2000)

67. The dihedral angle between two C—H bonds in the staggered conformation of ethane is

(*a*) 180° (*b*) 0°

(*c*) 120° (*d*) 60°

(C.B.S.E. P.M.T. 2000)

68. What is the ratio of π- and σ-bonds in benzene ?

(*a*) 1 : 4 (*b*) 2 : 1

(*c*) 1 : 1 (*d*) 2 : 2

(I.M.S. B.H.U. 2000)

69. Among chair, half chair, twist boat and boat conformations, the one that is most stable is

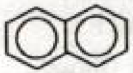
(*a*) Chair (*b*) Half chair

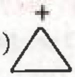
(*c*) Twist boat (*d*) Boat

(J.I.P.M.E.R. 2000)

70. The chemical system that is non-aromatic is

(*a*) 

(*b*) 

(*c*) 

(*d*) 

(J.I.P.M.E.R. 2000)

71. In Friedel-Crafts synthesis of toluene, reactants in addition to anhydrous $AlCl_3$ are

(*a*) $C_6H_6 + CH_4$ (*b*) $C_6H_6 + CH_3Cl$

(*c*) $C_6H_5Cl + CH_3Cl$ (*d*) $C_6H_5Cl + CH_4$.

(C.B.S.E. P.M.T. 2000)

72. Which one is/are weaker acid than water ?

(*a*) Alcohols (*b*) Terminal alkynes

(*c*) Both (*a*) and (*b*) (*d*) Mercaptans.

(D.C.E. 2000)

73. Identify the compounds A and B in the following reaction sequence.

$$CaC_2\,(s) + H_2O\,(l) \longrightarrow A\,(g) \xrightarrow[HgSO_4]{H_2SO_4} B\,(l)$$

(*a*) A is ethylene, B is acetaldehyde

(*b*) A is acetylene, B is propionaldehyde

(*c*) A is ethane, B is ethanol

(*d*) A is acetylene, B is acetaldehyde.

(C.P.M.T. 2000)

74. When 2-butyne is treated with dil. $H_2SO_4/HgSO_4$, the product formed is

(*a*) Butanol-1 (*b*) Butanol-2

ANSWERS

59. *b*	**60.** *d*	**61.** *d*	**62.** *a*	**63.** *d*	**64.** *c*	**65.** *c*	**66.** *b*	**67.** *d*	**68.** *a*
69. *a*	**70.** *c*	**71.** *b*	**72.** *c*	**73.** *d*					

(c) 2-Butanone (d) Butanal.

(Haryana C.E.E.T. 2000)

75. When propyne is treated with $HgSO_4/HgSO_4$, the product is

(a) Propenol (b) Propanal

(c) Propanone (d) Propanoic acid.

(Haryana C.E.E.T. 2000)

76. Tetrabromoethane on heating with Zn gives

(a) Ethyl bromide (b) Ethane

(c) Ethene (d) Ethyne.

(I.M.S.B.H.U. 2000)

77. Which of th following compounds will exhibit geometrical isomerism ?

(a) 1-Phenyl-2-butene (b) 3- Phenyl-1-butene

(c) 2-Phenyl-1-butene

(d) 1, 1-Diphenyl-1-propene

(I.I.T. 2000)

78. Propyne and propene can be distinguished by

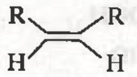
(a) conc. H_2SO_4 (b) Br_2 in CCl_4

(d) dil. H_2SO_4 (d) $AgNO_3$ in ammonia.

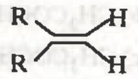
(I.I.T. 2000)

79. Which of the following alkenes will react fastest with H_2 under catalytic condition ?

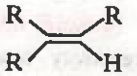
(a)



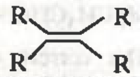
(b)



(c)



(d)



(I.I.T. 2000)

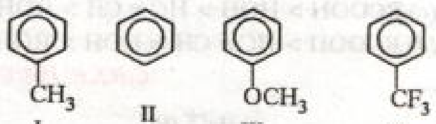
80. An alkane C_7H_{16} is produced by the reaction of lithium di (3-pentyl)cuprate with ethylbromide. The structural formula of the product is

(a) 3-Ethylpentane (b) 2-Methylpentane

(c) 3-Methylhexane (d) 2-Methylhexan

(e) Heptane (Kerala M.E.E. 2000)

81. Among the following compounds, the decreasing order of reactivity towards electrophilic substitution is



I II III IV

(a) III > I > II > IV (b) IV > I > II > III

(c) I > II > III > IV (d) II > I > III > IV

(C.B.S.E. P.M.T. 20000)

82. In chlorination of benzene, the reactive species is

(a) Cl^+ (b) Cl^-

(c) Cl_2 (d) Cl_2^-

(M.P. P.M.T. 2000)

83. An organic compound on treatment with Br_2 in CCl_4 gives bromoderivative of an alkene. The compound will be

(a) $CH_3—CH = CH_2$ (b) $CH_3CH = CHCH_3$

(c) $HC \equiv CH$ (d) $H_2C = CH_2$

(D.C.E. 2001)

84. Which alkene on ozonolysis gives CH_3CH_2CHO and CH_3COCH_3 ?

(a) $CH_3CH_2CH = C(CH_3)_2$

(b) $CH_3CH_2CH = CHCH_2CH_3$

(c) $CH_3CH_2CH = CHCH_3$

(d) $(CH_3)_2C = CHCH_3$ (C.B.S.E. P.M.T. 2001)

85. The number of isomers for the compound with molecular formula $C_2BrClFI$ is

(a) 3 (b) 4

(c) 5 (d) 6 (I.I.T. 2001)

86. Which of the following compounds exhibits stereoisomerism ?

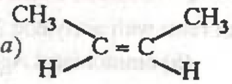
(a) 2-methylbutene-1 (b) 3-methylbutyne-1

(c) 3-methylbutanoic acid

(d) 2-methylbutanoic acid (I.I.T. 2002)

87. Which of the following hydrocarbons has the lowest dipole moment ?

(a)

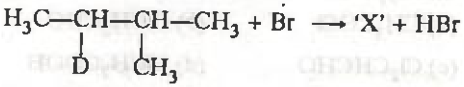


(b) $CH_3C \equiv CCH_3$

(c) $CH_3CH_2C \equiv CH$ (d) $CH_2 = CH—C \equiv CH$

(I.I.T. 2002)

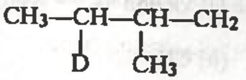
88. Consider the following reaction,



$$H_3C—\underset{D}{\underset{|}{CH}}—\underset{CH_3}{\underset{|}{CH}}—CH_3 + \dot{B}r \longrightarrow \text{'X'} + HBr$$

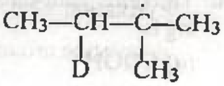
Identify the structure of the major product 'X'

(a)



$$CH_3—\underset{D}{\underset{|}{CH}}—\underset{CH_3}{\underset{|}{CH}}—CH_2$$

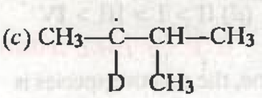
(b)



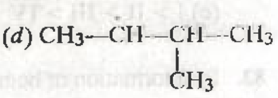
$$CH_3—\underset{D}{\underset{|}{CH}}—\underset{CH_3}{\underset{|}{C}}—CH_3$$

ANSWERS

74. c 75. c 76. d 77. a 78. d 79. a 80. a 81. a 82. a 83. c
84. a 85. d 86. d 87. b



(c) $CH_3—\dot{C}(D)—CH(CH_3)—CH_3$



(d) $CH_3—\dot{C}H—CH(CH_3)—CH_3$

(I.I.T. 2002)

89. Identify the reagent from the following list which can easily distinguish between 1-butyne and 2-butyne

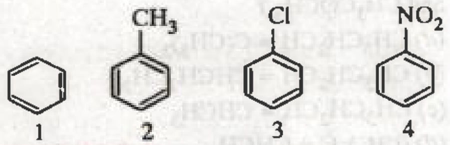
(a) bromine, CCl_4

(b) H_2, Lindler catalyst

(c) dilute H_2SO_4, $HgSO_4$

(d) ammoniacal Cu_2Cl_2 solution (I.I.T. 2002)

90. Identify the correct order of reactivity in electrophilic substitution reactions of the following compounds :



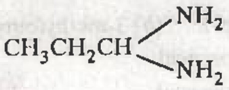
(a) 1 > 2 > 3 > 4 (b) 4 > 3 > 2 > 1

(c) 2 > 1 > 3 > 4 (d) 2 > 3 > 1 > 4

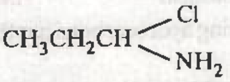
(I.I.T. 2002)

91. When $CH_3CH_2CHCl_2$ is treated with $NaNH_2$, the product formed is

(a) $CH_3—CH = CH_2$ (b) $CH_3—C \equiv CH$



(c) $CH_3CH_2CH(NH_2)_2$



(d) $CH_3CH_2CH(Cl)(NH_2)$ (C.B.S.E. P.M.T. 2002)

92. Which of these will not react with acetylene ?

(a) NaOH (b) ammoniacal $AgNO_3$

(c) Na (d) HCl

(A.I.E.E.E. 2002)

93. What is the product formed when acetylene reacts with hypochlorous acid ?

(a) CH_3COCl (b) $ClCH_2CHO$

(c) Cl_2CHCHO (d) $ClCH_2COOH$

(A.I.E.E.E. 2002)

94. The *ortho/para*-directing group among the following is

(a) COOH (b) CN

(c) $COCH_3$ (d) $NHCOCH_3$

(A.I.I.M.S. 2003)

95. The treatment of benzene with isobutene in the presence of sulphuric acid gives

(a) Isobutylbenzene (b) *tert*-Butylbenzene

(c) *n*-Butylbenzene (d) No reaction

(A.I.I.M.S. 2003)

96. Butene-1 may be converted to butane by reaction with

(a) Pd/H_2

(b) Zn—HCl

(c) Sn—HCl

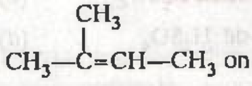
(d) Zn—Hg (A.I.E.E.E. 2003)

97. On mixing certain alkane with chlorine and irradiating it with ultraviolet light, one forms only one monochloroalkane. The alkane could be

(a) neopentane (b) propane

(c) pentane (d) isopentane

(A.I.E.E.E. 2003)



98. The compound, $CH_3—C(CH_3)=CH—CH_3$ on reaction with $NaIO_4$ in presence of $KMnO_4$ gives

(a) CH_3COCH_3

(b) $CH_3COCH_3 + CH_3COOH$

(c) $CH_3COCH_3 + CH_3CHO$

(d) $CH_3CHO + CO_2$ (C.B.S.E. P.M.T. 2003)

99. The correct order of reactivity towards the electrophilic substitution of the compounds aniline (I), benzene (II) and nitrobenzene (III) is

(a) III > II > I

(b) II > III > I

(c) I < II > III

(d) I > II > III (C.B.S.E. P.M.T. 2003)

100. Which one of the following order of acid strength is *correct* ?

(a) RCOOH > ROH > HOH > HC ≡ CH

(b) RCOOH > HOH > ROH > HC ≡ CH

(c) RCOOH > HOH > HC ≡ CH > ROH

(d) RCOOH > HC ≡ CH > HOH > ROH

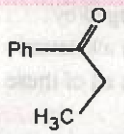
(C.B.S.E. P.M.T. 2003)

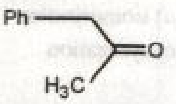
101. $Ph—C \equiv C—CH_3 \xrightarrow{Hg^{2+}/H^+} A$

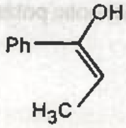
A is

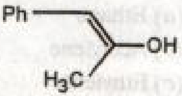
ANSWERS

88. *b* **89.** *d* **90.** *c* **91.** *b* **92.** *a* **93.** *c* **94.** *d* **95.** *b* **96.** *a* **97.** *a*
98. *b* **99.** *d* **100.** *b*

(a) 

(b) 

(c) 

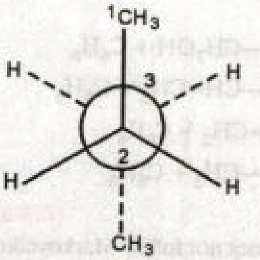
(d) 

(I.I.T. 2003 ; J & K C.E.T. 2004)

102. 2-Hexyne gives *trans*-2-hexene on treatment with
(*a*) Li/NH_3 (*b*) $Pd/BaSO_4$
(*c*) $LiAlH_4$ (*d*) Pt/H_2 (I.I.T. 2004)

103. 2-Phenylpropene on acidic hydration gives
(*a*) 2-Phenyl-2-propanal (*b*) 2-Phenyl-1-propanal
(*c*) 3-Phenyl-1-propanal (*d*) 1-Phenyl-2-propanal
(I.I.T. 2004)

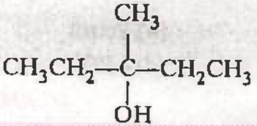
104. C_2 is rotated anticlockwise 120° about C_2—C_3 bond

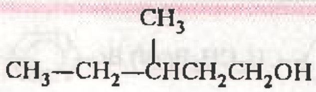


The resulting conformer is
(*a*) Partially eclipsed (*b*) Eclipsed
(*c*) Gauche (*d*) Staggered
(I.I.T. 2004)

105. Which of the following has the minimum boiling point ?
(*a*) *n*-Butane (*b*) 1-Butyne
(*c*) 1-Butene (*d*) 1-Isobutene
(A.I.E.E.E. 2004)

106. Among the following compounds which can be dehydrated very easily is
(*a*) $CH_3CH_2CH_2CH_2CH_2OH$
(*b*) $CH_3CH_2CH_2—CHOH—CH_3$

(*c*) 
$CH_3CH_2-\overset{CH_3}{\underset{OH}{\overset{|}{\underset{|}{C}}}}-CH_2CH_3$

(*d*) 
$CH_3-CH_2-\overset{CH_3}{\overset{|}{C}}HCH_2CH_2OH$

(A.I.E.E.E. 2004)

107. The addition of unsymmetrical reagents to unsymmetrical alkenes occurs in such a way that the negative part of the addendum goes to that carbon atom of the double bond which carries lesser number of hydrogen atoms, is called by
(*a*) Saytzeff rule (*b*) Markovnikov's rule
(*c*) Kharasch effect (*d*) Anti-Saytzeff rule
(A.F.M.C. 2004)

108. Benzene can be obtained by heating either benzoic acid with X or phenol with Y. X and Y respectively are
(*a*) Zinc dust and soda-lime
(*b*) Soda-lime and zinc dust
(*c*) Zinc dust and sodium hydroxide
(*d*) Soda-lime and copper (Karnataka C.E.T. 2004)

109. On heating a mixture of two alkyl halides with sodium metal in dry ether, 2-methylpropane was obtained. The alkyl halide is
(*a*) 2-Chloropropane and chloromethane
(*b*) 2-Chloropropane and chloroethane
(*c*) Chloroethane and chloroethane
(*d*) Chloromethane and 1-chloropropane
(Karnataka C.E.T. 2004)

110. The first fraction obtained during the fractionation of petroleum is
(*a*) hydrocarbon gases (*b*) kerosene oil
(*c*) gasoline (*d*) diesel oil
(Karnataka C.E.T. 2004)

111. Which of the following compounds is not aromatic ?

(*a*) 

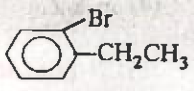
(*b*) 

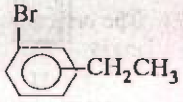
(*c*) 

(*d*) 

(J & K C.E.T. 2004)

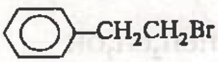
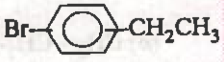
112. Ethylbenzene with bromine in presence of $FeBr_3$, predominantly gives

(*a*) 

(*b*) 

ANSWERS

101. *a* **102.** *a* **103.** *a* **104.** *c* **105.** *a* **106.** *c* **107.** *b* **108.** *b* **109.** *a* **110.** *a*
111. *c*

(c)  (d) 

(J & K C.E.T. 2004)

113. Which of the following compounds will exhibit *cis-trans-* isomerism ?
(a) 2-Butene
(b) 2-Butyne
(c) 2-Butanol
(d) Butanone
(e) Butanol

(Kerala M.E.E. 2004)

114. Propyne when passed through a hot iron tube at 400°C produces
(a) Benzene
(b) Methylbenzene
(c) Dimethylbenzene
(d) Trimethylbenzene
(e) Polypropene

(Kerala E.E.E. 2004)

115. $CH \equiv CH \xrightarrow{O_3} X \xrightarrow{Zn/CH_3OH} Y$, Y is
(a) $CH_2OH—CH_2OH$ (b) CH_3COOH
(c) C_2H_5OH (d) $CH_3—CH_3$

(M.G.I.M.S. Wardha 2004)

116. Debromination of *meso*-dibromobutane will give the product as
(a) *n*-butane (b) 2-butyne
(c) *cis*-2-butene (d) *trans*-2-butene

(M.G.I.M.S. Wardha 2004)

117. Pick out the alkane which differs from the other members of the group
(a) 2, 2-Dimethylpropane
(b) Pentane
(c) 3-Methylbutane
(d) 2, 2-Dimethylbutane

(Karnataka 2004)

118. Among the following the aromatic compound is

(a)  (b) 

(c)  (d) 

(A.I.I.M.S. 2004)

119. Octane number can be changed by
(a) isomerisation (b) alkylation
(c) cyclization (d) all of these

(A.F.M.C. 2004)

120. 1, 2-Dibromoethane with alcoholic potash gives
(a) Ethane
(b) Acetylene
(c) Ethylene
(d) Methane
(e) None of the above

(Kerala M.E.E. 2004)

121. Photochemical chlorination is initiated by a process of
(a) Pyrolysis
(b) Substitution
(c) Cracking
(d) Peroxidation
(e) Homolysis

(Kerala M.E.E. 2004)

122. Using anhydrous $AlCl_3$ as catalyst, which one of the following reactions produces ethylbenzene (PhEt) ?
(a) $CH_3—CH_2OH + C_6H_6$
(b) $CH_3—CH=CH_2 + C_6H_6$
(c) $H_2C=CH_2 + C_6H_6$
(d) $CH_3—CH_3 + C_6H_6$

(C.B.S.E. P.M.T. 2004)

123. Which does not follow Markovnikov's rule ?
(a) $CH_3CH=CH_2$
(b) $CH_3CH=CHCH_3$
(c) $(CH_3)_2CH—CH=CH_2$
(d) $CH_3CH_2CH=CH_2$

(Orissa J.E.E. 2004)

124. Which of the following reactions will yield 2, 2-dibromopropane ?
(a) $CH_2 = CHBr + HBr$
(b) $CH_3C \equiv CCH_3 + 2\,HBr$
(c) $CH_3C \equiv CH + 2\,HBr$
(d) $CH_3CH = CHBr + HBr$

(C.P.M.T. 2004)

125. Term 'Hexadecane' in petroleum is commonly called as
(a) Octane (b) Petrol
(c) Cetane (d) LPG

(C.P.M.T. 2004)

ANSWERS

112. *d*	**113.** *a*	**114.** *d*	**115.** *a*	**116.** *d*	**117.** *d*	**118.** *a*	**119.** *d*	**120.** *b*	**121.** *e*
122. *a*	**123.** *b*	**124.** *c*	**125.** *c*						

HINTS/EXPLANATIONS to Multiple Choice Questions

6. In conformations of hydrocarbons, for example, in ethane, only the bond distance between, the non-bonded hydrogens changes (for example, in eclipsed form, distance = 229 pm while in staggered form it is 310 pm) while all bond distances and bond angles, however, remain to be the same. Similarly in boat form of cyclohexane, the distance between fragpole H-atoms is only 183 pm which is much smaller than the distance between similar H-atoms in chair conformation.

9. Larger the branching, higher the octane number.

10. Toluene because it is aromatic.

14. Since it has the largest number of carbon atoms.

15. *p*-Xylene being symmetrical packs closely in the crystal lattice.

16. Because ammoniacal CuCl reacts with ethyne but not with ethene.

18. Only terminal alkynes react.

19. Markovnikov's addition

20. Let the heat of hydrogenation per double bond $= x$ kcal mol^{-1}. $\therefore$ Total heat evolved when three double bonds of the benzene ring are hydrogenated $= 3x$ kcal mol^{-1}. But the actual heat evolved $= 49\cdot8$ kcal mol^{-1} and resonance energy $= 36\cdot0$ kcal mol^{-1}.

$\therefore\ 3x - 36 = 49\cdot8$ or $3x = 49\cdot8 + 36\cdot0 = 85\cdot8$

or $x = 28\cdot6$ kcal mol^{-1}.

21. Only but-2-ene is symmetrical therefore, Markovnikov's and anti- Markovnikov's products are the same.

22. *n*-Octane and 2, 2, 3, 3-tetramethylbutane have eight carbon atoms each but *n*-octane has a straight chain while 2, 2, 3, 3-tetramethylbutane is higly branched.

25. Both ethane and hexachloroethane contain C—C bonds and hence have less hindered rotation than about C = C in ethylene and C ≡ C bond in actylene. Out of ethane and hexachloroethane, the latter has higher hindered rotation because of bigger size of Cl atoms.

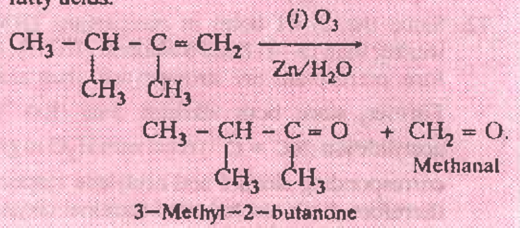
26. Markovnikov's and anti-Markovnikov's addition of HBr gives two structural isomers, *i.e.*,

$$CH_3C\equiv CCH_2CH_3 \xrightarrow{HBr} CH_3CH=C(Br)CH_2CH_3 + CH_3C(Br)=CHCH_2CH_3$$

Each of these two isomers can exist as a pair of *cis, trans*-isomers and hence there are four configurational isomers.

30. Vegetable oil is a mixture of triglycerides of higher fatty acids.

32.



$$CH_3-\underset{\displaystyle CH_3}{CH}-\underset{\displaystyle CH_3}{C}=CH_2 \xrightarrow[Zn/H_2O]{(i)\ O_3} CH_3-\underset{\displaystyle CH_3}{CH}-\underset{\displaystyle CH_3}{C}=O + \underset{\text{Methanal}}{CH_2=O}.$$

3−Methyl−2−butanone

33. Refer to the text on page 15/57.

39. Terminal alkyne containing $(CH_3)_2CH$ group.

40. It has least number of C-atoms.

41. Cleavage on either side of each double bond gives : CH_3CHO, CH_3COCHO and CH_2O.

42. Since it is non-terminal.

43. As expected first a mixture of *o*- and *p*-xylenes is obtained which subsequently undergo rearrangement to give the thermodynamically more stable *m*-xylene.

44. $(CH)_2(COOH)_2$ actually represents HOOC—CH = CH—COOH which shows geometrical isomersm.

46. Only (*b*) has a conjugated system of 6 π- electrons. While cyclopentadienyl cation has only 4 π-electrons.

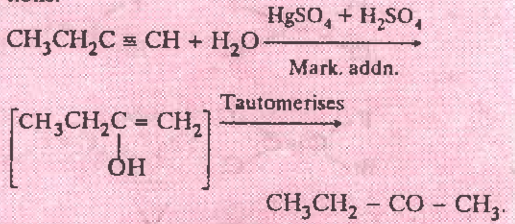
48. $(CH_3)_3CMgCl + D_2O \longrightarrow (CH_3)_3CD + Mg\,(OD)\,Cl.$

50. Only - COOH is *m*-directing, rest are all *o, p*-directing.

51. Terminal alkynes on oxidation give a mixture of CO_2 and a carboxylic acid with one C-atom less than that of the starting alkyene.

56. Arenes undergoes electrophilic substitution reactions.

58.



$$CH_3CH_2C\equiv CH + H_2O \xrightarrow[\text{Mark. addn.}]{HgSO_4 + H_2SO_4} \left[CH_3CH_2\underset{\displaystyle OH}{C}=CH_2\right] \xrightarrow{\text{Tautomerises}} CH_3CH_2-CO-CH_3.$$

59. C_2H_4 decolourises $KMnO_4$ solution but does not give ppt. with $AgNO_3$ solution.

61. β-Chlorovinyldichloroarsine and Lewisite are names of the same compound.

64. The option (*d*) implies F.C. acylation.

70. Compound (*c*) has no π-electrons, compound shown in option (*d*) is called azulene in which both the rings have six π-electrons and hence azulene is an aromatic compound. So are benzene (*a*) and naphthalene (*b*).

72. Since the S—H bond in mercaptans (RSH) is weaker than O—H bond is alcohols (ROH); therefore, mercaptans are stronger acid than alcohols. Further, since both alkoxide ions (RO^-) and acetylide ion ($RC \equiv C^-$) react with H_2O to give the corresponding alcohol and acetylene respectively, therefore, both alcohols and terminal alkynes are weaker acid than water.

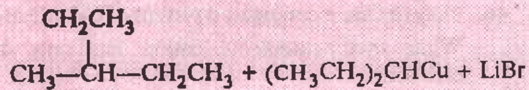
74. $CH_3C \equiv CCH_3 + H_2O \xrightarrow{H_2SO_4/HgSO_4} CH_3COCH_2CH_3.$

78. $AgNO_3$ in NH_3 reacts with propyne to give white ppt. to silver propynide while propene does not.

79. During catalytic hydrogenation, the hydrogens are transferred from the catalyst to the same side of the double bond thereby giving *cis*-alkenes. Evidently smaller the number of R substituents, lesser is the steric hindrance and hence faster is the rate of hydrogenation.

80. $[(CH_3CH_2)_2CH_2]_2CuLi + BrCH_2CH_3 \longrightarrow$

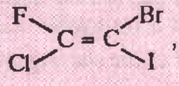
Lithium di(3−pentyl)cuprate

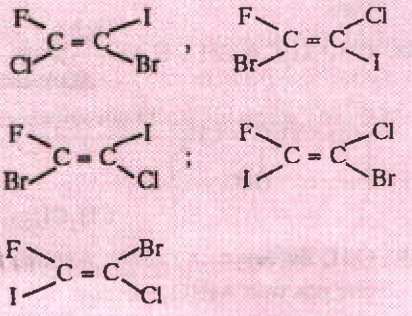


$CH_3-\underset{}{\overset{CH_2CH_3}{\overset{|}{C}}}H-CH_2CH_3 + (CH_3CH_2)_2CHCu + LiBr$

3−Ethylpentane
(M.F. C_7H_{16})

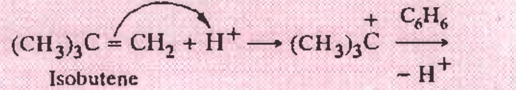
81. Reactivity towards electrophilic substitution decreases as the electron density in the benzene ring decreases. Thus, option (*a*) is correct, *i.e.* III > I > II > IV.

85. Six isomers are  ,



and

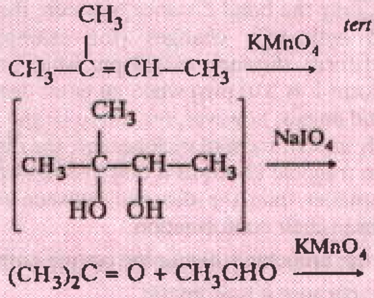
87. $CH_3C \equiv CCH_3$ being linear and symmetrical has lowest (or zero) dipole moment.

95. 

$(CH_3)_3C=CH_2 + H^+ \longrightarrow (CH_3)_3\overset{+}{C} \xrightarrow[-H^+]{C_6H_6}$

Isobutene

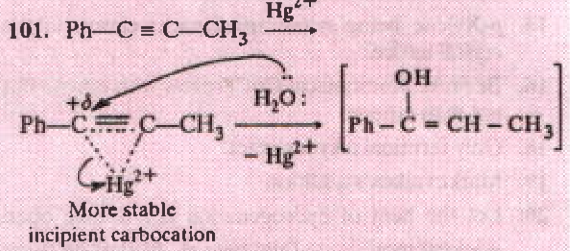
$(CH_3)_3C-C_6H_5$
tert−Butylbenzene

98. 

$CH_3-\overset{CH_3}{\overset{|}{C}}=CH-CH_3 \xrightarrow{KMnO_4} \left[CH_3-\underset{HO}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-\underset{OH}{\underset{|}{CH}}-CH_3\right] \xrightarrow{NaIO_4}$

$(CH_3)_2C=O + CH_3CHO \xrightarrow{KMnO_4}$

$(CH_3)_2C=O + CH_3COOH$

101. 

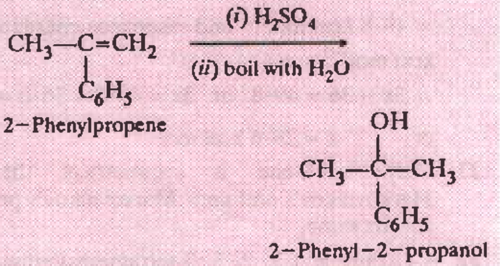
$Ph-C\equiv C-CH_3 \xrightarrow{Hg^{2+}}$

$Ph-\overset{+\delta}{C}\equiv C-CH_3 \xrightarrow[-Hg^{2+}]{H_2\ddot{O}:} \left[Ph-\overset{OH}{\overset{|}{C}}=CH-CH_3\right]$

Hg^{2+}

More stable
incipient carbocation

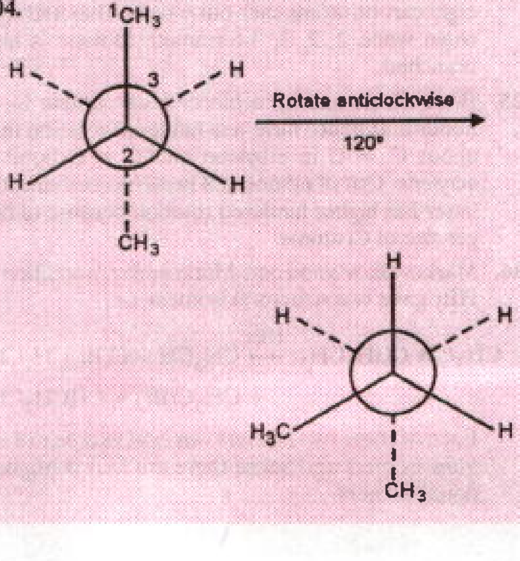
$\xrightarrow{\text{Tautomerises}} Ph-CO-CH_2CH_3$

103. 

$CH_3-\underset{C_6H_5}{\underset{|}{C}}=CH_2 \xrightarrow[(ii)\text{ boil with } H_2O]{(i)\ H_2SO_4} CH_3-\underset{C_6H_5}{\underset{|}{\overset{OH}{\overset{|}{C}}}}-CH_3$

2−Phenylpropene

2−Phenyl−2−propanol

104. 

105. Because of greater polarizability, alkenes and alkynes have higher boiling points than their isomeric alkanes.

111. (*a*), (*b*) and (*d*) have a cyclic cloud of six π-electrons and hence aromatic while (*b*) has 4 π-electrons and hence antiaromatic.

115. $CH \equiv CH \xrightarrow{O_3} OHC{-}CHO \xrightarrow[(Reduction)]{Zn/CH_3OH} \underset{\text{Ethane}-1,2-\text{diol}}{H_2OCH_2{-}CH_2OH}$

116. Addition of Br_2 to 2-butene gives *meso*-2, 3-dibromobutane by *trans*-addition (refer to page 15/34). Conversely, debromination of *meso*-2, 3-dibromobutane also occurs by *trans*-elimination. mechanism to form *trans*- 2-butene.

117. (*a*), (*b*) and (*c*) are all isomers but (*d*) is not.

118. Only (*a*) has 2 π-electrons and hence is aromatic. All others have 4 π electrons and hence *anti-aromatic*.

122. In presence of anhyd. $AlCl_3$, ethanol gives $CH_3CH_2^+$ which attacks the benzene ring to give ethylbenzene (Refer to page 15/73).

123. Symmetrical alkenes, *i.e.*, 2-butene does not follow Markovnikov's rule.

ADDITIONAL QUESTIONS

For All Competitive Examinations

Assertion-Reason Type Questions

The following questions consist of an 'Assertion' in column 1 and the 'Reason' in column 2. Use the following key to choose the appropriate answer.

(*a*) If both assertion and reason are CORRECT, but reason is not the CORRECT explanation of the assertion.

(*b*) If both assertion and reason are CORRECT, but reason is not the CORRECT explanation of the assertion.

(*c*) If assertion is CORRECT, but reason is INCORRECT.

(*d*) If assertion is INCORRECT, but reason is CORRECT.

(*e*) If both assertion and reason are FALSE.

	Assertion	**Reason**
1.	C_4H_6 represents a bicycloalkane.	The general formula for bicycloalkanes is C_nH_{2n}.
2.	But-1-ene and 2-methylprop-1-ene are position isomers.	Position isomers have same molecular formula but differ in the position of the functional group.
3.	$CHBr = CHCl$ exhibits geometrical isomerism but $CH_2Br{-}CH_2Cl$ does not.	Presence of double bond is one of the conditions of geometrical isomerism.
4.	All the carbon atoms of but-2-ene lie in one plane.	All the carbon atoms in but-2-ene are sp^2-hybridized.
5.	2-Butene shows geometrical isomerism.	*cis* and *trans*-2-butene are diastereomers.
6.	Alkanes having more than three carbon atoms exhibit chain isomerism.	All carbon atoms in alkanes are *sp*-hybridized. ***(A.I.I.M.S. 1994)***
7.	Cycloutane is less stable than cyclopentane.	Presence of 'bent bonds' causes loss of orbital overlap ***(A.I.I.M.S. 1995)***
8.	Lactic acid shows geometrical isomerism.	It has a C = C bond. ***(A.I.I.M.S. 1997)***

	Assertion	**Reason**
9.	A solution of bromine in CCl_4 is decolourised on bubbling acetylene through it.	Bromine is expelled from the solution as gas by acetylene.
10.	In Kolbe's electrolytic decarboxylation reaction, there are *n*-carbon atoms in the parent compound, the alkane produced will have (*n*—1) carbon atoms.	Kolbe's electrolytic method can also be employed for producing ethene and ethyne.
11.	Treatment of 1, 3-dibromopropane with zinc produces cyclopropane.	The reaction of alkyl halides with zinc metal is called Corey-House reaction.
12.	Acetylene reacts with dilute H_2SO_4 in presence of $HgSO_4$ to give acetaldehyde.	Acetylene is a feeble acid.
13.	Propene and HBr react in the presence of benzoyl peroxide to give 1-bromopropane.	In presence of peroxides, addition of HBr occurs anti to Markownikov's rule.
14.	Both toluene and *n*-propylbenzene give the same product on oxidation with $KMnO_4$.	$KMnO_4$ oxidises alkyl side chains of arenes irrespective of their length to — COOH group.
15.	The acidity of C—H bond varies in the order : $CH \equiv CH > CH_2 = CH_2 > CH_3-CH_3$	Higher the bond order greater the bond strength.
16.	Addition of Br_2 to 1-butene gives two optical isomers.	The product contains one asymmetric carbon. ***(I.I.T. 1998)***
17.	Dimethyl sulphide is commonly used for the reduction of an ozonide of an alkene to get the carbonyl compounds.	It reduces the ozonide giving water soluble dimethyl sulphoxide and excess of it evaporates. ***(I.I.T. 2001)***
18.	Alkylbenzene is not prepared by Friedel-Crafts alkylation of benzene.	Alkyl halides are less reactive than acyl halides. ***(A.I.I.M.S. 2003)***
19.	*trans*-2-Butene on reaction with Br_2 gives *meso*-2, 3-dibromobutane.	The reaction involves *syn*-addition of bromine. ***(A.I.I.M.S. 2003)***
20.	*cis*-1, 3-Dihydroxycyclohexane exists in boat conformation.	In the chair form, there will not be hydrogen bonding between the two hydroxyl groups. ***(A.I.I.M.S. 2003)***

True/False Statements

Which of the following statements are true and which are false ? Rewrite the false statements correctly.

1. 2, 2-Dimethylbutane and 2-methylbutane are chain isomers of hexane.

2. Acetylene is a tetrahedral molecule.

3. Like alkenes, alkynes also show geometrical isomerism.

4. Staggered and eclipsed conformation of ethane can be separated.

5. In benzene, carbon uses all the three *p*- orbitals for hybridization. ***(I.I.T. 1987)***

6. The most accepted theory about the origin of petroleum is believed to be of organic origin.

7. Branching in hydrocarbon chain decreases the octane number.

8. Gasoline directly obtained by refining of crude petroleum is called straight run gasoline.

9. Reforming involves conversion of aliphatic into aromatic hydrocarbons.

10. In Fischer Tropsch process, synthetic petroleum is obtained by the hydrogenation of coal.

11. Wurtz reaction can be used to prepare alkanes with odd number of carbon atoms.

12. Hydration of ethyne in presence of dil. H_2SO_4 and $HgSO_4$ as catalyst at 333 K gives ethanal.

13. Polyvinyl chloride is a polymer of chloroethane.

14. A mixture of conc. HNO_3 and conc. H_2SO_4 is used for sulphonation of arenes.

15. LPG does not contain methane since it cannot be easily compressed.

16. Acetylene is more acidic than ethylene. ***(B.I.T. Ranchi 1992)***

17. Photobromination of 2-methylbutane gives a mixture of 1-bromo-2-methylpropane and 2-bromo-2-methylpropane in the ratio 9 : 1. ***(I.I.T. 1993)***

Fill In The Blanks

1. A quarternary carbon atom is attached to .... other carbon atoms.
2. In methane, carbon exhibits .... hybridization and the four hybrid orbitals are inclined at angle of ....
3. Chain isomerism arises due to different arrangements of the ....
4. Infinite number of spatial arrangements of atoms obtained by rotation about carbon-carbon single bond are called ....
5. The two extreme conformations of ethane are called .... and ....
6. Restricted rotation about carbon-carbon double bond gives rise to .... isomerism.
7. Resonance energy is a measure of extra stability conferred on the molecule due to .... of electrons.
8. Lewis structures which differ in the position of electrons and not in the position of atoms are called ....
9. Organic compounds which contain at least one benzene ring are called .... compounds.
10. The real structure of benzene is a .... of two ...... structures.
11. The three isomers of xylene are called ..., ..., and ....
12. Isomers which differ in the spatial orientation of the atoms or groups are called .....
13. Carbon-carbon bond length in benzene is .... which is intermediate between carbon-carbon single bond length of .... and carbon-carbon double bond length of ....
14. Petroleum is a valuable source of ..... hydrocarbons.
15. Coal is the chief source of ..... hydrocarbons.
16. The process used to increase the octane number of gasoline is called ....
17. Gasoline obtained by ..... has a higher octane number than straight run gasoline.
18. An alkene is expected to have a ..... melting point than the corresponding alkane due to greater ....
19. The boiling points of hydrocarbons are low because of weak ..... forces of attraction.
20. A .... chain alkane has usually a lower boiling point than the corresponding .... chain alkane.
21. Out of isopentane and neopentane, ... has higher boiling point because of larger surface area.
22. Removal of H_2O from ethyl alcohol is an example of an .... reaction.
23. Alkanes undergo .... reactions whereas alkynes give......... ..... reactions.
24. .... is a versatile method for locating the position of the double bond in an alkene.
25. .... is more acidic than ammonia but less acidic than water.
26. The hydrogen atoms in acetylene are .... due to greater ..... of the carbon atoms.
27. Benzene gives .... reaction like .... hydrocarbons.
28. 1, 3-Migration of a hydrogen atom from one polyvalent atom to the other within the same molecule is called...........
29. The valence atomic orbital on carbon in silver acetylide is ..... hybridized. *(I.I.T. 1990)*
30. Addition of water to acetylenic compounds is catalysed by ..... and .... *(I.I.T. 1993)*
31. $R-C\equiv C-R \xrightarrow[\text{Lindlar catalyst}]{H_2}$ *(I.I.T. 1994)*

Matching Type Questions

Match the entries in column X with those in column Y.

X	Y
1. Cyclic conjugated polyenes with $(4n + 2)$ π-electrons.	1. Delocalization of π-electrons
2. Naphthalene	2. Aromatic compounds
3. *o*-Dichlorobenzene does not exist as two isomers	3. Moth repellent.
4. Tetraethyl lead	4. Alkyl halides in presence of metallic sodium
5. Friedel-Crafts reaction	5. Arenes and alkyl halides in presence of anhydrous $AlCl_3$
6. Wurtz reaction	6. Anti-knocking agent.
7. Ozonolysis	7. Location of double bond in an alkene.

ANSWERS

ASSERTION-REASON TYPE QUESTIONS

1. (*c*) **2.** (*d*) **3.** (*b*) **4.** (*c*) **5.** (*b*) **6.** (*c*) **7.** (*a*) **8.** (*d*) **9.** (*c*) **10.** (*d*) **11.** (*c*) **12.** (*b*)
13. (*a*) **14.** (*a*) **15.** (*b*) **16.** (*a*) **17.** (*a*) **18.** (*b*) **19.** (*c*) **20.** (*e*)

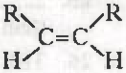
TRUE/FALSE STATEMENTS

1. False, 2, 2-dimethylbutane and 2, 3- dimethylbutane **2.** False, actylene is a linear molecule **3.** False, alkynes do not show geometrical isomerism **4.** False, cannot be separated **5.** False, only two *p*-orbitals **6.** True **7.** False, increases the octane number **8.** True **9.** True **10.** False, is obtained from water gas **11.** False, even number of carbon atoms **12.** True **13.** False, polymer of chloroethene (vinyl chloride) **14.** False, nitration of arenes **15.** True **16.** True **17.** False.

FILL IN THE BLANKS

1. Four **2.** sp^3 , 109° – 28′ **3.** carbon chain **4.** conformations **5.** staggered, eclipsed **6.** geometrical **7.** delocalization **8.** canonical or resonating structures **9.** aromatic **10.** resonance hybrid, Kekule **11.** 1, 2 ; 1, 3-and 1, 4- dimethylbenzenes. **12.** stereoisomers **13.** 1·39 Å, 1·54 Å and 1·34 Å **14.** aliphatic **15.** aromatic **16.** cracking or reforming **17.** cracking **18.** higher, polarizability **19.** van der waals' **20.** branched, straight **21.** isopentane **22.** elimination **23.** substitution, addition **24.** Ozonolysis **25.** acetylene **26.** acidic, electronegativity **27.** substitution, saturated **28.** Tautomerism

29. *sp* **30.** Hg^{2+} salts and dilute acids **31.**



$$\begin{matrix} R & & R \\ & C=C & \\ H & & H \end{matrix}$$

cis– alkene

MATCHING TYPE QUESTIONS

1—2, 2—3, 3—1, 4—6, 5—5, 6—4 and 7—7.

HINTS/EXPLANATIONS to Assertion-Reason Type Questions

1. *Correct reason.* The general formula for bicycloalkanes in C_nH_{2n-2}.

3. *Correct explanation.* Geometrical isomerism arises due to hindered rotation about single bond (in cyclic compounds) and double bonds.

4. *Correct reason.* Only the carbon atoms of the double bond in but-2-ene are sp^2-hybridized.

5. *Correct explanation.* 2-Butene has restricted rotation about C = C bond.

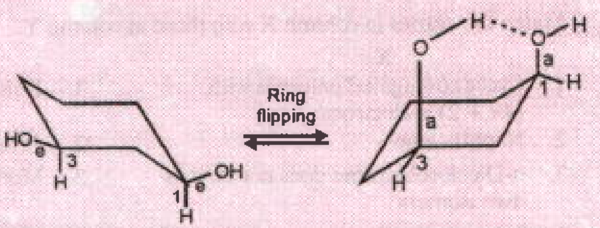
6. *Correct reason.* There are more than one way in which more than three carbon atoms can be connected.

18. *Correct explanation* : Due to +I-effect of the alkyl groups, alkylbenzenes are more reactive than benzene and hence readily undergo further alkylation to form polyalkylation products.

19. *Correction reason* : The reaction involves *trans*-addition of bromine, (refer to page 15/34 for explanation).

20. *Correct assertion* : *cis*-1, 3-Dihydroxycyclohexane exists in the chair firm.

Correct reason : Due to flipping of the ring, the two equatorial hydroxyl groups become axial and thus come closer to form H-bonds as shown below :



cis-1, 3-Dihydroxycyclohexane (diequatorial form) *cis*-1, 3-Dihydroxycyclohexane (diaxial form)