15. Hydrocarbons

The compounds which contains carbon and hydrogen as the only elements are called hydrocarbons.

Hydrocarbons can be **open chain** or **cyclic**. In accordance with presence or absence of carbon-carbon multiple bond (C=C and/ or C≡C) the hydrocarbons are called **unsaturated** or **saturated**. Cyclic unsaturated hydrocarbon can be either **aromatic** or **nonaromatic** (Fig. 15.1).

Fig. 15.1 : Classification of hydrocarbon
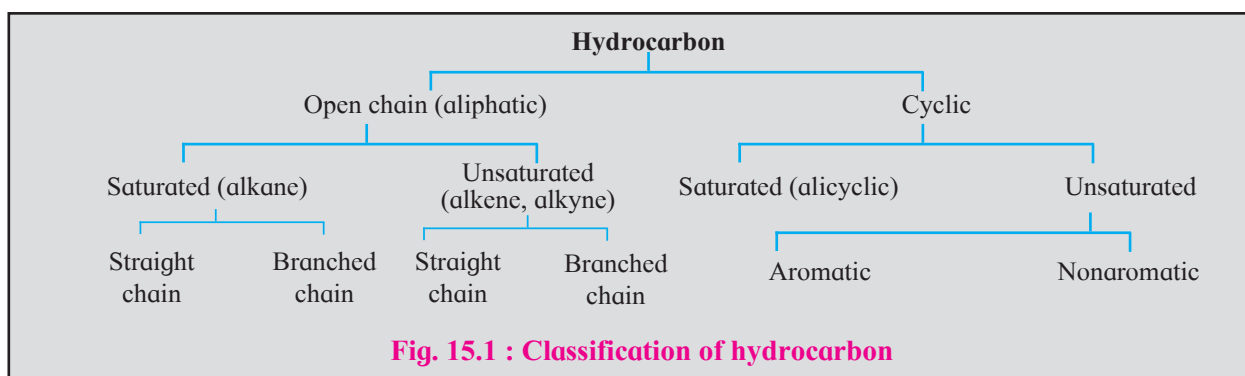
Do you know ?

Why are alkanes called paraffins?
Alkanes contain only carbon-carbon and carbon-hydrogen single covalent bonds. They are chemically less reactive and do not have much affinity for other chemicals. Hence they are called paraffins.

15.1 Alkanes

Alkanes are aliphatic saturated hydrocarbons containing carbon-carbon and carbon-hydrogen single covalent bonds. You have learnt in Chapter 14 that alkanes have general formula C_nH_{2n+2} where 'n' stands for the number of carbon atoms in the alkane molecule.

15.1.1 Isomerism in alkanes

Alkanes with more than three carbon atoms generally exhibit, structural isomerism and in particular, the chain isomerism (refer to section 14.5.1)
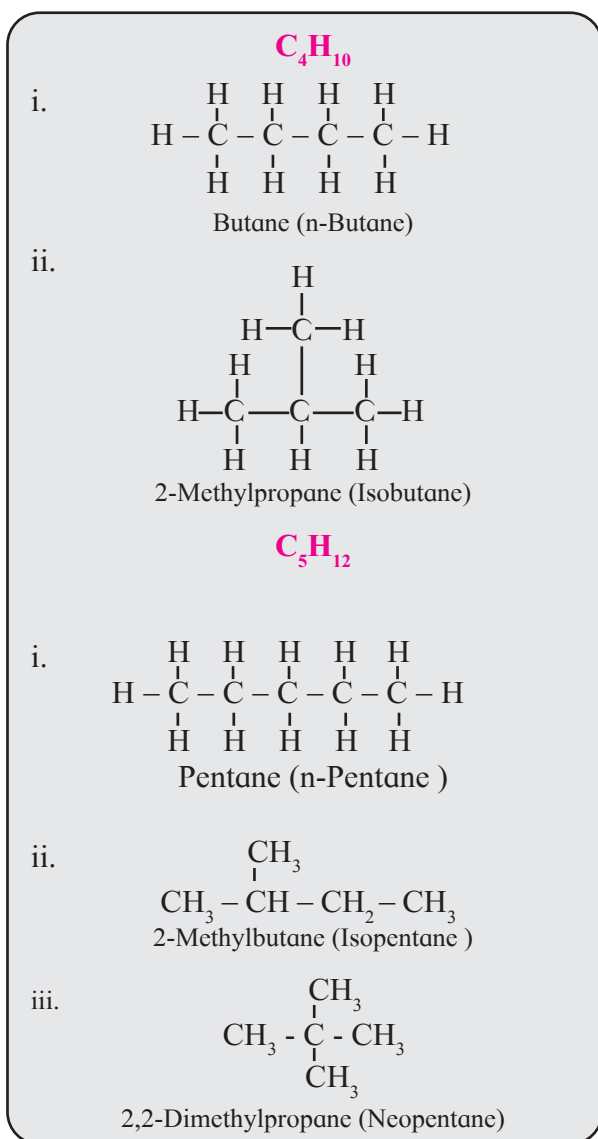
Internet my friend

Collect information about Hydrocarbon

Figure 15.2 shows IUPAC and common names of stuctural isomers of C_4H_{10} and C_5H_{12}.

The number of possible structural isomers increases rapidly with the increase in the number of carbon atoms. (See the Table 15.1).

Table 15.1 : Alkanes and isomer number

Number of Carbon	Alkane	Number of isomers
1	Methane	No structural isomer
2	Ethane	No structural isomer
3	Propane	No structural isomer
4	Butane	Two
5	Pentane	Three
6	Hexane	Five

C₄H₁₀

i.
$$H–\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}–\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}–\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}–\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}–H$$

Butane (n-Butane)

ii.

$$\begin{array}{c}H\\|\\H{-}C{-}H\\ \;\;|\\ H\;\;\;\;\;H\\ |\;\;\;\;\;|\\ H{-}C{-}C{-}C{-}H\\ |\;\;\;\;|\;\;\;\;|\\ H\;\;\;\;H\;\;\;\;H\end{array}$$

2-Methylpropane (Isobutane)

C₅H₁₂

i.
$$H–\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}–\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}–\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}–\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}–\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}–H$$

Pentane (n-Pentane)

ii.
$$CH_3 – \underset{\underset{CH_3}{|}}{CH} – CH_2 – CH_3$$

2-Methylbutane (Isopentane)

iii.
$$CH_3 - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} - CH_3$$

2,2-Dimethylpropane (Neopentane)

Fig. 15.2 : Structural isomers of butane and pentane

15.1.2 Conformations in alkanes : Alkanes have only single bonded atoms. You have learnt that a single covalent bond is formed by coaxial overlap of orbital and is called sigma (σ) bond (Refer to Chapter 5). As a direct consequence of coaxial overlap of orbitals, a sigma bond is cylindrically symmetrical and the extent of orbital overlap is unaffected by rotation about the single bond and therefore C-C bonds undergo rotation. The atoms bonded to one carbon of a C-C single bond change their relative position with reference to the atoms on the other carbon of that bond on rotation of that C-C single bond.

The resulting arrangements of the atoms in space about the C - C single bond are called conformations. Innumerable **conformations** result on complete rotation of a C - C single bond through 360°.

In chapter 14 you have learnt about **isomerism**. The phenomenon of existence of conformation is a type of **stereoisomerism**. In conformational isomerism the conformations (or **conformational isomers**) interconvert by rotation about a C - C single bond. Out of infinite **conformations of ethane** molecule two are extreme and called **staggered and eclipsed** conformation. They are represented by **Sawhorse formula** and **Newman projection formula** as shown in Fig. 15.3. Conformational isomerism in other alkanes is more complex.
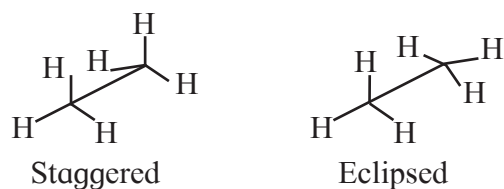
Staggered   Eclipsed
(a) Sawhorse formula
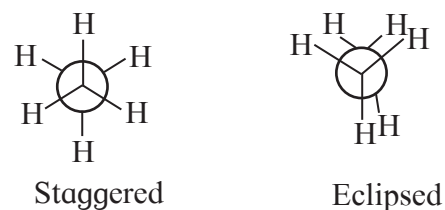
Staggered   Eclipsed
(b) Newman Projection formula

Fig. 15.3 : Representation of staggered and eclipsed conformation of ethanes

15.1.3 Industrial preparation of alkanes

a. Industrial source : Crude petroleum and natural gas are the source of alkanes. Dead plants buried under earth billions of year ago got converted into crude oil under the high temperature and pressure conditions. The crude oil collected in dome shaped cavities under the earth surface, which we call oil wells. Alkanes are obtained by fractional distillation of crude oil in oil refineries.
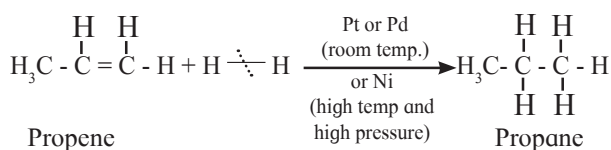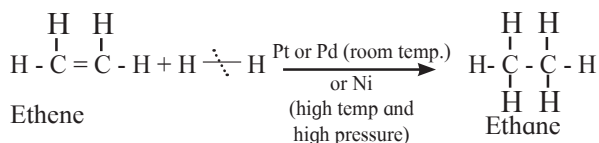
b. Methods of preparation of alkanes :
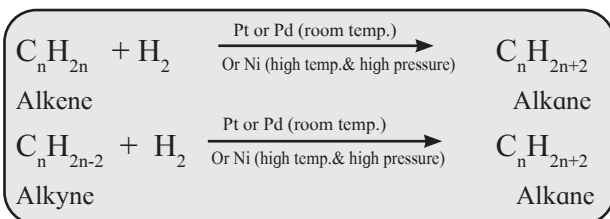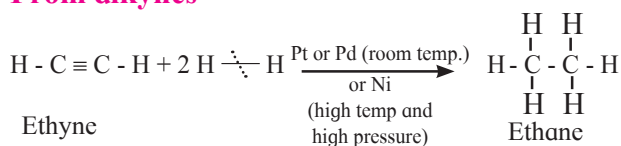
Can you recall?

- What is a catalyst ?
- What is addition reaction ?

1. From unsaturated hydrocarbons : Catalytic hydrogenation of alkenes or alkynes with dihydrogen gas gives corresponding alkane. Finely divided powder of platinum (Pt) or palladium (Pd) catalyse the hydrogenation of alkenes and alkynes at room temperature. Relatively high temperature and pressure are required with finely divided nickel as the catalyst.

From alkenes

Ethene → Ethane (Pt or Pd (room temp.) or Ni (high temp and high pressure))

Propene → Propane

From alkynes

Ethyne → Ethane

$$C_nH_{2n} + H_2 \xrightarrow[\text{Or Ni (high temp.\& high pressure)}]{\text{Pt or Pd (room temp.)}} C_nH_{2n+2}$$

Alkene → Alkane

$$C_nH_{2n-2} + H_2 \xrightarrow[\text{Or Ni (high temp.\& high pressure)}]{\text{Pt or Pd (room temp.)}} C_nH_{2n+2}$$
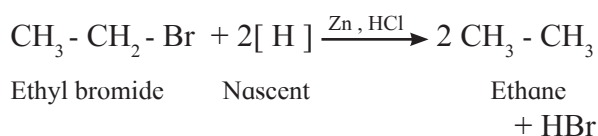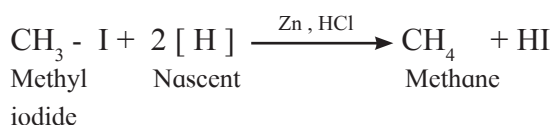
Alkyne → Alkane

Try this

Transform the following word equation into balanced chemical equation and write at least 3 changes that occur at molecular level during this chemical change.

$$2\text{-Methylpropene} + \text{Hydrogen} \xrightarrow{\text{catalyst}} \text{Isobutane}$$
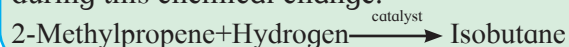
2. From alkyl halides

a. By reduction of alkyl halides : Alkyl halides on reduction with zinc and dilute hydrochloric acid form alkanes. The reduction of alkyl halides is due to nascent hydrogen obtained from the reducing agent Zn and dilute HCl.
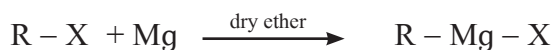
$$CH_3 - I + 2[H] \xrightarrow{Zn, HCl} CH_4 + HI$$

Methyl iodide   Nascent   Methane

$$CH_3 - CH_2 - Br + 2[H] \xrightarrow{Zn, HCl} 2\, CH_3 - CH_3$$

Ethyl bromide   Nascent   Ethane + HBr

b. By using reactive metal : In 19th century alkyl halides were transformed to alkane having double the number of carbons by Wurtz coupling reaction using the reactive metal sodium.

$$CH_3 \vdots Br + 2Na + Br \vdots CH_3 \xrightarrow{\text{dry ether}}$$
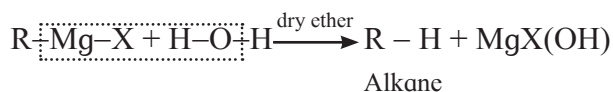$$CH_3 - CH_3 + 2NaBr$$
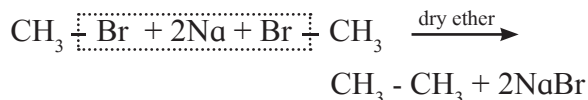
Later bettter methods using metals such as Mg, Li were developed. Grignard reaction is one of the new methods widely employed for preparation of alkanes.
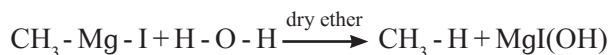
Alkyl magnesium halides (Grignard reagent) are obtained by treating alkyl halides with dry metal magnesium in the presence of dry ether. These on treatment with water give alkanes.

$$R - X + Mg \xrightarrow{\text{dry ether}} R - Mg - X$$

Alkyl halide   Alkyl magnesium halide

$$R\vdots Mg-X + H-O\vdots H \xrightarrow{\text{dry ether}} R - H + MgX(OH)$$

Alkane

$$CH_3 - Mg - I + H - O - H \xrightarrow{\text{dry ether}} CH_3 - H + MgI(OH)$$

Methyl magnesium iodide   Methane

Fig. 15.4 : Relative surface area of straight chain and branched alkanes

15.1.4 Physical properties of alkanes

i. Polarity : The electronegativity of carbon and hydrogen is nearly the same. C-H and C-C bonds are non-polar covalent bonds and alkanes are, thus, nonpolar. The forces which hold non-polar molecules together are the van der Waals forces. Those are usually weak. Larger the surface area of molecules, stronger are such intermolecular van der Waals forces.

The intermolecular forces are relatively stronger in straight chain alkanes than in branched alkanes (See Fig. 15.4).
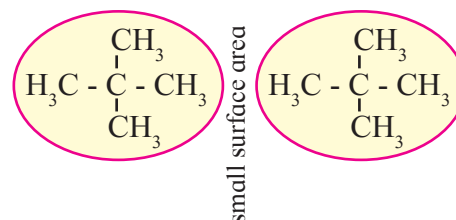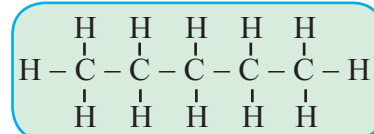Therefore straight chain alkanes have higher melting and boiling points.

Branched alkanes have lower melting and boiling points. Intermolecular forces are overcome partly during melting process and completely during boiling process. Table 15.2 shows the melting and boiling points of some alkanes. Alkanes are colourless and odourless. At room temperature, the first four alkanes are gases, next alkanes having 5 to 17 carbons are liquids and carbons 18 onwards are solids.

Use your brain power

Why are alkanes insoluble in water and readily soluble in organic solvents like chloroform or ether ?

Table 15.2 : Melting and Boiling points in alkanes

Molecular formula	Name	Molecular mass/u	b.p. (K)	m.p. (K)
CH_4	Methane	16	111.0	90.5
C_2H_6	Ethane	30	184.4	101.0
C_3H_8	Propane	44	230.9	85.3
C_4H_{10}	Butane	58	272.4	134.6
C_4H_{10}	2-Methylpropane	58	261.0	114.7
C_5H_{12}	Pentane	72	309.1	143.3
C_5H_{12}	2-Methylbutane	72	300.9	113.1
C_5H_{12}	2,2-Dimethylpropane	72	282.5	256.4
C_6H_{14}	Hexane	86	341.9	178.5

15.1.5 Chemical properties of alkanes :

Alkanes are relatively unreactive towards acids, bases, oxidizing and reducing agents. They undergo the following reactions under specified conditions.

1. Halogenation of alkanes : The reactions in which an atom or group of atoms in a molecule is replaced by another atom or group of atoms are known as **substitution reactions**. Substitution of H atoms of alkanes by X (halogen, X= Cl, Br, I and F) atom is called **halogenation of alkanes**. Alkanes react with halogens in presence of UV light or diffused sunlight or at higher temperature (573 To 773 K) to give mixture of alkyl halides.
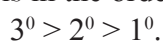
Chlorination of methane :

$$H - \underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}} - H + Cl - Cl \xrightarrow[\text{or } \Delta]{\text{UV light}} H - \underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}} - Cl + H - Cl$$

Methane Chlorine   Chloromethane   Hydrogen
                          (Methyl chloride) chloride

$$H - \underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}} - Cl + Cl - Cl \xrightarrow[\text{or } \Delta]{\text{UV light}} H - \underset{\underset{Cl}{|}}{\overset{\overset{H}{|}}{C}} - Cl + H - Cl$$

Chloromethane   Dichloromethane

$$H - \underset{\underset{Cl}{|}}{\overset{\overset{H}{|}}{C}} - Cl + Cl - Cl \xrightarrow[\text{or } \Delta]{\text{UV light}} H - \underset{\underset{Cl}{|}}{\overset{\overset{Cl}{|}}{C}} - Cl + H - Cl$$

Dichloromethane   Trichloromethane

$$H - \underset{\underset{Cl}{|}}{\overset{\overset{Cl}{|}}{C}} - Cl + Cl - Cl \xrightarrow[\text{or } \Delta]{\text{UV light}} Cl - \underset{\underset{Cl}{|}}{\overset{\overset{Cl}{|}}{C}} - Cl + H - Cl$$
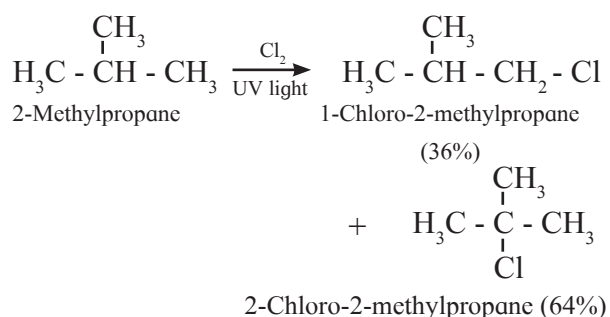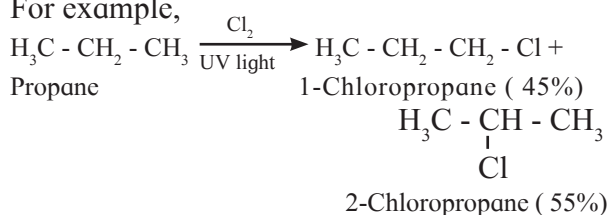
Trichloromethane   Tetrachloromethane
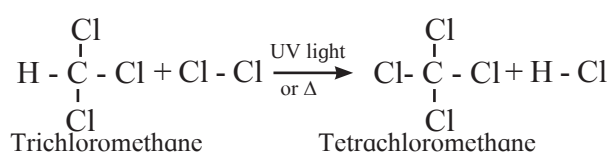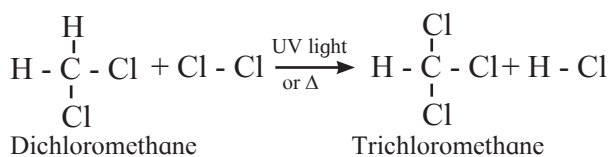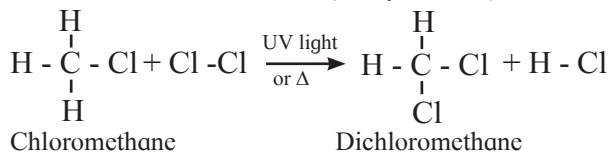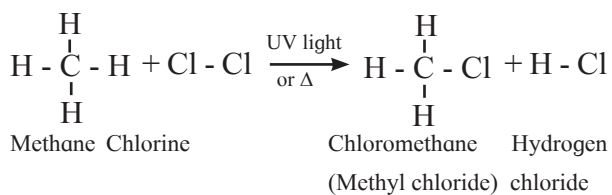
Tetrachloromethane is a major product when excess of chlorine is used. Chloromethane is obtained as major product when excess of methane is employed. The reactivity of halogens toward alkanes follows the order
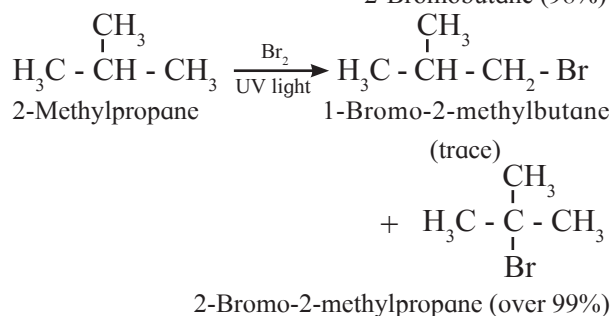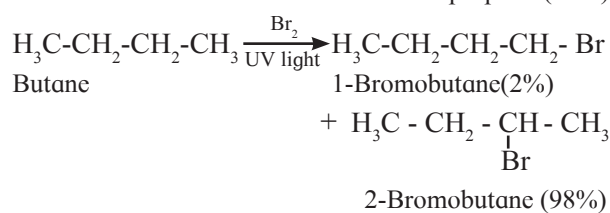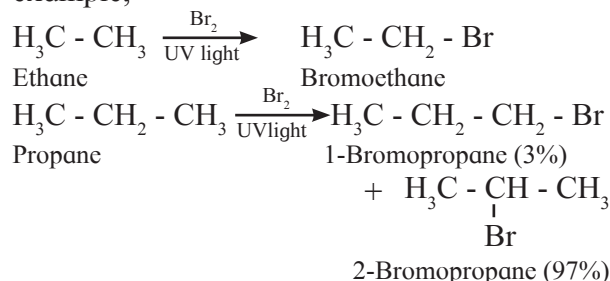
$$F_2 > Cl_2 > Br_2 > I_2.$$
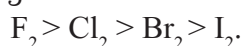
The ease of replacement of hydrogen atoms from the carbon is in the order of

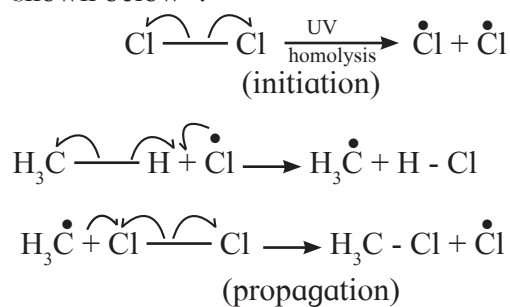$$3^0 > 2^0 > 1^0.$$

For example,

$$H_3C - CH_2 - CH_3 \xrightarrow[\text{UV light}]{Cl_2} H_3C - CH_2 - CH_2 - Cl +$$

Propane   1-Chloropropane (45%)

$$H_3C - \underset{\underset{Cl}{|}}{CH} - CH_3$$

2-Chloropropane (55%)

$$H_3C - \underset{\overset{|}{CH_3}}{CH} - CH_3 \xrightarrow[\text{UV light}]{Cl_2} H_3C - \underset{\overset{|}{CH_3}}{CH} - CH_2 - Cl$$

2-Methylpropane   1-Chloro-2-methylpropane
                          (36%)

$$+ \quad H_3C - \underset{\underset{Cl}{|}}{\overset{\overset{CH_3}{|}}{C}} - CH_3$$

2-Chloro-2-methylpropane (64%)

Bromination gives corresponding bromides, but in different proportions. For example,

$$H_3C - CH_3 \xrightarrow[\text{UV light}]{Br_2} H_3C - CH_2 - Br$$

Ethane   Bromoethane

$$H_3C - CH_2 - CH_3 \xrightarrow[\text{UVlight}]{Br_2} H_3C - CH_2 - CH_2 - Br$$

Propane   1-Bromopropane (3%)

$$+ \quad H_3C - \underset{\underset{Br}{|}}{CH} - CH_3$$

2-Bromopropane (97%)

$$H_3C-CH_2-CH_2-CH_3 \xrightarrow[\text{UV light}]{Br_2} H_3C-CH_2-CH_2-CH_2- Br$$

Butane   1-Bromobutane(2%)

$$+ \quad H_3C - CH_2 - \underset{\underset{Br}{|}}{CH} - CH_3$$

2-Bromobutane (98%)

$$H_3C - \underset{\overset{|}{CH_3}}{CH} - CH_3 \xrightarrow[\text{UV light}]{Br_2} H_3C - \underset{\overset{|}{CH_3}}{CH} - CH_2 - Br$$

2-Methylpropane   1-Bromo-2-methylbutane
                          (trace)

$$+ \quad H_3C - \underset{\underset{Br}{|}}{\overset{\overset{CH_3}{|}}{C}} - CH_3$$

2-Bromo-2-methylpropane (over 99%)

In bromination, there is high degree of selectivity as to which hydrogen atoms are replaced. Halogenation of alkanes follows the free radical mechanism. Homolysis of halogen molecule (X_2) generates halogen atoms, that is, halogen free radicals. The mechanism of the first step of chlorination of methane is shown below :
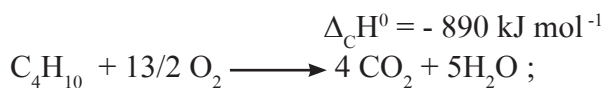
$$Cl \frown \frown Cl \xrightarrow[\text{homolysis}]{\text{UV}} \overset{\bullet}{Cl} + \overset{\bullet}{Cl}$$
(initiation)

$$H_3\overset{\frown}{C} \frown\frown H + \overset{\bullet}{Cl} \longrightarrow H_3\overset{\bullet}{C} + H - Cl$$

$$H_3\overset{\bullet}{C} + \overset{\frown}{Cl} \frown \frown Cl \longrightarrow H_3C - Cl + \overset{\bullet}{Cl}$$
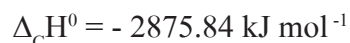(propagation)

2. Combustion : Alkanes on heating in the presence of air or dioxygen are completely oxidized to carbon dioxide and water with the evolution of a large amount of heat. That is why alkanes are good fuels.
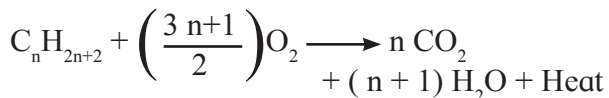
$$CH_4 + 2 O_2 \longrightarrow CO_2 + 2 H_2O ;$$
Methane

$$\Delta_C H^0 = - 890 \text{ kJ mol}^{-1}$$

$$C_4H_{10} + 13/2 O_2 \longrightarrow 4 CO_2 + 5H_2O ;$$
Butane

$$\Delta_C H^0 = - 2875.84 \text{ kJ mol}^{-1}$$

A representative combustion equation for alkane is

$$C_nH_{2n+2} + \left(\frac{3 n+1}{2} \right) O_2 \longrightarrow n CO_2 + (n + 1) H_2O + \text{Heat}$$

3. Pyrolysis : Alkanes on heating at higher temperature in absence of air decompose to lower alkanes, alkenes and hydrogen, etc. This is known as **pyrolysis or cracking**.

$$C_6H_{14} \xrightarrow{773 \text{ K}} \begin{cases} C_6H_{12} + H_2 \\ C_4H_8 + C_2H_6 \\ C_3H_6 + C_2H_4 + CH_4 \end{cases}$$
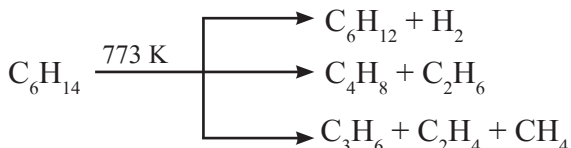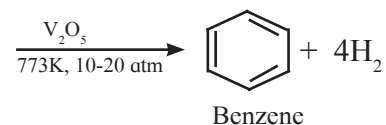
4. Reforming : Straight chain alkanes containing 6 to 10 carbon atoms are converted to benzene and its homologues on heating under 10 to 20 atm pressure at about 773 K in the presence of V_2O_5, Cr_2O_3, Mo_2O_3 etc. supported over alumina. The reaction involves simultaneous dehydrogenation and cyclization. This reaction is known as **aromatization or reforming** .

$$H_3C - CH_2 - CH_2 - CH_2 - CH_2 - CH_3$$
n-Hexane

$$\xrightarrow[\text{773K, 10-20 atm}]{V_2O_5} \quad \text{Benzene} \quad + 4H_2$$
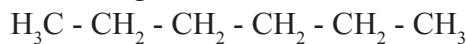
This process is used in refineries to produce high quality gasoline (the fuel used in automobiles).

15.1.6 Uses of alkanes :
1. First four alkanes are used as a fuel mainly for heating and cooking purpose. for example, LPG and CNG.
2. CNG, petrol, diesel are used as fuels for automobiles.
3. Lower liquid alkanes are used as solvent.
4. Alkanes with more than 35 C atoms (tar) are used for road surfacing.
5. Waxes are high molecular weight alkanes. They are used as lubricants.They are also used for the preparation of candles and carbon black that is used in manufacture of printing ink, shoe polish, etc.

15.2 Alkenes : Alkenes are unsaturated hydrocarbons containing at least one carbon-carbon double bond. Alkenes with one carbon-carbon double bond, contain two hydrogen atoms less than corresponding alkanes.They have general formula C_nH_{2n}.where n= 2,3,4... etc. You have also learnt about the IUPAC names of alkenes in Chapter 14.


Do you know ?

1. Alkenes are also known as olefins, because the first member ethylene or ethene reacts with chlorine to form oily substance.
2. The aliphatic unsaturated hydrocarbon containing two or three carbon-carbon double bonds are called alkadienes and alkatrienes, respectively. for example,
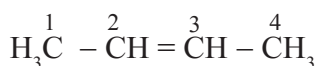
$$\overset{\displaystyle CH_3}{\underset{\displaystyle |}{H_2C = C - CH = CH_2}} \quad \text{Methylbuta-1,3-diene (Isoprene)}$$
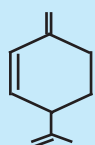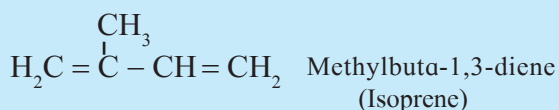
β-Phellandrene (oil of eucalyptus)

15.2.1 Isomerism in alkenes : Alkenes with more than three carbon atoms show both **structural isomerism** and **geometrical isomerism**.
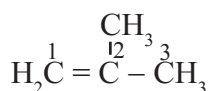
i. Structural isomerism : Alkenes with molecular formula C_4H_8 is butene. The structural formulae for C_4H_8 can be drawn in three diffferent ways :

$$\overset{1}{H_2C} = \overset{2}{CH} - \overset{3}{CH_2} - \overset{4}{CH_3}$$
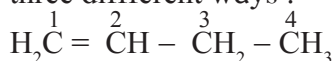
(I) But-1-ene (Chain of 4 carbon atoms)

$$\overset{1}{H_3C} - \overset{2}{CH} = \overset{3}{CH} - \overset{4}{CH_3}$$

(II) But-2-ene (Chain of 4 carbon atoms)

$$\overset{\displaystyle CH_3}{\underset{\displaystyle |}{\overset{1}{H_2C} = \overset{2}{C} - \overset{3}{CH_3}}}$$

(III) 2-Methylprop-1-ene (Chain of 3 carbon atoms)

Structure I and III along with II and III are the examples of chain isomerism. They differ in carbon chain length. Structure I and II are the examples of position isomerism because they differ in the position of double bond in the same carbon chain.

ii. Geometrical isomerism

The isomerism which arises due to the difference in spatial arrangement of atoms or groups about doubly bonded carbon (C=C) atoms is called *geometrical isomerism*. If the two atoms or groups bonded to each end of the C=C double bond are different, then molecule can be represented by two different special arrangements of the groups as follows :

(A)   (B)
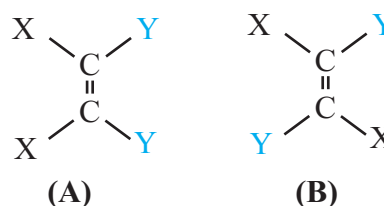
In structure (A), two identical atoms or groups lie on the same side of the double bond. **The geometrical isomer in which two identical or similar atoms or groups lie on the same side of the double bond is called** *cis-isomer*.

In structure (B), two identical atoms or groups lie on the opposite side of the double bond. **The geometrical isomer in which two identical or similar atoms or groups lie on the opposite side of the double bond is called trans-isomer.** Due to different arrangement of atoms or groups in space, these isomers differ in their physical properties like melting point, boiling point, solubility etc. Geometrical or cis-trans isomers of but-2-ene are represented as :
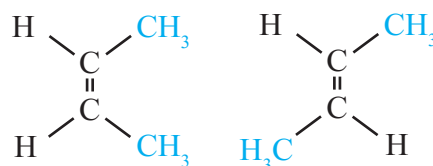
cis-But-2-ene   trans- But-2-ene
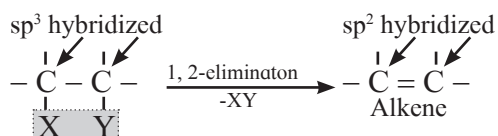(b.p. = 277 K)   (b.p. = 274 K)

239

15.2 Preparation of alkenes

a. Industrial sources : The most important alkenes for chemical industry are ethene, propene and buta-1,3-diene. Alkenes containing upto four carbon atoms can be obtained in pure form from the petroleum products. Ethene is produced from natural gas and crude oil by cracking.

b. Methods of preparation of alkenes

(I) Elimination reactions : (1,2 -elimination) The reactions in which two atoms or groups are eliminated or removed from adjacent carbon atoms are called **1,2 - elimination reactions**.

sp^3 hybridized   sp^2 hybridized

$$-\overset{|}{\underset{X}{C}}-\overset{|}{\underset{Y}{C}}- \xrightarrow[\text{-XY}]{1,\,2\text{-eliminaton}} -\overset{|}{C}=\overset{|}{C}-$$
Alkene

Remember

1. The carbon - carbon double bond can be generated from a carbon -carbon single bond by elimination reaction.
2. During elimination reaction sp^3 carbon atom changes to sp^2 carbon atom.
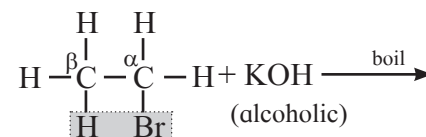
Some elimination reactions useful to prepare alkenes are described below.
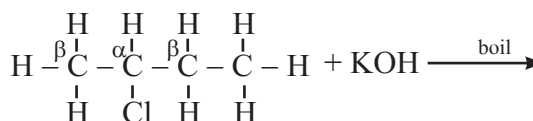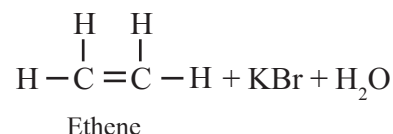
i. Dehydrohalogenation of alkyl halides

Dehydrohalogenation means removal of hydrogen (H) atom and halogen (X) atom from adjacent carbon atoms. The carbon carrying X is called α-carbon atom.

The hydrogen atom from adjacent carbon called β-carbon atom, is removed and the reaction is known as β-elimination.

Dehydrohalogenation suffers from the disadvantage that -H can be eliminated from the carbon on either side of the α-carbon bearing the -X. When an alkyl halide is boiled with a hot concentrated alcoholic solution of a strong base like KOH or NaOH, alkene is formed with removal of water molecule.
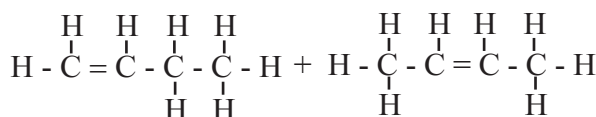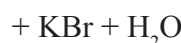
$$H-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{\overset{\beta}{C}}}-\overset{\overset{H}{|}}{\underset{\underset{Br}{|}}{\overset{\alpha}{C}}}-H+ KOH \xrightarrow{\text{boil}}$$
(alcoholic)

Bromoethane

$$H-\overset{\overset{H}{|}}{C}=\overset{\overset{H}{|}}{C}-H + KBr + H_2O$$
Ethene

$$H-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{\overset{\beta}{C}}}-\overset{\overset{H}{|}}{\underset{\underset{Cl}{|}}{\overset{\alpha}{C}}}-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{\overset{\beta}{C}}}-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-H + KOH \xrightarrow{\text{boil}}$$

2-Chlorobutane   alcoholic

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

But-1-ene (20%)   But-2-ene (80%)

$$+ KBr + H_2O$$

In dehydrohalogenation of 2-Chlorobutane, but-2-ene (disubstituted alkene) is the preferred product because it is formed faster than but-1-ene (monosubstituted alkene). This is in accordance to with Saytzeff rule.

Saytzeff rule : *In dehydrohalogenation the preferred product is the alkene that has the greater number of alkyl groups attached to doubly bonded carbon atoms.*

The ease of dehydrohalogenation of alkyl halides accordingly is in the order $3^0 > 2^0 > 1^0$

The ease of formation of alkenes :
R$_2$C = CR$_2$ > R$_2$C= CHR > R$_2$C = CH$_2$, RCH=CHR > RCH=CH$_2$
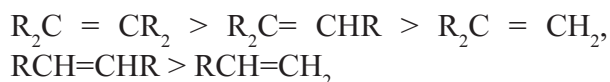
The stability of alkenes :
R$_2$C = CR$_2$ > R$_2$C= CHR > R$_2$C = CH$_2$, RCH=CHR > RCH=CH$_2$ > CH$_2$ = CH$_2$
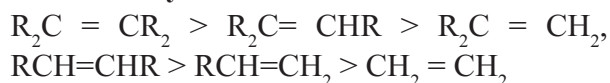
Can you recall?

- What are alcohols ?
- What is a dehydration reaction?
- What is a catalyst ?

Can you tell?

1. Explain by writing a reaction, the main product formed on heating 2-methylbutan-2-ol with concentrated sulphuric acid.
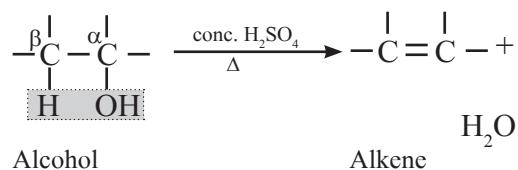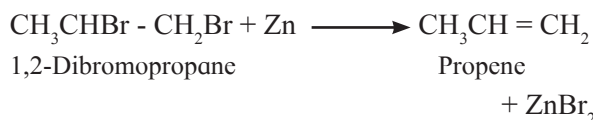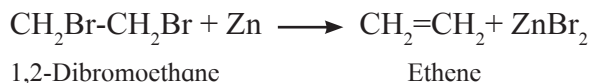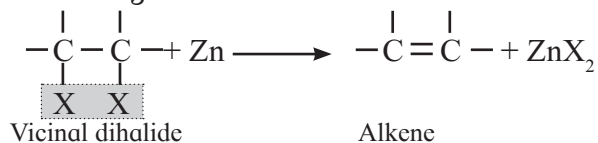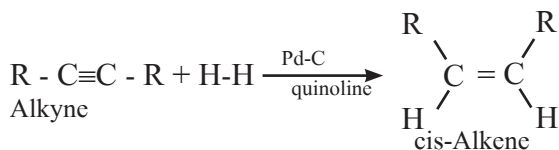2. Will the main product in the above reaction show geometrical isomerism?

ii. Dehydration of alcohols : Alcohols on heating with sulphuric acid form alkenes with elimination of water molecule. The reaction is known as catalyzed dehydration of alcohols. The exact conditions of dehydration depend upon the alcohol.

Dehydration of alcohol is an example of β-elimination since OH group from α-carbon along with a H atom from β-carbon atom is removed.

$$-\overset{\beta}{C}-\overset{\alpha}{C}- \xrightarrow[\Delta]{\text{conc. } H_2SO_4} -C=C-+$$
$$\underset{H\ \ OH}{} \qquad\qquad H_2O$$

Alcohol   Alkene

The ease of dehydration of alcohols is in the order $3^0 > 2^0 > 1^0$

$$H_3C-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{\overset{\beta}{C}}}-\overset{H}{\underset{OH}{\overset{\alpha}{C}}}-H \xrightarrow[413\ K]{75\%\ H_2SO_4}$$

$$H_3C-CH_2-CH=CH_2+H_2O$$
Butan-1-ol   But-1-ene (main product)

$$H_3C-\overset{H}{\underset{H}{\overset{\beta}{C}}}-\overset{H}{\underset{OH}{\overset{\alpha}{C}}}-\overset{H}{\underset{H}{\overset{\beta}{C}}}-H \xrightarrow[373K]{60\%\ H_2SO_4}$$

$$H_3C-CH=CH-CH_3+H_3C-CH_2-CH=CH_2$$
(major)   (minor) $+H_2O$

$$H-\overset{H}{\underset{H}{\overset{\beta}{C}}}-\overset{\beta\ CH_3}{\underset{OH}{\overset{\alpha}{C}}}-\overset{H}{\underset{H}{C}}-H \xrightarrow[363K]{20\%\ H_2SO_4}$$
2-Methylpropan-2-ol

$$H_3C-\overset{CH_3}{\underset{}{C}}=CH_2 + H_2O$$
2-Methylprop-1-ene

iii. By dehalogenation of vicinal dihalides : Removal of two halogen atoms from adjacent carbon atoms is called dehalogenation. The dihalides of alkane in which two halogen atoms are attached to adjacent carbon atoms are called vicinal dihalides. Vicinal dihalides on heating with zinc metal form alkenes.

$$-\overset{|}{\underset{X}{C}}-\overset{|}{\underset{X}{C}}-+ Zn \longrightarrow -C=C-+ ZnX_2$$
Vicinal dihalide   Alkene

$$CH_2Br-CH_2Br + Zn \longrightarrow CH_2=CH_2+ ZnBr_2$$
1,2-Dibromoethane   Ethene

$$CH_3CHBr-CH_2Br + Zn \longrightarrow CH_3CH=CH_2$$
1,2-Dibromopropane   Propene
$$+ ZnBr_2$$

(II) Addition reactions : By partial reduction of alkynes (or controlled hydrogenation of alkynes) :

The $C \equiv C$ triple bond of alkynes can be partially reduced to a $C = C$ double bond with calculated quantity of dihydrogen in presence of Lindlar's catalyst (palladised charcoal deactivated partially with quinoline or sulfur compound). The *Cis* isomer is obtained by this method.

$$R-C\equiv C-R + H-H \xrightarrow[\text{quinoline}]{Pd-C} \underset{\underset{\text{cis-Alkene}}{H}}{\overset{R}{\underset{}{C}}}=\overset{R}{\underset{H}{C}}$$
Alkyne

Trans alkene is obtained from alkyne on reduction with sodium in liquid ammonia.

$$R-C\equiv C-R \xrightarrow[\text{liquid } NH_3]{Na} \underset{\underset{\text{trans-alkene}}{H}}{\overset{R}{C}}=\overset{H}{\underset{R}{C}}$$
Alkyne
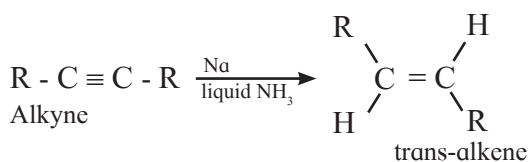
Table 15.3 : Melting point and boiling point of alkenes

Fornula	Name	Molecular mass (u)	b.p. (K)	m.p. (K)
$CH_2=CH_2$	Ethene	28	171	104
$CH_2 = CHCH_3$	Propene	42	225	88
$CH_2 =CHCH_2CH_3$	But-1-ene	56	267	--
$CH_2 = CH(CH_2)_2CH_3$	Pent-1-ene	70	303	--
$CH_2 =CH(CH_2)_3CH_3$	Hex-1-ene	84	337	135
cis $CH_3CH = CH\ CH_3$	cis-But-2-ene	56	277	134
trans $CH_3CH = CHCH_3$	trans-But-2-ene	56	274	167
$CH_2 = C(CH_3)_2$	Isobutylene	56	266	132

15.2.3 Physical properties of alkenes : Alkenes are nonpolar or weakly polar compounds those are insoluble in water, and soluble in non-polar solvents like benzene, ether, chloroform. They are less dense than water. From Table 15.3, it is clear that the boiling point of alkene rises with increasing number of carbons. Branched alkenes have lower boiling point than the corresponding straight chain alkane. The boiling point of alkene is very nearly the same as that of alkane with the same carbon skeleton.
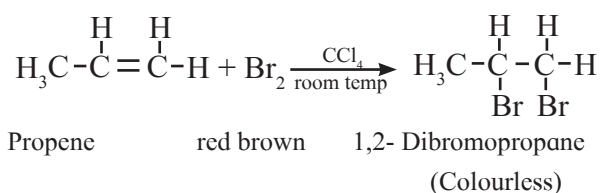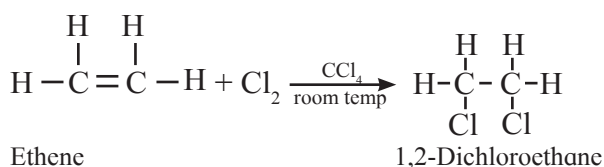
15.2.4 Chemical properties of alkenes :

Alkenes are more reactive than alkene due to the presence of pi (π) electrons. They undergo electrophilic addition reactions. The different reactions of alkenes are given below:

1. Addition of dihydrogen/hydrogenation (see section 15.1.4).

2. Addition of halogens/halogenation. Alkenes are converted into the corresponding vicinal dihalides by addition of halogens ($X_2 = Cl_2$ or Br_2) .
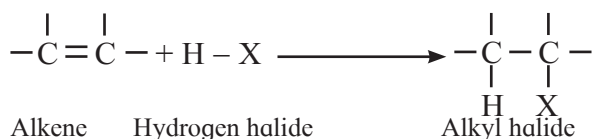
$$-\overset{|}{C}=\overset{|}{C}- + \ X_2 \xrightarrow[\text{room temp}]{CCl_4} -\overset{|}{\underset{X}{C}}-\overset{|}{\underset{X}{C}}-$$

Alkene   Vicinal dihalide
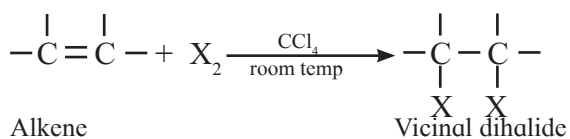
Iodine generally fails to react.

$$H-\overset{H}{\overset{|}{C}}=\overset{H}{\overset{|}{C}}-H + Cl_2 \xrightarrow[\text{room temp}]{CCl_4} H-\overset{H}{\overset{|}{\underset{\underset{Cl}{|}}{C}}}-\overset{H}{\overset{|}{\underset{\underset{Cl}{|}}{C}}}-H$$

Ethene   1,2-Dichloroethane

$$H_3C-\overset{H}{\overset{|}{C}}=\overset{H}{\overset{|}{C}}-H + Br_2 \xrightarrow[\text{room temp}]{CCl_4} H_3C-\overset{H}{\overset{|}{\underset{\underset{Br}{|}}{C}}}-\overset{H}{\overset{|}{\underset{\underset{Br}{|}}{C}}}-H$$

Propene   red brown   1,2- Dibromopropane
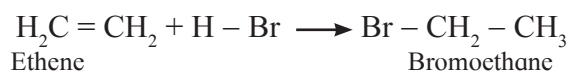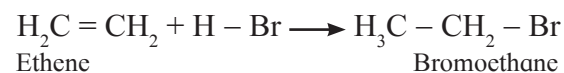   (Colourless)

Addition of bromine is useful test for detection C = C in unknown compounds. Red brown colour of bromine rapidly disappears in carbontetrachloride solution if a C = C double bond is present in the compound.

3. Addition of hydrogen halides/ hydrohalogenation : Addition of hydrogen halides (HX) like hydrogen chloride, hydrogen bromide and hydrogen iodide converts alkene into the corresponding alkyl halides.

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

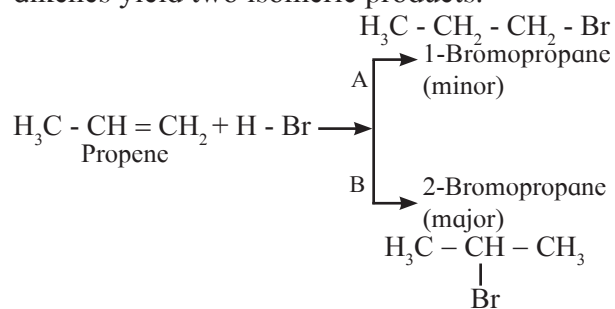Alkene   Hydrogen halide   Alkyl halide

The order of reactivity of hydrogen halides is HI > HBr > HCl

Addition reaction of HBr to symmetrical alkenes : The addition of HBr to symmetrical alkenes yield only one product.

$$H_2C = CH_2 + H-Br \longrightarrow H_3C - CH_2 - Br$$
Ethene   Bromoethane

$$H_2C = CH_2 + H-Br \longrightarrow Br - CH_2 - CH_3$$
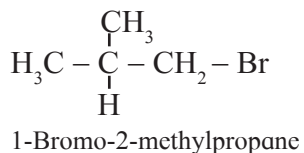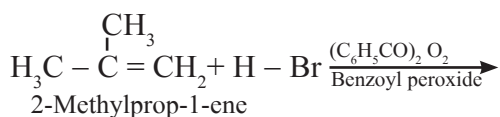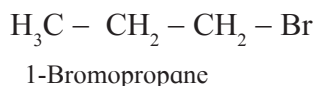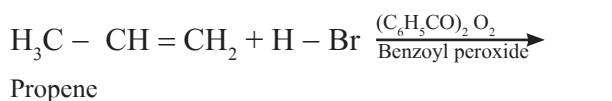Ethene   Bromoethane

Addition reaction of HBr to unsymmetrical alkenes : Addition of HBr to unsymmetrical alkenes yield two isomeric products.

$$H_3C - CH = CH_2 + H - Br \longrightarrow$$
Propene

A → $H_3C - CH_2 - CH_2 - Br$
1-Bromopropane (minor)

B → 2-Bromopropane (major)
$$H_3C - CH - CH_3$$
$$\qquad \quad | $$
$$\qquad \quad Br$$

Experimentally it has been found that 2-Bromopropane is the major product. Russian chemist Markovnikov studied hydrohalogenation of a number of an unsymmetrical alkenes and formulated a geneneral rule (1869) as follows :

Markovnikov's rule : When an unsymmetrical reagent is added to unsymmetrical alkene, the negative part $(X^{\ominus})$ of the reagent gets attached to the carbon atom which carries less number of hydrogen atoms.

Anti- Markovnikov addition Or peroxide effect or Kharasch - Mayo effect : In 1933, M. S. Kharasch and F. R. Mayo discovered that the addition of HBr to unsymmetrical alkene in the presence of organic peroxide (R-O-O-R) takes place in the opposite orientation to that suggested by Markovnikov 's rule.
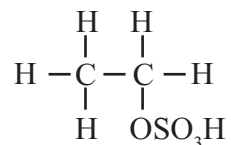
$$H_3C - CH = CH_2 + H - Br \xrightarrow{\frac{(C_6H_5CO)_2 \, O_2}{\text{Benzoyl peroxide}}}$$
Propene

$$H_3C - CH_2 - CH_2 - Br$$
1-Bromopropane

$$\overset{\displaystyle CH_3}{\underset{\displaystyle}{H_3C - \overset{|}{C} = CH_2}} + H - Br \xrightarrow{\frac{(C_6H_5CO)_2 \, O_2}{\text{Benzoyl peroxide}}}$$
2-Methylprop-1-ene

$$H_3C - \overset{\displaystyle CH_3}{\underset{\displaystyle H}{\overset{|}{\underset{|}{C}}} - CH_2 - Br}$$
1-Bromo-2-methylpropane

www Internet my friend

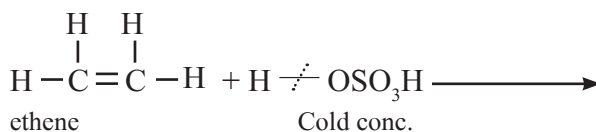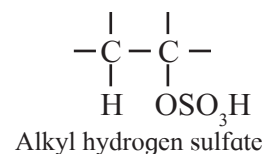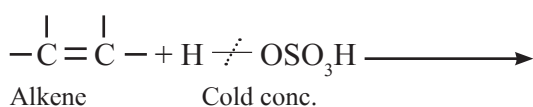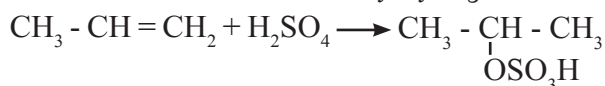https://www.britanicacom>science>hydrocarbon

Remember

1. The orientation of addition of HBr to unsymmetrical alkene is determined by the presence or absence of peroxide.
2. The peroxide has no effect upon the addition of HCl and HI.

4. Addition of sulfuric acid

Alkenes react with cold concentrated sulphuric acid to form alkyl hydrogen sulfate ($ROSO_3H$). The addition takes place according to **Markovnikov's rule**.

$$\overset{\displaystyle | \quad |}{-C = C -} + H \, \dashv \, OSO_3H \longrightarrow$$
Alkene   Cold conc.

$$\overset{\displaystyle | \quad |}{-\underset{\displaystyle H \quad OSO_3H}{\overset{|}{C} - \overset{|}{C} -}}$$
Alkyl hydrogen sulfate

$$H - \overset{\displaystyle H \quad H}{\overset{|}{C} = \overset{|}{C}} - H + H \, \dashv \, OSO_3H \longrightarrow$$
ethene   Cold conc.

$$H - \overset{\displaystyle H \quad H}{\underset{\displaystyle H \quad OSO_3H}{\overset{|}{C} - \overset{|}{C}} - H}$$
ethyl hydrogen sulfate

$$CH_3 - CH = CH_2 + H_2SO_4 \longrightarrow CH_3 - \underset{\displaystyle OSO_3H}{\overset{|}{CH}} - CH_3$$
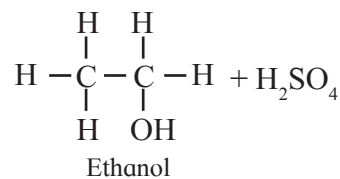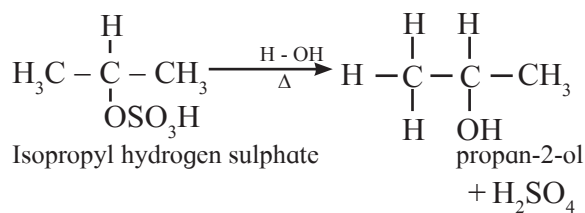isopropyl hydrogen sulfate

If alkyl hydrogen sulfate is diluted with water and heated, then an alcohol having the same alkyl group as the original alkyl hydrogen sulfate is obtained. This is an excellent method for the large scale manufacture of alcohols.
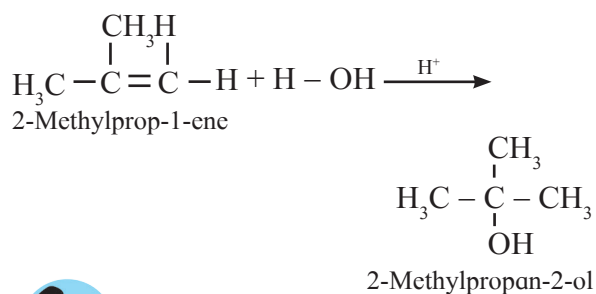
$$CH_3 - CH_2 - OSO_3H \xrightarrow[\Delta]{H - OH}$$
Ethyl hydrogen sulfate

$$H - \overset{\displaystyle H \quad H}{\underset{\displaystyle H \quad OH}{\overset{|}{C} - \overset{|}{C}} - H} + H_2SO_4$$
Ethanol

$$H_3C - \underset{\underset{OSO_3H}{|}}{\overset{\overset{H}{|}}{C}} - CH_3 \xrightarrow[\Delta]{H-OH} H - \underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}} - \underset{\underset{OH}{|}}{\overset{\overset{H}{|}}{C}} - CH_3$$

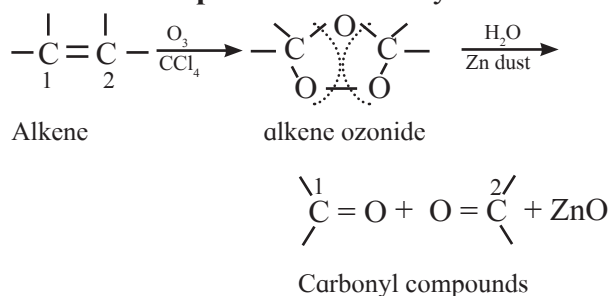Isopropyl hydrogen sulphate   propan-2-ol
$$+ H_2SO_4$$

Reactive alkenes on adding water molecules in the presence of concentrated sulphuric acid, form alcohol.The addition of water takes place according to **Markovnikov's rule**.This reaction is known as hydration of alkenes.
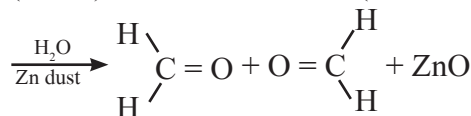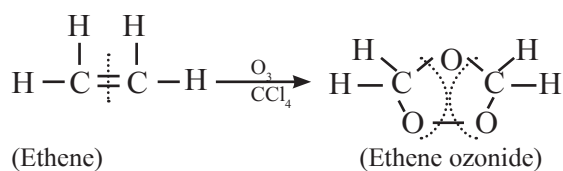
$$H_3C - \underset{\underset{}{\overset{\overset{CH_3 H}{|\quad |}}{C=C}}}{} - H + H - OH \xrightarrow{H^+}$$

2-Methylprop-1-ene

$$H_3C - \underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}} - CH_3$$

2-Methylpropan-2-ol

🗣 Can you tell?

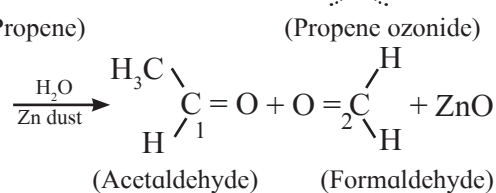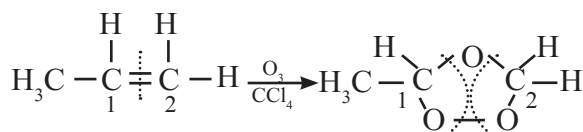Why are Propan-1-ol and 2-Methypropan-1-ol are not prepared by this method ?

5. Ozonolysis of alkenes : The C = C double bond gets cleaved on reaction with ozone followed by reduction. This overall process of formation of ozonide by reaction of ozone with alkene in the **first step** and then decomposing it to the carbonyl compounds by reduction in the **second step** is called ozonolysis.

$$-\underset{1}{\overset{|}{C}}=\underset{2}{\overset{|}{C}}- \xrightarrow[CCl_4]{O_3} -\overset{}{\underset{}{C}}\overset{O}{\underset{O\;O}{\diamond}}\overset{}{\underset{}{C}}- \xrightarrow[Zn\,dust]{H_2O}$$

Alkene   alkene ozonide

$$\overset{1}{\underset{}{C}}=O + O=\overset{2}{\underset{}{C}} + ZnO$$

Carbonyl compounds

Ozone gas is passed into solution of the alkene in an inert solvent like carbon tetrachloride, unstable alkene ozonide is obtained. This is subsequently treated with water in the presence of a reducing agent zinc dust to form carbonyl comounds, namely, aldehydes and/or ketones .

$$H - \underset{}{\overset{\overset{H}{|}}{C}} \vdots \underset{}{\overset{\overset{H}{|}}{C}} - H \xrightarrow[CCl_4]{O_3} H - C \overset{O}{\underset{O\;O}{\diamond}} C - H$$

(Ethene)   (Ethene ozonide)

$$\xrightarrow[Zn\,dust]{H_2O} \underset{H}{\overset{H}{>}}C=O + O=C\overset{H}{\underset{H}{<}} + ZnO$$

(Formaldehyde) (Formaldehyde)

$$H_3C - \underset{1}{\overset{\overset{H}{|}}{C}} \vdots \underset{2}{\overset{\overset{H}{|}}{C}} - H \xrightarrow[CCl_4]{O_3} H_3C - \underset{1}{C} \overset{O}{\underset{O\;O}{\diamond}} \underset{2}{C} - H$$

(Propene)   (Propene ozonide)

$$\xrightarrow[Zn\,dust]{H_2O} \underset{H}{\overset{H_3C}{>}}\underset{1}{C}=O + O=\underset{2}{C}\overset{H}{\underset{H}{<}} + ZnO$$

(Acetaldehyde)   (Formaldehyde)

🧠 Remember

1. In the cleavage products a carbonyl group (C =O) is formed at each of the original doubly bonded carbon atoms.
2. Knowing the number and arrangement of carbon atoms in these aldehydes and ketones produced, we can identify the structure of original alkene.
3. The role of zinc dust is to prevent the formation of hydrogen peroxide which oxidizes aldehydes to corresponding acids.
4. This reaction is used to locate the position and determine the number of double bonds in alkenes.
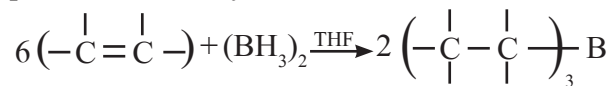
🧠 Use your brain power

On ozonolysis an alkene forms the following carbonyl compounds. Draw the structure of unknown alkene from which these compounds are formed.
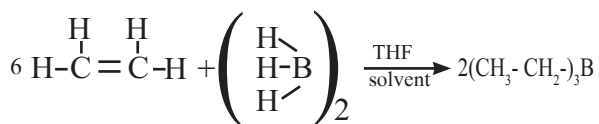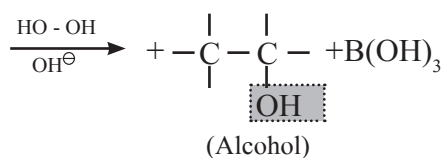HCHO and $CH_3COCH_2CH_3$

6. Hydroboration- oxidation of alkene
Alkenes with diborane in tetrahydrofuran (THF) solvent undergo hydroboration to form trialkylborane, which on oxidation with
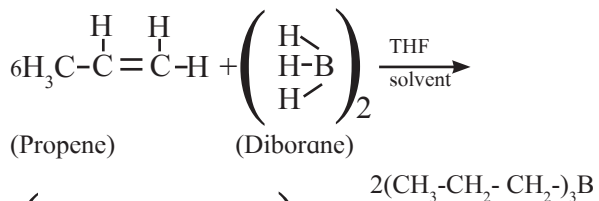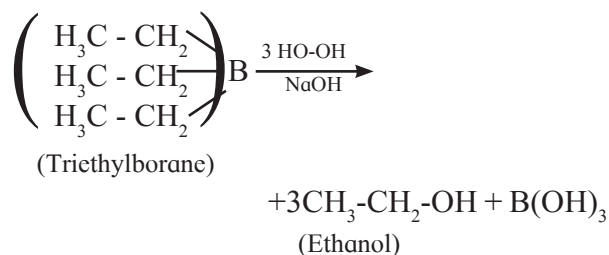
alkaline peroxide forms primary alcohol. The overall reaction gives **Anti-Markovnikov's** product from unsymmetrical alkenes
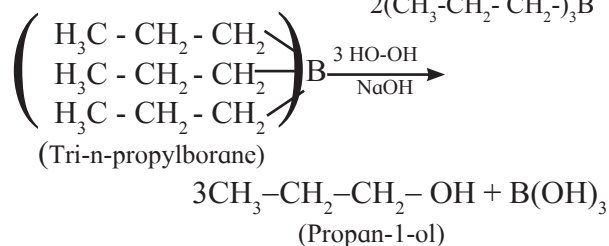
$$6\left(-\overset{|}{C}=\overset{|}{C}-\right)+(BH_3)_2 \xrightarrow{THF} 2\left(-\overset{|}{C}-\overset{|}{C}-\right)_3 B$$

(Alkene)   (Diborane)   (Trialkylborane)

$$\xrightarrow[OH^\ominus]{HO-OH} + -\overset{|}{C}-\overset{|}{C}- +B(OH)_3$$
$$\boxed{OH}$$
(Alcohol)

$$6\ H-\overset{H}{\underset{}{C}}=\overset{H}{\underset{}{C}}-H + \left(\overset{H}{\underset{H}{\diagdown}}_{H-B}\right)_2 \xrightarrow[solvent]{THF} 2(CH_3- CH_2-)_3B$$

(Ethene)   (Diborane)

$$\left(\begin{array}{c} H_3C - CH_2 \\ H_3C - CH_2 \\ H_3C - CH_2 \end{array}\!\!B\right) \xrightarrow[NaOH]{3\ HO-OH}$$

(Triethylborane)

$$+3CH_3-CH_2-OH + B(OH)_3$$
(Ethanol)

$$6H_3C-\overset{H}{\underset{}{C}}=\overset{H}{\underset{}{C}}-H + \left(\overset{H}{\underset{H}{\diagdown}}_{H-B}\right)_2 \xrightarrow[solvent]{THF}$$

(Propene)   (Diborane)

$$2(CH_3-CH_2- CH_2-)_3B$$

$$\left(\begin{array}{c} H_3C - CH_2 - CH_2 \\ H_3C - CH_2 - CH_2 \\ H_3C - CH_2 - CH_2 \end{array}\!\!B\right) \xrightarrow[NaOH]{3\ HO-OH}$$

(Tri-n-propylborane)

$$3CH_3-CH_2-CH_2- OH + B(OH)_3$$
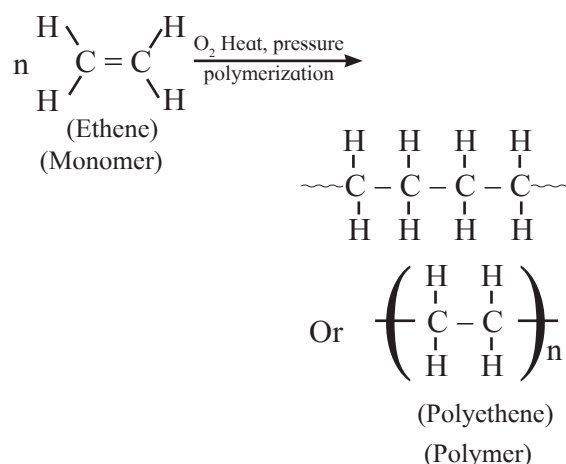(Propan-1-ol)

7. Polymerization : The process in which large number of small molecules join together and form very large molecules with repeating units is called **polymerization**. The compound having very large molecules made of large number repeating small units is called **polymer** and the simple compound forming the repeating units in the polymer is called **monomer**.

For example, ethene at high temperature and under high presssure interacts with oxygen, and undergoes polymerization giving high molecular weight polymer called polyethene.

$$n\ \overset{H}{\underset{H}{\diagdown}}C=C\overset{H}{\underset{H}{\diagup}} \xrightarrow[polymerization]{O_2\ Heat,\ pressure}$$

(Ethene)
(Monomer)

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

Or
$$\left(\begin{array}{cc} H & H \\ | & | \\ C & - C \\ | & | \\ H & H \end{array}\right)_n$$

(Polyethene)
(Polymer)

Here n represents the number of repeating units and is a large number.
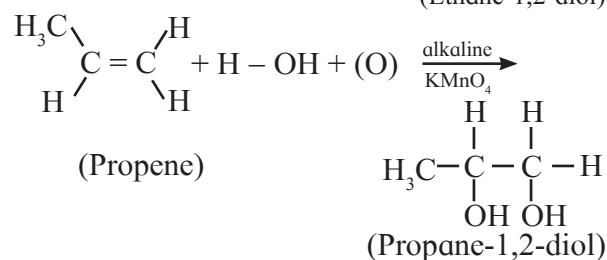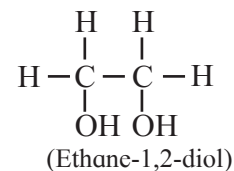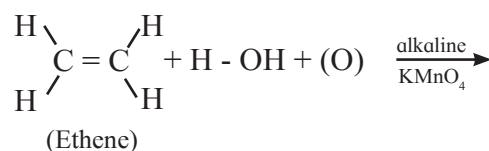
Use your brain power

Write the structure of monomer from which each of the following polymers are obtained.

a. Teflon $-(CF_2-CF_2)-$

b. Polypropene
$$\left(\begin{array}{cc} CH_3 & H \\ | & | \\ C & - C \\ | & | \\ H & Cl \end{array}\right)_n$$

c. Polyvinyl chloride
$$\left(\begin{array}{cc} H & H \\ | & | \\ C & - C \\ | & | \\ H & Cl \end{array}\right)_n$$

8. Hydroxylation : Alkenes react with cold and dilute alkaline potassium permanganate to form glycols.

$$\overset{H}{\underset{H}{\diagdown}}C=C\overset{H}{\underset{H}{\diagup}} + H-OH + (O) \xrightarrow{\underset{KMnO_4}{alkaline}}$$

(Ethene)

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

(Ethane-1,2-diol)

$$\overset{H_3C}{\underset{H}{\diagdown}}C=C\overset{H}{\underset{H}{\diagup}} + H-OH + (O) \xrightarrow{\underset{KMnO_4}{alkaline}}$$

(Propene)

$$H_3C-\overset{H}{\underset{OH}{C}}-\overset{H}{\underset{OH}{C}}-H$$

(Propane-1,2-diol)

Hydroxylation of alkenes is the most important method for the synthesis of 1,2-diols (Glycols). During this reaction the purple colour of $KMnO_4$ disappears. Hence such reaction serves as qualitative test for detecting the presence of double bond in the compound under test. This is known as **Baeyer's test**.

9. Oxidation : Alkenes on oxidation with acidic $KMnO_4$ or acidic potassium dichromate form ketones and / or acids.

$$H_3C - CH = CH_2 \xrightarrow[(O)]{KMnO_4, H^\oplus} H_3C - \overset{\overset{O}{\|}}{C} - OH$$
(Prop-1-ene) (Ethanoic acid)
$$+ CO_2 + H_2O$$

$$H_3C - \overset{\overset{CH_3}{|}}{C} = CH - CH_3 \xrightarrow[(O)]{KMnO_4, H^\oplus}$$
(2-Methylbut-2-ene)

$$H_3C - \overset{\overset{CH_3}{|}}{C} = O + H_3C - \overset{\overset{O}{\|}}{C} - OH$$
Propan-2-one   Ethanoic acid
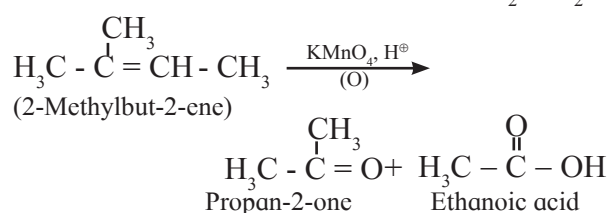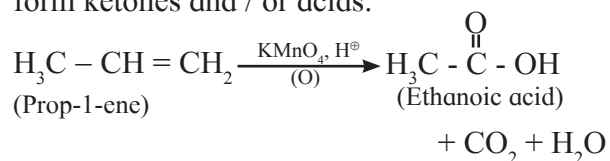
15.2.5 Uses of alkenes
1. Alkenes, are used as starting materials for preparation of alkyl halides, alcohols, aldehydes, ketones , acids etc.
2. Ethene and propene are used to manufacture polythene, polypropylene those find use in bags, toys, bottles, etc.
3. Ethene is used for artificial ripening of fruits, such as mangoes.

Can you tell?
- What are aliphatic hydrocarbons?
- Compare the proportion of carbon and hydrogen atoms in ethane, ethene and ethyne. Which compound is most unsaturated with hydrogen ?

15.3 Alkynes : Alkynes are aliphatic unsaturated hydrocarbons containing at least one $C \equiv C$. The number of hydrogen atoms is still less in alkynes as compared to alkenes. Their general formula is C_nH_{2n-2} . Table 15.4 shows names and formulae of lower alkynes.

15.3 Isomerism in alkynes : Alkynes show position isomerism which is a type of structural isomerism. For example 1-butyne and 2-butyne. 1-Alkynes are also called terminal alkynes.

Table 15.4 : Lower alkynes

| n	Molecular formula	Structural formula and Common name	IUPAC name
2	C_2H_2	H-C ≡ C-H Acetylene	Ethyne
3	C_3H_4	CH_3-C≡ CH Methyl acetylene	Propyne
4	C_4H_6	CH_3-CH_2-C≡CH Ethyl acetylene	But-1-yne
5	C_4H_6	C H$_3$ - C ≡ C - C H$_3$ Dimethyl acetylene	But-2-yne

Do you know ?

1. Simplest alkyne is ethyne which is known as acetylene.

2. The carbon-carbon triple bond is a functional group.

3. The aliphatic unsaturated hydrocarbons containing two or three carbon-carbon triple bonds are called alkadiynes and alkatriynes, respectively.

4. Cicutoxin from poisonous plants 'water hemlock'.

$$HO - (CH_2)_3 - C \equiv C - C \equiv C - (C_{10}H_{14}) -OH$$

15.3.2 Preparation of alkynes
a. Industrial sources :
i. Ethyne is industrially prepared by controlled, high temperature partial oxidation of methane.

$$6CH_4 + 2O_2 \xrightarrow{1773K} 2H - C \equiv C - H + 2 CO_2 + 10 H_2$$
Methane   Ethyne
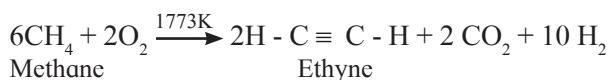
ii. From calcium carbide : Industrially the alkyne ethyne is prepared by reaction of calcium carbide with water.
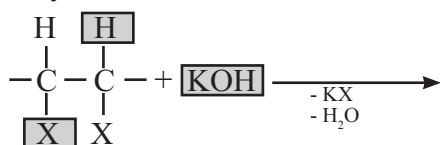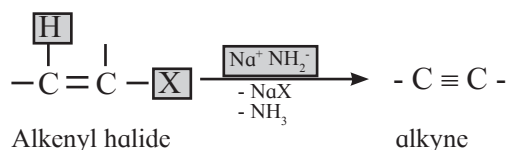
$$CaC_2 + 2H_2O \longrightarrow C_2H_2 + Ca (OH)_2$$

b. Methods of preparation of alkynes

1. By dehydrohalogenation of vicinal dihalides : Removal of H and X from adjacent carbon atoms is called dehydrohalogenation. Vicinal dihalides react with alcoholic solution of potassium hydroxide to form alkenyl halide which on further treating with sodamide forms alkyne.
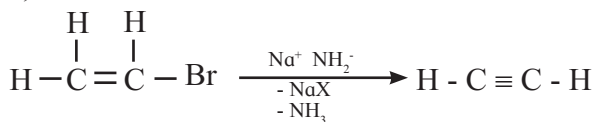
$$-\overset{H}{\underset{X}{\underset{|}{\overset{|}{C}}}}-\overset{\boxed{H}}{\underset{X}{\underset{|}{\overset{|}{C}}}}-+\boxed{KOH} \xrightarrow[\text{- H}_2\text{O}]{\text{- KX}}$$

Vicinal dihalide (Alcoholic)

$$-\overset{\boxed{H}}{\underset{|}{C}}=\overset{|}{\underset{|}{C}}-\boxed{X} \xrightarrow[\substack{\text{- NaX} \\ \text{- NH}_3}]{\boxed{Na^+\ NH_2^-}} -C\equiv C-$$

Alkenyl halide   alkyne

$$H-\overset{H}{\underset{Br}{\underset{|}{\overset{|}{C}}}}-\overset{H}{\underset{Br}{\underset{|}{\overset{|}{C}}}}-H + KOH \xrightarrow[\text{(Alcoholic) - H}_2\text{O}]{\text{- KBr}}$$

1,2-Dibromoethane

$$H-\overset{H}{\underset{|}{C}}=\overset{H}{\underset{|}{C}}-Br \xrightarrow[\substack{\text{- NaX} \\ \text{- NH}_3}]{Na^+\ NH_2^-} H-C\equiv C-H$$

Bromoethene   Ethyne

$$H_3C-\overset{H}{\underset{Cl}{\underset{|}{\overset{|}{C}}}}-\overset{H}{\underset{Cl}{\underset{|}{\overset{|}{C}}}}-H + KOH \xrightarrow[\text{(Alcoholic) - H}_2\text{O}]{\text{- KCl}}$$

1,2-Dichloropropane

$$H_3C-\overset{H}{\underset{|}{C}}=\overset{H}{\underset{|}{C}}-Cl \xrightarrow[\substack{\text{- NaCl} \\ \text{- NH}_3}]{Na^+\ NH_2^-} H_3C-C\equiv C-H$$
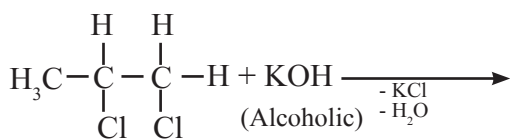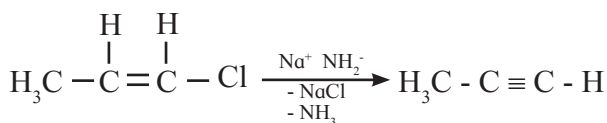
1-Chloropropene   Propyne

🗣 Can you tell?

Why sodamide is used in second step to remove HX from alkenyl halide in place of alcoholic KOH?

2. From terminal alkynes : Terminal alkynes are the compounds in which hydrogen atom is directly attached to triply bonded carbon atom.

$$H-C\equiv C-H$$
$$R-C\equiv C-H$$
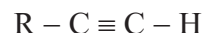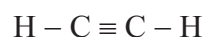
Such hydrogen atom shows appreciable acidity and can be given away as proton on reaction with sufficiently strong base.

In this method a smaller terminal alkyne first reacts with a very strong base like lithium amide to form metal acetylide (Lithium amide is easier to handle than sodamide).
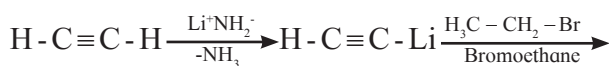
Higher alkynes are obtained by reacting metal acetylides (alkyn-1-yl lithium) with primary alkyl halides.

$$R-C\equiv C-\boxed{H}+Li^+\boxed{NH_2^-} \longrightarrow R-C\equiv C-Li+\boxed{NH_3}$$

Terminal alkyne   Lithium amide   Alkyn-1-yl lithium

$$R-C\equiv C-\boxed{Li}+R^1-\boxed{X} \longrightarrow R-C\equiv C-R^1+\boxed{LiX}$$

Alkyn-1-yl lithium   Primary alkyl halide   Higher alkyne

$$H-C\equiv C-H \xrightarrow[\text{-NH}_3]{Li^+NH_2^-} H-C\equiv C-Li \xrightarrow[\text{Bromoethane}]{H_3C-CH_2-Br}$$

Ethyne   Ethynyllithium

$$H-C\equiv C-CH_2-CH_3 + LiBr$$
But-1-yne

$$H_3C-C\equiv C-H \xrightarrow[\text{-NH}_3]{Li^+NH_2^-} H_3C-C\equiv C-Li$$
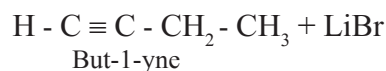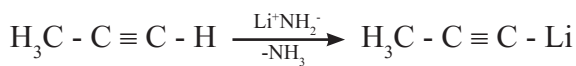
Propyne   Prop-1-yn-1-yl lithium
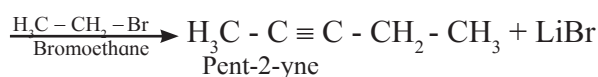
$$\xrightarrow[\text{Bromoethane}]{H_3C-CH_2-Br} H_3C-C\equiv C-CH_2-CH_3 + LiBr$$
Pent-2-yne

🧠 Use your brain power

Convert : 1-Bromobutane to Hex-1yne.

15.3.3 Physical properties of alkynes : The physical properties of alkynes are similar to those of alkanes and alkenes. They are less dense than water. They are insoluble in water and quite soluble in less polar organic solvents like ether, benzene, carbon tetrachloride. The melting points and boiling points of alkynes increase with an increase in molecular mass (Table 15.5).
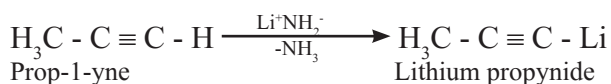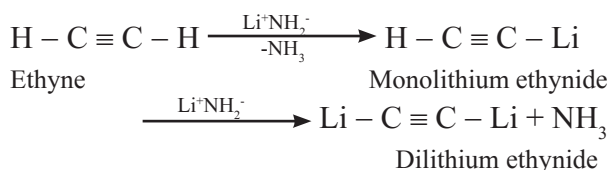
Table 15.5 : Melting point and Boiling point of alkynes

Fornula	Name	Molecular mass/u	Physical State	b.p.(K)	m.p.(K)
CH =CH	Ethyne	26	Gas	198	191
CH = CCH$_3$	Propyne	40	Gas	250	171.5
CH =CCH$_2$CH$_3$	But-1-yne	54	Gas	282	151
CH = C(CH$_2$)$_2$CH$_3$	Pent-1-yne	68	Liquid	313	175
CH =C(CH$_2$)$_3$CH$_3$	Hex-1-yne	82	Liquid	345	149

15.3.4 Chemical properties of alkynes :

1. Acidity of alkynes :

The hydrogen bonded to C ≡ C triple bond has acidic character. Lithium amide (LiNH$_2$) is very strong base and it reacts with terminal alkynes to form lithium acetylides with the liberation of hydrogen indicating acidic nature of terminal alkynes. Why is it so ? In terminal alkynes, hydrogen atom is directly attached to *sp* hybridized carbon atom. In *sp* hybrid orbital, the percentage of s- character is 50%. An electron in s-orbital is very close to the nucleus and is held tightly. The sp hybrid carbon atom in terminal alkynes is more electronegative than the sp^2 carbon in ethene or the sp^3 carbon in ethane. Due to high electronegative character of carbon in terminal alkynes, hydrogen atom can be given away as proton (H$^+$) to very strong base.

Examples

$$H - C \equiv C - H \xrightarrow[-NH_3]{Li^+NH_2^-} H - C \equiv C - Li$$

Ethyne   Monolithium ethynide

$$\xrightarrow{Li^+NH_2^-} Li - C \equiv C - Li + NH_3$$

Dilithium ethynide

$$H_3C - C \equiv C - H \xrightarrow[-NH_3]{Li^+NH_2^-} H_3C - C \equiv C - Li$$

Prop-1-yne   Lithium propynide

The relative acidity of alkanes, alkenes and alkynes follows the order

$$H - C \equiv C - H > H_2C = CH_2 > H_3C - CH_3$$
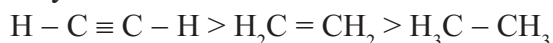
Can you tell?

Alkanes and alkenes do not react with lithium amide. Give reason.

Use your brain power

Arrange following hydrocarbons in the increasing order of acidic character.
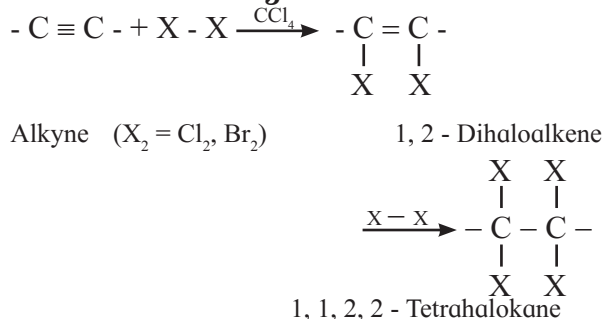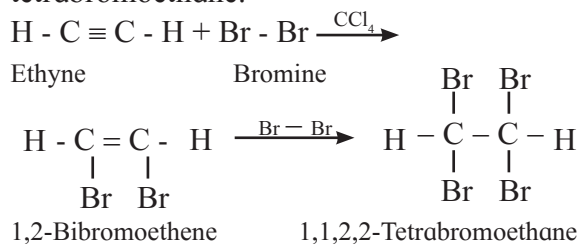propane, propyne, propene.

Do you know ?

Acidic alkynes react with certain heavy metal ions like Ag$^+$ and Cu$^+$ and form insoluble acetylides. On addition of acidic alkyne to solution of AgNO$_3$ in alcohol form a precipitate which indicates that the hydrogen atom is attached to triply bonded carbon. This reaction is used to differentiate terminal alkynes and non-terminal alkynes.

2. Addition of dihydrogen (See method of preparation of alkenes from unsaturated hydrocarbons)
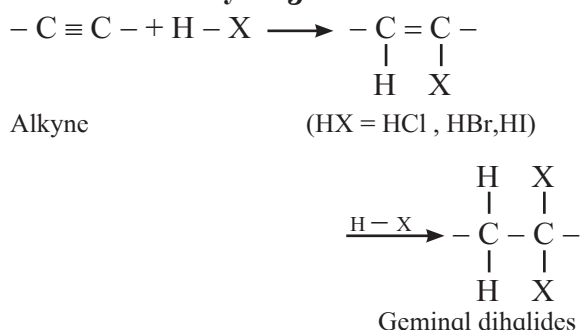
3. Addition of halogens

$$- C \equiv C - + X - X \xrightarrow{CCl_4} \begin{array}{c} - C = C - \\ | \quad | \\ X \quad X \end{array}$$

Alkyne   (X$_2$ = Cl$_2$, Br$_2$)   1, 2 - Dihaloalkene

$$\xrightarrow{X-X} \begin{array}{c} X \quad X \\ | \quad | \\ - C - C - \\ | \quad | \\ X \quad X \end{array}$$

1, 1, 2, 2 - Tetrahalokane

Ethyne reacts with bromine in inert solvent such as carbon tetrachloride to give tetrabromoethane.

$$H - C \equiv C - H + Br - Br \xrightarrow{CCl_4}$$

Ethyne   Bromine

$$\begin{array}{c} H - C = C - H \\ | \quad | \\ Br \quad Br \end{array} \xrightarrow{Br-Br} \begin{array}{c} Br \quad Br \\ | \quad | \\ H - C - C - H \\ | \quad | \\ Br \quad Br \end{array}$$

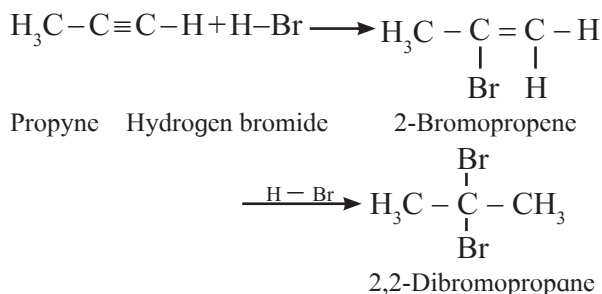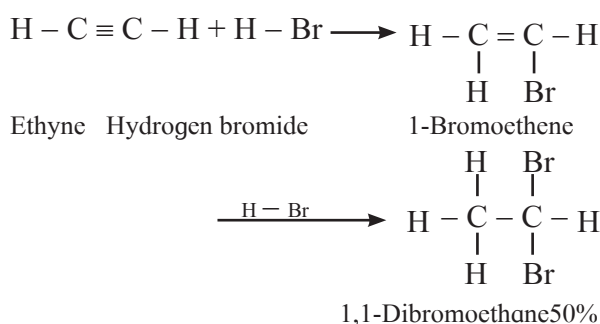1,2-Bibromoethene   1,1,2,2-Tetrabromoethane

Red-brown colour of solution of bromine in carbon tetrachloride disappears. This test can be used to detect the presence of unsaturation in given compound.
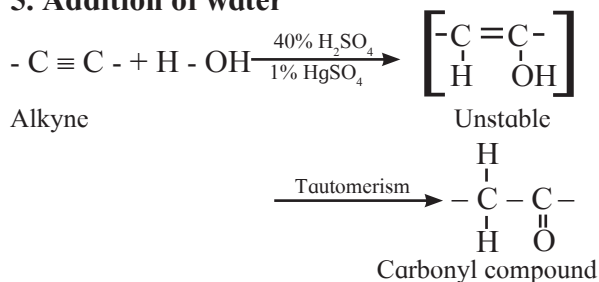
4. Addition of hydrogen halides

$$- C \equiv C - + H - X \longrightarrow \begin{array}{c} - C = C - \\ | \quad | \\ H \quad X \end{array}$$

Alkyne $\qquad\qquad$ (HX = HCl , HBr,HI)

$$\xrightarrow{H - X} \begin{array}{c} H \quad X \\ | \quad | \\ - C - C - \\ | \quad | \\ H \quad X \end{array}$$

Geminal dihalides

Hydrogen halides (HCl, HBr and HI) add to alkynes across carbon-carbon triple bond in two steps to form geminal dihalides (in which two halogen atoms are attached to the same carbon atom).The addition of HX in both the steps takes place according to **Markovnikov's rule**.

$$H - C \equiv C - H + H - Br \longrightarrow \begin{array}{c} H - C = C - H \\ | \quad | \\ H \quad Br \end{array}$$

Ethyne $\quad$ Hydrogen bromide $\qquad$ 1-Bromoethene

$$\xrightarrow{H - Br} \begin{array}{c} H \quad Br \\ | \quad | \\ H - C - C - H \\ | \quad | \\ H \quad Br \end{array}$$

1,1-Dibromoethane50%

$$H_3C - C \equiv C - H + H - Br \longrightarrow \begin{array}{c} H_3C - C = C - H \\ | \quad | \\ Br \quad H \end{array}$$

Propyne $\quad$ Hydrogen bromide $\qquad$ 2-Bromopropene

$$\xrightarrow{H - Br} \begin{array}{c} Br \\ | \\ H_3C - C - CH_3 \\ | \\ Br \end{array}$$

2,2-Dibromopropane

The order of reactivity of hydrogen halides is HI > HBr > HCl

5. Addition of water

$$- C \equiv C - + H - OH \xrightarrow[1\% \text{ HgSO}_4]{40\% \text{ H}_2\text{SO}_4} \begin{bmatrix} -C = C- \\ | \quad | \\ H \quad OH \end{bmatrix}$$

Alkyne $\qquad\qquad$ Unstable

$$\xrightarrow{\text{Tautomerism}} \begin{array}{c} H \\ | \\ - C - C - \\ | \quad \| \\ H \quad O \end{array}$$

Carbonyl compound

Alkynes react with water in presence of 40% sulphuric acid and 1% mercuric sulphate to form aldehydes or ketones i.e. carbonyl compounds.

$$H - C \equiv C - H + H - OH \xrightarrow[1\% \text{ HgSO}_4]{40\% \text{ H}_2\text{SO}_4}$$

Ethyne

$$\begin{bmatrix} \begin{array}{c} H \\ | \\ H - C = C - H \\ \quad | \\ \quad O - H \end{array} \end{bmatrix} \xrightarrow{\text{Tautomerisation}}$$

Vinyl alcohol

$$\begin{array}{c} \qquad\qquad H \\ \qquad\qquad | \\ H - C - C - H \\ \quad \| \quad | \\ \quad O \quad H \end{array}$$

Ethanal

$$H_3C - C \equiv C - H + H - OH \xrightarrow[1\% \text{ HgSO}_4]{40\% \text{ H}_2\text{SO}_4}$$

Propyne

$$\begin{bmatrix} \begin{array}{c} H \\ | \\ H_3C - C = C - H \\ \quad | \\ \quad O - H \end{array} \end{bmatrix} \xrightarrow{\text{Tautomerisation}}$$

$$\begin{array}{c} H_3C - C - CH_3 \\ \| \\ O \end{array}$$
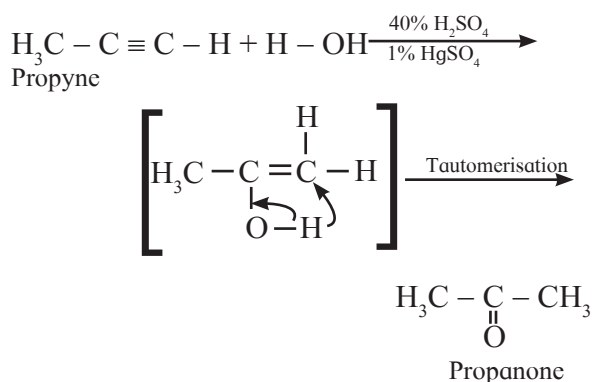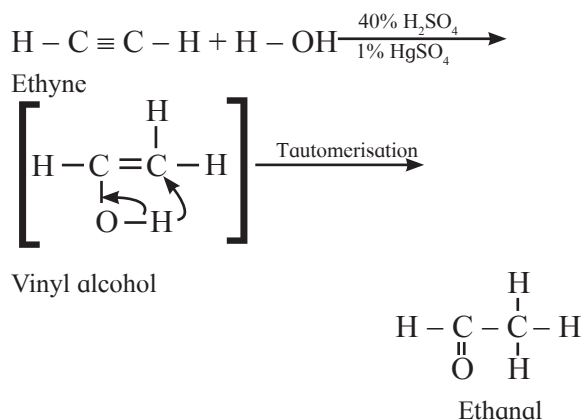
Propanone

Use your brain power

Convert : 3-Methylbut-1-yne into 3-Methylbutan-2-one.

15.3.5 Uses of acetylene :
1. Ethyne (acetylene) is used in preparation of Ethanal (acetaldehyde), Propanone (acetone), ethanoic acid (acetic acid).
2. It is used in the manufacture of polymers, synthetic rubber, synthetic fibre, plastic etc.
3. For artificial ripening of fruits.
4. In oxy-acetylene (mixture of oxygen and acetylene) flame for welding and cutting of metals.

15.4 Aromatic Hydrocarbons :

Can you recall?

- What are aromatic hydrocarbons?
- What are benzenoid and non-benzenoid aromatics ?

Many organic compounds obtained from natural sources like resins, balsams, oil of wintergreen, etc. possessing pleasant fragrance (aroma = smell) are named as aromatic compounds. Aromatic hydrocarbons (also called arenes) contain only carbon and hydrogen. Benzene is the simplest aromatic compound.

Benzene and all compounds that have structures and chemical properties resembling benzene are classified as aromatic compounds. Examples are :

CH$_3$ Br
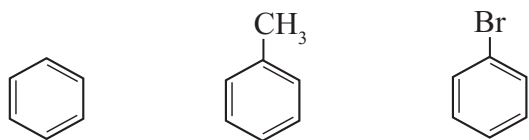
(Benzene) (Methylbenzene) (Bromobenzene)

OH
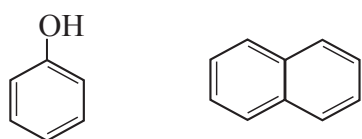
(Phenol)   (Naphthalene)

15.4.1 Benzene : The molecular formula of benzene is C$_6$H$_6$. Benzene is parent compound of most of the aromatic compounds.

Coal-tar and petroleum are the two large-scale sources of benzene (and aromatic compounds like toulene , phenol, naphthalene.).

Remember

1. Aromatic compounds contain planar cyclic rings.
2. Not all compounds those resemble benzene have pleasant odour (smell).
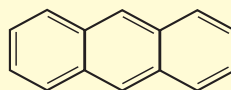
Anthracene is odourless.

3. Many compounds having pleasant odour do not resemble benzene.

$$H_3C - \overset{\overset{O}{\|}}{C} - O - CH_3$$
(Methyl acetate)

$$H_3C - \overset{\overset{O}{\|}}{C} - O - C_2H_5$$
(Ethyl acetate)

$$H - \overset{\overset{Cl}{|}}{\underset{Cl}{C}} - Cl$$
(Trichloromethane or chloroform)
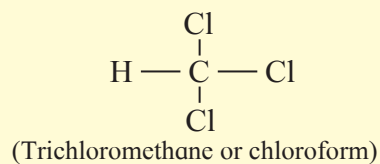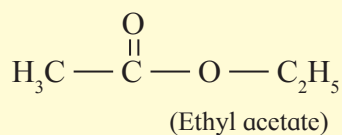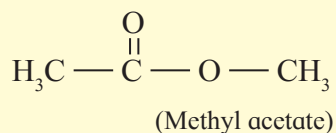
It is a colourless liquid having characteristic odour. Its boiling point is 353K.

It was synthesized by Berthelot (1870) from acetylene. Benzene was originally called **phene** and hence C$_6$H$_5$ is called **phenyl group**.

Table 15.6 : Difference between aromatic and aliphatic compounds

Aromatic compounds	Aliphatic compounds
1. Aromatic compounds contain higher percentage of carbon.	1. Aliphatic compounds contain lower percentage of carbon.
2. They burn with sooty flame.	2. They burn with non-sooty flame.
3. They are cyclic compounds with alternate single and double bonds.	3. They are open chain compounds.
4. They are not attacked by normal oxidizing and reducing agents.	4. They are easily attacked by oxidizing and reducing agents.
5. They do not undergo addition reactions easily. They do not decolourise dilute alkaline aqueous KMnO$_4$ and Br$_2$ in CCl$_4$, though double bonds appear in their structure.	5. Unsaturated aliphatic compounds undergo addition reactions easily.They decolourise dilute aqueous alkaline KMnO$_4$ and Br$_2$ in CCl$_4$.
6. They prefer substitution reactions.	6. The saturated aliphatic compounds give substitution reactions.

15.4.2 Structure of benzene :

1. Molcular formula of benzene, C_6H_6, indicates the high degree of unsaturation.

2. Open chain structure NOT possible : Open chain or cyclic structure having double and triple bonds can be written for C_6H_6. But benzene does not behave like alkenes or alkynes (see Table 15.7). This indicates that benzene can not have the open chain structure.

### Table 15.7 : Comparative reactivity of alkenes and benzene

Reaction	Alkene	Benzene
With dil. alka. $KMnO_4$	Decolourisation of purple colour of $KMnO_4$	No decolourisation
With Br_2 in CCl_4	Decolourisation of red brown colour of bromine	No decolourisation
With H_2O in acidic medium	Addition of H_2O molecule	No reaction

3. Evidence of cyclic structure : Benzene yields only one and no isomeric monosubstituted bromobenzene (C_6H_5Br) when treated with equimolar bromine in $FeBr_3$. This indicates that all the six hydrogen atoms in benzene are identical.

$$C_6H_6 + Br_2 \xrightarrow{FeBr_3} C_6H_5Br + HBr$$
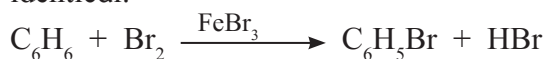
This is possible only if benzene has cyclic structure of six carbons bound to one hydrogen atom each.

Benzene on catalytic hydrogenation gives cyclohexane.

$$C_6H_6 + 3H_2 \xrightarrow[\Delta]{Ni} C_6H_{12}$$
(Benzene)   (Cyclohexane)
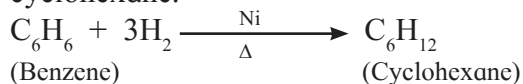
This confirms the cyclic structure of benzene and three C = C in it.

4. Kekulé structure of benzene :

August Kekulé in 1865 suggested the structure for benzene having a cyclic planar ring of six carbon atoms with alternate single and double bonds and hydrogen atom attached to each carbon atom.

Usually written as
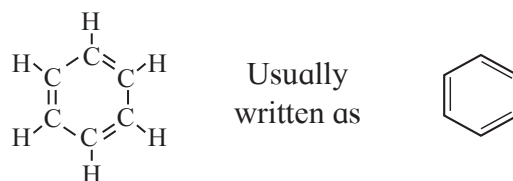
The Kekulé structure indicates the possibility of two isomeric 1,2-dibromobenzenes. In one of the isomers, the bromine atoms would be attached to the doubly bonded carbon atoms whereas in the other, they would be attached to single bonded carbons.
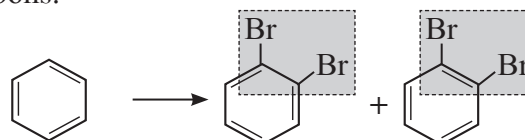
However, benzene was found to form only one ortho-disubstituted benzene. This problem was overcome by Kekule' by suggesting the concept of oscillating nature of double bonds in benzene as given below.

Even with this modification, Kekule' structure of benzene failed to explain unusual stability and preference to substitution reactions rather than addition reactions, which was later explained by resonance.

5. Stability of benzene:

Benzene is a hybrid of various resonance srtuctures.The two structures, A and B given by Kekulé are the main contributing structures. The resonance hybrid is represented by inserting a circle or a dotted circle inscribed in the hexagon as shown in (C). The circle represents six electrons delocalized over the six carbon atoms of benzene ring.


(A)   (B)   (C)
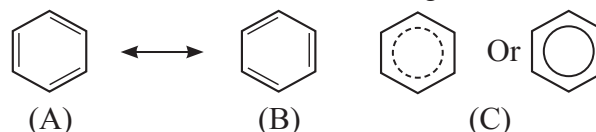
A double headed arrow between the resonance structures is used to represent the resonance phenomenon.

Stability of benzene : The actual molecule is more stable than any of its resonance structures. For benzene, the stability due to resonance

is so high that π-bonds of the molecule resist breaking. This explains lack of reactivity of benzene towards addition.

The orbital overlap gives us better picture of structure of benzene. All six carbon atoms in benzene are sp^2 hybridised. Two sp^2 hybrid orbitals of carbons overlap and form carbon-carbon sigma (σ) bond and the remaining third sp^2 hybrid orbital of each carbon overlaps with s orbital of a hydrogen atom to form six C-H sigma bonds.
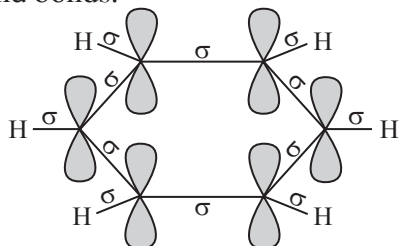
The unhybrid p orbitals of carbon atoms overlap laterally forming π bonds. There are two possibilities of forming three π bonds by overlap of p orbitals of C_1-C_2, C_3-C_4, C_5-C_6 or C_2-C_3, C_4-C_5, C_6-C_1, respectively, as shown in Fig. 15.5; both are equally probable. According to **resonance theory** (Chapter 5) these are two resonance structures of benzene.
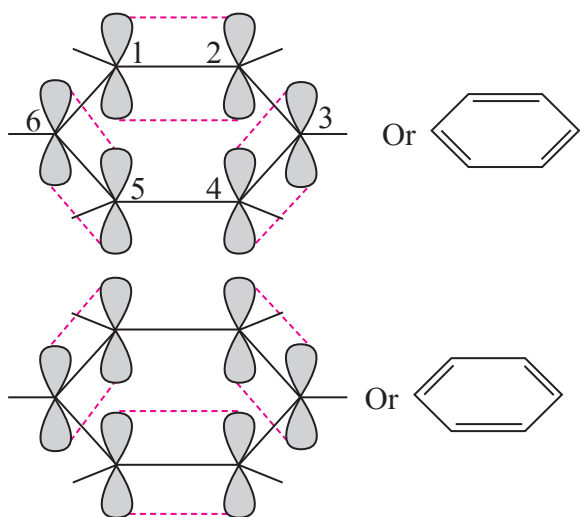
Fig. 15.5 Overlap of p orbitals in benzene

According to **molecular orbital (MO) theory** (Chapter 5) the six p orbitals of six carbons give rise to six molecular orbitals of benzene. Shape of the most stable MO is as shown in Fig. 15.6.

Three of these π molecular orbitals lie above and the other below those of free carbon atom energies.
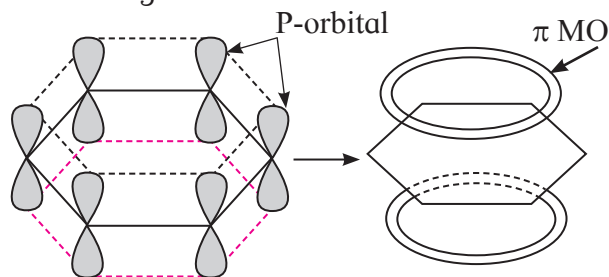
Fig 15.6 : Representative π molecular orbital in benzene

Remember

In benzene , a. All carbon and hydrogen atoms lie in the same plane.
b. Six sigma (σ) bonds lie in the same plane.
c. All bond angles are 120^0
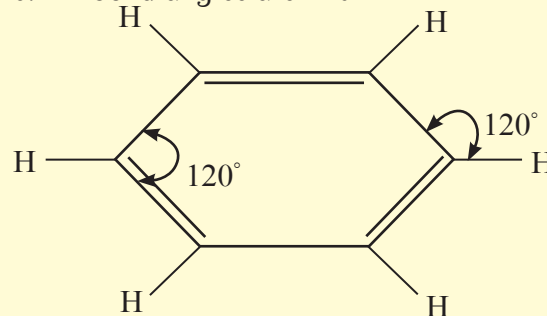
The six electrons of the p orbitals cover all the six carbon atoms and are said to be delocalized. Delocalization of π electrons results in stablity of benzene molecule.

6. Bond parameters of benzene : X-ray diffraction data indicate that all C-C bond lengths in benzene are equal (139 pm) which is an intermediate between C-C (154 pm) and C=C bond (133pm). Thus absence of pure double bond in benzene accounts for its reluctance to addition reactions under normal conditions, which explains unusual behaviour of benzene (Refer to sec.14.6.5).

1.54 A°
Single-bond lenght

1.39 A°
Benzene-bond length
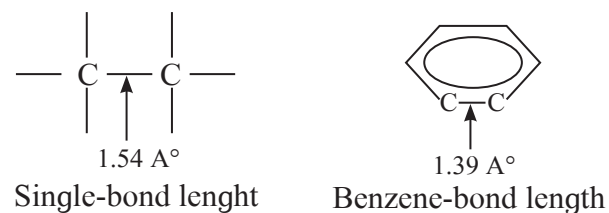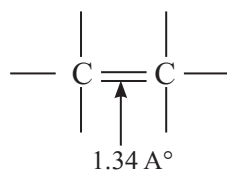
1.34 A°
Double-bond length

15.4.3 Aromatic character (Huckel Rule) :

Benzene undergoes substitution reaction rather than addition reactions. This property is common to all aromatic compounds and is referred to as **aromaticity** or **aromatic character**. The aromatic character of benzene is correlated to its structure.

Aromaticity is due to extensive cyclic delocalization of p electrons in planar ring structures.

The following **three rules of aromaticity** are useful in predicting whether a particular compound is

aromatic or non-aromatic.

1. Aromatic compounds are cyclic and planar (all atoms in ring are sp^2 hybridized).

2. Each atom in aromatic ring has a p-orbital. The p-orbitals must be parallel so that continuous overlap is possible around the ring.

3. Huckel Rule : The cyclic π molecular orbital formed by overlap of p-orbitals must contain (4n + 2) p electrons, where n= integer 0,1,2,3 ...etc.

Let us apply these rules to the following compounds

Benzene   Naphthalene
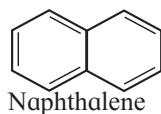
1. Benzene : It is cyclic and planar. It has three double bonds and six π electrons. It has a p orbital on each carbon of the hexagonal ring. Hence a continuous overlap above and below the ring is posssible.
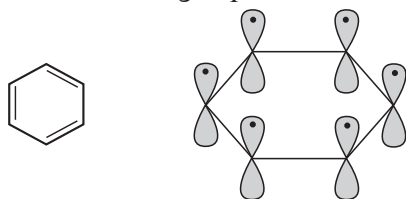
This compound is aromatic, 4n + 2 = Number of π electrons.

4n + 2 = 6, $\therefore$ 4n = 6-2 =4
n = 4/4 = 1, Here 'n' comes out to be an integer. Hence benzene is aromatic.

2. Naphthalene : It is cyclic and planar. It has 5 double bonds and 10 π electrons.It has p orbital on each carbon atom of the ring. Hence a continuous overlap around the ring is posssible. This is in accordance with Huckel rule.

4n + 2 = Number of π electrons
4n + 2 = 10, $\therefore$ 4n = 10 -2 = 8
n = 8/4 = 2, Here 'n' comes out to be an integer. Hence napthalene is aromatic.

3. Pyridine : Pyridine has three double bonds and 6 π electrons. The six p orbital containing six electrons form delocalized p molecular orbital. The unused sp^2 hybrid orbital of nitrogen containing two non-bonding electrons is as it is.

Non bonding
electron pair
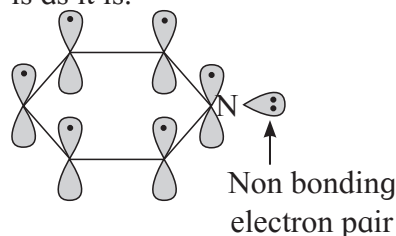
4n + 2 = Number of p electrons
4n + 2 = 6, $\therefore$ 4n = 6 -2 = 4
n = 4/4 = 1, Here 'n' comes out to be an integer. Hence pyridine is aromatic.

4. Cycloheptatriene : It is cyclic and planar. It has three double bonds and 6 π electrons. But one of the carbons is saturated (sp^3 hybridized) and does not possess a p orbital. Hence a continuous overlap around the ring is not possible.Therefore, it is non- aromatic.

sp^3 hybridized
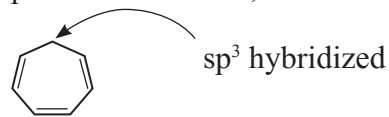
15.4.4 Preparation of aromatic compounds

a. Industrial source of aromatic compounds
Coal tar and petroleum are major sources of aromatic compounds.

b. Methods of preparation of benzene

1. From ethyne (By trimerization) : Alkynes when passed through a red hot iron tube at 873 K, polymerize to form aromatic hydrocarbons.

Ethyne when passed through a red hot iron tube at 873 K undergoes trimerization to form benzene.
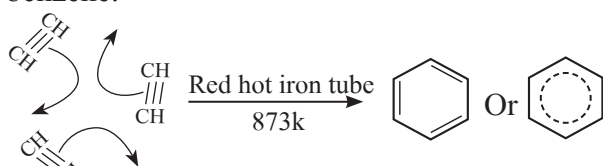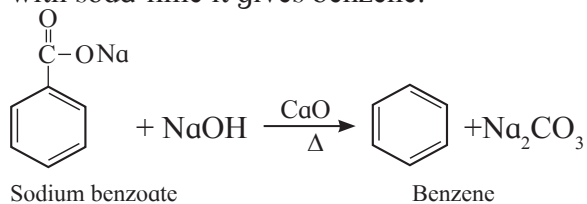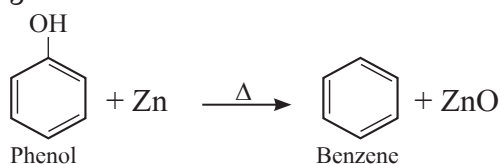

Can you recall?

What is decarboxylation ?

2.From sodium benzoate :
(By decarboxylation)
When anhydrous sodium benzoate is heated with soda-lime it gives benzene.

Sodium benzoate   Benzene

3. From phenol (By reduction) : When vapours of phenol are passed over heated zinc dust, it gives benzene.

Phenol   Benzene

15.4.5 Physical properties of benzene
1. Benzene is colourless liquid.
2. Its boiling point is 353K and melting point is 278.5 K.
3. It is isoluble in water. It forms upper layer when mixed with water.
4. It is soluble in alcohol, ether, and chloroform.
5. Benzene vapours are highly toxic which on inhalation lead to unconsciousness.

15.4.6 Chemical properties of benzene
Aromatic compounds are characterised by electrophilic substitution reactions. However, they undergo addition and oxidation reactions under special conditions. Some reactions of benzene are discussed below.

I. Addition reactions
i. Addition of chlorine : Benzene when treated with chlorine in presence of bright sunlight or UV light, adds up three molecules of chlorine

to give benzene hexachloride .
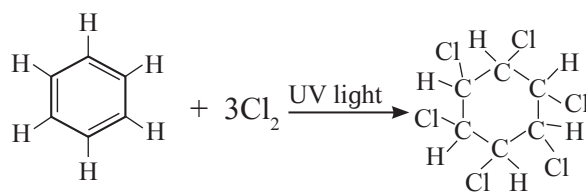
Benzene   Benzene hexachloride (BHC)

γ - isomer of benzene hexachloride is called **gammexane** or **lindane** which is used as insecticide.

ii. Addition of hydrogen : When a mixture of benzene and hydrogen gas is passed over heated catalyst nickel at 453 K to 473 K,cylohexane is formed.

Benzene (C_6H_6)   Cyclohexane
                                    (C_6H_{12})
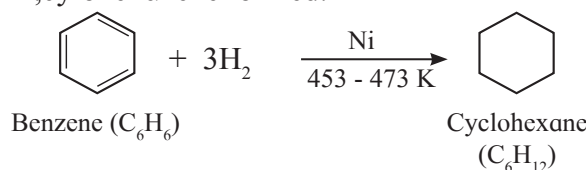
iii. Addition of ozone : When benzene is treated with ozone in presence of an inert solvent carbon tetrachloride, benzene triozonide is formed which is then decomposed by zinc dust and water to give glyoxal.
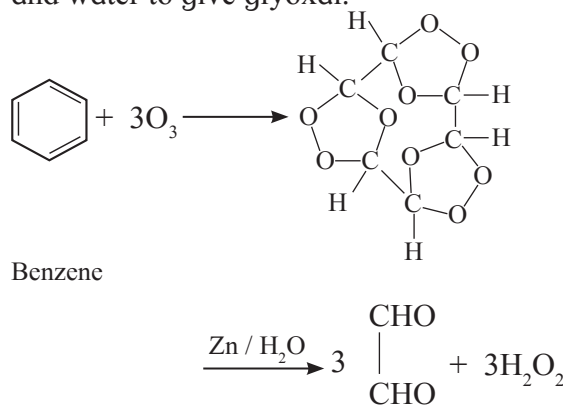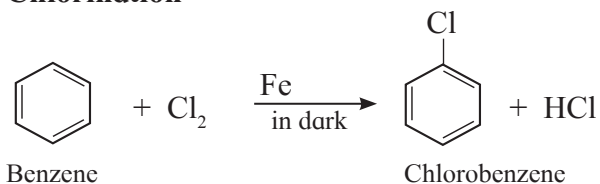

Benzene

Ethanedial or glyoxal

II. Substitution reactions : Benzene shows electrophilic substitution reactions, in which one or more hydrogen atoms of benzene ring are replaced by **electrophilic groups** like -Cl, -Br, $-NO_2$, $-SO_3H$, -R (alkyl group) , -COR (Acyl group) etc. (see Chapter 14).

i. Halogenation : In this reaction, hydrogen atom of benzene ring is replaced by halogen atom .
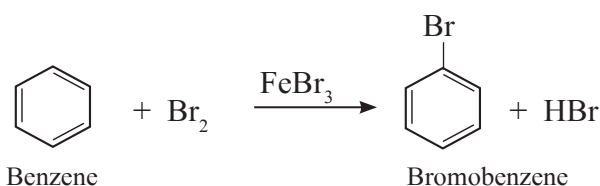
Chlorination

Benzene $+$ Cl$_2$ $\xrightarrow[\text{in dark}]{\text{Fe}}$ Chlorobenzene $+$ HCl

Chlorine reacts with benzene in dark in the presence of iron or ferric chloride or anhydous aluminium chloride or red phosphorous as catalyst to give chlorobenze .

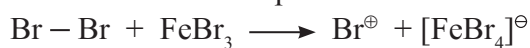Electrophile : Cl$^\oplus$, Chloronium ion

Formation of the electrophile :

$Cl - Cl + FeCl_3 \longrightarrow Cl^\oplus + [FeCl_4]^\ominus$

Bromination of benzene is similar to chlorination :

Benzene $+$ Br$_2$ $\xrightarrow{\text{FeBr}_3}$ Bromobenzene $+$ HBr

Electrophile : Br$^\oplus$,

Formation of electrophile :

$Br - Br + FeBr_3 \longrightarrow Br^\oplus + [FeBr_4]^\ominus$

Iodination of benzene is **not possible** as it is reversible process.

With excess of chlorine, benzene gives hexachlorobenzene.

Benzene $+$ 6 Cl$_2$ $\xrightarrow{\text{anhy.AlCl}_3}$

Hexachlorobenzene $+$ 6 HCl

ii. Nitration :

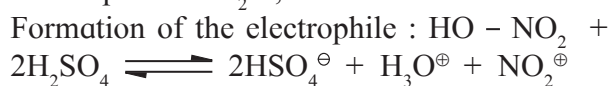Benzene $+$ HO-NO$_2$ Conc. $\xrightarrow[\text{Heat}]{\text{Conc. H}_2\text{SO}_4}$
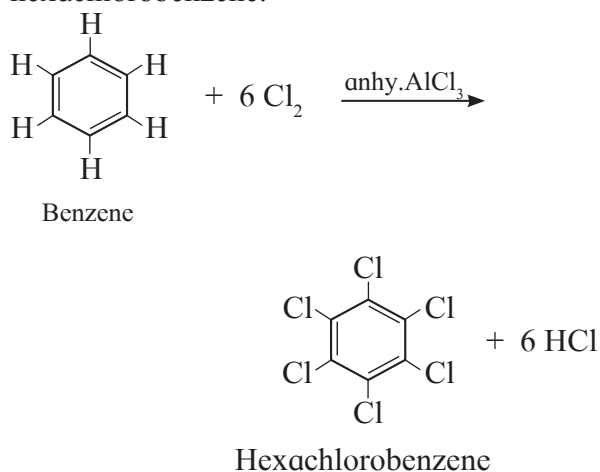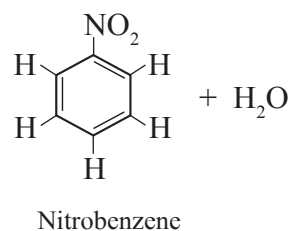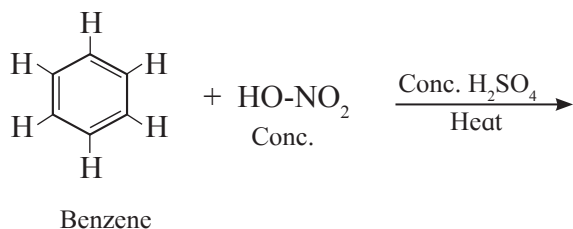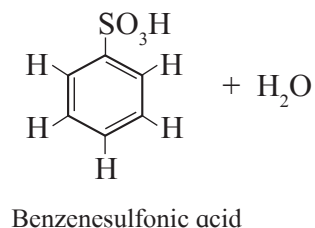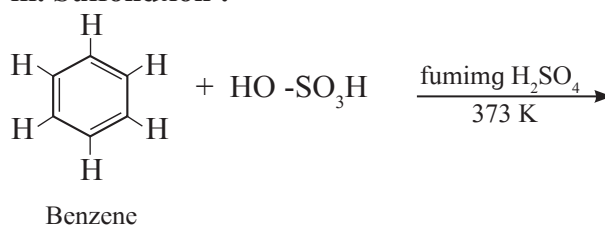

Nitrobenzene $+$ H$_2$O

When benzene is heated with a mixture of concentrated nitric acid and concentrated sulfuric acid (nitrating mixture) at about 313 K to 333 K , it gives nitrobenzene.

Electrophile : NO$_2$$^\oplus$, nitronium ion.

Formation of the electrophile : $HO - NO_2 + 2H_2SO_4 \rightleftharpoons 2HSO_4^\ominus + H_3O^\oplus + NO_2^\oplus$

iii. Sulfonation :

Benzene $+$ HO -SO$_3$H $\xrightarrow[\text{373 K}]{\text{fumimg H}_2\text{SO}_4}$
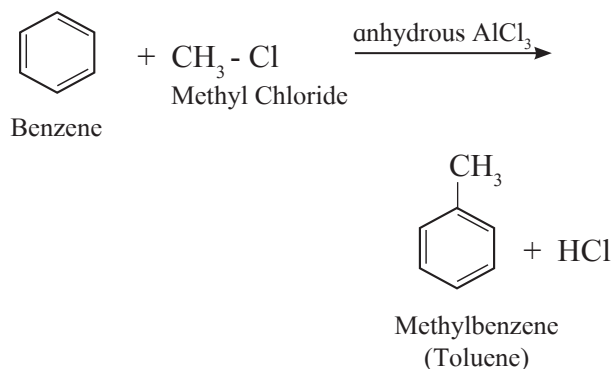

Benzenesulfonic acid $+$ H$_2$O

When benzene is heated with fuming sulfuric acid (oleum) at 373 K, it gives benzene sulfonic acid.

Electrophile : SO$_3$, free sulfur trioxide

Formation of the electrophile :

$2H_2SO_4 \longrightarrow H_3O^\oplus + HSO_4^\ominus + SO_3$

iv. Friedel-Craft's alkylation reaction :

Benzene $+$ CH$_3$- Cl (Methyl Chloride) $\xrightarrow{\text{anhydrous AlCl}_3}$

Methylbenzene (Toluene) $+$ HCl

When benzene is treated with an alkyl halide like methyl chloride in the presence of anhydrous aluminium chloride, it gives toluene.
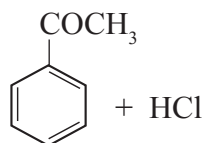
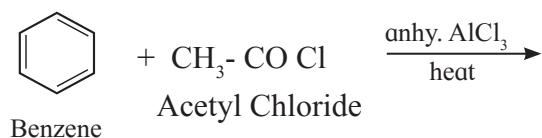The reaction is used to extend the chain outside the benzene ring.
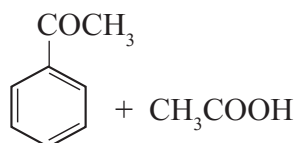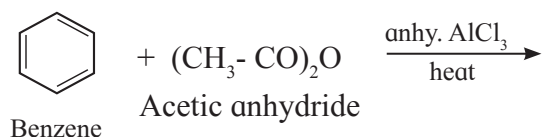
Electrophile : $R^{\oplus}$

Formation of the electrophile :

$$R - Cl + AlCl_3 \longrightarrow R^{\oplus} + AlCl_4^{\ominus}$$

v. Friedel-Craft's acylation reaction :

Benzene $+ CH_3- CO \ Cl$ Acetyl Chloride $\xrightarrow[\text{heat}]{\text{anhy. AlCl}_3}$

COCH₃ structure $+ HCl$

1- Phenylethanone or Acetophenone

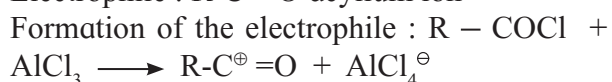Benzene $+ (CH_3- CO)_2O$ Acetic anhydride $\xrightarrow[\text{heat}]{\text{anhy. AlCl}_3}$
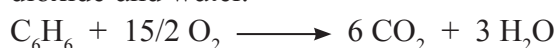
COCH₃ structure $+ CH_3COOH$

1- Phenylethanone or Acetophenone

When benzene is heated with an acyl halide or acid anhydride in the presence of anhydrous aluminium chloride, it gives corresponding acyl benzene.
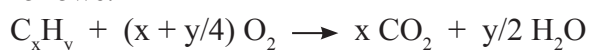
Electrophile : $R\text{-}C^{\oplus}=O$ acylium ion

Formation of the electrophile : $R - COCl + AlCl_3 \longrightarrow R\text{-}C^{\oplus}=O + AlCl_4^{\ominus}$

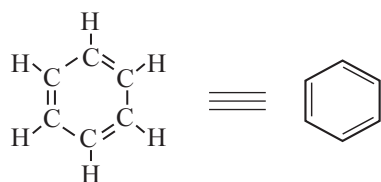**6. Combustion :** When benzene is heated in air , it burns with sooty flame forming carbon dioxide and water.

$$C_6H_6 + 15/2 \ O_2 \longrightarrow 6 \ CO_2 + 3 \ H_2O$$

General combustion reaction for any hydrocarbon (C_xH_y) can be represented as follows:

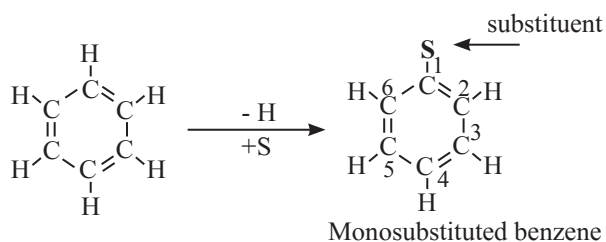$$C_xH_y + (x + y/4) \ O_2 \longrightarrow x \ CO_2 + y/2 \ H_2O$$

15.4.7 Directive influence of a functional group in monosubstituted benzene

Structure of benzene :

In benzene, all hydrogen atoms are equivalent. Therefore, only one product is possible when it undergoes electrophilic substitution reactions.

Monosubstituted benzene :

Monosubstituted benzene

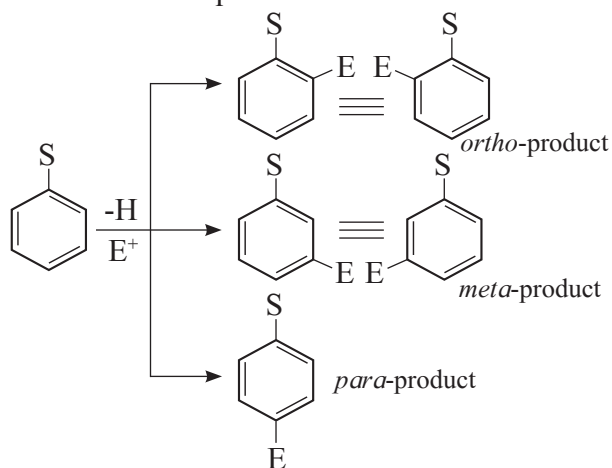**Positions of carbon atoms in mono substituted benzene :**

The positions 2 and 6 are equivalent and give ortho (o-) products.

The position 3 and 5 are equivalent and give meta (m-) products.

The position 4 is unique and and gives para (p-) product.

Now in benzene , five positions are available for electrophilic substitution.

When monosubstituted benzene is subjected to further electrophilic substitution, the second substituent i.e. electrophile (see Chapter 14) or incoming group (E) can occupy any of these positions and give three disubstituted products. But these products are not formed in equal amounts.

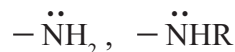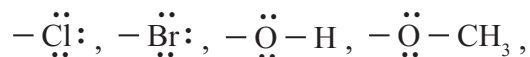ortho-product

meta-product

para-product

Two types of behaviour are observed.

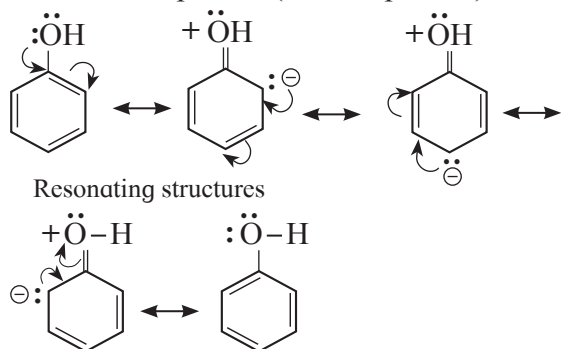**a. ortho- and para - products or b. meta-products are found as major products :**

This behaviour mainly depends on the nature of the substituent (S) already present in the benzene ring and not on the nature of second substituent (E) i.e. incoming group.

Ortho and para directing groups :

$$-\overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}: , \ -\overset{\cdot\cdot}{\underset{\cdot\cdot}{Br}}: , \ -\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}-H , \ -\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}-CH_3 ,$$

$$-\overset{\cdot\cdot}{N}H_2 , \ -\overset{\cdot\cdot}{N}HR$$
$$-CH_3 , \ -C_2H_5 , \ -R \ etc.$$

The groups which direct the incoming group to ortho and para positions are called ortho and para directing groups.

Ortho and para directive influence of -OH group : The resonance theory clearly explains why certain substituents are ortho/para or meta directing. Let us study the various resonance structures of phenol (see Chapter 14).

Resonating structures

It is clear from the above resonance structures that the ortho and para positions have a greater electron density than the meta positions. Therefore, -OH group activates the benzene ring for the attack of second substituent E at these electron-rich centres.

Remember

Due to -I effect of -OH group (see Chapter 14), the electron density on ortho positions of the benzene ring gets slightly reduced. Thus resonance effect and inductive effect of OH group act opposite to each other but +R effect of -OH is more powerful than -I effect.
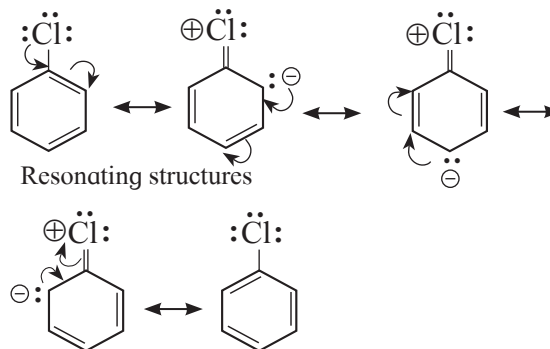
All ortho and para directing groups possess nonbonding electron pair on the atom which is directly attached to aromatic ring.

Methyl group is an exception : The only exception to above rule is methyl or alkyl groups. It is ortho and para directing, although
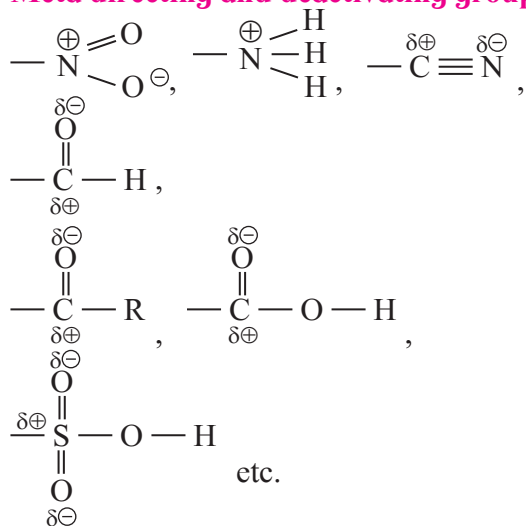
it has no nonbonding electron pair on the key atom. This is explained on the basis of special type of resonance called hyperconjugation or no bond resonance (see Chapter 14).

In case of **aryl halides**, halogens are moderately deactivating. Because of their strong -I effect, overall electron density on the benzene ring decreases. It makes the electrophilic substitution difficult. However, due to resonance the electron density on ortho and para positions is greater than meta positions. Halogens are ortho and para directing.

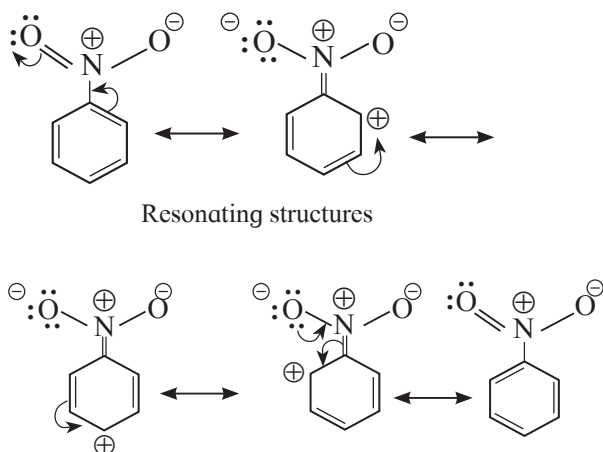Let us study the various resonating structures of chlorobenzene.

Resonating structures

Meta directing and deactivating groups

$$-\overset{\oplus}{N}\overset{O}{\underset{O^\ominus}{\diagup}} , \quad -\overset{\oplus}{N}\overset{H}{\underset{H}{\overset{H}{\diagup}}} , \quad -\overset{\delta\oplus}{C}\equiv\overset{\delta\ominus}{N} ,$$

$$-\overset{\overset{\delta\ominus}{O}}{\underset{\delta\oplus}{\overset{\|}{C}}}-H ,$$

$$-\overset{\overset{\delta\ominus}{O}}{\underset{\delta\oplus}{\overset{\|}{C}}}-R , \quad -\overset{\overset{\delta\ominus}{O}}{\underset{\delta\oplus}{\overset{\|}{C}}}-O-H ,$$

$$\overset{\delta\oplus}{\underset{\overset{\|}{\underset{O}{\delta\ominus}}}{\overset{\overset{\delta\ominus}{O}}{\overset{\|}{S}}}}-O-H$$
etc.

All meta directing groups have positive (or partial positive) charge on the atom which is directly attached to an aromatic ring.

The groups which direct the incoming group to meta positions are called **meta directing groups**.

Metadirective influence of -NO₂ group can be explained by resonance theory : Meta directing group withdraws electrons from the aromatic ring by resonance, making the ring electron-deficient. Therefore, meta groups are ring deactivating groups. Due to -I effect , -NO₂ group reduces electron density in benzne ring on ortho and para positions.So the attack of incoming group becomes difficult at ortho and para positions. Incoming group can attack on meta positions more easily. Let us study the various resonance structures of nitrobenzene.

Resonating structures

It is clear from the above resonance structures that the ortho and para positions have comparatively less electron density than at meta positions. Hence, the incoming group/ electrophile attacks on meta positions.

15.4.8 Carcinogenicity and Toxicity of benzene :

Benzene is both toxic and carcinogenic (cancer causing). In fact, it might be considered "the mother of all carcinogens" as a large number of carcinogens have structures those include benzene rings. Several polycyclic aromatic compounds (containing more than two fused benzene rings) are produced by incomplete combustion of tobacco, coal and petroleum. In liver, benzene is oxidized to an epoxide. Benzopyrene is converted into an epoxy diol. These substances are carcinogenic and can react with DNA which can induce mutation leading to uncontrolled growth of cancer cells.

Internet my friend

1. chemed.chem.purdue.edu>1organic>Organic Chemistry
2. www.ncert.nic.in>ncerts>kech206(pdf)
3. https://www.britannica.com>science>benzene
4. https://pubchem.ncbi.nlm.nih.gov>Benzene

Exercises

1. Choose correct options

A. Which of the following compound has highest boiling point ?
  a. n-pentane
  b. iso-butane
  c. butane
  d. neopentane

B. Acidic hydrogen is present in :
  a. acetylene
  b. ethane
  c. ethylene
  d. dimethyl acetylene

C. Identify 'A' in the following reaction:
$$CH_3 - \underset{\underset{CH_3}{|}}{C} = CH_2 \xrightarrow{A} CH_3 - \underset{\overset{||}{O}}{C} - CH_3$$
$$+ CO_2 + H_2O$$
  a. $KMnO_4/H^+$
  b. alkaline $KMnO_4$
  c. dil. $H_2SO_4/1\%$ $HgSO_4$
  d. $NaOH/H_2O_2$

D. Major product of chlorination of ethyl benzene is :
  a. m-chlorethyl benzene
  b. p - chloroethyl benzene
  c. chlorobenzene
  d. o - chloroethylbenzene

E. 1 - chloropropane on treatment with alc. KOH produces :
  a. propane
  b. propene
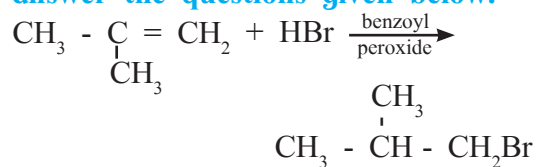 c. propyne
  d. propyl alcohol

2. Name the following :

A. The type of hydrocarbon that is used as lubricant.

B. Alkene used in the manufacture of polythene bags.

C. The hydrocarbon said to possess carcinogenic property.

D. What are the main natural sources of alkane?

E. Arrange the three isomers of alkane with malecular formula C_5H_{12} in increasing order of boiling points and write their IUPAC names.

F. Write IUPAC names of the products obtained by the reaction of cold concentrated sulphuric acid followed by water with the following compounds.
  a. propene   b. but-l-ene

G. Write the balanced chemical reaction for preparation of ethane from
  a. Ethyl bromide
  b. Ethyl magnesium iodide

H. How many monochlorination products are possible for
  a. 2-methylpropane ?
  b. 2-methylbutane   ?
  Draw their structures and write their IUPAC names.

I. Write all the possible products for pyrolysis of butane.

J. Which of the following will exhibit geometical isomerism ?
  a. $CH_3- CH_2 - \underset{\underset{CH_2}{||}}{C} - CH_3$

  b $(CH_3)_2 C = CH_2$

  c. $CH_3- \underset{\underset{C_2H_5}{|}}{C} = \underset{\underset{C_2H_5}{|}}{C} - CH_3$

K. What is the action of following on ethyl iodide ?
  a. alc, KOH
  b. Zn, HCl

L. An alkene 'A' an ozonolysis gives 2 moles of ethanal. Write the structure and IUPAC name of 'A'.

M. Acetone and acetaldehyde are the ozonolysis products of an alkene. Write the structural formula of an alkene and give IUPAC name of it.

N. Write the reaction to convert
  a. propene to nypropylalcohol.
  b. propene to isoproyl alcohol.

O. What is the action of following on but-2-ene ?
   a. dil alkaline $KMnO_4$
   b. acidic $KMnO_4$
P. Complete the following reaction sequence :
   $$HC \equiv CH \xrightarrow{LiNH_2} A \xrightarrow{CH_3CH_2Cl} B \xrightarrow{HBr} C$$
   Comment on the acidic nature of B.
Q. Write the balanced chemical reactions to get benzene from
   a. Sodium benzoate.
   b. Phenol.
R. Predict the possible products of the following reaction.
   a. chlorination of nitrobenzene,
   b. sulfonation of chlorobenzene,
   c. bromination of phenol,
   d. nitration of toluene.
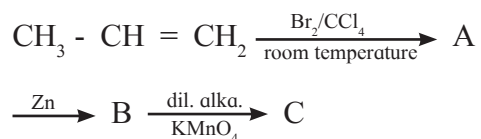
3. **Identify the main product of the reaction**

a. $CH_3\text{-}CH_2\text{-}CH_3 \xrightarrow[\Delta]{O_2}$

b. $CH_3 - \underset{\underset{OH}{|}}{CH} - CH_3 \xrightarrow[373K]{60\% \ H_2SO_4}$

c. $HC \equiv C\text{-}CH_3 \xrightarrow[Pd\text{-}C/quinoline]{H_2}$

d. $H\text{-}C\text{-}H + H_2O \xrightarrow[1\% \ HgSO_4]{40\% \ H_2SO_4}$

4. **Read the following reaction and answer the questions given below.**

$CH_3 - \underset{\underset{CH_3}{|}}{C} = CH_2 + HBr \xrightarrow[peroxide]{benzoyl}$

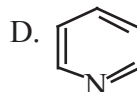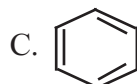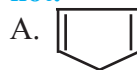$CH_3 - \underset{\underset{CH_3}{|}}{CH} - CH_2Br$

a. Write IUPAC name of the product.
b. State the rule that governs formation of this product.

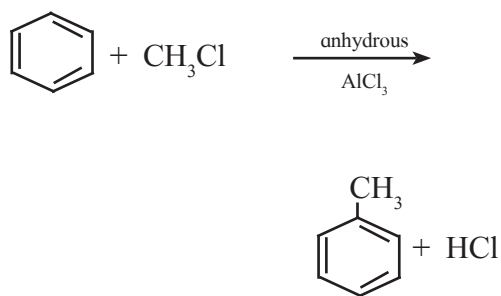**5.** **Identify A, B, C in the following reaction sequence :**

$$CH_3 - CH = CH_2 \xrightarrow[room\ temperature]{Br_2/CCl_4} A$$

$$\xrightarrow{Zn} B \xrightarrow[KMnO_4]{dil.\ alka.} C$$

6. **Identify giving reason whether the following compounds are aromatic or not.**

A.

B.

C.

D.

7. **Name two reagents used for acylation of benzene.**

8. **Read the following reaction and answer the questions given below.**

$+ CH_3Cl \xrightarrow[AlCl_3]{anhydrous}$

$+ HCl$

A. Write the name of the reaction.
B. Identify the electrophile in it.
C. How is this electrophile generated?

Activity :

Prepare chart of hydrocarbons and note down the characteristics.