UNIT 16

HYDROCARBONS

Learning Outcomes:

After carefully studying this unit and working the exercise, the student will be able to:

- Classify hydrocarbons as aliphatic and aromatic.
- Deseribe nomenclature of alkanes and cycloalkanes.
- Explain the shapes of alkanes and cycloalkanes exemplified by ethane and cyclopropane.
- Explain unreactive nature of alkanes towards polar reagents.
- Define homolytic and heterolytic fission, free radical initiation, propagation and termination.
- Describe the mechanism of free radical substitution in alkanes exemplified by methane and ethane.
- Identify organic redox reactions.
- Explain what is meant by a chiral centre and show that such a centre gives rise to optical isomerism.
- Identify chiral centres in given structural formula of a molecule.
- Explain the nomenclature of alkenes.
- Explain the shape of ethene molecule in terms of sigma and pi C–C bonds.

- Describe the structure and reactivity of alkenes as exemplified by ethane.
- Define and explain with suitable examples the terms isomerism, stereoisomerism and structural isomerism.
- Explain dehydration of alcohols and dehydrohalogenation of RX for the preparation of ethene.
- Describe the chemistry of alkenes by the following reactions of ethane Hydrogenation, Hydrohalogenation, hydration, Halogenation, Halohydration, Epoxidation, ozonolysis, polymerization.
- Explain the concept of conjugation in alkenes, having alternate double bonds.
- Use the IUPAC Naming system for alkenes.
- Explain the shape of benzene molecule (MOT).
- Define resonance, resonance energy and relative stability.
- Compare the reactivity of benzene with alkanes and alkenes.
- Describe what is meant by term delocalized electrons in the context of benzene ring.
- Describe addition reactions of benzene and toluene.
- Describe the mechanism of electronphilic substitution in benzene.
- Discuss the chemistry of benzene and toluene by nitration, sulphanation, halogenations, Friedel –Craft's alkylation and acylation.
- Apply the knowledge of positions of substituents in the electrophilic substitution of benzene.
- Use the IUPAC naming system of alkynes.
- Compare the reactivity of alkynes with alkenes, alkenes and arenes.
- Discuss the shape of alkynes in terms of sigma and pi $C-C$ bonds.

- Describe the preparation of alkynes, using elimination reactions.
- Describe acidity of alkynes.
- Discuss the chemistry of alkynes by hydrogenation, hydrohalogenation, hydration, bromination, ozonlysis and reaction with metals.
- Describe and differentiate between substitution and addition reactions.
- Explain isomerism in alkanes, alkenes, alkynes and substituted benzene.
- Identify and link uses of various hydrocarbons in daily life and also their significance as fuels for the future energy needs of Pakistan.

Introduction:

Hydrocarbons are the organic compounds which contain carbon and hydrogen only. For example methane (CH_4), benzene (C_6H_6) etc. These compounds are thought to serve as basis for all other organic compounds. That is, all other organic compounds are the derivatives of hydrocarbons where one or more hydrogen atoms have been replaced by another atom or group of atoms. Petroleum, natural gas and coal are the main natural sources of hydrocarbons. These sources are frequently found in under ground deposits. The significance of hydrocarbons can be realized by their uses in daily life and in industries and power generation as fuel and as raw materials for synthesis of many other organic compounds. If the fossil fuels are simply bound to produce heat, which is then used to produce power and heat up our homes, we need not be concerned with the molecular make up of these substances. But to appreciate the treatments these gas, liquid and solid materials receive and the roles, the products from these play, you must know about their molecular make up and their chemical reactions.

16.1 Types of Hydrocarbons:

Hydrocarbons are divided into two major categories i.e.

(A) Aliphatic hydrocarbons (B) Aromatic hydrocarbons.

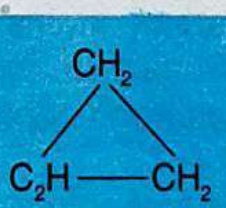
A. Aliphatic Hydrocarbons:

These include the open chain (acyclic) compounds and those cyclic compounds which resemble the open chain compounds in their chemical properties e.g.

$CH_3-CH_2-CH_3$

n-propane

(Acyclic compound)



Cyclopropane

(Cyclic compound)

i. Open chain or acyclic hydrocarbons:

In these hydrocarbons, the carbon atoms are linked together in the form of chains which may either be:

i. Straight Chain:

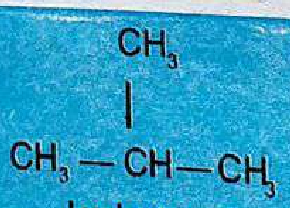
In this case no carbon atom is linked directly to more than two carbons atoms.

$CH_3-CH_2-CH_2-CH_3$

Butane

ii. Branched Chain:

In this case, at least one carbon atom is linked directly to three or four carbon atoms. For example.



$$\begin{array}{c} \phantom{CH_3-{}}CH_3 \\ \phantom{CH_3-{}}| \\ CH_3-CH-CH_3 \end{array}$$

Isobutane

Both straight and branched hydrocarbon may be:

a. Saturated hydrocarbons:

These are also called alkanes and in these compounds all the carbon atoms are bonded to each other by single bonds and hence each carbon is bonded to four other atoms. They are calle saturated because their valencies are fully satisfied e.g.

$CH_3-CH_2-CH_2-CH_3$

Butane

They can be represented by the general formula C_nH_{2n+2}, where n is the number of carbon atoms.

b. Unsaturated hydrocarbons:

In these hydrocarbons, the chain contains carbon–carbon multiple bonds.

$CH_3-CH=CH_2$ Propene

$CH_3-C\equiv C-CH_3$ Butyne

Unsaturated hydrocarbons, having carbon–carbon double bond are called alkenes, represented by general formula C_nH_{2n}, while those having carbon–carbon triple bond are called alkynes, represented by general formula C_nH_{2n-2}

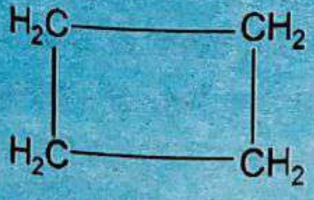
ii. Closed Chain or Cyclic Hydrocarbons:

In these hydrocarbons the carbon atoms are bonded together in such a way that they form a ring or cyclic structure. Like open chain hydrocarbons, they may also be classified as

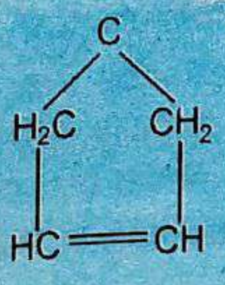
i. Saturated

ii. Unsaturated

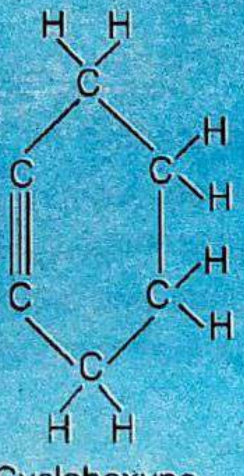
For example,



Cyclobutane (saturated)



Cyclopentene (unsaturated)

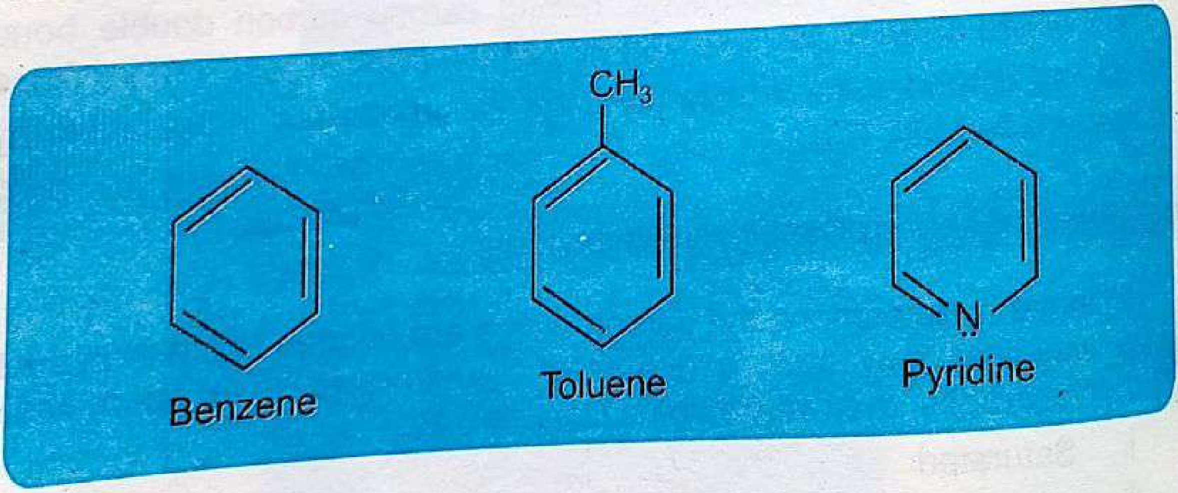


Cyclohexyne (Unsaturated)

Saturated cyclic hydrocarbon are called cycloalkanes, unsaturated are called cycloalkenes and cycloalkynes.

B. Aromatic Hydrocarbons:

Benzene (C_6H_6) is the parent member of this class and hence aromatic is the term used for benzene and all those compounds that resemble benzene in their chemical properties e.g.



16.2 Alkanes and Cycloalkanes:

Alkanes are open chain saturated hydrocarbons, which can be represented by the general formula C_nH_{2n+2} (where "n" is the number of carbon atoms), while cycloalkanes are cyclic saturated hydrocarbons represented by the general formula C_nH_{2n} (n is the number of carbon atoms; and $n \geq 3$). It is to be noted that cyclo alkanes are two $H-$atoms less than the corresponding alkanes, in their formula.

16.2.1 Nomenclature:

The systematic process of naming a compound is called nomenclature. At the beginning of organic chemistry, each new compound was given an individual name, which was based on its source, some property or other trivial reason. For example, the compound "HCOOH" was given the name formic acid because it was obtained from red ants. (Latin, formica = ants). Similarly the compound "CH_3COOH" was named as acetic acid (Greek, Acetum = vinegar). These names, which are based on the source of the compounds are called common names or trivial names.

With the increase in the number of organic compounds it became impossible to give names to such a large number of organic compounds. Moreover trivial names do not give any information about the structure of the compounds. Need was, therefore, felt to name organic compounds in a systematic way. Thus, the "International Union of pure and Applied chemistry" (IUPAC) in 1957, set rules for giving systematic names to organic compounds on the basis of structure. This is known as the IUPAC system of nomenclature.

Alkanes:

Alkanes are named by the following two systems.

(A) Common System (B) IUPAC System.

A. Common System:

The first four members of the series $(C_1 \text{ to } C_4)$ are named as methane (CH_4), ethane (C_2H_6), propane (C_3H_8) and butane (C_4H_{10}) while the rest are named by using the Greek prefixes that indicate number of carbon atoms in the molecule. Thus the prefix penta (5) is used for the compound having five carbon atoms, hexa (6) for six, hepta (7) for seven, octa (8) for eight, nona (9) for nine and deca (10) for ten carbon atoms (see table 16.1) the prefix is followed by the ending "ane".

Table 16.1 Name and formulae of first 10 alkanes

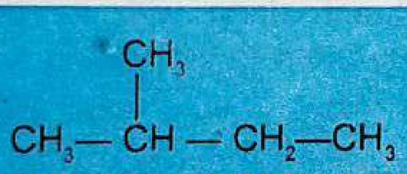
No. of Carbon Atoms	Name	Molecular Formula	Structural Formula
1	Methane	CH_4	CH_4
2	Ethane	C_2H_6	CH_3CH_3
3	Propane	C_3H_8	$CH_3CH_2CH_3$
4	Butane	C_4H_{10}	$CH_3CH_2CH_2CH_3$
5	Pentane	C_5H_{12}	$CH_3CH_2CH_2CH_2CH_3$
6	Hexane	C_6H_{14}	$CH_3CH_2CH_2CH_2CH_2CH_3$
7	Heptane	C_7H_{16}	$CH_3CH_2CH_2CH_2CH_2CH_2CH_3$
8	Octane	C_8H_{18}	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$
9	Nonane	C_9H_{20}	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$
10	Decane	$C_{10}H_{22}$	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$

i. The prefix n – is used for those alkanes in which all the carbon atoms are in one continuous chain (straight chain or normal alkanes)

$CH_3-CH_2-CH_2-CH_3$, n-butane

$CH_3-CH_2-CH_2-CH_2-CH_3$ n-pentane

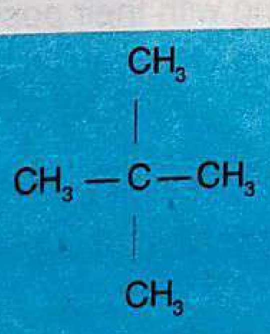
ii. The prefix iso is used for those alkanes which have a methyl group $(-CH_3)$ attached to the second last carbon atom of the continuous chain.



$$CH_3-\overset{\overset{\large CH_3}{|}}{C}H-CH_2-CH_3$$

isopentane

iii. The prefix neo is used for those alkanes which have two methyl groups attached to the second last carbon atom of the continuous chain.



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

neopentane

B. IUPAC System:

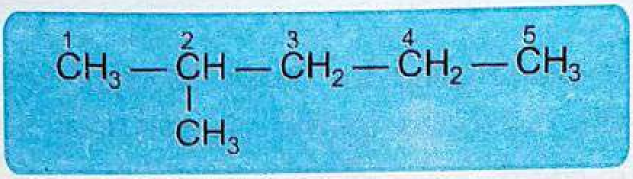
In this system the parent names of the alkanes are retained such as methane, ethane, propane, butane, pentane, hexane and so on while the branching (if any) is treated as substitutuent, attached to the main continuous carbon chain.

Rules for naming alkanes are:

1. Select the longest continuous chains of carbon atoms and consider it as a parent compound.

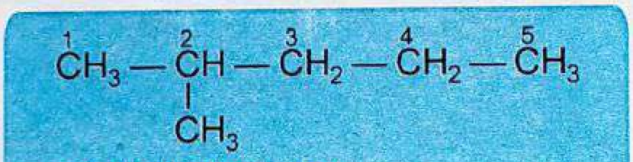
$$C-C-C-C-C$$

2. Number the longest chain from one end or the other, so as to give the carbon carrying the substituent (alkyl group), the lowest possible number.



$$\overset{1}{C}H_3-\overset{2}{C}H-\overset{3}{C}H_2-\overset{4}{C}H_2-\overset{5}{C}H_3 \quad (CH_3 \text{ on } C2)$$

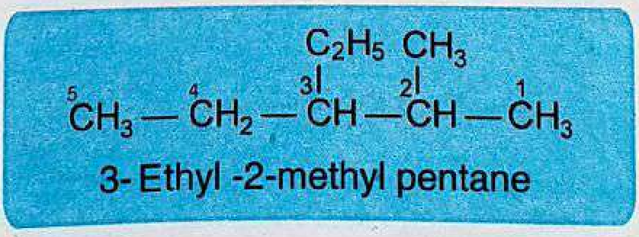
3. Name the substitutuant along with its position by indicating the number of the carbon atom to which it is attached, before the parent name.



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

2-Methylpentane

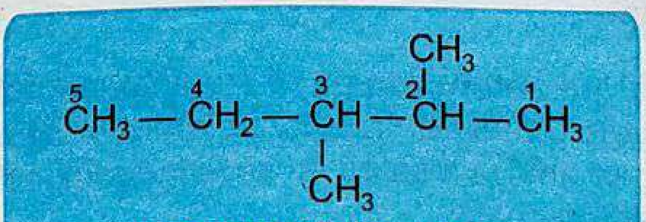
4. When two or more different substituents are attached, they are named in alphabetical order along with their positions before the parent name.



$$\overset{5}{C}H_3-\overset{4}{C}H_2-\overset{C_2H_5}{\overset{3|}{C}H}-\overset{CH_3}{\overset{2|}{C}H}-\overset{1}{C}H_3$$

3- Ethyl -2-methyl pentane

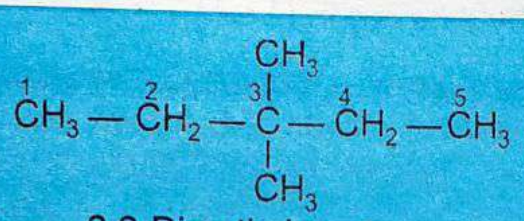
5. When the same substituent is present more than once, a prefix di, tri, tetra etc is used before the substitutent name and position of each substituent is indicated by a separate number.



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

2,3- Dimethyl pentane

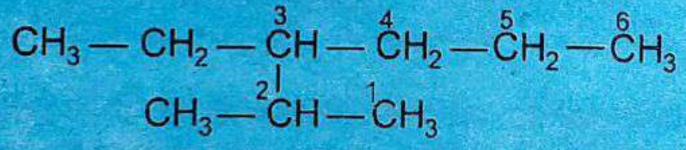
6. When two substitutents (same or different) are attached to the same carbon atom, the number of that carbon atom is repeated.



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

3,3-Dimethyl pentane

7. When there are more than one longest chains, select the chain which carries more substituents.

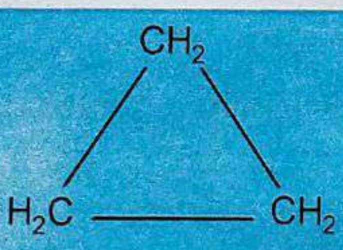


$$CH_3-CH_2-\underset{\underset{CH_3-\overset{2}{C}H-\overset{1}{C}H_3}{|}}{\overset{3}{C}H}-\overset{4}{C}H_2-\overset{5}{C}H_2-\overset{6}{C}H_3$$

3-Ethyl -2-methyl hexane

Cycloalkanes:

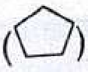
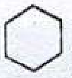
1. Cycloalkanes are named by placing the prefix “cyclo –” to the name of alkane having the same number of carbon atoms as in the ring.



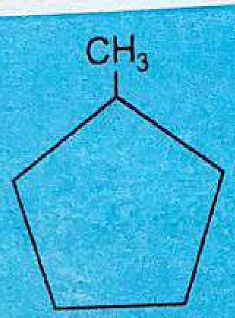
Cyclopropane

For convenience, cyloalkanes are represented by geometric figures. Each corner represents a -CH_2 group.

- Cyclopropane is represented by a triangle (△)

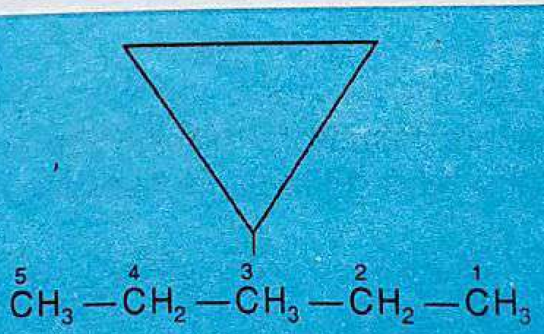
- Cyclopentane by a pentagon ()
- Cyclohexane by a hexagon ()

2. Substituted cycloalkanes are named as alkylcycloalkanes e.g.



Methylcyclopentane

3. The ring is taken as substitutuants, if the side chain contains greater number of carbon atoms than the ring.



3-Cyclopropylpentane

16.2.2 Physical Properties:

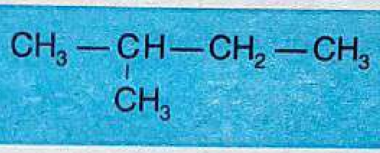
(A) Alkanes:

1. First four members $(C_1 - C_4)$ of the alkane series methane, ethane, propane and butane are colourless gases. Next thirteen members $(C_5 - C_{17})$ are colourless liquids. Higher alkanes are wax like (soft) solids.

2. Alkanes, being non polar, are soluble in nonpolar solvents like CCl_4 and C_6H_6 but they are insoluble in polar solvents such as water.

3. The boiling points of normal alkanes increase with the increase in molecular weight. Moreover, straight chain alkanes have higher boiling points than the isomeric branched alkanes.

$CH_3CH_2CH_2CH_2CH_3$



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

4. The melting points of alkanes also increase with increasing molecular weight. However, there is no regularity in the change in melting point with the number of carbon atoms in a molecule.

5. The specific gravities of alkanes, in general , increase with increasing molecular weight.

6. Viscosity also increases with increase in the number of carbon atoms in the molecule.

Table 16.2 Boiling and Melting points of some alkanes:

Alkane	Formula	Boiling Point (°C)	Melting Point (°C)
Methane	CH_4	–161.5	–182.5
Ethane	CH_3-CH_3	–88.6	–172
Propane	$CH_3-CH_2-CH_3$	–42.1	– 188
Butane	$CH_3(CH_2)_2CH_3$	0.00	– 138
Pentane	$CH_3(CH_2)_3CH_3$	36.0	– 130
Hexane	$CH_3(CH_2)_4CH_3$	68.7	–95.3

(B) Cycloalkanes:

1. First two members i.e. Cyclopropane and cyclobutane are gases at room temperature and atmospheric pressure, while remaining cycloalkanes are liquids.
2. They are insoluble in water but dissolve in ethanol and ether.
3. Their melting and boiling points show a gradual increase with the increases the molecular weight.

Table 16.3 Boiling and Melting points of some cycloalkanes:

Cycloalkane	Boiling Points (°C)	Melting Points (°C)
Cyclopropane	– 33	– 127
Cyclobutane	+ 13	–50
Cydopentane	+ 49.2	–94
Cyclohexane	+ 81	6.7

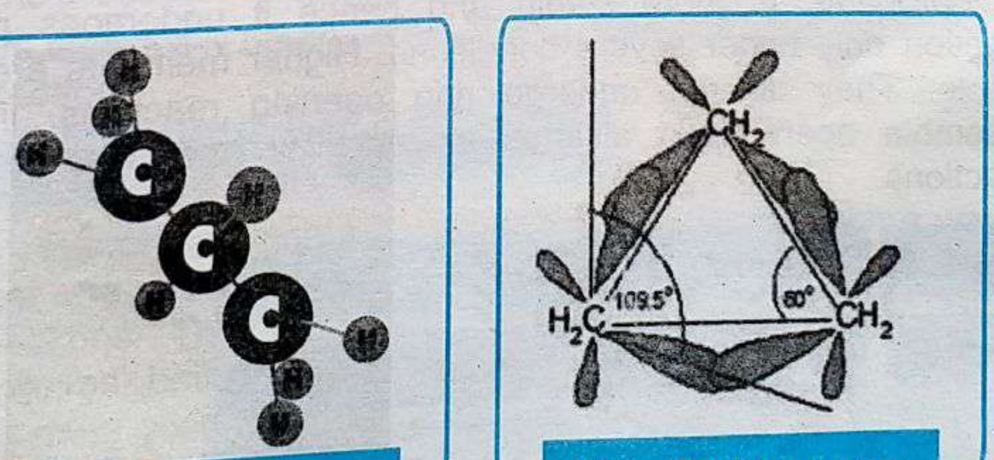
16.2.3 Structure:

(A) Let us consider ethane (CH_3-CH_3) for illustrating the orbital structure of alkanes. In ethane, each carbon atom is bonded to four other atoms, so it uses sp^3 hybrid orbitals to form these bonds. There are six $C-H$ covalent bonds and one $C-C$ covalent bond. Each of the $C-H$ bonds, is the result of linear overlap of an sp^3 hybrid orbital of carbon and an 's' orbital of hydrogen. The $C-C$ bond is formed due to the overlap of sp^3 orbitals, one from each carbon atom (Fig.16.1). All the $C-H$ and $C-C$ bonds are sigma (δ) bonds. All the bond angles are 109.5° (tetrahedral geometry). The $C-C$ bond length is $1.54°A$ and each $C-H$ bond length is $1.09°A$.

Fig. 16.1 Structure of ethane

(B) In cyclopropane (C_3H_6), each carbon atom, like alkanes, is bonded to four other atoms, so it uses sp^3 hybrid orbitals to form these bonds. However, in this case, the $sp^3 - sp^3$ overlap of $C-C$ bond is not maximum as in the case of alkanes. This is due to the fact that in cyclopropane the $C-C-C$ bond angle is $60°$ and not $109.5°$ (true tetrahadred angle) due to which orbitals do not overlap exactly along their axes (Fig. 16.2). Thus the small bond angles of cyclopropane indicate that the overlap of sp^3orbitals of carbon is less than the overlap of sp^3- orbitals of carbon in alkanes (e.g. propane).

In cylopropane the three carbon atoms occupy the corners of an equilateral triangle, which results in the $C-C-C$ bond angles to be of $60°$. This compression (deviation) from the normal tetrahedral angle of $109{\cdot}5°$ to $60°$ is called the "Angle Strain".



(a) Propane

(b) Cyclopropane

Fig 16.2 Overlap between sp^3 orbitals in (a) Propane (b) Cyclopropane: Maximum overlap occurs in propane.

16.2.4 Relative Stability and Reactivity:

(A) Alkanes:

The carbon atoms in alkanes are fully saturated due to which alkanes are quite inert. Moveover, due to comparable electronegativities of carbon (2.5) and hydrogen (2.1) the electrons in the C – H bonds are practically shared equally between them, and the bond is almost non polar. Consequently polar reagents do not react with alkanes under normal conditions. Furthermore the C – H and C – C bonds are strong bonds and hence alkanes are relatively stable to common reagents such as acids, alkalies and oxidizing agents at room temperature. That is why they are also called paraffins (latin Parum = Little, affins = affinity or reactivity.

(B) Cycloalkanes:

Cycloalkanes resemble alkanes in their chemical behaviour except for cyclopropane and cyclobutane. The strength of bond and hence the stability, depends on the extent of overlap of orbitals. In the case of cyclopropane and cyclobutane, the extent of overlap of orbitals is not maximum due to greater angle strains and are unstable Cyclopropane undergoes ring opening reactions with H_2/Ni and HBr to give open –chain addition products. Cyclobutane, having less angle strain than that of cyclopropane, is more stable and hence it undergoes ring opening reaction only under severe conditions. Higher members are even more stable. They do not undergo ring opening reactions. Instead, they resemble open chain alkanes in reactivity and undergo substitution reactions.

16.2.5 Rreaction of alkanes:

16.2.5.1 Radical Substitution Reactions:

16.2.5.1.1 Substitution reactions:

Substitution reactions are those reactions in which an atom or group of atoms, directly attached to the carbon in the substrate molecule is replaced by another atom or group of atoms. (The term substrate is used for the reactant molecule, undergoing chemical change).

For example,

$$\underset{\text{Methane}}{CH_4 + Cl_2} \xrightarrow{h\upsilon} \underset{\text{Chloromethane}}{CH_3Cl + HCl}$$

A hydrogen atom of the methane molecule is replaced by a chlorine atom.

A substitution reaction may be initiated by nucleophile, electrophile or free radical.

1. Homolytic and heterolytic bond fission

Bond breaking (fission) is an endothermic process. If sufficient amount of energy is available, a covalent bond $(\delta - \text{bond})$ can undergo fission in two ways.

a. Homolytic fission or Homolysis:

In Homolysis when a chemical bond breaks in such a way that each of the two bonded atoms acquires one of the bonding electrons.

$$\overset{\curvearrowleft\curvearrowright}{A-A} \rightarrow A^{\bullet} + A^{\bullet}$$

The products $A^{\bullet}$ and $A^{\bullet}$ are called the free radicals, which are electrically neutral species and have one unpaired electron.

b. Heterolytic fission or Heterolysis:

In Heterolysis when a chemical bond breaks in such a way that one of the bonded atoms acquires both of the bonded electrons. The atom with high electronegativity, usually, acquires both the bonding electrons. The arrow in the following general example indicates that the sigma electrons are leaving A and becoming a property of the B.

$$A \overset{\curvearrowright}{-} B \rightarrow A^{+} + B^{-}$$

The product in this case are the ions.

2. Electrophile: (Electron loving)

A reagent which can accept an electron pair in a reaction is called an electrophile. An electrophile may be positive ion or neutral molecule with an electron–deficient centre. Examples are;

$$H^+, C\ell^+, Br^+, I^+, NO_2^+, R_3C^+, \overset{+}{S}O_3H, A\ell C\ell_3, BF_3 \text{ etc}$$

3. Nucleophile (Nucleus –Loving):

A reagent which can donate an electron –pair in a reaction, is called a nucleophite. A nucleophile may be negative ion or neutral molecule with lone pair of electrons. Examples are,

$$C\ell^-, Br^-, I^-, \bar{C}N, \bar{O}H, R-\ddot{N}H_2, \ddot{N}H_3, H_2\ddot{O}:, R\ddot{O}H \text{ etc}$$

16.2.5.1.2 Mechanism of Free Radical Substitution Reactions:

The step wise description of a chemical reaction, showing the breaking of older bonds and making of new bonds in the substrate leading to the formation of the final product, through transitory intermediates (if any) is called mechanism of the reaction.

Substitution reactions, which are initiated by a free radical are called the free radical substitution reactions. One of the examples of such reactions is the chlorination of methane and ethane in the presence of ultraviolet (u.v.) light.

$$\underset{\text{Methane}}{CH_4} + C\ell_2 \xrightarrow{\text{U.V. Light}} \underset{\text{Methyl Chloride}}{CH_3C\ell} + HC\ell$$

The mechanism involve the following steps:

Step 1. Initiation: A chlorine molecule undergoes homolytic fission in the presence of u.v. light to give chlorine free radicals.

$$C\ell_2 \xrightarrow{U.V} 2C\ell^\bullet$$

Step 2. Propagation: (a) A chlorine free radical attacks the methane molecule to give methyl free radicals and $HC\ell$.

$$C\ell^{\bullet} + CH_4 \longrightarrow \dot{C}H_3 + HC\ell$$

Methyl free radical

(b) The methyl free radical $(\dot{C}H_3)$, thus produced attacks a chlorine molecule to form methyl chloride and chlorine free radical.

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

Methyl chloride

These propagation steps are repeated again and again.

Step 3. Termination: The above chain reaction comes to an end, when any two free radicals combine to form stable products.

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

In actual practice the above reaction does not stop at $CH_3 - C\ell$ stage. The remaining three hydrogen atoms of methyl chloride can be successively replaced by chlorine atoms.

$$CH_3 - Cl + Cl_2 \longrightarrow CH_2Cl_2 + HCl$$

Methylene chloride
(Dichlomethane)

$$CH_2 - Cl_2 + Cl_2 \longrightarrow CHCl_3 + HCl$$

Chloroform
(Trichloro methane)

$$CHCl_3 + Cl_2 \longrightarrow \underset{\text{Carbon tetrachloride}}{CCl_4} + HCl$$

Thus a mixture of all the four substitution products (CH_3Cl, CH_2Cl_2, $CHCl_3$ and CCl_4) is obtained. The extent of their concentration in the mixture depends on the relative amounts of chlorine and methane. If $C\ell_2$ is taken in excess, the reaction goes to the final substitution product and carbon tetrachloride is the major product. On the contrary, when $C\ell_2$ is limited (or CH_4 is taken in excess), the major product of the reaction is $CH_3C\ell$.

16.2.5.2 Oxidation of Organic Compounds (Combustion):

Alkanes like all other hydrocarbons, burn in air to produce carbon dioxide and water. The reaction is highly exothermic and large quantity of heat is evolved. For example,

$$\underset{\text{Methane}}{CH_4} + 2O_2 \xrightarrow[\text{Ignition}]{\text{Flame or}} CO_2 + 2H_2O + 890.95\ kJ/mol$$

$$\underset{\text{Ethane}}{2CH_3CH_3} + 7O_2 \xrightarrow{\text{Flame}} 4CO_2 + 6H_2O + 1559\ kJ/mol$$

The reaction is of high significance, as it provides basis for their use as fuels to get heat and power. When there is an insufficient supply of oxygen, alkanes on combustion, form carbon monoxide and water or carbon soot and water.

$$2CH_4 + \underset{\text{(Limited)}}{3O_2} \xrightarrow{\text{Flame}} 2CO + 4H_2O + \text{Heat}$$

$$CH_4 + \underset{\text{(Very limited)}}{O_2} \longrightarrow C + 2H_2O + \text{Heat}$$

16.3 Alkenes:

Alkenes are the unsaturated hydrocarbons which contain a carbon–carbon double bond. They can be represented by the general formula C_nH_{2n}. They are also known as olefins because their lower members form oily products on treatment with chlorine or bromine.

16.3.1 Nomenclature:

There are two systems for naming alkenes.

(A) Common System (B) IUPAC System

(A) Common System:

1. The common names of fist four members are derived from those of the corresponding alkanes by replacing the ending "ane" with "–ylene".

$$CH_2=CH_2$$

Ethylene

2. Greek letters, α, β, γ etc are used to distinguish isomers having double bonds at different positions.

$$\overset{\alpha}{C}H_2=\overset{\beta}{C}H-\overset{\gamma}{C}H_2-\overset{\delta}{C}H_3,$$

α–Butylene

$$\overset{\alpha}{C}H_3-\overset{\beta}{C}H=\overset{\gamma}{C}H-\overset{\delta}{C}H_3$$

β–Butylene

(B) IUPAC System:

The IUPAC rules for naming alkenes are same as those for alkanes except the following.

1. The longest continuous carbon chain must include the double bond.

2. The name given to the longest chain will act as parent name, whereby the ending "ane" of the corresponding alkane is replaced by "ene".

3. Number the chain from that end that will confer upon atom holding the $-C=C,-$ the smallest possible number.

4. Since double bond appears between two carbon atoms, therefore its position is indicated by the number of that carbon atom, bearing lower number and this number is written before -ene.

5. If there are more than one double bonds in the molecule, these are indicated by the prefixes di, tri, tetra etc before –ene.

For example:

i

$CH_2=CH_2$

Ethene

ii

$CH_3-CH=CH_2$

Propene

iii

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

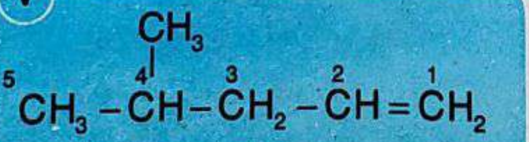
1–Butene
OR
But-1-ene

iv

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

2–Butene
OR
But-2-ene

v



$$\overset{5}{C}H_3-\overset{\overset{CH_3}{|}}{\overset{4}{C}}H-\overset{3}{C}H_2-\overset{2}{C}H=\overset{1}{C}H_2$$

4–Methyl–1–pentene
(or 4–Methyl–Pent–1–ene)

vi

$\overset{1}{C}H_2=\overset{2}{C}H-\overset{3}{C}H=\overset{4}{C}H-\overset{5}{C}H_3$

1,3–Pentadiene
OR
Pent -2,3-diene

16.3.2 Relative Stability of Alkenes:

Various alkenes differ in stability. The extent of stability of alkenes depends upon the following factors.

i. Position of the double bond in the molecule.

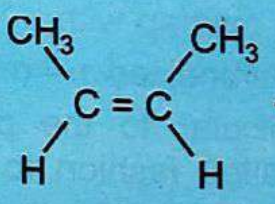
ii. Number and nature of substituents, attached.

iii. Relative positions of the substituents on the doubly bonded carbon atoms.

Measurment and comparison of the heats of hydrogenation of different alkenes, give us a clue about the relative stability of these alkenes. The stabilities of alkenes, which give the same products on combustion can be compared as follows.

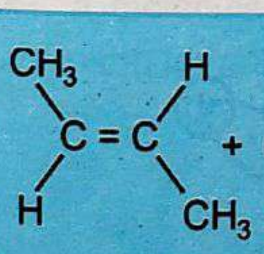
$CH_3-CH_2-CH=CH_2+6O_2 \longrightarrow 4CO_2+4H_2O+2719\,kJ/mol$

1-Butene



$+\,6O_2 \longrightarrow 4CO_2+4H_2O+2712\,kJ/mol$

cis-2-Butene



$+\,6O_2 \longrightarrow 4CO_2+4H_2O+2707\,kJ/mol$

trans-2-Butene

$(CH_3)_2C=CH_2+6O_2 \longrightarrow 4CO_2+4H_2O+2703\,kJ/mol$

Isobutylene

Comparison of the heats of combustion of butenes show that 1-butene evolves the largest amount of heat of combustion. In other words, 1-butene possess the highest energy and is thus the least stable of the butenes. Similarly isobutylene is the most stable of the four isomers.

However, it has been observed that the stabilizing effect increases with increasing the number of substitutions in the molecules. In general, the greater the number of alkyl groups attached to the double bonded carbons, the greater is the stability of alkene.

16.3.3 Structure of Alkenes:

Consider ethene $(CH_2 = CH_2)$ to illustrate the structure of alkenes. In ethene, each carbon atom has three sp^2– hybridized orbitals which are coplanar. One of the sp^2 hybrid orbitals of one carbon atom overlaps linearly with that of another carbon atom to form a sigma (δ) bond. The other two sp^2 hybrid orbitals of each carbon atom overlap with "s" orbitals of hydrogen atoms to form sigma bonds. The unhybridized p–orbitals of the two carbon atoms, which remain perpendicular to the plane of hybridized orbitals, overlap in a side wise (parallel) fashion to form a pi(π) bond between the two carbon atoms. (Fig.16.3).

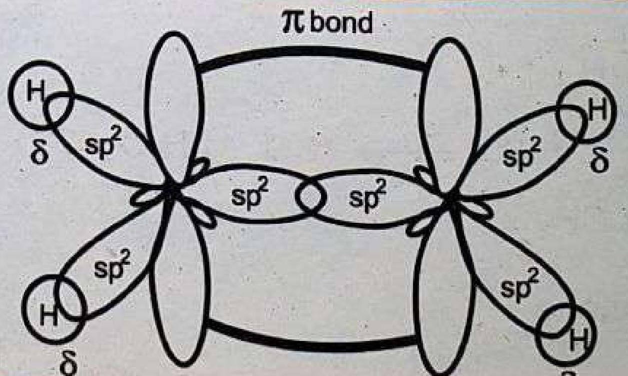


Fig. 16.3 Structure of ethene molecule

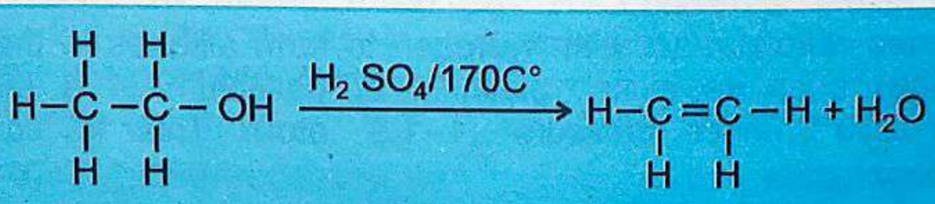
The overall structure of ethene is planar in which H–C–C and H–C–H bond angles are approximately equal to 120°. The carbon-carbon double bond length is 1.34A° and the C–H bond lengths are 1.09A° each.

16.3.4 Preparation of Alkenes:

Alkenes can be prepared by the following methods.

16.3.4.1 By Dehydration of Alcohols:

When an alcohol is heated at 170°C, in the presence of sulphuric acid, a water molecule is eliminated, resulting in the formation of an alkene.



$$H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-OH \xrightarrow{H_2SO_4/170C^\circ} H-\underset{H}{C}=\underset{H}{C}-H + H_2O$$

Ethyl alcohol Ethene

16.3.4.2 By Dehydrohalogenation of Alkyl Halides:

When an alkyl halide is heated with alcoholic solution of KOH or NaOH, a molecule of hydrogen halide (HX) is eliminated which results in the formation of an alkene.

$$CH_3-CH_2-Br+KOH \xrightarrow[\Delta]{Alcohol} CH_2=CH_2+KBr+H_2O$$

Ethyl bomide Ethene

16.3.5 Reactivity of Alkenes:

Alkenes are more reactive than alkanes due the presence of π-bond in the alkene molecules. The electron density of pi (π) bond lies above and below the bond axis. It is therefore, more exposed and easily accessible to an external electrophilic (electron seeking) reagent, commonly known as electrophile. Secondly, the overlap of atomic orbitals forming the π bond is not as effective as that in δ-bonds. Thus π bond is weaker than a sigma bond and more easily broken. It is, therefore, favourable for alkenes to add an electrophile across the double bond by breaking the weak π bond and to produce a saturated compound. Such reactions in which unsaturated hydrocarbons (alkenes) are converted into saturated compounds, are called addition reactions.

16.3.6 Reactions of Alkenes:

16.3.6.1 Hydrogenation (Addition of Hydrogen):

Alkenes readily react with hydrogen to form alkanes in the presence of catalyst such as nickel, platinum or palladium at a temperature of 200 – 250°C, under pressure (1–1.5 atm). This is called catalytic hydrogenation.

$$\underset{\text{Ethene}}{H_2C=CH_2} + H_2 \xrightarrow[\text{or Pt or Pd/25°C}]{\text{Ni/200–250°C}} \underset{\text{Ethane}}{CH_3-CH_3}$$

$$\underset{\text{Propene}}{CH_3-CH=CH_2} + H_2 \xrightarrow[\text{Pt or Pd or/25°C}]{\text{Ni 200–250°C}} \underset{\text{Propane}}{CH_3-CH_2-CH_2}$$

The hydrogenation of alkenes is industrially used for the conversion of vegetable oils into ghee.

$$\text{Vegetable oil} + H_2 \xrightarrow[\text{200–250°C}]{\text{Ni}} \text{vegetable ghee.}$$

16.3.6.2 Hydrohalogenation (Addition of halogen acids, HX):

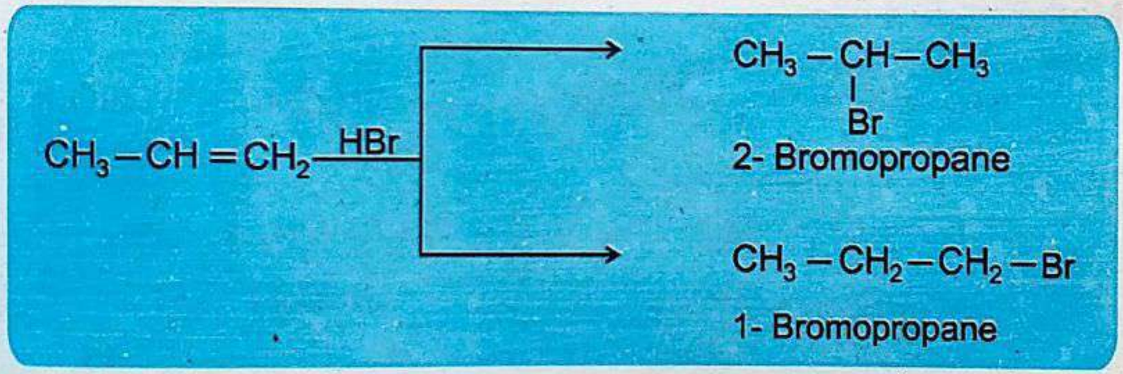
Alkenes react with halogen acids (HCℓ, HBr, or HI) to form alkyl halides.

$$CH_2=CH_2+HBr \longrightarrow CH_3-CH_2Br$$

Ethene Ethyl bromide

Mechanism:

The order of reactivity of halogen acids is $HI > HBr > HCl > HF$. When the alkene is symmetrical (as in the case of ethene), the product formed is the same, no matter which way $H-X$ becomes attached to the alkene. But if the alkene is unsymmetrical, two different isomeric products are possible. For example, propene can react with $H-Br$ in the following two ways.

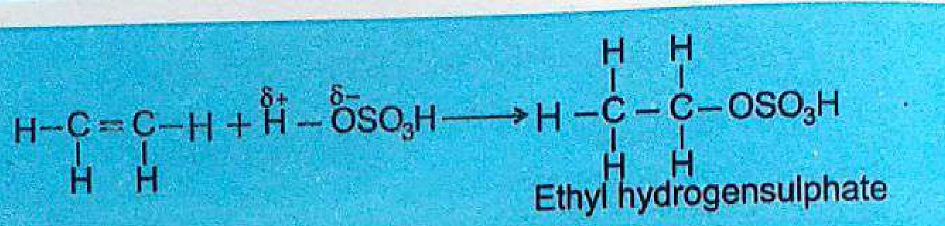


However, experimentally it has been found that $2-$Bromopropane is the major product. In fact this is in accordance with the Markovnikov's rule.

Markovnikov's Rule: It states that when an unsymmetrical (or Polar) reagent is added to an unsymmetrical alkene, the positive part of the reagent attaches itself to that carbon atom involved in the double bond, holding greater number of hydrogen atoms.

16.3.6.3 Hydration (Addition of Water):

Alkenes react with sulphuric acid to produce alkyl hydrogen sulphates, which on hydrolysis yield alcohols, at 100°C.



$$H-\underset{H}{C}=\underset{H}{C}-H+\overset{\delta+}{H}-\overset{\delta-}{O}SO_3H\longrightarrow H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-OSO_3H$$

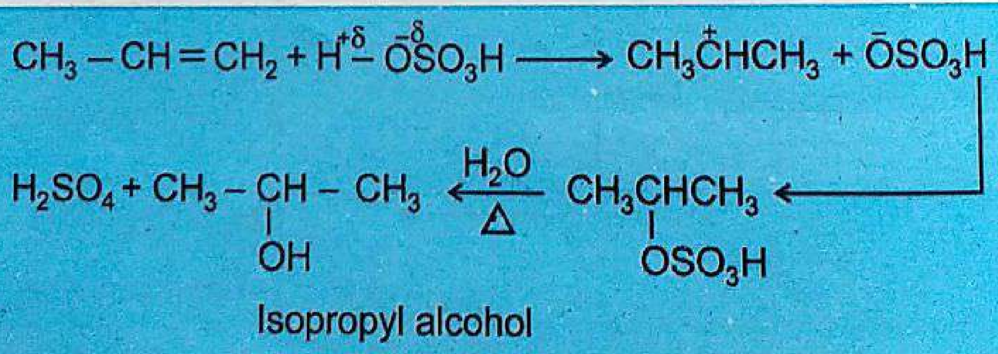
Ethyl hydrogensulphate

$$CH_3-CH_2-SO_3H+HOH\xrightarrow{100^{\circ}C}CH_3-CH_2OH+H_2SO_4$$

Ethyl alcohol

The overall result of the above reaction appears to be the addition of H_2O (hydration) to the double bond.

In case of unsymmetrical alkenes, the reaction follows the Markovnikov's rule.



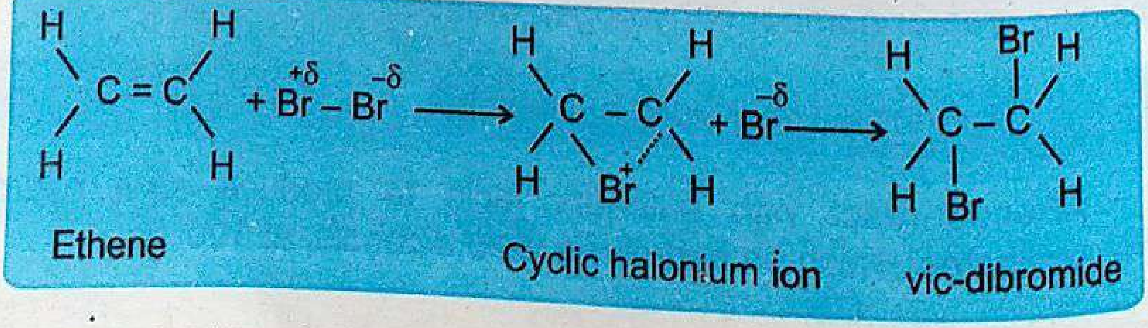
$$CH_3-CH=CH_2+\overset{+\delta}{H}-\overset{-\delta}{O}SO_3H\longrightarrow CH_3\overset{+}{C}HCH_3+\bar{O}SO_3H$$

$$H_2SO_4+CH_3-\underset{OH}{CH}-CH_3\xleftarrow[\Delta]{H_2O}CH_3\underset{OSO_3H}{C}HCH_3$$

Isopropyl alcohol

16.3.6.4 Halogenation (Addition of Halogens):

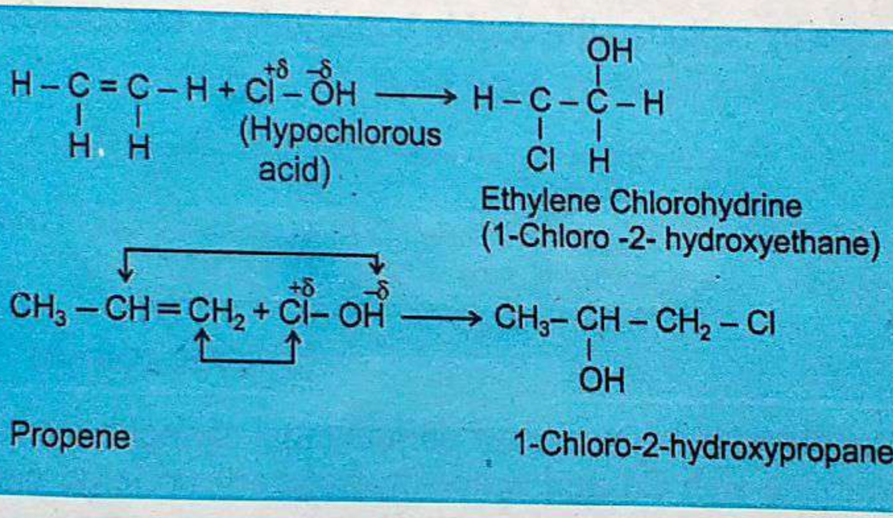
Alkenes react with halogens $(C\ell_2$ or $Br_2)$ in the presence of an inert solvent (CCl_4) to form dihaloalkanes (vicinal dihalides).



The bromination of alkenes provides a useful test for the presence of a double bond in the molecules. The colour of bromine rapidly discharges as the colorless dibromo compound is formed. The order of reactivity of various halogens with alkenes is $F_2 > Cl_2 > Br_2 > I_2$.

16.3.6.5 Halohydration: (Addition of Hypohalous acids, X – OH)

Alkenes react with hypohalous acids $(X-OH)$ to form halohydrins. Halohydrins are the organic compounds having hydroxyl group and halogen at the adjacent carbon atoms. The Markovinkov's rule is followed in case of unsymmetrical alkenes.

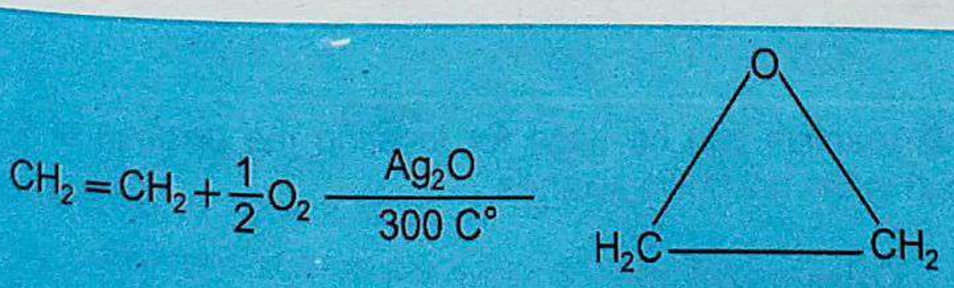


$$H_2C=CH_2 + \overset{+\delta}{Cl}-\overset{-\delta}{OH} \longrightarrow ClCH_2-CH_2OH$$

$$CH_3-CH=CH_2 + \overset{+\delta}{Cl}-\overset{-\delta}{OH} \longrightarrow CH_3-CH(OH)-CH_2-Cl$$

16.3.6.6 Epoxidation (Addition of O_2):

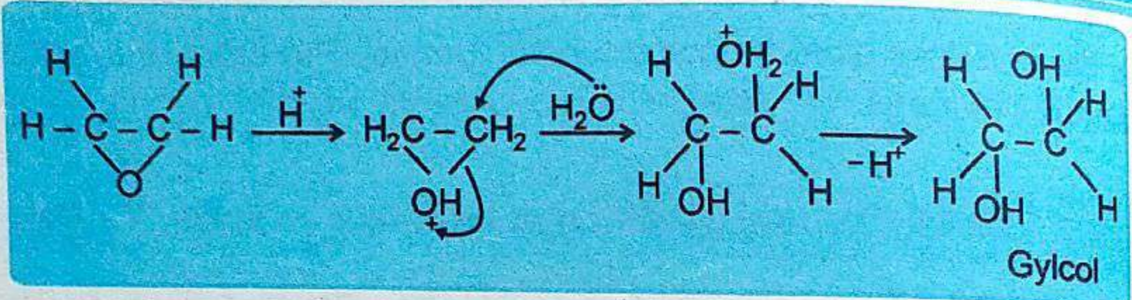
Alkenes react with oxygen in the presence of silver (Ag) catalyst at temperature 300C° to form epoxides.



$$CH_2=CH_2 + \frac{1}{2}O_2 \xrightarrow[300\ C^\circ]{Ag_2O}$$

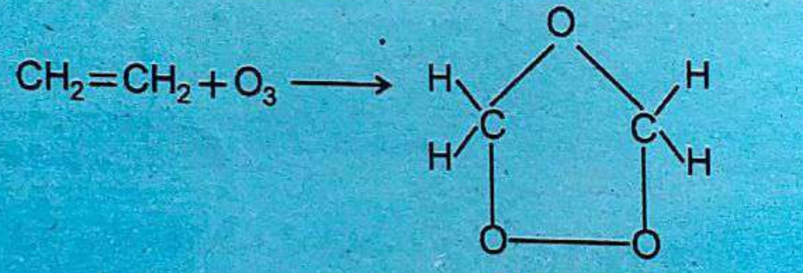
Ethylene oxide
(Epoxide)

The epoxides are very important compounds. They on acid hydrolysis produce glycols.

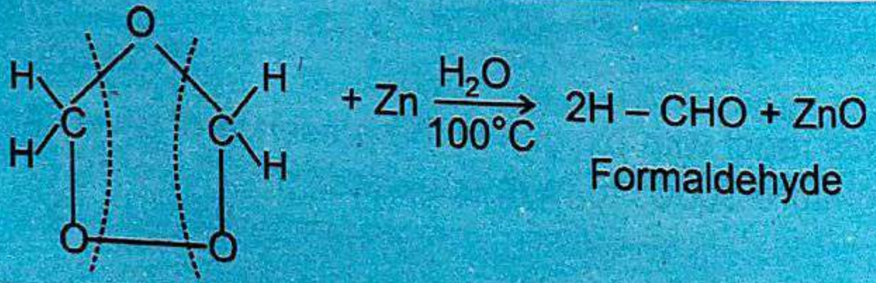


16.3.6.7 Ozonolysis:

When ozone (O_3) is passed through an alkene in an inert solvent, it adds by rupturing the double bond, to form an ozonide.


Ethylene ozonide

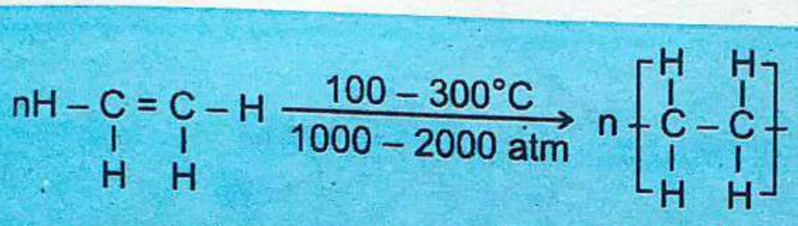
Ozonides, being explosive compounds, cannot be isolated. They on warming with Zn and water (hydrolyzed) undergo cleavage at the position of the double bond to form carbonyl compounds.



This reaction can be used for locating the position of the double bond in the unknown alkenes.

16.3.6.8 Polymerization:

The process by which simple molecules (molecules of low molecular weight) chemically join together to form large molecules with high molecular weight, is called polymerization. The simple molecules that undergo the process are called monomers and the bigger molecule is called the polymer. Simple alkenes when subjected to high temperature $(100-300°C)$ and pressure $(1000-2000\ \text{atm})$ in the presence of a catalyst, form long chain addition polymers, (Molecular weight approximately 20,000 or more).



$$nH-\underset{H}{\underset{|}{C}}=\underset{H}{\underset{|}{C}}-H \xrightarrow[1000-2000\ \text{atm}]{100-300°C} n\left[\begin{array}{cc} H & H \\ | & | \\ C & -C \\ | & | \\ H & H \end{array}\right]$$

Polyethene

Polyethylene is commercially known as "polyethene" and is used as plastic material in the industries. It is used in the manufacture of buckets, dustbins, carpet backing, packing materials and cable insulation.

16.3.7 Conjugation in Alkenes:

Conjugated compounds are those compounds in which the carbon atoms are linked alternatively by single and double bonds. For example, 1,3 –butadiene.

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

1,3-butadiene

All the four carbon atoms in this compound are sp^2 hybridized. The $C-C$ and $C-H$ sigma bonds are the result of the overlap of sp^2 hybrid orbitals with each other and with "s" orbitals of the hydrogen atoms. All the carbon and hydrogen atoms lie in the same plane.

Each of the four carbon atom also possess an unhybridized $p-$orbital, which are perpendicular to the plane of $\delta-$bonds. The $p-$orbitals of the second and third carbon atoms can overlap on either side. Thus all four $p-$orbitals overlap to form a large π molecular orbital (MO) (Fig 16.4). Each pair of π electrons is thus attracted not by two, but all four carbons. We can say that the π electrons are delocalized. The delocalization of π electrons is responsible for greater stability of $1,3-$butadiene. The $C-C$ single bonds in 1,3 –butadiene are shorter $(1.48\,\text{Å})$ than the normal

(1.54 Å) C–C single bonds, while the C–C double bonds are longer (1.37 Å) than normal (1.33 Å) isolated C–C double bonds.

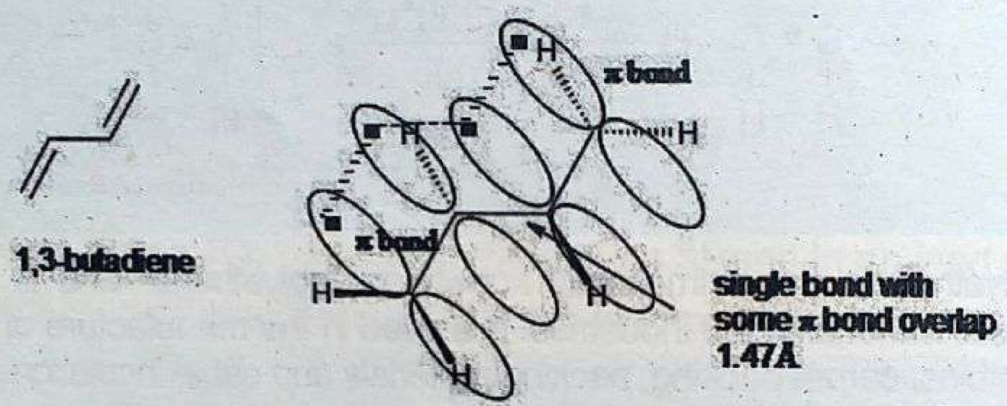


Fig 16.4

16.4 Isomerism:

Many of the organic compounds contain equal number of like atoms and thus have the same molecular formula but they different from each other in their structure, physical and chemical properties. Such compounds are called isomers and this phenomenon is called isomerism.

16.4.1 Types of isomerism

There are two main types of isomerism.

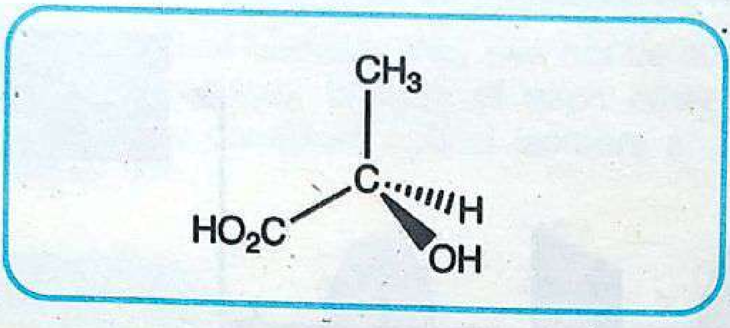
1. Structural isomerism
2. Stereoisomerism

16.4.1.1 Chiral Centres:

A structural feature within a molecule that is responsible for its chirality is called chiral centre, of the molecule.

16.4.1.2 Carbon based Chiral Centres:

A carbon atom which is bonded to four different groups is called a chiral carbon atom or asymmetric carbon atom. For example,



The chirality of lactic acid (described in optical isomerism) is due to the presence of a chiral carbon atom in the molecule. However, a chiral atom is not necessary condition for chiralty. A molecule may not have a chiral atom but still be chiral. On the other hand a molecule may have more than one chiral atoms but still be achiral.

16.4.1.3 Optical Activity:

Ordinary light is an electromagnetic radiation composed of waves vibrating in many different planes. The oscillating waves are of different wave lengths in all possible planes perpendicular to the direction of propagation. It becomes monochromatic (light of a single wave length) when it is passed through a monochromator but it still has waves in all the planes. When it is passed through a polarizer such as Nicol prism (made of calcite, $CaCO_3$), the light is found to vibrate only in one plane, and is said to be plane –polarized or simply polarized light. (Fig 16.5).

Solutions of some organic compounds have the ability to rotate the plane of polarized light. These compounds are said to be optically active, and this property of a compound is called optical activity. Optical activity of a compound is measured by an instrument called polarimeter.

An optically active compound can exist in two isomeric forms, which rotate the plane of polarized light in opposite directions. These are called optical isomers. The isomer which rotates the plane of polarized light to the right (clockwise direction) is said to be dextrorotatory isomer or (+) isomer and the isomer which rotates the plane of polarized light to the left (anticlockwise direction) is said to be levorotatory isomer or (–) isomer.

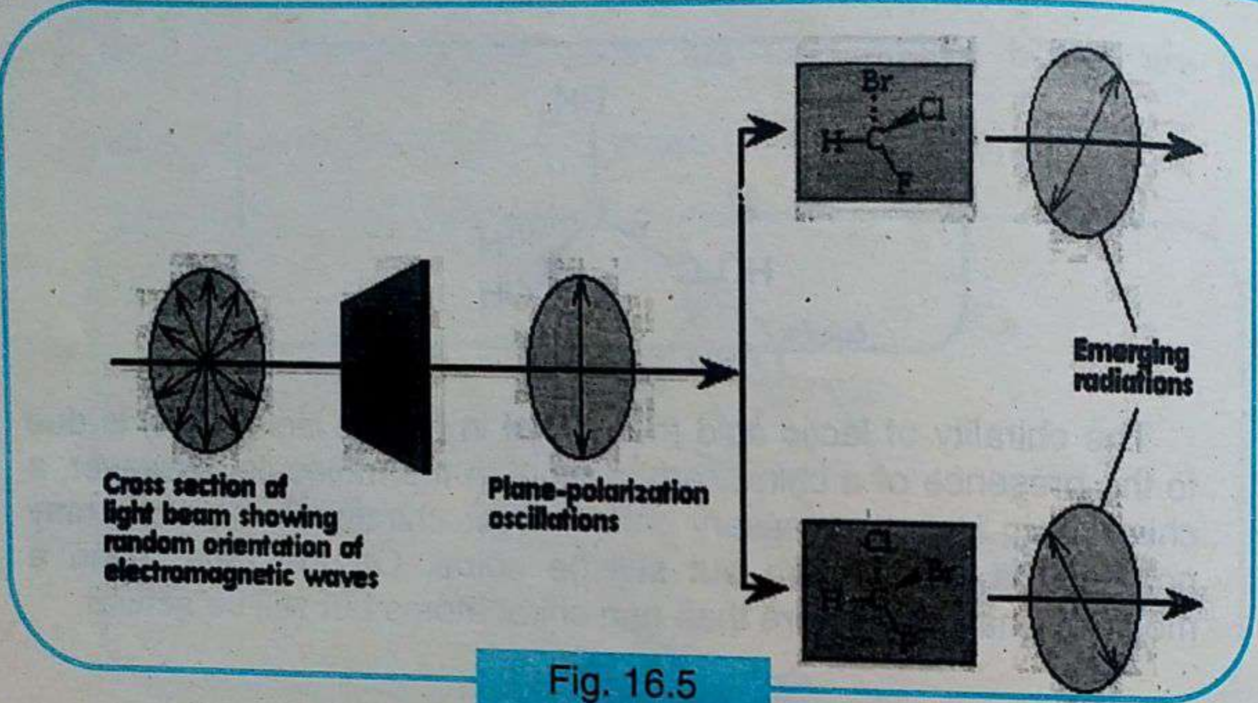
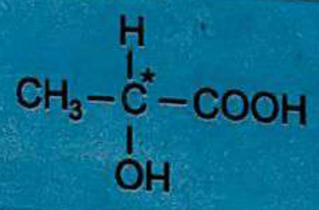


Fig. 16.5

16.4.1.4 Optical Isomerism:

Optical isomerism is a type of Isomerism in which the isomers differ in their interaction towards plane polarized light.

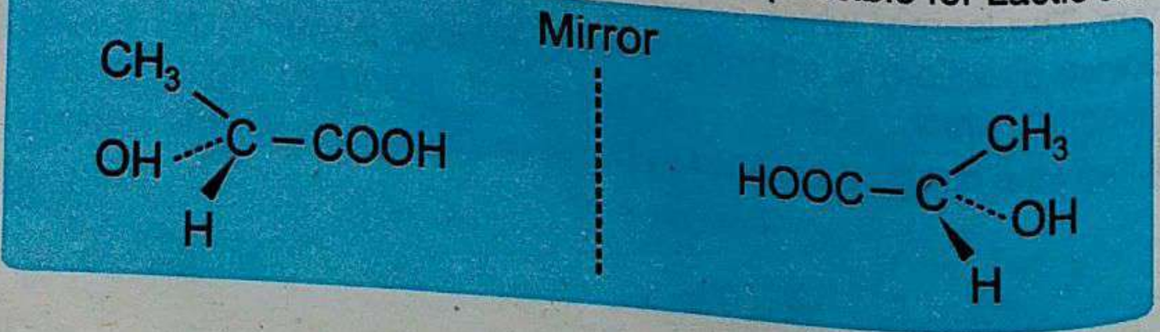
Lactic acid (2–Hydroxy Propanoic acid) is an example of a compound which shows optical isomerism. It contains one asymmetric carbon atom, shown by asteric in the following structure.



$$CH_3-\overset{\overset{H}{|}}{\underset{\underset{OH}{|}}{C^*}}-COOH$$

A carbon atom which is bonded to four different groups is called Asymmetric or chiral carbon atom.

The following three –dimensional structures are possible for Lactic acid.



These structures are not identical because they can not be superimposed on each other. They are the mirror images of each other. Such non superimposable mirror images constitute optical isomers and are called enantiomers of each other.

16.4.2 Stereoisomerism:

When isomerism is caused by different arrangement of atoms or groups in space, the phenomenon is called stereoisomerism. Thus the stereoisomers have the same structural formula (and of course the same molecular formula) but differ in the arrangement of atoms or groups in space. In other words, the isomers have different configuration (Three dimensional arrangement of atoms is space is called configuration).

Stereoisomerism is of two types.

i. Geometric or cis –trans isomerism.

ii. Optical isomerism.

Geometrical Isomerism (or cis –trans Isomerism):

The type of isomerism, where isomers possess the same structural formula containing double bond and differ only in respect of arrangement of atoms or groups about the double bond.

These isomers occur when there is restriction to the rotation somewhere in the molecule. For example, 2 – butene can be written in two isomeric form.

These are two different compounds, as they have different boiling points. These two compounds are referred to as the geometric isomer. The isomers in which the two similar groups are on the same side of the double bond is called the cis isomer, while trans isomer has got them on the opposite sides of the double bond. Consequently this type of isomerism is also called cis –trans isomerism.

Geometric isomerism in alkenes is possible only when each double bonded carbon atom is attached to two different atoms or groups, thus propene does not have geometric isomers.

16.4.3 Structural Isomerism:

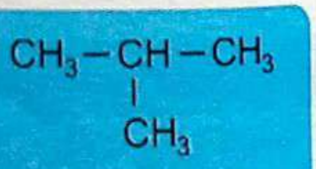
In this type of isomerism, the isomers (compounds) have the same molecular formula but different structural formula i.e. the arrangement of atoms is different in different isomers without any reference to space. Structural isomerism is of five types.

i. Chain Isomerism (Skeletal Isomerism):

Compounds which have same molecular formula but different carbon chains or skeletons are said to be chain isomers and the phenomenon is called chain isomerism. For example;

$CH_3-CH_2-CH_2-CH_3$

n-Butane



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

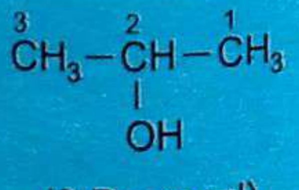
Isobutane

ii. Position Isomerism:

Position isomers have the same molecular formula but differ in the position of a functional group or the position of double or triple bound. For example;

$\overset{3}{C}H_3-\overset{2}{C}H_2-\overset{1}{C}H_2-OH$

(1-Propanol)



$\overset{3}{C}H_3-\underset{OH}{\underset{|}{\overset{2}{C}H}}-\overset{1}{C}H_3$

(2-Propanol)

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

1-Butene

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

2-Butene

iii. Functional group Isomerism:

Functional group isomerism involves compounds, having the same molecular formula but different functional groups. For example,

CH_3-CH_2-OH Ethyl alcohol	CH_3-O-CH_3. Dimethyl ether
CH_3-CH_2-CHO Propionaldehyde	$CH_3-CO-CH_3$ Acetone

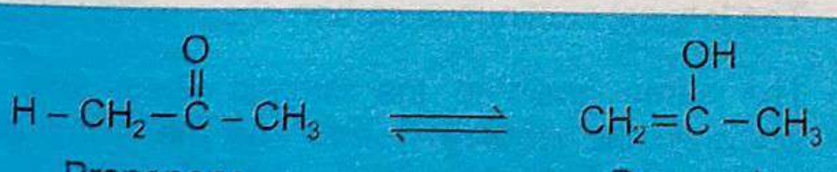
iv. Metamerism:

This type of isomerism is exhibited due to the unequal distribution of carbon atoms or (alkyl groups) on either side of the functional group. Isomers belong to the same homologous series. For example,

$CH_3-CH_2-O-CH_2-CH_3$ Diethyl ether	$CH_3-O-CH_2-CH_2-CH_3$ Methylpropyl ether

v. Tautomerism:

It is a special type of functional group isomerism, in which the isomers are in dynamic equilibrium with each other. For example



$$H-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 \rightleftharpoons CH_2=\overset{\overset{\displaystyle OH}{|}}{C}-CH_3$$

Propanone (Keto form) Propenol (Enol form)

16.5 Alkynes:

Alkynes are unsaturated hydrocarbons which contain a carbon – carbon triple bond. They can be represented by the general formula

C_nH_{2n-2}. The first and most important member of this series is acetylene $(CH \equiv CH)$ and hence these are generally called acetylenes.

16.5.1 Nomenclature:

There are two systems for naming alkynes.

(A) Common System:

1. The first member of the alkyne series is named as acetylene.

$H-C \equiv C-H$

Acetylene

2. The higher alkynes are regarded as the alkyl derivatives of acetylene. For example,

$CH_3-C \equiv CH$

Methyl acetylene

,

$CH_3-C \equiv C-CH_3$

Dimethyl acetylene

(B) IUPAC System:

The IUPAC rules for naming akynes are the same as those for alkanes, except the following.

1. The longest continuous carbon chain must include the triple bond.
2. The name given to the longest chain acts as parent name, whereby the ending "–ane" of the corresponding alkane is replaced by "–yne".
3. Number the chain in such a way that triply bonded carbon atom $(-C \equiv C-)$ gets the smallest number.
4. The position of the triple bond is indicated by the number of that triply bonded carbon atom which bears lower number and this number is written before"–yne".

5. For more than one triple bonds in the molecule, the prefix di, tri, tetra etc are used before "–yne".

The following examples will illustrate the above rules.

(i) $CH \equiv CH$

Ethyne

(ii) $CH_3 - C \equiv CH$

Propyne

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

1-butyne

(iv) $\overset{1}{C}H_3 - \overset{2}{C} \equiv \overset{3}{C} - \overset{4}{C}H$

2-buty~~e~~ne

16.5.2 Relative Stabilities of alkynes:

Like alkenes, the alkynes also exhibit stability to varying degree. The stability of alkynes, also depends on the following factors.

i. Position of the triple bond in the molecule.

ii. Number and nature of the substitutuents, attached.

The stabilities of various isomers of an alkyne (having same molecular mass), can be compared, by measuring their heats of hydrogenation or heats of combustion.

16.5.3 Structure:

In acetylene each carbon atom has two sp hybrid orbitals which lie on the same line .Each carbon atom also has two unhybridized p–orbitals, which are perpendicular to each other and to the plane of sp–hybrid orbitals. One sp–hybrid orbital of one carbon atom linearly overlaps with the sp hybrid orbital of the other carbon atom to form δ–bond between the two carbon atoms. The other sp–hybrid orbitals of both the carbon atoms overlaps with the "s" orbitals of the two hydrogen atoms to form two C–H δ bonds.

The two p –orbitals (unhybridized) of both the carbon atoms approach each other in a sidewise manner $(p_y - p_y \text{ and } p_z - p_z)$ to form two pi(π) bonds. (Fig 16.6)

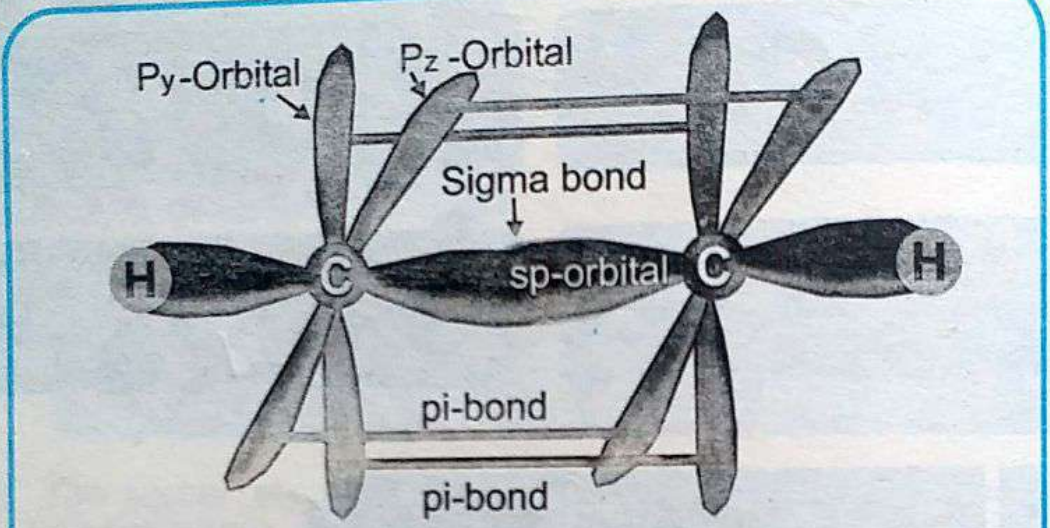


Fig: 16.6 Structure of acetylene

Thus the carbon –carbon triple bond is made up of one sigma (δ) and two pi(π) bonds. The acetylene molecules has linear geometry with $C-C-H$ bond angle of 180°. The carbon –carbon triple bond length is 1.19Å and that of $C-H$ bond is 1.09Å

16.5.4 Physical Properties:

1. The first three members (ethyne, propyne and butynes) are gases, next eight $(C_5 - C_{17})$ are liquids and higher alkynes are solids at room temperature and pressure.
2. With the exception of acetylene which has garlic like odour, all other alkynes are odourless and colourless.
3. They are soluble in organic solvents such as acetone, benzene, ethanol etc but only slightly soluble in water.
4. The boiling points of alkynes are slightly higher than the corresponding alkenes, and increase regularly with increase in the number of carbon atoms in the alkynes. However, their melting points do not follow a

regular sequence. Instead, they change irregularly with increase in the number of carbon atoms (Table 16.4).

5. They are slightly more denser than the corresponding alkanes and alkenes.

Table 16.4 Boiling and melting points of some alkynes.

Name	Formula	M.P(°C)	B.P(°C)
Acetylene	$CH \equiv CH$	–82	–75
Propyne	$CH_3-CH \equiv CH$	–102	–23
1–Butyne	$CH \equiv C-CH_2-CH_3$	–122	09
1Pentyne	$CH_3-CH_2-CH_2-C \equiv CH$	–98	40

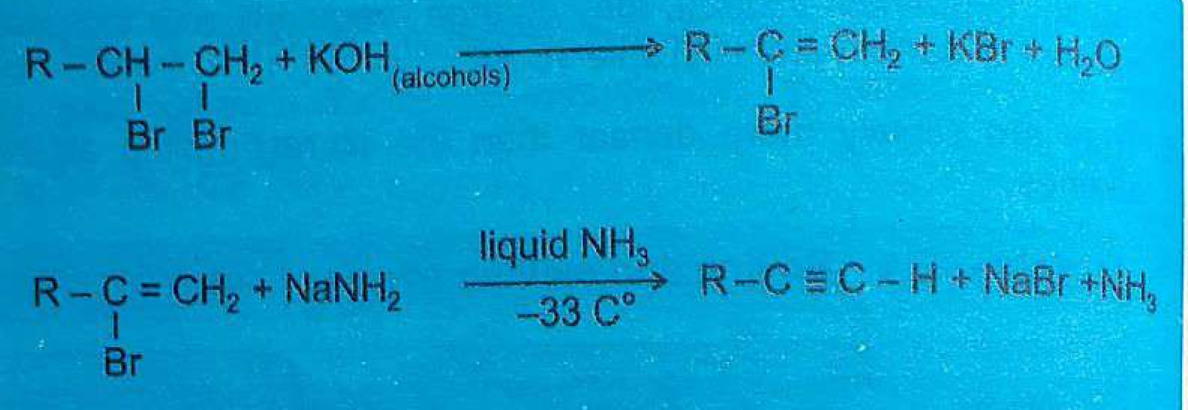
16.5.5 Preparation of Alkynes by Elimination Reactions:

Elimination reactions involve the removal of atoms or groups from two adjacent carbon atoms. These reactions result in the formation of unsaturated compounds. Alkyne can be prepared by the following elimination reactions.

1. By the dehydrohalogenation of Vicinal Dihalides:

Compounds having two halogen atoms on adjacent carbon atoms are called vicinal dihalides.

These compounds, when treated with alcoholic KOH followed by sodium amide ($NaNH_2$) in liquid ammonia form alkynes. It is a two step reaction. The elimination product of the first step (vinyl halide), being unreactive, is treated with stronger base ($NaNH_2$) to remove another HX molecule.

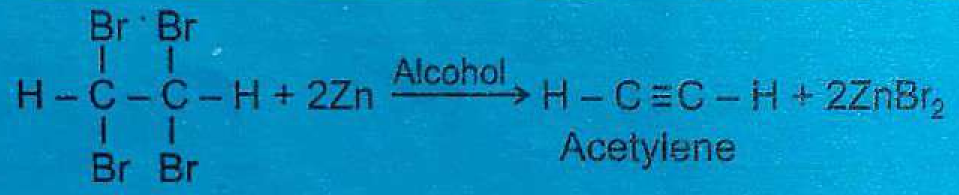


$$\mathrm{R-\underset{\underset{Br}{|}}{CH}-\underset{\underset{Br}{|}}{CH_2}+KOH_{(alcohols)}\longrightarrow R-\underset{\underset{Br}{|}}{C}=CH_2+KBr+H_2O}$$

$$\mathrm{R-\underset{\underset{Br}{|}}{C}=CH_2+NaNH_2\xrightarrow[-33\ C^{\circ}]{liquid\ NH_3}R-C\equiv C-H+NaBr+NH_3}$$

2. By the dehalogenation of Tetrahalides:

When tetrahalides are heated with zinc dust in alcohol, alkynes are formed.



$$\mathrm{H-\overset{\overset{Br}{|}}{\underset{\underset{Br}{|}}{C}}-\overset{\overset{Br}{|}}{\underset{\underset{Br}{|}}{C}}-H+2Zn\xrightarrow{Alcohol}\underset{Acetylene}{H-C\equiv C-H}+2ZnBr_2}$$

1,1,2,2-Tetrabromoethane

16.5.6 Reactivity of Alkynes:

Alkynes are unsaturated hydrocarbons like alkenes. Thus they resemble alkenes in most of their reactions. For example, alkyne add hydrogen, halogens, and halogen acids much like the addition of these reagents to alkenes. However, unlike alkenes which add one molecules of these reagents, alkynes add two molecules in a step-wise manner.

It is to be noted that a carbon–carbon triple bond (alkynes), in general, is less reactive than a carbon–carbon double bond (alkenes) towards electrophillic reagents. This is due to the following two reasons.

i. In alkynes, there are two π-bonds, the four lobes of which merge to form a single electron cloud. This cloud is cylindrically symmetrical about the internuclear axis and occupies a big volume. (Fig 16.7). Thus electron –density per unit volume becomes low.

Due to decrease in the electron density, π–electrons are not easily available to an electrophile. Hence alkynes are less reactive towards electrophilic addition reactions.

ii. The carbon atom in alkynes are sp – hybridized while in alkenes are sp^2 hybridized. Greater the s – character of an orbital, the more highly the electrons in that orbital are held by the nucleus. Thus π electrons in alkynes (50% s – character) are more strongly held by the carbon atom than in case of alkenes (33% s – character) and are less easily available for reactions with electrophile. This makes alkynes less reactive than alkenes in electrophilic reactions.

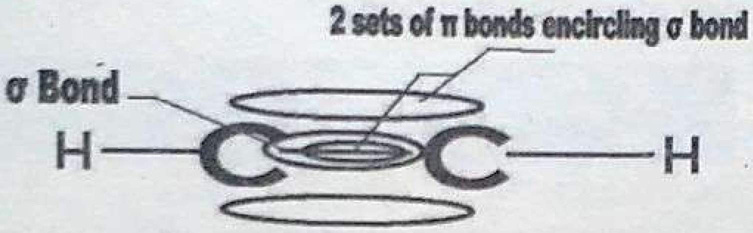


Fig: 16.7

16.5.7 Acidity of Terminal Alkynes:

Alkynes in which the triple bond is at the end of the chain, are refered to as terminal or 1 – alkynes.

$H-C\equiv C-H$	$R-CH_2-C\equiv CH$
Acetylene	terminal alkyne

Terminal alkynes and acetylene are acidic in nature. They readily donate proton to a strong base. Thus if acetylene or a terminal alkyne is treated with a solution of sodium amide ($NaNH_2$) in liquid ammonia, sodium acetylide is obtained.

$$\underset{\text{Acetylene}}{H-C\equiv C-H} + NaNH_2 \xrightarrow{\text{Liq. }NH_3} \underset{\text{Sodium acetylide}}{H-C\equiv \overset{-}{C}\overset{+}{Na}} + NH_3$$

$$R-C\equiv C-H + NaNH_2 \xrightarrow{Liq.\ NH_3} R-C\equiv CNa + NH_3$$

1−Alkyne Sodium alkynide

In ethyne and other terminal alkynes, the hydrogen atom is bonded to the carbon atom with sp-s overlap. An sp hybrid orbital has 50% s character in it and renders the carbon atom more electronegative than sp^2 and sp^3 hybridized carbons. As a result, the sp hybridized carbon atom of a terminal alkyne pulls the electrons more strongly making the attached hydrogen atom slightly acidic.

$$R-C\equiv \overset{-\delta}{C}-\overset{+\delta}{H}$$

Because of acidic nature, acetylene and 1−alkynes react with ammoniacal solutions of cuprous chloride and silver nitrate to form acetylides and alkynides of these metals.

$$CH\equiv CH + Cu_2Cl_2 + 2\,NH_4OH \longrightarrow \overset{+}{Cu}\overset{-}{C}\equiv\overset{-}{C}\overset{+}{Cu} + 2\,NH_4Cl + 2H_2O$$

Copper acetylide
(red ppt.)

$$HC\equiv CH + 2\,Ag(NO_3)_2 + 2NH_4OH \longrightarrow \overset{+}{Ag}\,\overset{-}{C}\equiv\overset{-}{C}\,\overset{+}{Ag} + 2\,NH_4NO_3 + 2H_2O$$

Silver acetylide
(White ppt)

Copper and silver acetylides are highly explosive in dry condition. They can however, be decomposed by acids such as HNO_3 to regenerate acetylene.

Since other alkynes (non−terminal) do not form acetylides (alkynides), this reaction can be used as a test to distinguish 1−alkynes from non −terminal alkynes.

16.5.8 Addition Reactions of Alkynes:

1. Hydrogenation (Addition of Hydrogen):

Two molecules of hydrogen are added to alkynes stepwise, initially forming the corresponding alkenes and finally alkanes. This reaction takes place in the presence of catalysts such as Pt, Pd or Ni.

$$H-C\equiv C-H+H_2 \xrightarrow[\text{Pt/ Pd}]{\substack{230-250^\circ C \\ Ni}} CH_2=CH_2$$

Ethyne Ethene

$$CH_2=CH_2+H_2 \xrightarrow[\text{Pt/Pd}]{\substack{230-250^\circ C \\ Ni}} CH_3-CH_3$$

Ethane

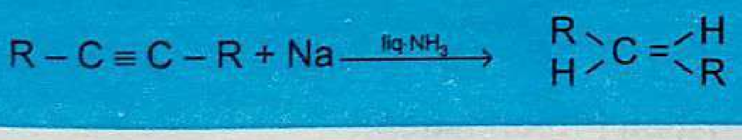
The reaction can be stopped at the alkene stage by poisoning Pd catalyst with $BaSO_4$ + quinoline (Lindlar's catalyst).

2. Reduction by Dissolving Metal (Salt Formation):

1–alkynes and acetylene, react with metals in liquid ammonia such as sodium, to form salts called alkynides or acetylides, however non-terminal alkynes give trans alkenes under this condition.

$$H-C\equiv C-H+Na \xrightarrow{\text{liq } NH_3} H-C\equiv CNa+1/2H_2$$

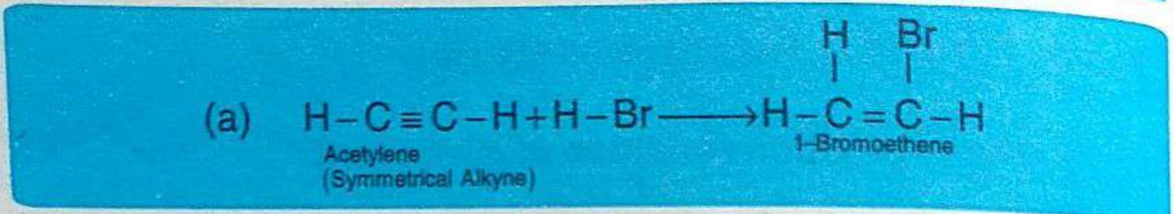
Acetylene Sodium acetylide

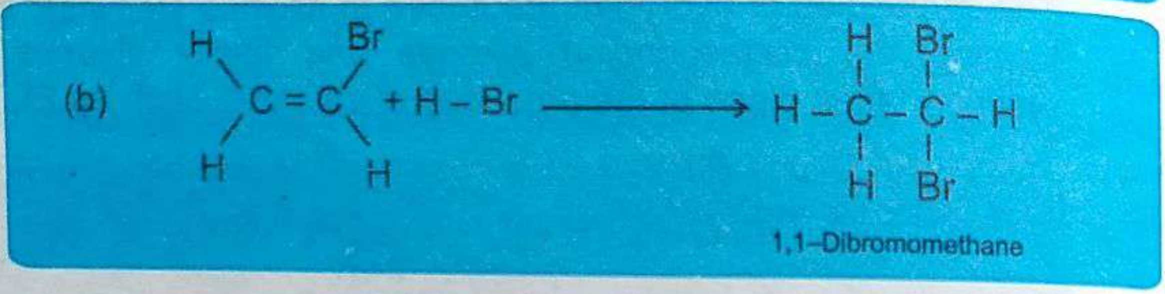


3. Hydrohalogenation (Addition of Halogen Acids):

Two molecules of halogen acids are added to alkynes in two steps. In case of symmetric alkyne, the second step follows the Markovnikov's rule. However addition of halogen acids, HX to unsymmetrical alkynes follows Markovnikov's rule in both the steps.

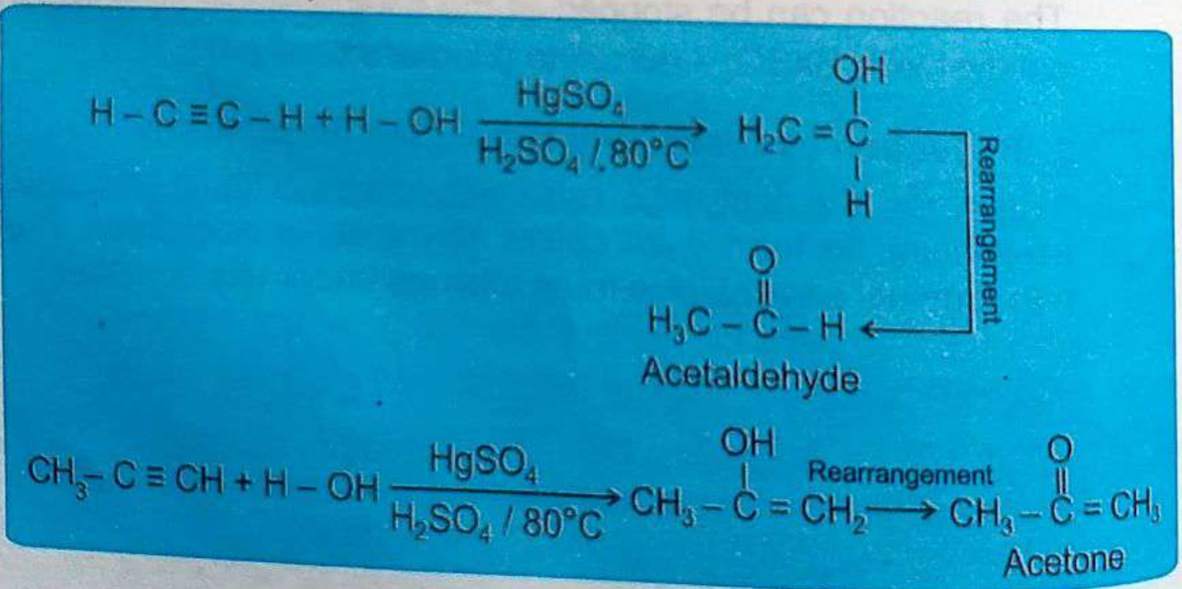
For symmetrical alkyne:





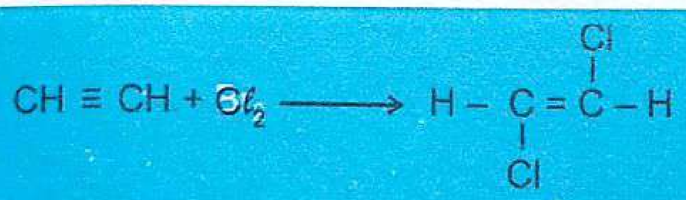
4. Hydration (Addition of Water):

Alkynes react with water in the presence of mercuric sulphate ($HgSO_4$) and sulphuric acid (H_2SO_4) to form a carbonyl compound (aldehyde or ketone).



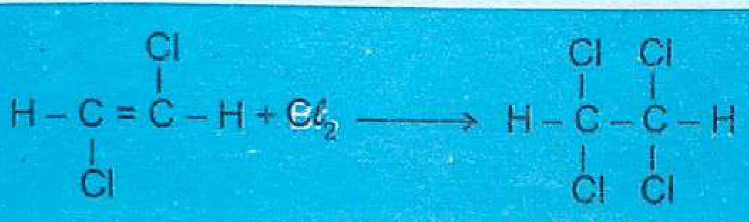
5. Halogenation (Chlorination):

Bromine adds to alkynes in two steps, forming dihalides (dihaloalkene) and then tetra halides (tetrahaloalkanes).



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

1,2-Dichloroethene

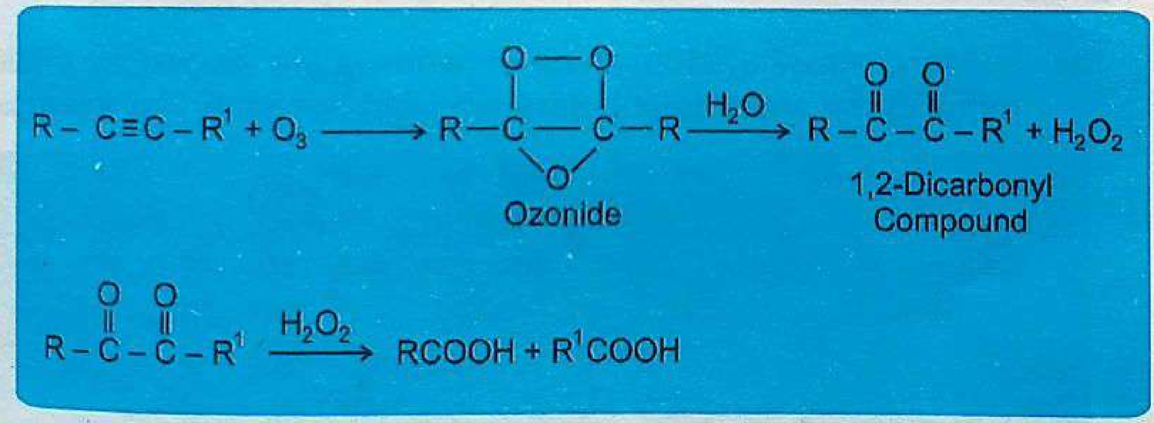


$$H-\underset{\underset{Cl}{|}}{C}=\overset{\overset{Cl}{|}}{C}-H + Cl_2 \longrightarrow H-\underset{\underset{Cl}{|}}{\overset{\overset{Cl}{|}}{C}}-\underset{\underset{Cl}{|}}{\overset{\overset{Cl}{|}}{C}}-H$$

1,1,2,2-Tetrachloroethane

6. Ozonolysis (addition of ozone, O_3):

Alkynes react with ozone (O_3) to form ozonides. The ozonides may be decomposed with water to give ketones, which are finally oxidized to acids by H_2O_2 produced in the reaction, resulting in formation of carboxylic acid.

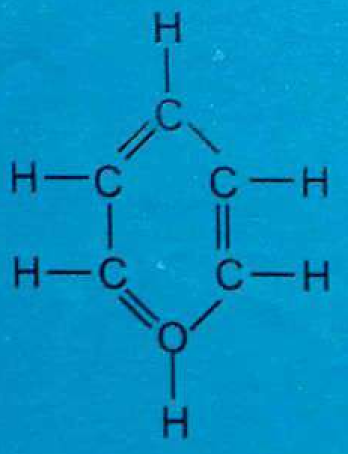


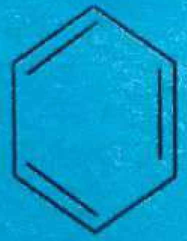
$$R-C\equiv C-R^1 + O_3 \longrightarrow \text{Ozonide} \xrightarrow{H_2O} R-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-R^1 + H_2O_2$$

$$R-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-R^1 \xrightarrow{H_2O_2} RCOOH + R^1COOH$$

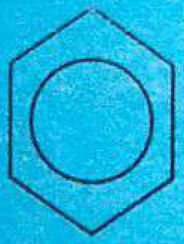
16.6 Benzene and Subtituted Benzenes:

Benzene is an aromatic hydrocarbon. Its molecular formula is C_6H_6. The following ring structure is usually written for benzene, where each corner represents a carbon atom.





or



It is understood that one hydrogen atom is bonded to each carbon atom. Mono substituted, disubstituted and polysubstituted benzene derivatives are formed by the replacement of one, two or more hydrogen atoms respectively.

16.6.1 Nomenclature:

Benzene and its substituted compounds are named by common names which are also accepted by the IUPAC System.

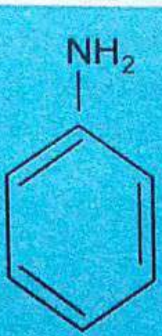
1. a. Mono substituted benzene derivatives are named by putting the name of the substituent before the word benzene. For example,

Bromobenzene

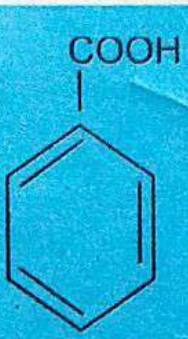
b. Some Mono substituted benzene derivatives have been given "Special names". They must be remembered as such. For examples,

Toluene

Phenol



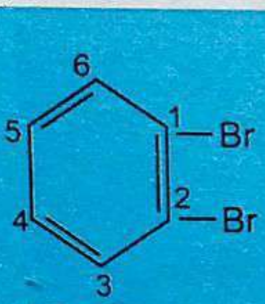
Aniline



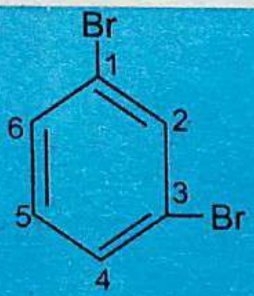
Benzoic Acid

2. In disubstituted benzene derivates, the relative substitutions are mentioned by using numbers $(1,2)(1,3)(1,4)$ or by using the prefixes ortho $(0-)$, meta $(m-)$ and para $(p-)$.

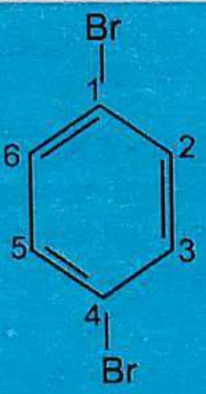
   a. For similar substituents, the prefix di is also used before the name of the substituents. For example



1,2 - Dibromobenzene
(o - Dibromobenzen)

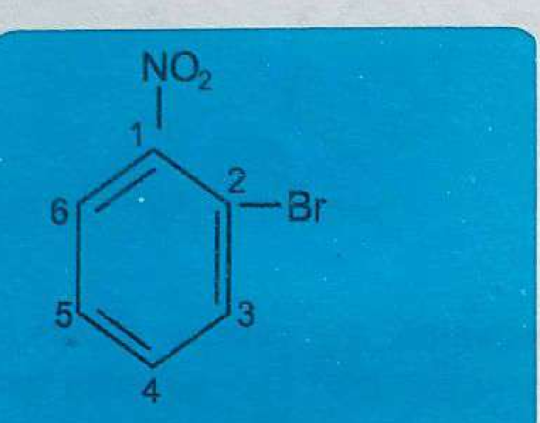


1,3 - Dibromobenzene
(m - Dibromobenzen)

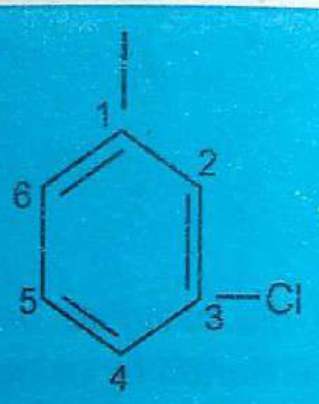


1,4 - Dibromobenzene
(p - Dibromobenzen)

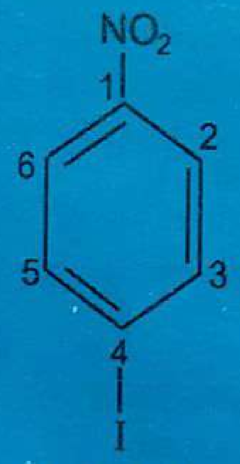
b. If the substituents are different, they are named in alphabatical order the last named substituent is understood to be at position 1. e.g;



2 - Bromonitrobenzene
(o - Bromonitrobenzene)

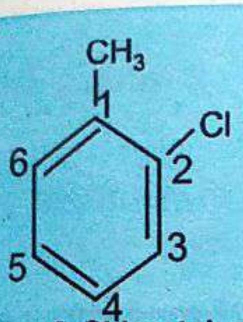


3 - Chloroiodobenzene
(m - Chloroiodobenzene)

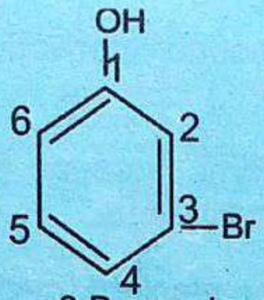


4 - Iodonitrobenzene
(p - Iodonitrobenzene)

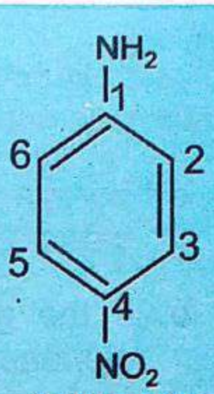
c. If one of the substiuent is such that it gives special name to the molecule then the special name is used as the parent name. The other substituent, alongwith its position, is mentioned before the parent name. For example,



2-Chlorotoluene
(o-Chlrorotoluene)

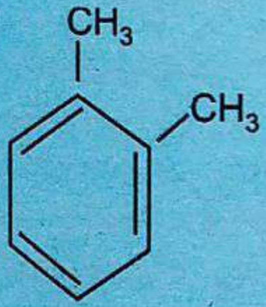


3-Bromophenol
(m-Bromophenol)

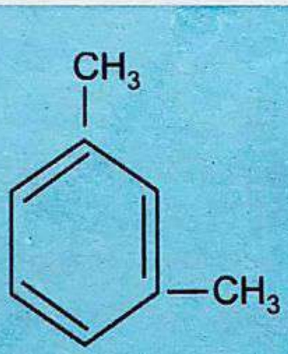


4-Nitroaniline
(p-Nitroaniline)

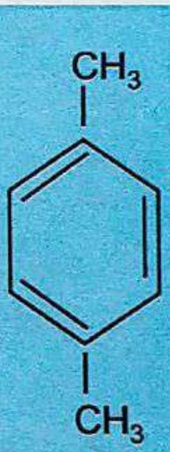
d. Some disubstituted benzene derivatives are given special names. For example,



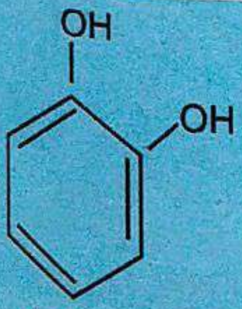
o-xylene
or
1,2-Dimethyl benzene



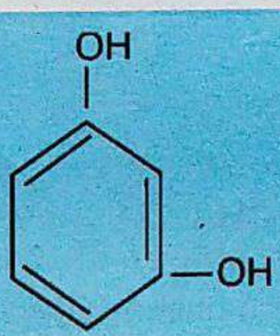
m-xylene
or
1,3-Dimethyl benzene



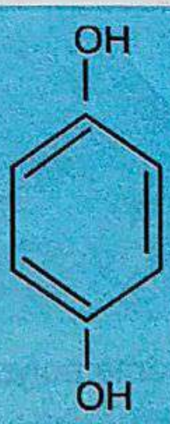
p-xylene
or 1,4-Dimethyl benzene



Catechol



Resorcinol



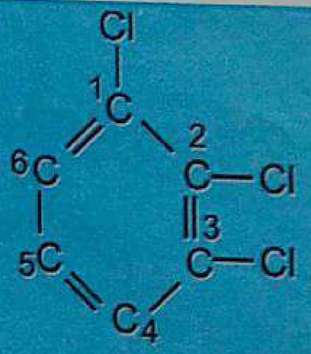
Hydroquinone
(Quinol)

3. Polysubstituted benzene derivatives, are invariably assigned systematic names.

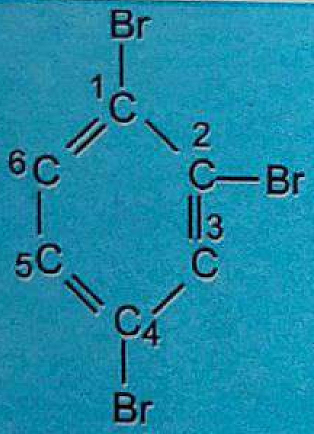
   a. For similar atoms / groups the prefix tri, tetra etc are used before the substitutents.

   b. If the groups attached, are different, they are named in alphabetical order. The last one in the order will be understood to be at position number one.

   c. To indicate the position of the substituents, the ring is numbered in such a way that all the numbers used in the name, give the lowest sum. For example,

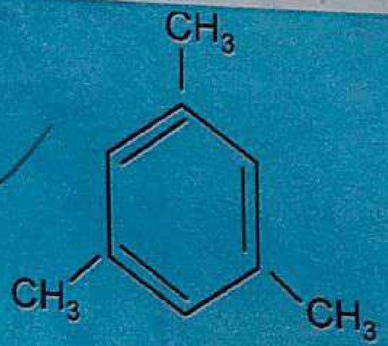


1,2,3-Trichlrobenzene

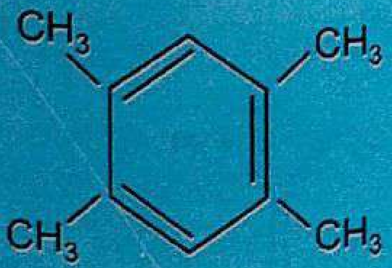


1,2,4-Tribromobenzene

   d. Even some polysubstituted benzene derivatives have been assigned special names. For example,

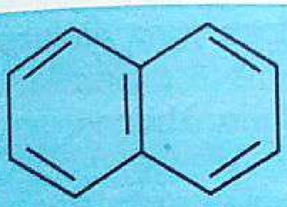


Mesitylene

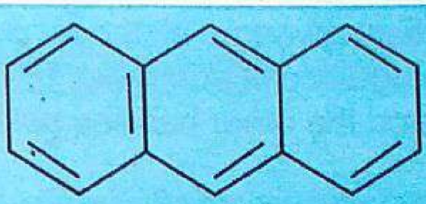


Durene

4. Some polycyclic aromatic hydrocarbons are:



Naphthalene



Anthracene

16.6.2 Physical Properties of Benzene:

At room temperature and atmospheric pressure, benzene is a colourless liquid. It has a peculiar smell and burning taste. The specific gravity of benzene is 0.8788. Benzene melts at 5.5°C and boils at 80·2°C. It is highly inflammable. Benzene is insoluble in water but soluble in ether, alcohol and petrol. It is used as solvent for many fats and resins.

16.6.3 Structure:

Molecular Orbital Aspects:

The structure of benzene can best be described in terms of the modern Molecular Orbital Theory (MOT). Each carbon atom of the ring is linked to others by sp^2 hybrid orbitals and with s orbitals of the six hydrogen atoms, forming six $C-C$ and six $C-H$ sigma bonds. (fig 16.8)

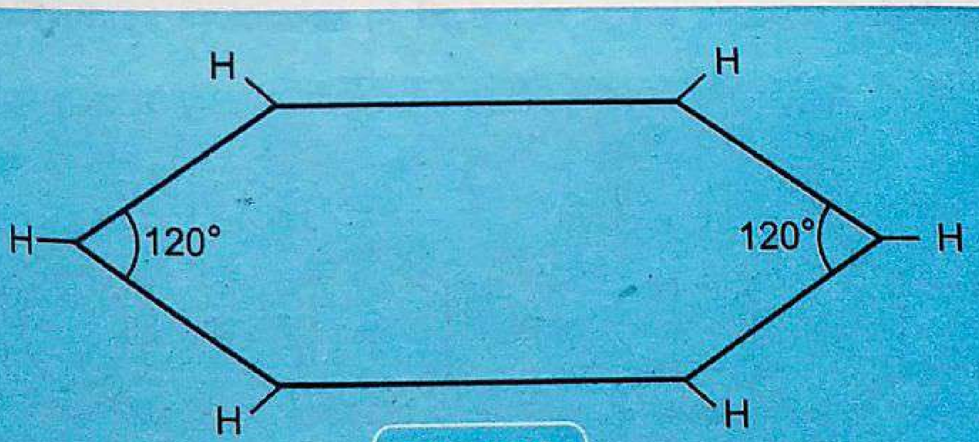


Fig. 16.8

Since the $\delta-$bond results from the overlap of planar sp^2 hybrid orbitals, all carbon and hydrogen atoms in benzene lie in the same plane. All $\delta-$bonds in benzene lie in one plane and all the bond angles are 120°.

Each carbon atom also possesses an unhybridized p orbital (containing one electron), which are perpendicular to the plane of δ bonds. The lateral (side wise) overlap of these p orbitals produces a π molecular orbital containing six electrons. (fig 16.9). one half of this π molecular orbital lies above and the other half lies below the plane of the δ bonds.

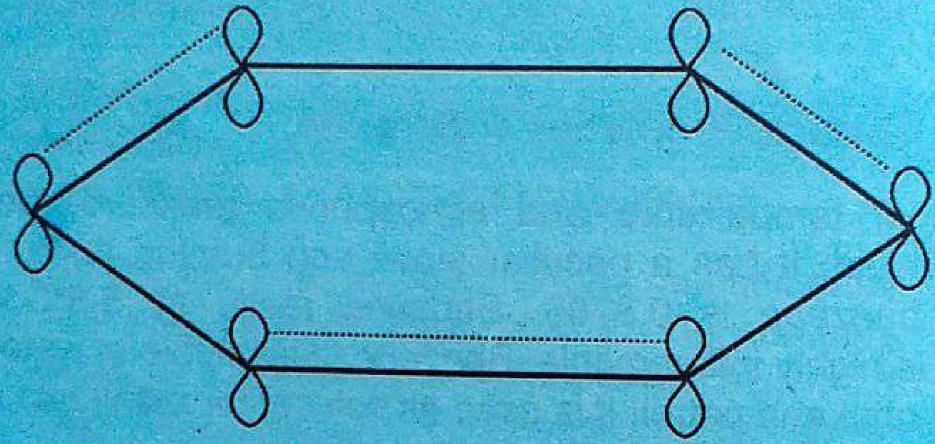
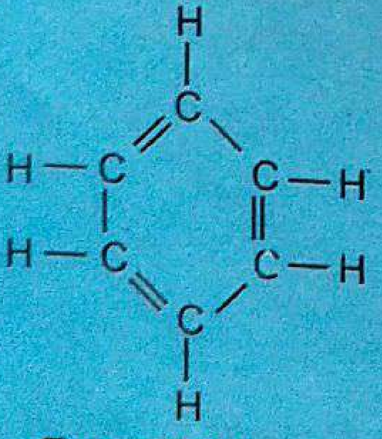


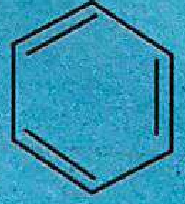
Fig. 16.9 Unhybridized p-p orbitals overlap to form π bonds

The six electrons of the p orbitals are associated with all the six carbon atoms and are said to be delocalized. Hence a stronger π bond and a more stable molecule of benzene is formed. It is this extensive π-electron delocalization which is responsible for the special chemical behavior of benzene. There are three ways in which benzene can be represented.



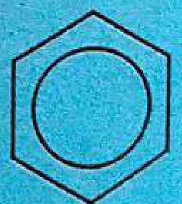
Expanded form

or



Kekule structure

or



Short hand representation

16.6.4 Resonance, Resonance Energy and Stabilization:

Resonance:

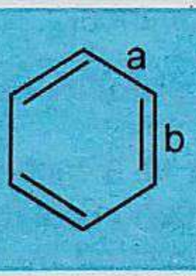
Generally, if the properties of compound are known, we can predict/draw its Lewis structure or if the lewis structure of a compound is known, we can guess its chemical properties. For example a compound with structure $CH_3-CH\overset{b}{=}CH\overset{a}{-}CH_2-OH$ should have the following properties.

i. It will react with carboxylic acids to form esters, by virtue of the presence of $-OH$ group.

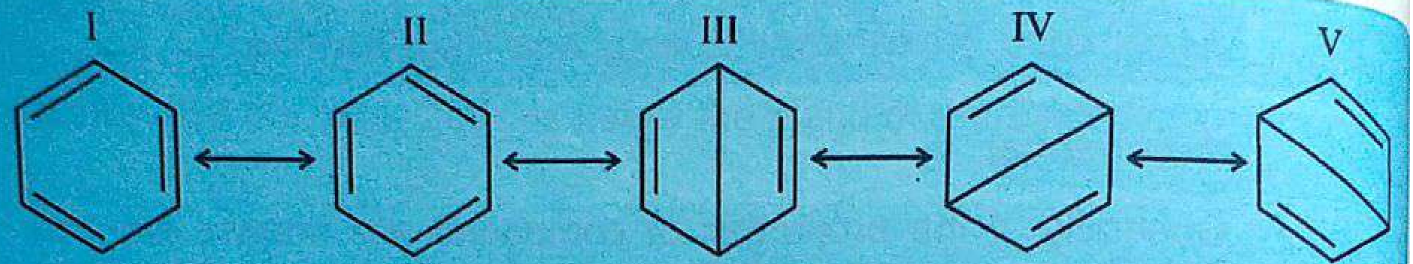
ii. It will add molecule of H_2 or Br_2 by virtue of the presence of double bond.

iii. The bond length of bonds "a" and "b" will be 1.54°A and 1.33°A respectively.

But this is not true for a compound, having a delocalized π electron system. For example, the following structure (which is in fact 1,3,5 −cyclohexatriene) commonly known as benzene is expected to add readily three molecules of Br_2 but in actual practice it does not do so.



Similarly the bond lengths of bonds "a" and "b" are not equal to 1.54A° and 1.33A°. Thus it can be said that the above structure is not the actual structure of benzene. In such a case we write more than one structures to represent the actual structure of the molecule. These structures together may explain the properties of the compound but none of them is the real structure of the compound. Thus for benzene the following structures (including the one written above) are suggested to better explain the behaviour of benzene.



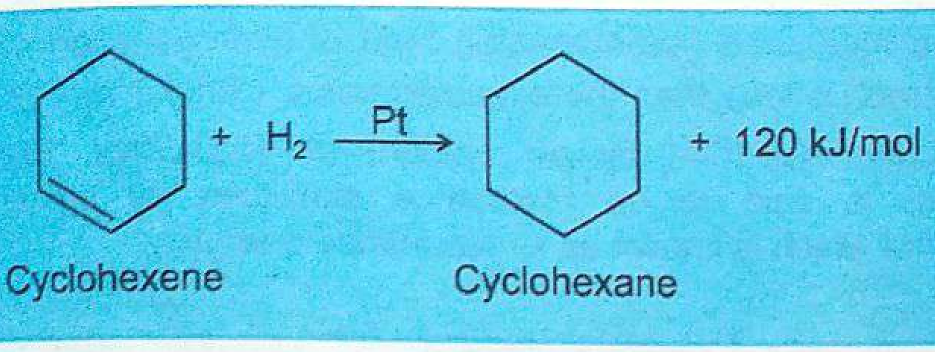
The real structure of the compound (benzene in this case) is considered to be a weighted average of all the contributing structures.

"The representation of a real structure as a weighted average of two or more contributing structures is called resonance".

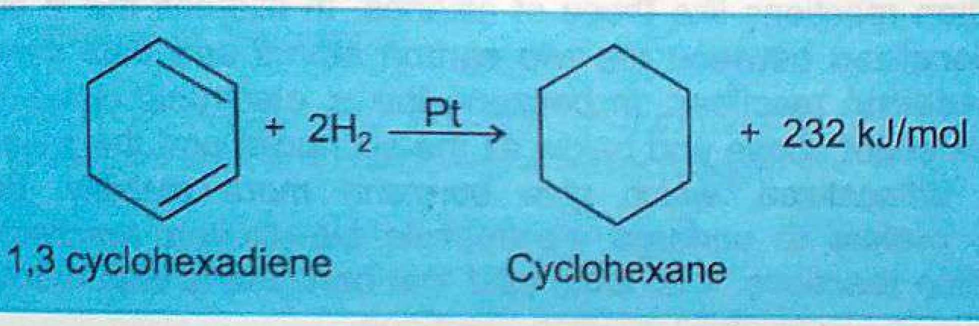
The contributing structures are called canonical forms and the real structure (which is actually not known) is called the resonance hybrid. It should be noted that all the canonical (contributing) forms do not have equal contribution and thus they are not of equal importance. For example, the contribution of structure I and II to the actual structure has been calculated to be 39% each, where as that of structures III, IV and V is 7.3% each. It should further be noted that the resonance concept of describing a molecule (as shown above in the case of benzene) does not mean that the structure rapidly shifts between the canonical forms, neither it means that some molecules are like one canonical form and other like another form. In fact, all the molecules of a substance have the same structure all the time, in which the electrons are delocalized over the whole system involved in the resonance.

Resonance Energy and stability of benzene:

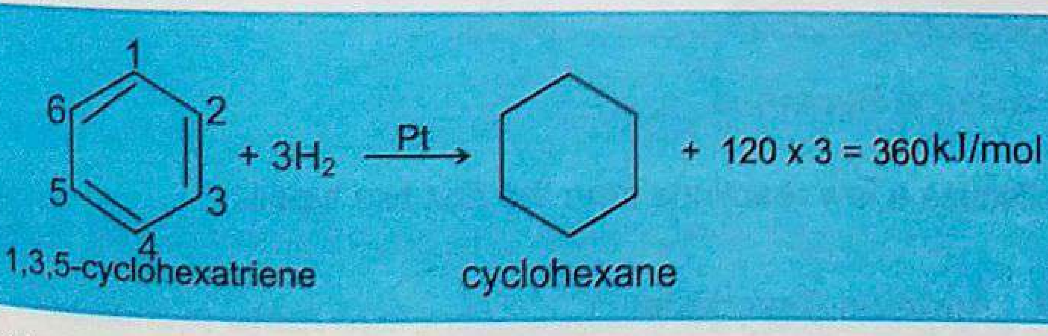
"The resonance energy of a molecules is the difference between the energy of the most stable canonical form and that of the actual molecule". For benzene it can be calculated by measuring its heat of hydrogenation and comparing it with that of the most stable canonical from. Hydrogenation of cyclohexene (having one double bond) evolves 120 kJ/mole heat energy to form cyclohexane.



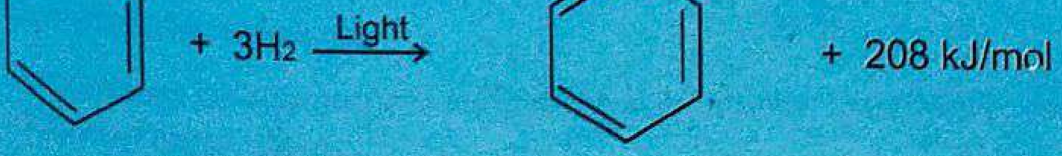
Hydrogenation of 1,3–cyclohexadiene (having two double bonds) evolves 232 kJ/mol to from cyclohexane, which is almost double of the value 120 kJ for cyclohexene.



The molecule 1,3,5–cyclohexatriene (kekule structure) normally written for benzene and having three double bonds, should release energy three times that of cyclohexane (i.e. $120 \times 3 = 360\ \text{kJ/mol}$, on hydrogenation).



But hydrogenation of benzene actually evolves only 208·0kJ/mol



Thus the measured (experimental) heat of hydrogenation of benzene (208 kJ/mol) is less than the expected value (360 kJ/mol) of the most stable canonical form by an amount of 152 kJ/mol. Benzene is, therefore, is said to be resonance stabilized by an amount of 152 kJ/mol which is known as its resonance energy.

16.6.5 Reactivity and Reactions:

Due to unusual stability (resonance stabilized), benzene does not give addition reactions like those of alkenes. In alkenes the π electronic cloud is localized between the two carbon atoms and thus they readily undergo addition reactions. In benzene the π electronic cloud makes a continuous sheet above and below all the six nuclei and the $\pi-$electrons are thus delocalized, which give benzene more stability. Benzene, therefore, prefers to undergo electrophilic substitution reactions rather than addition reactions. It is, thus, said that benzene is less reactive than alkenes during electrophilic addition reactions.

The main types of reactions of benzene are:

A. Addition Reactions.

B. Electrophilic Substitution Reactions.

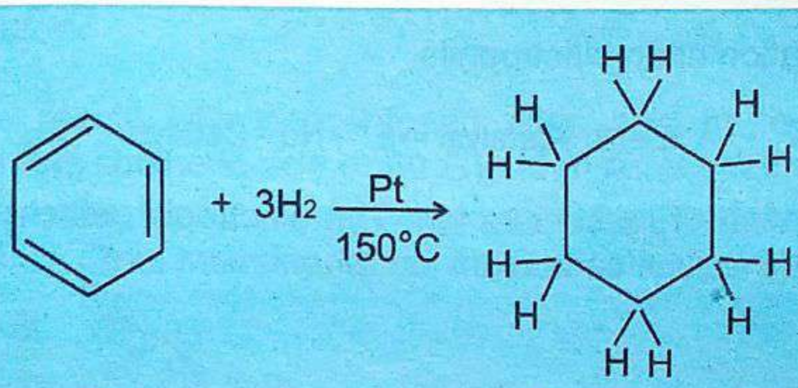
C. Oxidation Reactions.

We will discuss a few reactions from the first two types.

16.6.5.1 Addition Reactions:

1. Addition of Hydrogen:

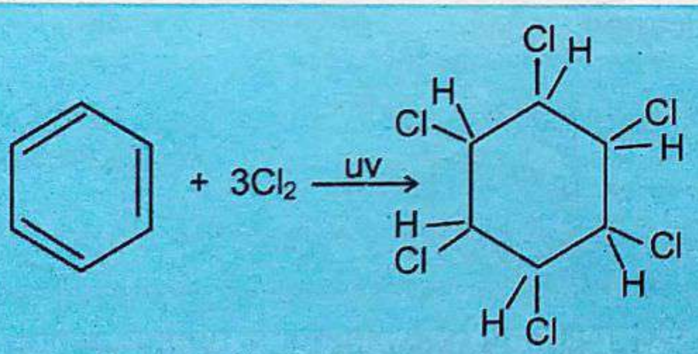
Benzene reacts with hydrogen in the presence of Ni or Pt catalyst at 150°C, under high pressure to form cyclohexane.



Cyclohexane

2. Addition of Halogens:

Benzene reacts with chlorine or bromine in the presence of ultraviolet light to form benzene hexachloride:



Benzenehexachloride
(1,2,3,4,5,6 hexachlorocyclo hexane)

16.6.5.2 Electrophillic Aromatic Substitution Reactions:

Reactions in which hydrogen atom of the aromatic ring is replaced by electrophiles are called electrophilic aromatic substitution reactions. Benzene ring with its delocalized π electrons is an electron rich system. It is attacked by electrophiles (electron–loving species), giving substituted products.

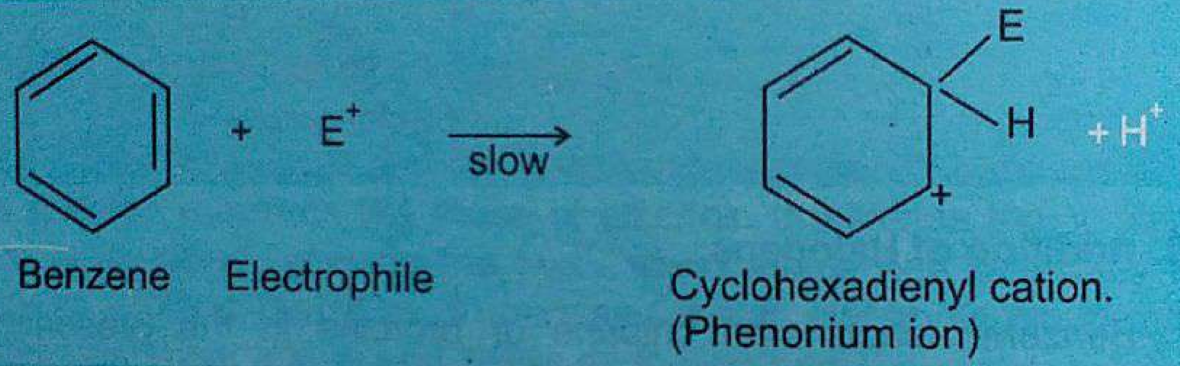
General Mechanism:

Mechanism of electrophilic aromatic substitution reaction involves the following three steps.

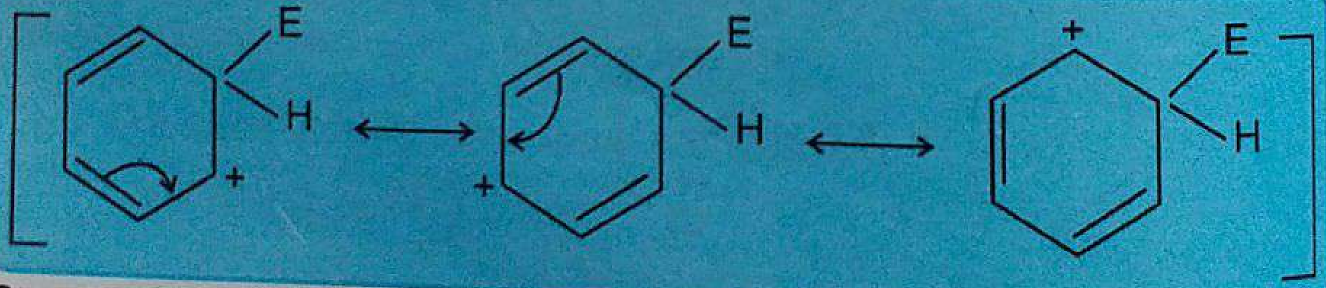
Step 1. Formation of an electrophile

$$E-Nu + catalyst \rightarrow E^{+} + Nu-Catalyst$$

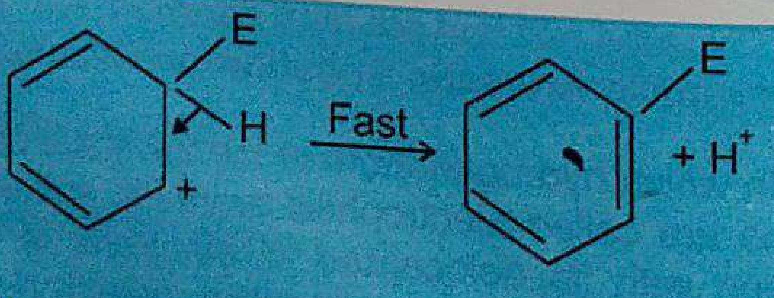
Step 2. Formation of carbonium ion: The electropile attacks the aromatic ring to produce carbonium ion (phenonium ion).



The intermediate carbonium ion is resonance stabilized and is a hybrid of the following three structures.



Step 3. Loss of proton to give substitution product. The intermediate carbonium ion is non aromatic species and is unstable. It loses a proton to form a stable aromatic substitution product.

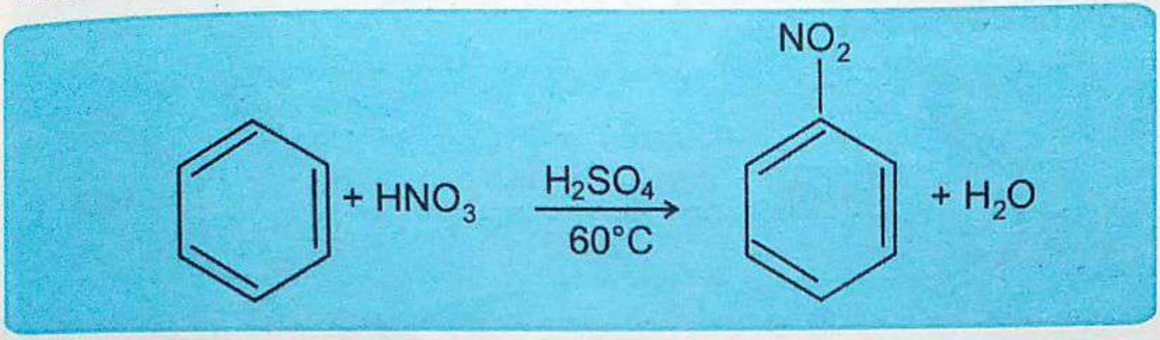


$$H^{+} + Nu-Catalyst \longrightarrow NuH + Catalyst$$

Now let us take a few electrophilic substitution reactions of benzene as an example.

1. Nitration:

Benzene reacts with concentrated nitric acid in the presence of concentrated sulphuric acid at 60°C to form nitrobenzene.

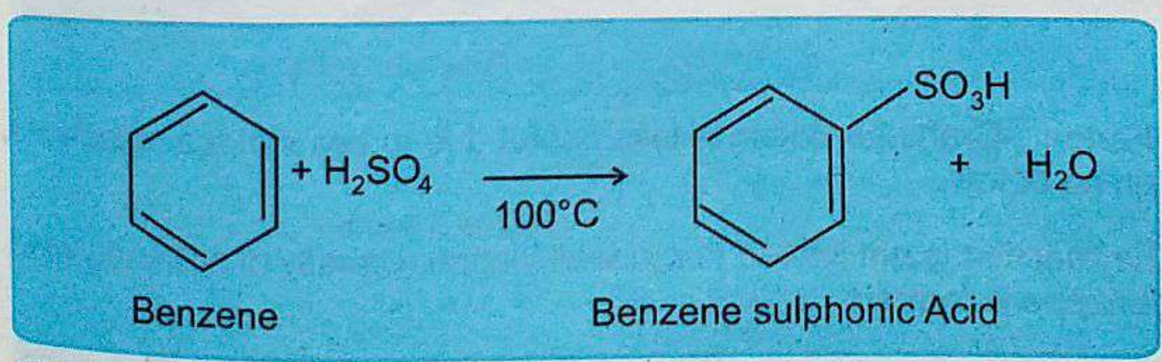


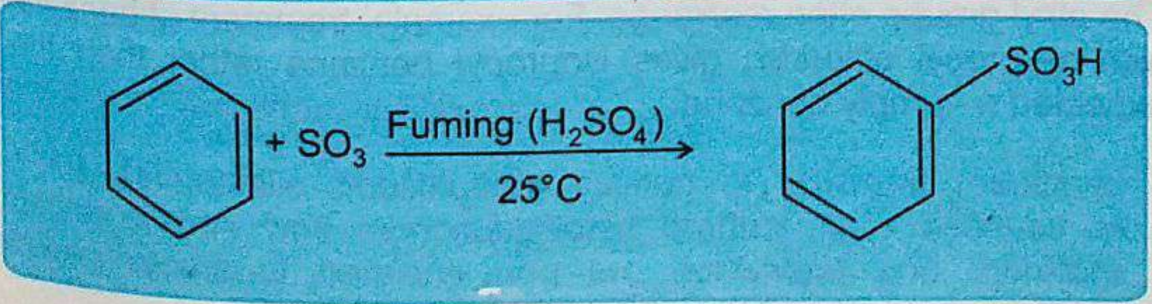
In this case the electrophile (NO_2^+) is produced by reaction of H_2SO_4 and HNO_3.

$$HNO_3 + 2\,H_2SO_4 \longrightarrow \overset{+}{N}O_2 + 2HSO_4^- + H_3\overset{+}{O}$$

2. Sulphonation:

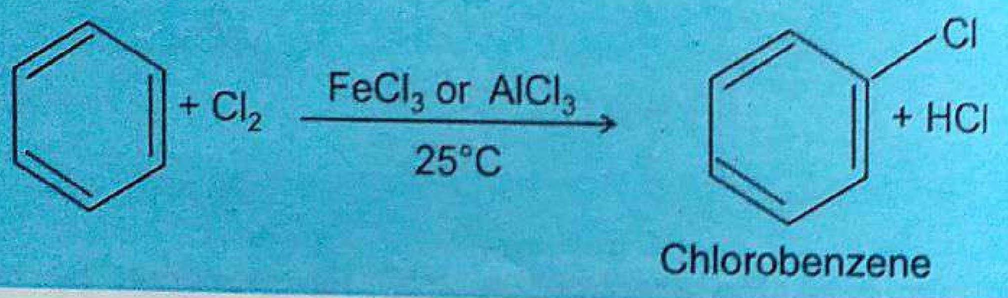
Benzene reacts with concentrated H_2SO_4 at 120°C or fuming H_2SO_4 at room temperature, to give benzene sulphonic acid. Fuming sulphuric acid is concentrated sulphuric acid in which SO_3 has been dissolved.





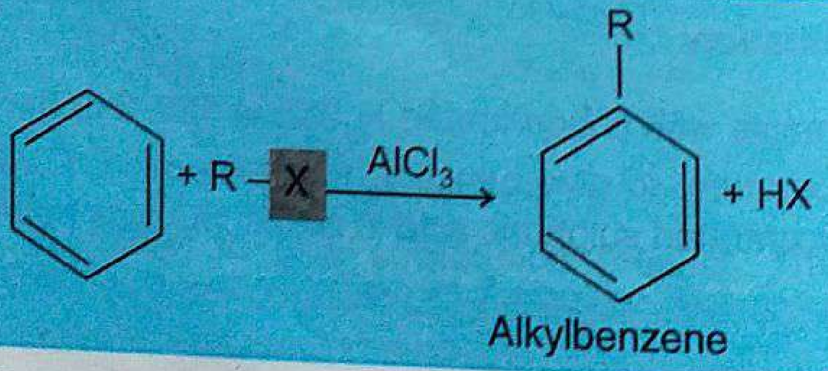
3. Halogenation:

Benzene is halogenated on treatment with molecular halogen in the presence of $FeCl_3$ or $AlCl_3$ (Lewis catalyst) at room temperature to form halobenzene.



4. Friedel –Craft's Alkylation:

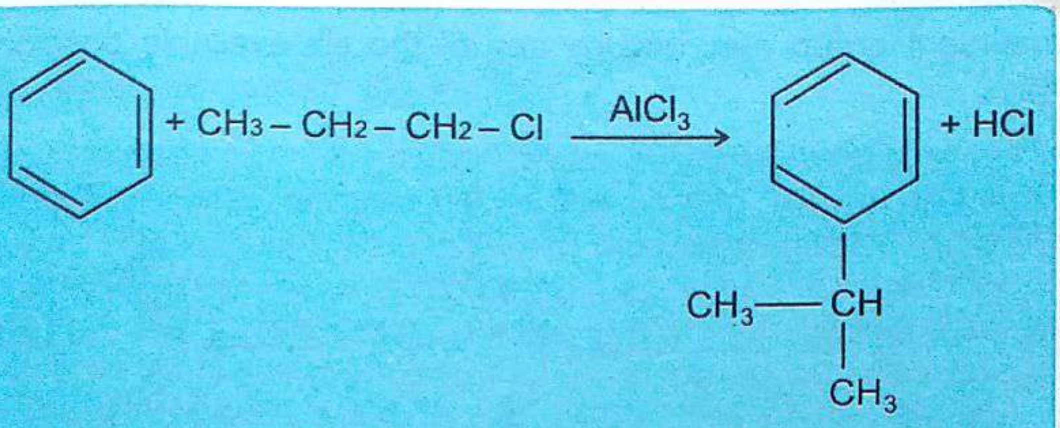
Benzene reacts with alkyl halides in the presence of $AlCl_3$ to form alkyl benzenes.



Feridel –Crafts alkylation is less useful due to two serious objections, given below.

i. The reaction is not limited to monoalkylation. Usually di or tri alkylated benzene is formed.

ii. The alkyl groups often rearrange. For example, treatment of benzene with n –propyl chloride, gives isopropyl benzene rather than the expected n –proply benzene.



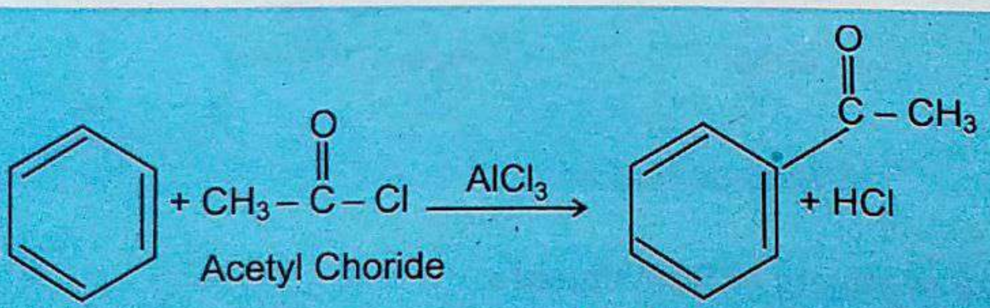
isopropyl benzene

This is because the reaction involves formation of carbonium ion which can undergo rearrangement before attacking the benzene ring.

Thus the possibility of rearrangement brings uncertainty about the actual products, formed.

5. Fridel –Crafts Acylation: (Substitution of acyl $\left(-\overset{\overset{\displaystyle O}{\|}}{C}-R\right)$ group).

Benzene reacts with acid halides (or anhydrides) in the presence of a Lewis acid catalyst $(AlCl_3)$ to give aromatic ketones. For example,

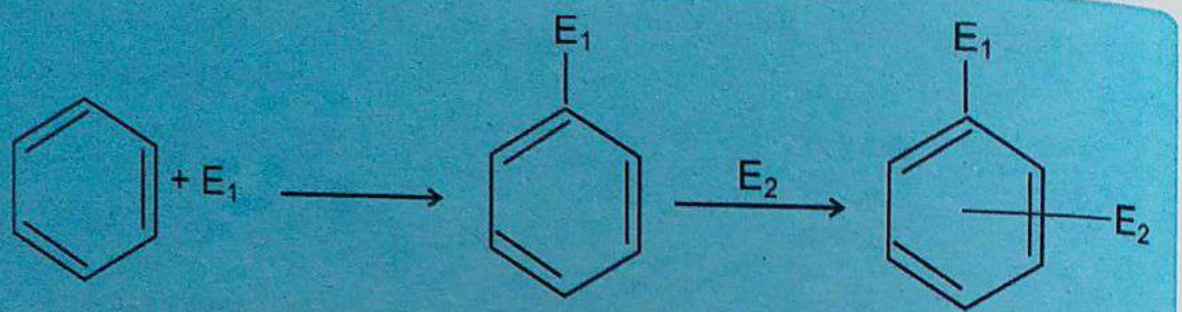


Acetyl Choride

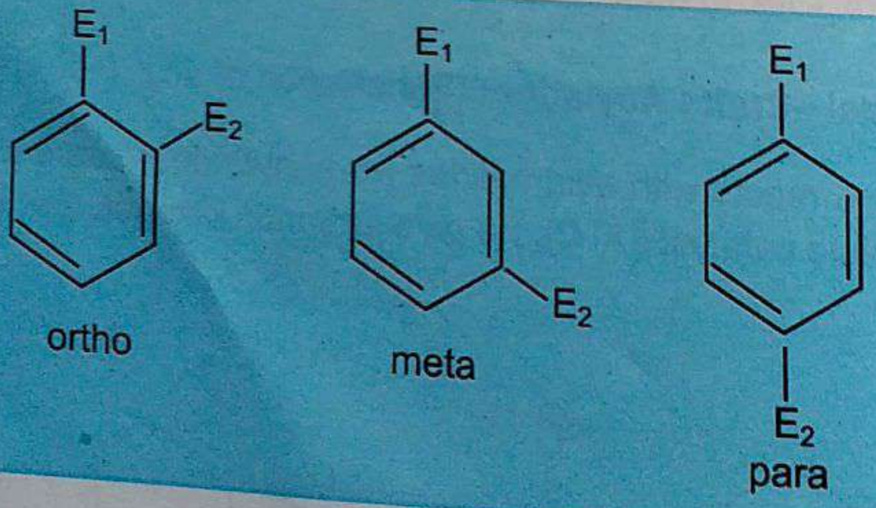
Acetophenone
(Methylphenyl ketone)

16.6.5.3 Substituent Effects:

An electrophilic Substitution reaction of benzene results in the formation of only one monosubstituted product. It is because all the hydrogen atoms of benzene ring are equivalent and therefore the substituent group may occupy any of the six available positions on the ring.



However, a second substituent, can occupy any of the remaining five positions to yield three isomeric disubstituted benzenes depending on whether the second group occupies ortho, meta or para position with respect to the first (already attached) group.



Types of effects of Substituents:

Effect of a substituent already present on the benzene ring on further substitution can be divided into two categories.

(A) Directive or orientation Effect.

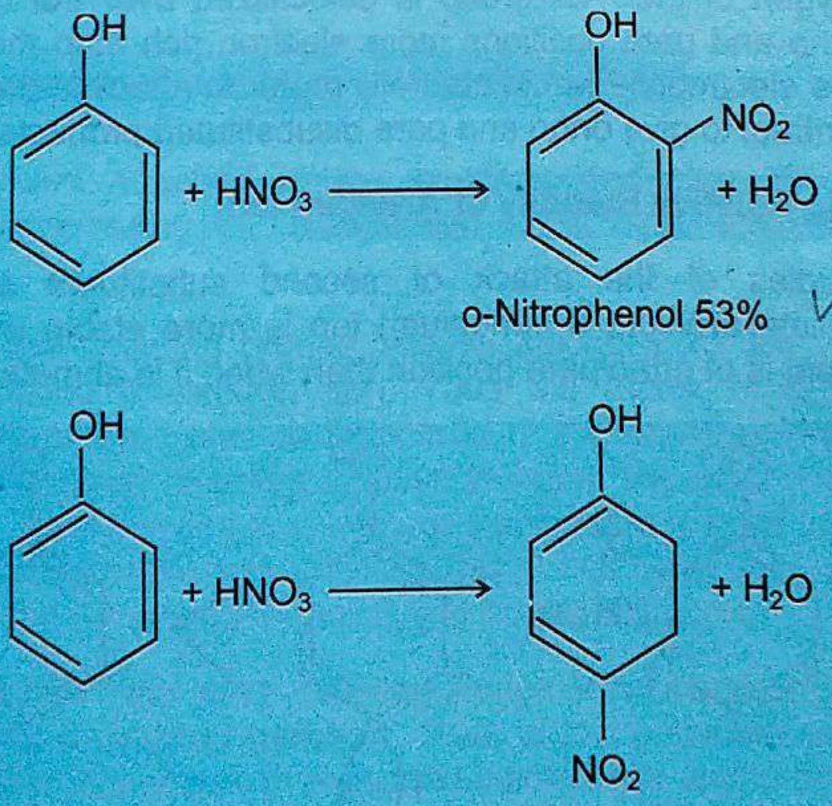
(B) Effect on reactivity of benzene ring.

(A) Directive or Orientation Effect:

The first substitutent (X) may direct the incoming substituent (Y) to ortho, meta or para position, depending on the nature of the first substituent. This is called the directive or orientation effect. It has been experimentally observed that some groups, when attached to the benzene ring, direct the second incoming substituent to either ortho and para positions or to the meta position. Thus the substituents (groups) can be divided into two classes.

i. Ortho/Para Directing/substituents

Substituents which direct the second substituent to the ortho and para positions simultaneously are called the ortho/para directing substituents. For example, when phenol is nitrated, the reaction yields only the o–Nitrophenol and p–Nitrophenol (in the ratio 53% : 47%) and no meta isomer is produced.



o-Nitrophenol 53% ✓

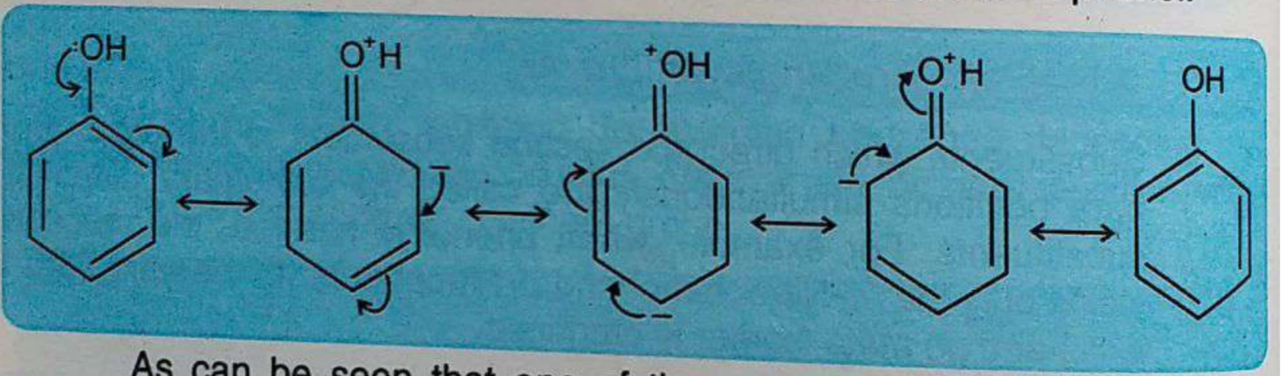
p-Nitropheol 47% ✓

Thus the substituent –OH which has directed the second substituent $-NO_2$ to ortho and para positions, is designated as ortho/para directing. Some common ortho/para directing groups are –Cl, –Br, –I, –OH, $-NH_2$ $-CH_3$, $-C_2H_5$ (Table 16.5).

The ortho/para directing effect can be explained in terms of (a) charge distribution and (b) Relative stability of arenium ion.

a. Charge Distribution:

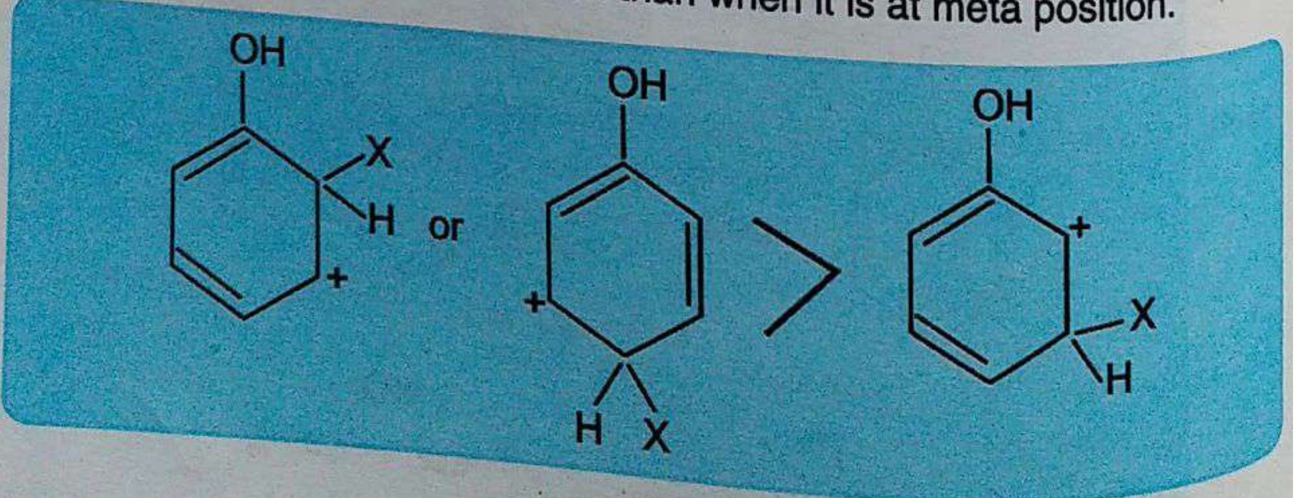
Consider, for example, the various resonance forms of phenol.



As can be seen that one of the non –bonding electron pairs of oxygen of the –OH group is delocalized over the ring, making the ortho and para positions more electron rich than the meta position. The electrophile would naturally prefer to attack at these electron rich centres, to give ortho and para disubstituted products.

b. Relative Stability of Arenium ion:

Studies of the attack of second substituent shows that the intermediate arenium (Phenonium) ion is more stable when the second substituent is at ortho/para position than when it is at meta position.



ii. Meta Directing Substituents:

The substituents which direct the second incoming substituent to meta position, are called meta–directing substituents. For example, nitration of nitrobenzene gives mainly meta dinitrobenzene (94%).

Thus the substituent $-NO_2$ group, which has directed the second $-NO_2$ group to the meta –position, is meta–Directing. Some common meta directing groups are. $-NO_2$, $-CN$, $-CHO$, $-COOH$ etc. (Table 16.5)

The meta –directing effect of a group may also be due to the following two reasons.

(a) Meta position of the ring has relatively more electronic density than ortho and para positions.

(b) Secondly, the arenium ion (Phenonium ion) with the second substituent at meta position is more stable than when the second subtituent is at ortho or para position.

(B) Effect of Substituent on the reactivity of the Ring

The substituent attached to the benzene ring also affects the reactivity of benzene ring in comparison with the unsubstituted benzene.

The ortho/para directing groups release electrons to the ring by resonance making it electron rich. Thus the attack of a second electrophile would be faster as compared to the benzene ring itself. That is the ortho/para directing species increase the reactivity of the benzene ring. They are ring activators and are referred to as activating groups. Halogens are the exceptions to this. It has been observed that halogens, though ortho/para directing, are ring deactivators.

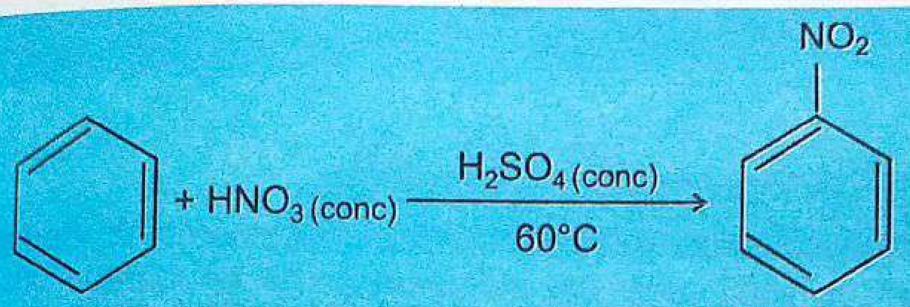
On the other hand, the meta–directing groups withdraw electrons from the ring making it electron deficient. Thus in the presence of meta–directing species, the attack of a second electrophile would be slower as compared to the benzene ring i.e. the meta–directing species decreases the reactivity of the benzene ring. These are ring deactivators and are referred to as deactivating groups. (Tabel 16.5).

Table 16.5 Orientation and activity effect of some Common Groups.

Ortho/Para directing		Meta directing	
Ring Deactivators	**Ring Activators**	**Ring Deactivators**	
$-F$	$-OR$	$-NO_2$	$-COR$
$-Cl$	$-C_6H_5$	$-CHO$	$-\overset{+}{N}H_3$
$-Br$	$-NHR$	$-COOH$	$-COOR$
$-I$	$-NR_2$	$-CN$	$-\overset{+}{N}R_3$
	$-CH_3$	$-SO_3H$	
	$-OH$		
	$-NH_2$		

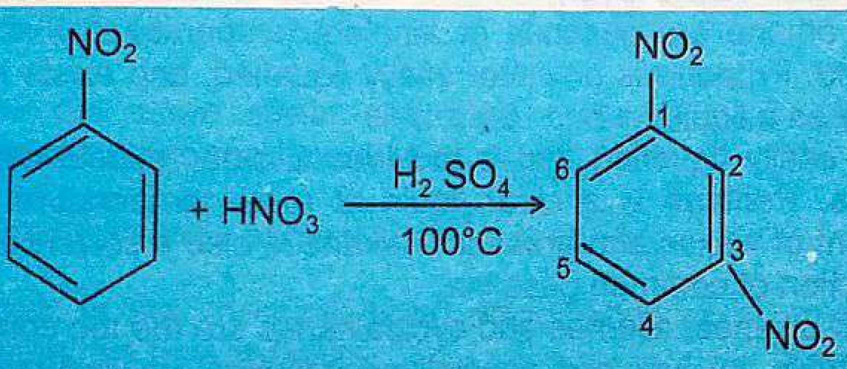
16.6.5.4 Making Polysubstituted Benzenes:

Polysubstituted benzenes are the derivatives of benzene in which two or more hydrogen atoms have been substituted by other atoms or group of atoms. These can be made under different conditions. The position of second, third etc substituents on the ring, relative to the first, depends on the nature of the first and successive substitutions already attached to the ring. Moreover, the reactivity of the ring also increases or decreases by the presence of preceding substituents attached to the ring. For example, using nitrating mixture (conc HNO_3 + conc H_2SO_4), benzene can be nitrated at 60°C, to form nitrobenzene.



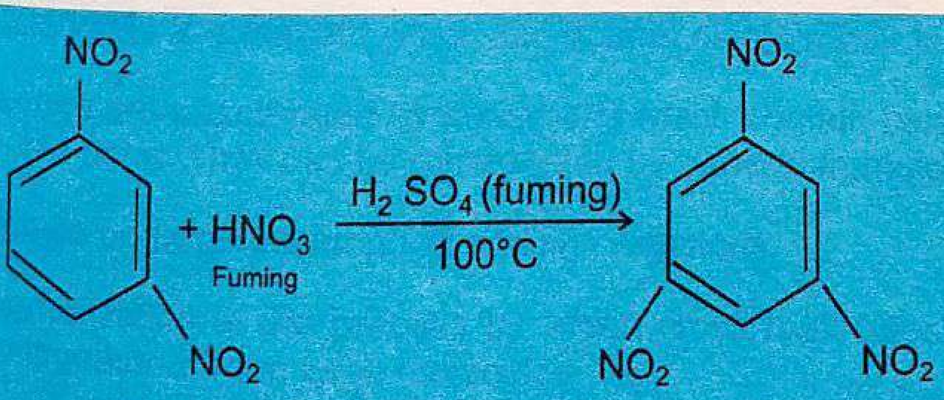
Nitrobenzene

Nitro group being deactivator, deactivates the benzene ring and further substitution becomes, difficult. Dinitrobenzene in obtained only if the reaction is carried out at higher temperature.



1,3-Dinitrobenzene

The second –NO$_2$ group further deactivates the ring. Thus trinitrobenzene is obtained only by using a mixture of fuming nitric acid and sulphuric acids.



1,3,5 - Trinitrobenzene

Similarly 2,4,6 –Trinitrotoluene (TNT) may be prepared by the nitration of toluene. TNT is widely used as a powerful explosive.

Society, Technology and Science

Hydrocarbons are a primary energy source for current civilizations. The predominant use of hydrocarbons is as a combustible fuel source. In their solid form, hydrocarbons take the form of asphalt used in road construction. Mixtures of volatile hydrocarbons are now used in preference to the chlorofluorocarbons as a propellant for aerosol sprays, due to negative impact of CFC's on ozone layer.

Methane and ethane are gaseous at ambient temperatures and cannot be readily liquefied. Propane is however easily liquefied, and exists in "propane bottles" mostly as a liquid.

Butane is so easily liquefied that it provides a safe, volatile fuel for small pocket lighters. Pentane is a clear liquid at room temperature, commonly used as solvent of waxes and greases. Hexane is also a solvent as well as a significant fraction of common gasoline.

The 6C to 10C alkanes, alkenes and cycloalkanes are the top components of gasoline, naphtha, jet fuel and specialized industrial solvent mixtures. The long chain hydrocarbons obtained from crude oil are used as lubricants, roofing compounds, pavement composition, wood preservatives, etc.

Key Points:

- Aliphatic hydrocarbons include the open chain (acyclic) and those cyclic compound which resemble the open chain in their chemical properties (Alicyclic).
- Aromatic hydrocarbons include benzene and those compounds which resemble benzene.
- Acyclic hydrocarbons contain saturated and unsaturated open chain hydrocarbons.
- Alkanes are open chain saturated hydrocarbons, which can be represented by general formula $C_n H_{2n+2}$.
- The general formula of cycloalkanes is $C_n H_{2n}$.
- Homolysis is the chemical bond dissociation of a neutral molecule generating two free radicals.
- Heterolysis is chemical bond cleavage of a neutral molecule generating cation and anion.
- Electrophile is a reagent which can accept electron pair in a reaction.
- Nucleophile is a reagent which can donate electron pair in a reaction.
- Alkenes are unsaturated hydrocarbons which contain carbon–carbon double bond. They can be represented by general formula $C_n H_{2n}$.
- Alkenes undergo electrophilic addition reactions.
- Polymerization is the process by which small molecules chemically join together to form large molecules.
- In conjugated compounds carbon atoms are linked alternatively by single and double bonds.

- Compounds having the same molecular formula but different structural formula are known as 'isomers' and this phenomenon is called "Isomerism".
- Tautomerism is a special type of functional group isomerism, in which isomers are in equilibrium with each other.
- Stereoisomerism is caused by different arrangements of atoms or groups in space.
- Carbon atom which is bonded to four different group is called chiral carbon.
- Alkynes contain carbon—carbon triple bond. They can be represented by general formula $C_n H_{2n-2}$.
- Benzene is aromatic hydrocarbon. Its molecular formula is C_6H_6.
- The representation of a real structure as a weighted average of two or more contributing structure is called resonance.
- The contributing structures are called canonical forms and real structure is called resonance hybrid.
- Electrophilic aromatic substitution reactions are those in which hydrogen is replaced by an electrophile.
- Carbonium ion is a positively charge organic ion in which most of positive charge is localized on carbon atom.
- Substituents which direct the second substituent to ortho and para position simultaneously are called ortho/para directing.
- The substituents which direct the second incoming substituent to meta position are called meta-directing.

Exercise

Q1. Select the correct option.

(i) Which one of the following deactivates benzene ring and is o/p-directing?

(a) $-NH_2$ (b) $-OH$ (c) $-OCH_3$ (d) $-Cl$

(ii) Which one of the following compounds is expected to exhibit geometrical isomerism.

(a) 1-butene (b) 2-butene (c) 2-methyl propane

(d) 2-butyne

(iii) The overlapping of orbitals in benzene is of the type of

(a) sp – sp (b) $sp^2 - sp^2$

(c) $sp^3 - sp^3$ (d) s – s

(iv) When acetylene is treated with HBr, we get.

(a) Methyl bromide (b) Methyl chloride

(c) Ethyl bromide (d) Ethylene bromide

(v) The general formula of cycloalkanes is

(a) C_nH_{2n+2} (b) C_nH_{2n}

(c) C_nH_{2n+1} (d) C_nH_{2n-2}

(vi) How many isomers are possible for C_2H_6O

(a) 2 (b) 4 (c) 8 (d) 5

(vii) Dehydrohalogenation of alkylhalide is carried out in presence of ________.

(a) Zn dust (b) H_2SO_4 (c) Alcoholic KOH

(d) aqueous KOH

(viii) The marsh gas mainly consists of ______.

(a) C_2H_4 (b) CH_4 (c) H_2S (d) SO_2

(ix) Ethene and Ethyne can be distinguished by

(a) Anh. $AlCl_3$ (b) Br_2 in CCl_4

(c) Cold. H_2SO_4 (d) $AgNO_3$ in NH_4OH

(x) The homolytic fission of C–C bond in ethane give an intermediate in which "C" is ______ hybiridized.

(a) sp^3 (b) sp^2 (c) sp (d) sp^2d

(xi) Which one of the following compound has planar structure?

(a) Alkane (b) Alkene (c) Alkyne (d) Cycloalkane

(xii) When carbon undergoes sp^2 hybridization then H–C–H bond angles are:

(a) 120 ° (b) 180° (c) 109.5° (d) 107.5°

(xiii) In the following reaction $C_6H_6 + Cl_2 \xrightarrow{AlCl_3} C_6H_5Cl + HCl$, what type of reaction has taken?

(a) Electrophilic substitution (b) Electrophilic addition

(c) Friedel-craft's alkylation (d) Non of these

(xiv) Nitrobenzene reacts with chlorine in presence of $AlCl_3$. The product obtained is.

(a) o-chloro nitrobenzene (b) m-chloronitrobenzene

(c) p-chloro nitrobenzene (d) All of them

2. Write short answers of the following questions.

(i) What is the difference between aliphatic and aromatic hydrocarbons?

(ii) What is meant by resonance?

(iii) How do you detect the unsaturation in Alkenes?

(iv) Why benzene is less reactive than ethene but more reactive than ethane?

(v) Why halogens are deactivating groups although they are ortho/para directing?

(vi) Why ethyne is less reactive towards electrophilic addition reaction than ethene.

(vii) What is meant by chirality?

(viii) Why there are no geometrical isomers of but-1-ene (1-butene)?

(ix) Why cyclopropane is more reactive than propane?

(x) Differentiate between Homolytic and heterolytic fission.

(xi) Write down the resonance structure of benzene.

(xii) Write down the two reasons of meta-directing effect.

(xiii) How can you distinguish 1-alkyne from other non-terminal alkynes?

(xvi) Why Lindlar's catalyst is used in hydrogenation of alkynes?

(xv) What is the main difference between tautomerism and metamerism?

Q.3 Long questions:

(i) Describe the mechanism of chlorination of methane in detail.

(ii) (a) Explain the structure and reactivity of cycloalkanes.

(b) Mention at least four physical properties of alkynes.

(iii) (a) What are hydrocarbons? How will you classify them? Give an example of each class.

(b) Write down the physical properties of alkanes and cyclo alkanes.

(iv) (a) Give methods of preparation of ethene from

(a) An alcohol (b) An alkylhalide

(b) Explain the relative stabilities of different alkenes.

(c) Starting from alkene how would you prepare the following compounds.

(a) Vicinal dihalide (b) Alcohol

(c) Ozonide (d) Epoxide

(v) (a) Describe any two methods of preparation of alkynes.

(b) Mention at least four physical properties of alkynes

(vi) (a) Describe the structure of benzene on the basis of MOT.

(a) How would you prepare the following compounds from Benzene?

(a) Acetophenone (b) Toluene

(b) Trinitrobenzene (d) Benzenesulphonic acid

(vii) (a) Describe mechanism of electrophilic substitution reaction in benzene.

(b) Explain the directive and activitating effect in mono substituted benzene.

(viii) Write notes on the following.

(a) Conjugation in alkenes

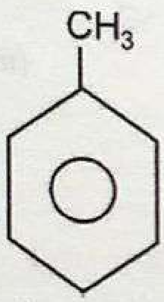
(b) Polymerization

(c) Resonance

(d) Structure of alkyne

Q.4 **Names the following compounds.**

i)



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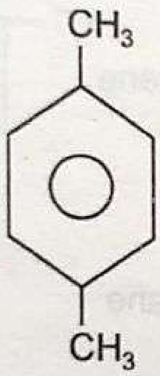

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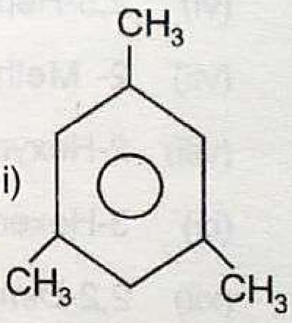

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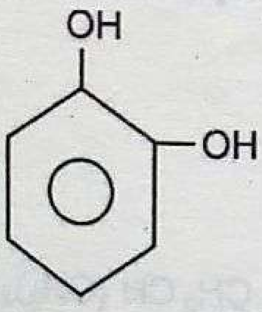

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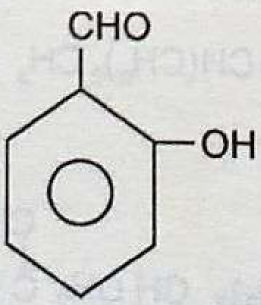

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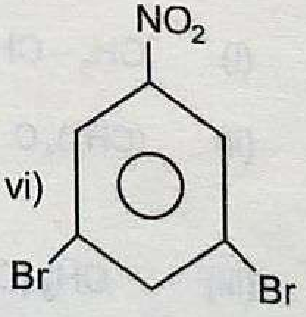

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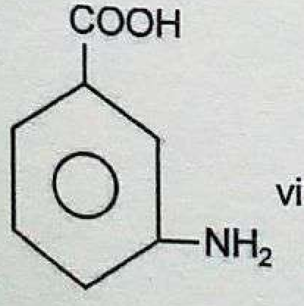

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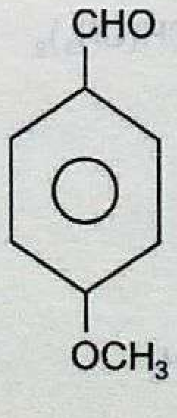

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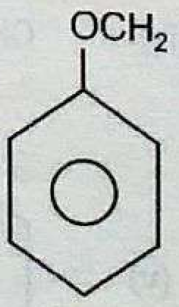


Q.5 **Draw the structural formula of the following compounds.**

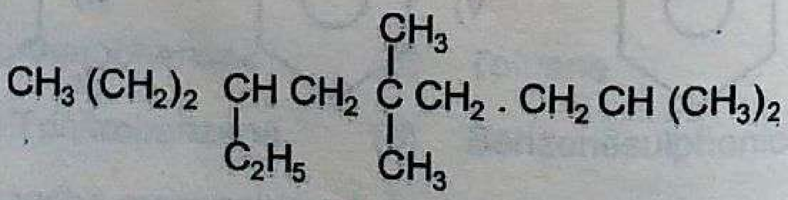
- (i) Anthracene
- (ii) Naphthalene
- (iii) 3- Phenyl pentane
- (iv) Isobutylene
- (v) 2,3,4-Trimethyl hexane
- (vi) 2,5-Heptadiene
- (vii) 2- Methyl-2-pentene
- (viii) 2-Hexyne
- (ix) 3-Hexen -1-yne
- (xii) 2,2-Dimethyl butane

Q.6 **Give IUPAC names to the following Hydrocarbons.**

(i) $CH_3-CH=CH(CH_2)_2CH_3$

(ii) $(CH_3)_4C$

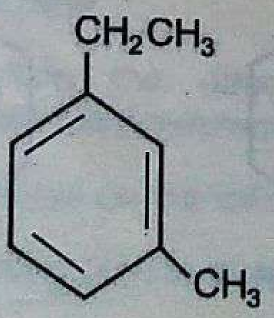
(iii)



$CH_3(CH_2)_2\underset{C_2H_5}{\underset{|}{CH}}CH_2\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}CH_2 . CH_2CH(CH_3)_2$

(iv) $CH_3-C\equiv C-CH(CH_3)_2$

(v)



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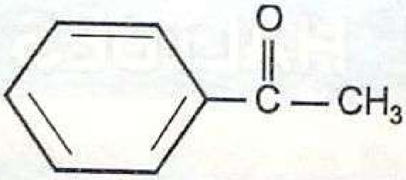

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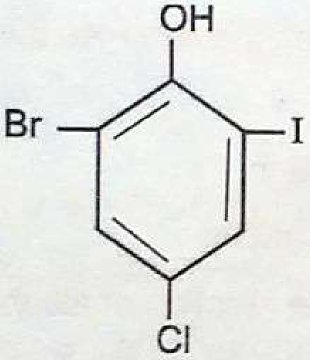

(viii) $(C_6H_5)_3\,CH$