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Syllabus

B. Sc. (Part I) Chemistry
CHEMISTRY-I : Organic Chemistry
SC-106

UNIT-I : STRUCTURE AND BONDING AND MECHANISM OF ORGANIC REACTIONS

Hybridization, bond lengths and bond angles, bond energy, vander Waals interactions, resonance, inductive and electrometric effects, hydrogen bonding, homolytic and heterolytic bond breaking. Types of reagents-electrophiles and nucleophiles.

UNIT-II : STEREOCHEMISTRY OF ORGANIC COMPOUNDS

Concept of isomerism. Types of isomerism

Optical isomerism elements of symmetry, molecular chirality, enantiomers, optical activity, diastereomers, meso compounds, racemization.

Relative and absolute configurations, D & L and R & S system of nomenclature.

Geometrical isomerism determination of configuration of geometrical isomers. E & Z system of nomenclature.

UNIT-III : ALKANES AND CYCLOALKANES

IUPAC nomenclature of branched and unbranched alkanes, the alkyl group, classification of carbon atoms in alkanes, method of formation (with special reference to Wurtz reaction. Kolbe reaction, decarboxylation of carboxylic acids). Physical properties and chemical reactions of alkanes.

Cycloalkanes Nomenclature, methods of formation, chemical reactions, Baeyer's strain theory and its limitations.

UNIT-IV : ALKENES AND ALKYNES

Nomenclature of alkenes, method of formation, mechanisms of dehydration of alcohols and dehydrohalogenation of alkyl halides, Hofmann elimination, physical properties and relative stabilities of alkenes. Chemical reactions of alkenes mechanisms involved in hydrogenation, electrophilic and free radical additions, Markownikoff's rule, ozonolysis, hydration, hydroxylation and oxidation with Polymerization of alkenes.

Nomenclature, structure and bonding in alkynes, methods of formation and chemical reactions of alkynes, Acidity of alkynes, Mechanism of electrophilic and nucleophilic addition reactions.

UNIT-V : ARENES AND AROMATICITY

Nomenclature of benzene derivatives. The aryl group. Aromatic nucleus and side chain, Structure of benzene; molecular formula and Kekule structure. Stability and carbon-carbon bond lengths of benzene, resonance structure, MO picture, aromaticity : Huckel rule, aromatic ions.

Aromatic electrophilic substitution general pattern of the mechanism, role of σ - and π -complexes. Mechanism of nitration, halogenation, sulphonation, mercuration and Friedel-Crafts reaction in arenes (taking benzene as example).

UNIT-VI : ARYL HALIDES

Methods of formation of aryl halides, nuclear and side chain reactions. The addition-elimination and the elimination-addition mechanisms of nucleophilic aromatic substitution reactions.

Synthesis and uses of DDT and BHC.

UNIT-VII : ARYL ALDEHYDES AND KETONES

Nomenclature and structure of the carbonyl group. Synthesis of aryl aldehydes and ketones with particular reference to the synthesis of aldehydes from acid chlorides, synthesis of aryl aldehydes and ketones using 1, 3-dithianes, synthesis of aryl ketones from nitriles and carboxylic acids, properties of aryl aldehydes and ketones.

Preparation, properties and uses of benzaldehyde, salicylaldehyde and acetophenone.

1

STRUCTURE, BONDING AND MECHANISM
OF ORGANIC REACTIONS

STRUCTURE

- Bond Length
- Bond Angle
- Bond Energy
- van der Waal's Forces
- Inductive Effect
- Electromeric Effect
- Hydrogen Bond
- Electrophiles and Nucleophiles
- Types of Organic Reactions
- Free Radicals
- Carbonium ion
- Carbanion
- Homolytic and Heterolytic Fission
- Mechanism of Organic Reactions
- Elimination Reactions
- Reaction Intermediates
- Carbenes
- Arynes or Benzyne
- Nitrenes or Imidogens
- Summary
- ✓ Student Activity
- Test Yourself

LEARNING OBJECTIVES

After going this unit you will learn :

- Bond length, bond angle and bond energy with their affecting factors and uses.
- Dipole-dipole interactions, dipole-induced dipole interactions and induced-dipole induced dipole interactions.
- Acid strength and base strength
- Intermolecular and intramolecular hydrogen bonding.
- Substitution reactions, addition reactions, elimination reactions and rearrangement reactions.
- Formation and characteristics of carbonium ion and carbanions.
- Free radical mechanism, ionic mechanism, nucleophilic substitution reactions and electrophilic substitution reactions.
- Formation of carbenes, benzyne and nitrenes.

• 1.1. BOND LENGTH

Covalent bond is formed between two atoms by the overlapping of atomic orbitals. This overlapping of atomic orbitals takes place at certain distances between two atoms. **The distance between the centres of two nuclei is called as bond length or bond distance.** Bond length is measured by X-ray diffraction, electron diffraction and by spectroscopic methods. The unit of bond length is Angstrom, Å ($1 \text{ \AA} = 10^{-8} \text{ cm}$). The bond length ensures the maximum stability of the bond.

The bond lengths of some common bonds like C—C, C=C, C≡C, C—H, O—H, C=O are 1.54, 1.34, 1.20, 1.09, 0.96 and 1.20 Å, respectively.

Factors Affecting Bond Length

Bond length mainly depends on the following factors:

(i) **Electronegativity** : If an atom is more electronegative than the other in a diatomic molecule, then the bond length will be comparatively shorter. For example, the bond length of C—F bond is found to be 1.36 Å, whereas it should be $0.77 + 0.64 = 1.41$ Å. The greater the difference in electronegativity between two atoms, the shorter will be the bond length.

(ii) **Bond order** : It is seen that as bond order or multiplicity of bond increases, the bond length decreases. For example, in $\text{CH}_3\text{—CH}_3$, the bond length of C—C bond (bond order = 1) is 1.54 Å, whereas in $\text{CH}_2\text{=CH}_2$, the bond length of C=C bond (bond order = 2) is 1.34 Å and in $\text{HC}\equiv\text{CH}$, the bond length of C≡C bond (bond order = 3) is 1.20 Å.

(iii) **Hybridisation** : Bond length depends on the hybridised state of the bonded atoms in a molecule. It is due to the *s*-character in different types of hybridised orbitals. In sp^3 -orbital, there is 25% *s*-character, while in sp -orbital there is 50% *s*-character. So, **greater the *s*-character, smaller will be the orbital and smaller will be the bond length.**

(iv) **Resonance and delocalisation** : Bond length is also affected by resonance. For example, the bond length of each C—C bond in benzene is 1.39 Å which is neither equal to C—C single bond (1.54 Å) nor to C=C double bond (1.34 Å). It is however, in between them, as benzene occurs in the following two resonance hybrids.

Uses of Bond Length Determination

Some of the uses of determination of bond length are as follows :

(i) **In deciding the correct structure of compounds** : The determination of bond length gives the nature of the compound and the presence of bonds, viz., single, double, triple bonds etc. This helps in deciding the correct structure of the compound.

(ii) **In explaining the stability of the compounds** : Bond length determination gives information about the stability and reactivity of a number of organic compounds. Compounds of normal bond length behave in a normal way. Compounds of shorter or longer bond lengths have abnormal reactivity. It is because such compounds show hybridisation, resonance or have lone pair of electrons. For example, the abnormal bond length between C—C bonds shows the presence of resonance and its exceptional stability. The bond lengths in hydrocarbons is in the order, C—C > C=C > C≡C

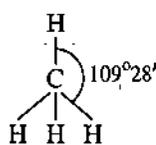
• 1.2. BOND ANGLE

The angle between two nearest atoms to central atom of a molecule is known as bond angle. It is represented in degree ($^\circ$). It can be determined by infrared spectroscopy, microwave spectroscopy and electron diffraction methods. The diatomic molecules are linear and therefore, in these there is no meaning of bond angle but for triatomic and polyatomic molecules, the bond angle is very important for determining the structure of molecules.

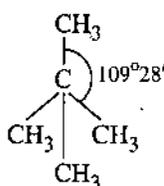
Factors Affecting Bond Angle

(i) **Hybridization of central atom** : The bond angle can be known by the hybridized state of central atom. The central carbon atom in C_2H_2 , C_2H_4 and CH_4 is in sp , sp^2 and sp^3 hybridized state, respectively and therefore, bond angle $\angle\text{HCH}$ in these compounds is 180° , 120° and $109^\circ 28'$.

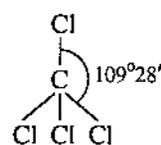
(ii) **Atoms or groups attached to central atom** : The bond angle in sp^3 hybridization is $109^\circ 28'$, in sp^2 it is 120° and in sp it is 180° . These bond angles are only when the atoms or groups attached to central atom are same.



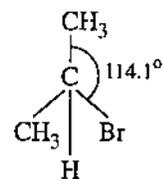
Methane



Neo-pentane



Carbon tetra chloride



2-bromo propane

The bond angle deviates if different atoms or groups are attached to central atom. For example, in 2-bromo propane $\angle\text{CCBr}$ is 114.1° . This

is due to difference in the electronegativity of atoms attached to central carbon atom.

(iii) **Number of bonded pair of electrons** : The electronegativity of an orbital containing lone pair of electron is least. In CH_4 , NH_3 and H_2O , there is an increase in the p -character of orbital attached to hydrogen, whereas there is an increase in the s -character of orbital containing lone pair of electron. In all these molecules, the central atom is sp^3 hybridized but the bond angle is 109.5° , 107° and 104.5° , respectively. The lone pair of electrons in CH_4 , NH_3 and H_2O are 0, 1 and 2 respectively.

(iv) **Electronegativity of bonded atoms** : The bond angle decreases on decreasing the electronegativity of central atom.

Compound	NH_3	PH_3	AsH_3	SbH_3
Bond angle	107°	93.3°	91.8°	91°

• 1.3. BOND ENERGY

Bond energy is defined as *the average amount of energy required to break a bond in one mole of the substance*. Each bond has a characteristic value of this energy and is a measure of strength of that bond. The greater the bond energy, the stronger is the bond. Bond energy is the scale of direct measurement of bond strength. It is expressed in kcal per mol or kJ per mol. The bond energies of some bonds like $\text{C}-\text{C}$, $\text{C}=\text{C}$, $\text{C}\equiv\text{C}$, $\text{O}-\text{H}$, are 83, 146, 199 and (i) kcal mol⁻¹ respectively.

Factors Affecting Bond Energy

The following factors affect the bond energy :

(i) **Electronegativity** : The greater the difference in electronegativities of the two atoms in a compound, the greater will be the bond energy. For example, the bond energy of HF is maximum (135.0 kcal/mol) and that of HI is minimum (70.4 kcal/mol).

(ii) **Atomic size** : Small atoms form smaller bonds and so the bonds formed between such atoms will have more bond strength. The atomic size of halogens is in the order of $\text{F} < \text{Cl} < \text{Br} < \text{I}$. Therefore, the order of bond energies of halogen acids will be $\text{H}-\text{F} > \text{H}-\text{Cl} > \text{H}-\text{Br} > \text{H}-\text{I}$.

(iii) **Type or extent of overlapping** : We know that σ -bond is more strong than π -bond. Therefore, compounds having σ -bonds form stronger bonds than those having π -bonds. So, the bond energy of compounds having σ -bonds is greater than that of compounds having π -bonds.

(iv) **Hybridisation** : The bond energy increases as the s -orbital contribution of the hybrid orbitals increases. Thus, the bond energy decreases in the order $sp > sp^2 > sp^3$.

(v) **Bond order** : The higher the bond order of a multiple bond, greater will be the bond energy. For example, the bond energies of $\text{C}-\text{C}$, $\text{C}=\text{C}$, $\text{C}\equiv\text{C}$ bonds are 347.2, 610.0, 815.1 kJ/mol, respectively.

Uses of Bond Energy Determination

Bond energy gives the following important informations—

(i) **Determination of the relative electronegativity of atoms** : If the normal calculated values of bond energy differ largely, there is a large difference in the electronegativities of the atoms. Thus electronegativity can be calculated.

(ii) **Mechanism of the reaction** : Bond energy helps in determining the mechanism of certain organic reactions.

(iii) **Calculation of heat of reaction and heat of formation** : It helps in the calculation of heat of reaction and heat of formation.

• 1.4. VAN DER WAAL'S FORCES

van der Waal's in 1873, pointed out that the forces of attraction also exist between non polar molecules. These forces are much weaker than chemical forces and are known as van der Waal's or intermolecular or cohesive forces. *These may be defined as the very short lived electrostatic attractive forces which exist between all kinds of atoms, molecules*

or ions when they are very close together. The magnitude of the forces decrease from solid to gas. van der Waal's forces involve the following three types of interactions :

(i) **Dipole-dipole interactions :** These forces are present in polar molecules such as HF , HCl , H_2O , NH_3 etc. The polar molecules have separate centres of positive and negative charge and they have permanent dipole moment. These forces arise due to electrostatic attraction between oppositely charged ends of the polar molecules. The positive end of one molecule attracts the negative end of the other molecule and vice versa as shown in figure (1).

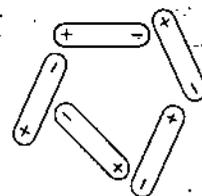


Fig. 1. Dipole dipole interactions

(ii) **Dipole-induced dipole interactions :** These forces are present in a mixture containing polar and non-polar molecules. When a polar molecule is brought near to a non-polar molecule (such as iodine molecule or inert gas), the positive end of polar molecule attracts the mobile electrons of non-polar molecule and thus, polarity is developed in the non-polar molecule as shown in figure (2).

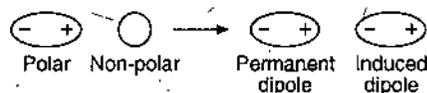


Fig. 2. Dipole-induced dipole interactions

(iii) **Induced dipole-induced dipole interactions :** These forces are present in non-polar molecules such as diatomic gases like H_2 , N_2 , O_2 , Cl_2 etc. and mono atomic inert gases. The van der Waal's forces in these molecules occur due to the development of an instantaneous or temporary dipole moment in them. In a non polar molecule, the electrons are symmetrically distributed around the nuclei of the atoms. These electrons are in continuous and rapid motion around the positively charged nuclei. Due to this, at any time positive charge may be concentrated in one region and negative charge in another region of the same molecule. Thus, a non-polar molecule may be polarised and may induce a polarity in a neighbouring molecule as shown in figure (3).

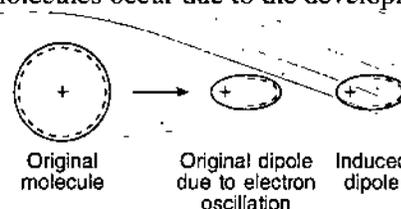


Fig. 3. Induced dipole-induced dipole interactions

Factors Affecting van der Waal's Forces

The factor affecting van der Waal's forces are :

(i) **Temperature :** The strength and magnitude of the forces increases with the decrease in the temperature.

(ii) **Pressure :** When the pressure is increased, the molecules come close to each other. Hence, the strength and magnitude of the forces increases with the increase in the pressure.

(iii) **Number of electrons present in the molecule :** The strength and magnitude of the forces increases with the increase in the number of electrons in the molecule.

(iv) **Molecular size :** The strength and magnitude of the forces increase with the increase in the molecular size.

• 1.5. INDUCTIVE EFFECT (I)

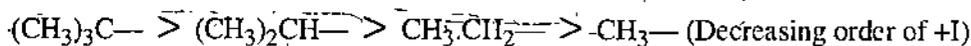
When a covalent bond is formed between similar atoms, e.g., $\text{H}-\text{H}$, $\text{Cl}-\text{Cl}$ etc., the bonded electron pair is equally shared between the two atoms, hence the bond is *non-polar*. However, a covalent bond formed between dissimilar atoms is *polar* since the sharing of electrons is not equal, the more electronegative part (atom) attracting a greater share, e.g., $\text{C} \rightarrow \text{Cl}$ bond. This displacement of bond electrons towards one direction is transmitted through the carbon atoms in a carbon chain, and is called *inductive effect*. Atoms or groups which are more electronegative than hydrogen, exert *negative inductive effect (-I)*, i.e., they pull electrons towards themselves. On the other hand, if the atom or group is less

electronegative than hydrogen, it exerts a *positive inductive effect (+I)*, i.e., they repel or release electrons away from themselves.

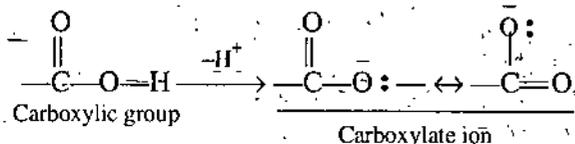
Some of the groups and atoms with their decreasing negative and positive inductive effects are given below :



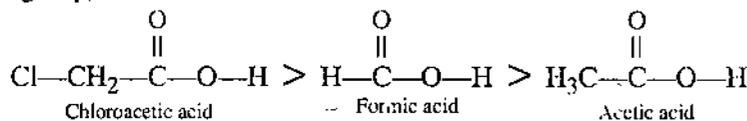
H (No inductive effect)



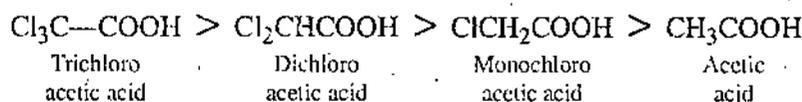
(a) **Acid strength** : An acid is a compound which releases H^+ . Acid strength is, therefore, the ease with which H^+ is released. Release of H^+ always depends upon the stability of the anion formed. Thus carboxylic (organic) acids release H^+ as the carboxylate ion stabilises due to dispersal of negative charge between two oxygen atoms.



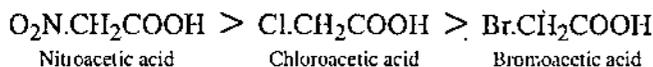
Any group or atom attached in a carboxylic acid can increase its acid strength if it shares the negative charge present on oxygen of its anion (It is possible due to the $-I$ effect of groups or atoms). On the other hand, if an atom or group present in a carboxylic acid increases negative charge on the oxygen atoms of its anion, makes it weakly acidic (It is possible due to $+I$ effect of group or atom). Thus, chloroacetic acid is stronger than formic acid ($-I$ effect of chlorine atom) which in turn is stronger than acetic acid ($+I$ effect of methyl group).



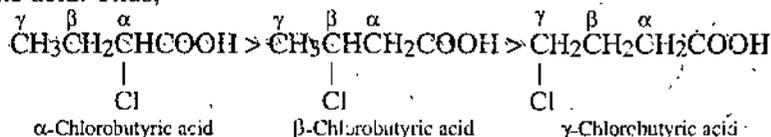
As the number of groups or atoms exerting $-I$ effect increases in an acid, the strength of acid also increases. Thus, amongst the following acids, the decreasing order of acid strength is :



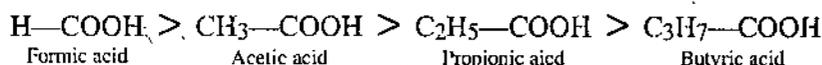
The acid strength of monosubstituted acids also depends on the $-I$ effect of the substituent. A substituent with greater $-I$ effect increases the acid strength, thus



The closer is the substituent, exerting $-I$ effect, to the carboxyl group, the stronger will be the acid. Thus,



Substituent exerting $+I$ effect decreases the acid strength. A substituent exerting greater $+I$ effect will decrease the acid strength more than a substituent with lesser $+I$ effect, thus



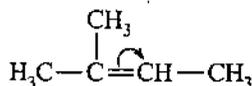
(b) **Base strength** : A base is a compound which accepts H^+ . Thus, the base strength is the ease with which H^+ is accepted. The acceptance of H^+ depends on the amount of electron density present on an atom of a molecule. Thus, an atom or group which increases electron density of an atom having lone pair of electrons increases the base strength of the

Some +E effect producing groups are $-F$, $-Cl$, $-Br$, $-I$, $-OH$, $-OR$, $-NR_2$ etc, where some $-E$ effect producing groups are $=NR_2$, $=NHR$, $=O$ etc.

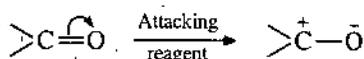
Actually, the displacement in the molecule would be to which side, depends upon (i) the nature of inductive effect of the substituent present and (ii) the relative stability of carbonium ion and carbanion formed, e.g., the displacement of electrons in propylene would be according to (i) and not (ii) due to +I of methyl group.



Similarly, the displacement of electrons in 2-methyl butene-2 is as given below, owing to relative stability of carbonium and carbanion formed.



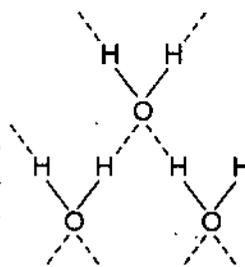
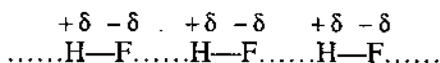
If a multiple bond is present between two dissimilar atoms, the displacement occurs always towards the more electronegative atom.



• 1.7. HYDROGEN BOND

In the compounds of hydrogen with strongly electronegative elements such as fluorine, oxygen and nitrogen, the shared pair of electrons is attracted more towards the electronegative atom. As a result, the electronegative atom acquires a partial negative charge

and hydrogen acquires a partial positive charge ($H-F$). Such a molecule behaves as a dipole because one end of the molecule carries a positive charge and the other carries a negative charge. If a number of such molecules are brought together, the positive end of one molecule will attract and will be attracted by the negative end of other molecule. In this way, two or more molecules will be associated together to form large clusters of molecules.

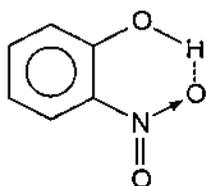


The attractive force that binds hydrogen atom of one molecule with electronegative atom of same or another molecule of the same substance is known as hydrogen bond. It is generally represented by dotted line.

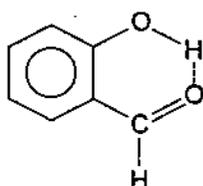
Types of hydrogen bonding : Hydrogen bonds are of two types :

(i) **Intermolecular hydrogen bonding :** When hydrogen bond is formed between two molecules of a compound, it is known as intermolecular hydrogen bonding. For example,

(ii) **Intramolecular hydrogen bonding :** When hydrogen bond is formed with in the same molecule, it is known as intramolecular hydrogen bonding. For example,



o-Nitro phenol



o-Hydroxy benzaldehyde

• 1.8. ELECTROPHILES AND NUCLEOPHILES

The completion of organic reactions depends very much on the nature of attacking reagents. The attacking reagents are generally of two types, viz., electrophilic reagents and nucleophilic reagents.

(1) **Electrophilic reagents** : The reagents which show the attraction towards electrons are called *electrophilic reagents* or *electrophiles*. (electro = electron, philic = loving). These reagents are short of a pair of electrons than the stable one. These reagents are of two types :

(a) **Positive electrophiles** : These are deficient in two electrons and carry a positive charge, e.g., $R-CH_2^+$, R_2CH^+ , R_3C^+ (carbonium ion), $:Br^+$ (bromonium ion), H^+ (hydrogenium), H_3O^+ (hydronium ion), NO_2^+ (nitronium ion), SO_3H^+ (sulphonium ion), NO^+ (nitrosylium ion) etc.

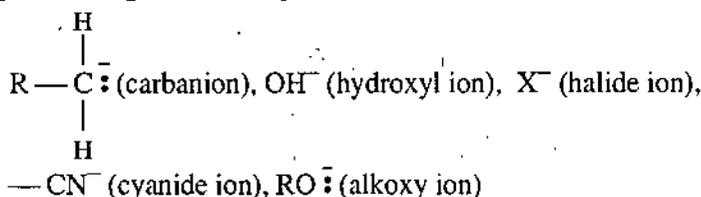
(b) **Neutral electrophiles** : In these the central atom has six electrons but have no charge, e.g., BF_3 (boron trifluoride), $AlCl_3$ (aluminium chloride), SO_2 (sulphur dioxide), SO_3 (sulphur trioxide), $>C=O$ (carbonyl group), $ZnCl_2$ (zinc chloride), $R-C \begin{array}{l} \text{O} \\ // \\ \text{Cl} \end{array}$ (acid chloride).

$:CH_2$ (carbene) etc.

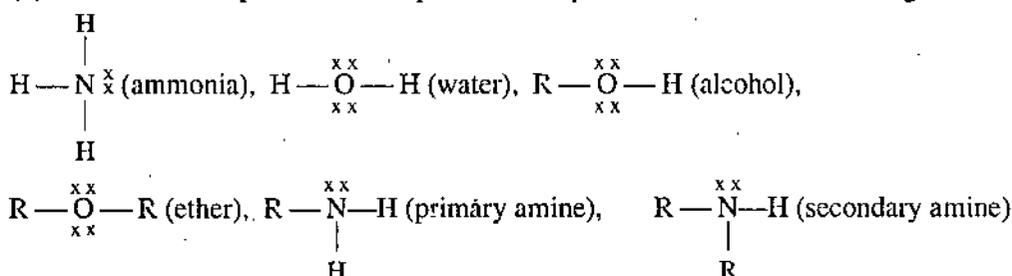
Both type of electrophiles can attack the ion or molecule which is electron rich.

(2) **Nucleophilic reagents** : The reagents which show the attraction towards nucleus are called *nucleophilic reagents* or *nucleophiles* (nucleo = nucleus, philic = loving). Since the nucleus is positively charged, these reagents will be negatively charged or electron rich substances. These are of two types :

(a) **Negative nucleophiles (Anions)** : These have an excess of electron pair and carry a negative charge. For example,



(b) **Neutral nucleophiles** : These possess lone pair of electrons but no charge.

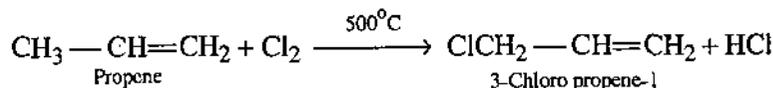
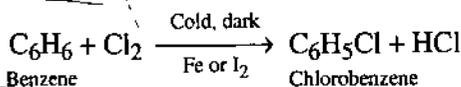
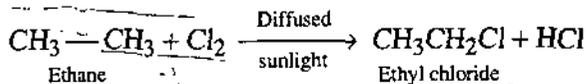


• 1.9. TYPES OF ORGANIC REACTIONS

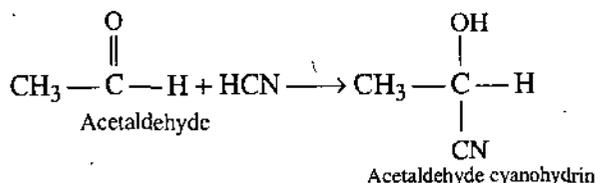
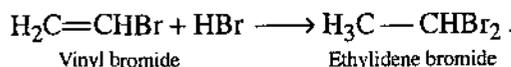
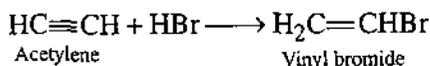
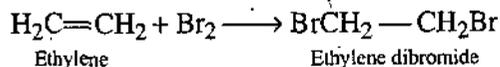
There are four types of organic reactions :

- Substitution reactions.
- Addition reactions.
- Elimination reactions.
- Rearrangement reactions.

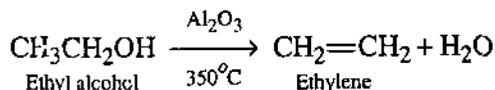
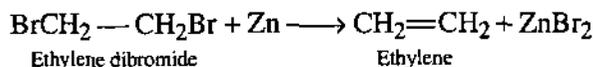
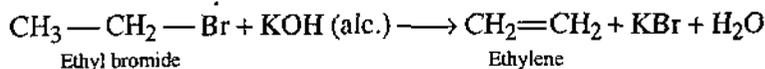
(a) **Substitution reactions** : The reactions in which one or more atoms or groups attached to a carbon atom are replaced by other atoms or groups are known as **substitution reactions**. The saturation or unsaturation of original compound remains unchanged during the reaction, i.e., the total number of double bonds and triple bonds in reactants and products remain the same.



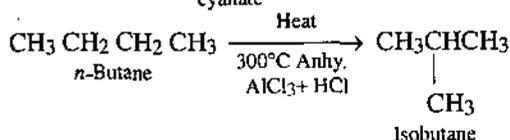
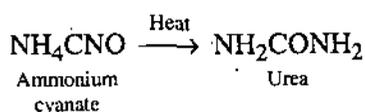
(b) **Addition reactions** : The reactions in which atoms or molecules are added to carbon atoms or other atoms, resulting in the formation of a more saturated product, are called as **addition reactions**, e.g.,

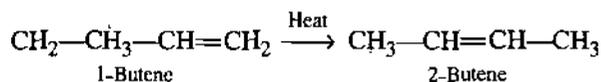


(c) **Elimination reactions** : Reactions in which atoms or groups attached to two adjacent carbon atoms are removed resulting in the formation of a more unsaturated product, are called **elimination reactions**. These reactions are just the reverse of addition reactions, e.g.,



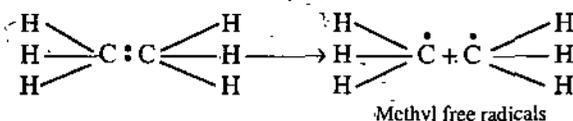
(d) **Rearrangement reactions** : Reactions in which some atoms or groups present in a molecule interchange their positions to form a new product are called **rearrangement reactions**.





• 1.10. FREE RADICALS

A neutral atom or group of atoms which have an odd or unpaired electron is called a free radical, e.g., if a carbon-carbon bond of ethane breaks in homolytic manner, two methyl radicals are formed:

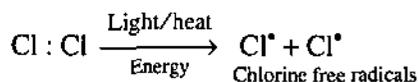


Characteristics of Free Radicals

- (i) Free radicals are formed in presence of sunlight and when the reactants are in the gaseous-state.
- (ii) Free radicals are highly unstable and reactive.
- (iii) They are highly unstable and immediately take an electron from a radical or molecule to form a stable bond.
- (iv) They are generally electrically neutral since the odd electron present on them is that electron which is used in the formation of a covalent bond.
- (v) The high reactivity of free radicals is due to the nature of odd electron to form a bond with any available electron.
- (vi) Free radicals are paramagnetic in nature, i.e., they are attracted by a magnetic field.

Formation of Free Radicals

Formation of free radical is always initiated by energy (heat or light), e.g., a molecule of chlorine breaks into chlorine free radicals in presence of sunlight or on heating.



Examples :

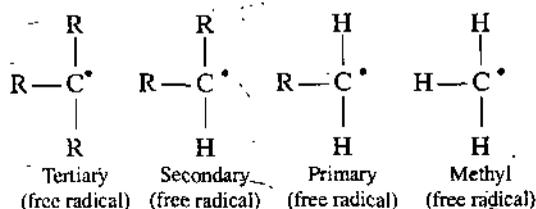
- (i) $\text{H}-\text{H} \xrightarrow{h\nu} 2\text{H}^\bullet$
Hydrogen molecule Hydrogen free radicals
- (ii) $\text{CH}_3-\text{H} \xrightarrow{h\nu} \text{CH}_3^\bullet + \text{H}^\bullet$
Methane Methyl free radical (Primary)
- (iii) $\text{CH}_3-\text{CH}_2-\text{CH}_3 \xrightarrow{h\nu} \text{CH}_3-\dot{\text{C}}\text{H}-\text{CH}_3 + \text{H}^\bullet$
Propane Iso-propyl free radical (Secondary)
- (iv) $\text{H}_2\text{C}=\text{CH}_2 \xrightarrow{h\nu} \dot{\text{C}}\text{H}_2-\dot{\text{C}}\text{H}_2$
Ethylene Ethylene di free radical
- (v) $\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_3-\text{C}-\text{CH}_3 \\ | \\ \text{H} \end{array} \xrightarrow{h\nu} \begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_3-\dot{\text{C}}-\text{CH}_3 \\ | \\ \text{H} \end{array} + \text{H}^\bullet$
Isobutane Tertiary butyl free radical (Tertiary)

Stability of Free Radicals

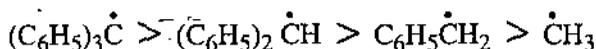
(1) The energy required for breaking the C—H bond is not always the same but it is generally different. To make CH_3^\bullet from CH_4 , the energy required is 102 kcal, $\text{C}_2\text{H}_5^\bullet$

from C_2H_6 , the value is 97 kcal, $CH_3-\dot{C}H-CH_3$ from C_3H_8 , the value is 94 kcal and to make $(CH_3)_3C^\bullet$ from $(CH_3)_3C-H$, the value is 91 kcal. So, electron repelling groups like methyl (alkyl) group increases the stability of free radicals.

The order of stability of primary, secondary and tertiary free radicals is as follows :



(2) Those free radicals which have resonance are comparatively more stable, e.g., phenyl free radical ($C_6H_5^\bullet$) is more stable than methyl free radical (CH_3^\bullet). The order of stability is,



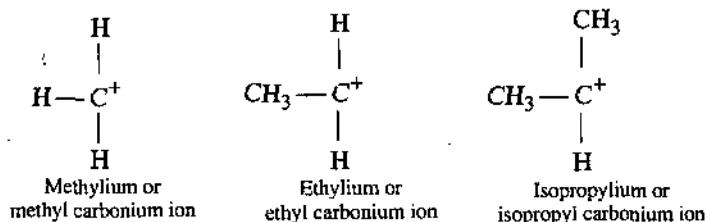
Difference between a free radical and an ion

Characteristics	Free radicals	Ions
1. Nature	These are electrically neutral, e.g., Cl^\bullet , CH_3^\bullet , $C_2H_5^\bullet$ etc.	These contain either positive or negative charge, e.g., CH_3^+ , CH_3^- , Cl^- , $C_2H_5^-$, $C_2H_5^+$ etc.
2. Magnetic property	These have one unpaired electron, so they are paramagnetic.	All the electrons are paired in ions, so they are diamagnetic.
3. Hybridisation	The carbon atom of alkyl group on which unpaired electron is present is sp^2 hybridised.	Positively charged carbon atom is sp^2 hybridised, while negatively charged carbon atom is sp^3 hybridised.
4. Method of preparation	These are formed by the homolytic fission of covalent bonds.	These are formed by the heterolytic fission of covalent bonds.

1.11. CARBONIUM ION

Carbonium ion or carbo-cations : An ion containing a positively charged carbon centre is called a carbonium ion or carbo-cations. These ions are named by adding the suffix 'ium' to the name of the parent alkyl group i.e., alkylium.

For example,



Characteristics of Carbonium Ion

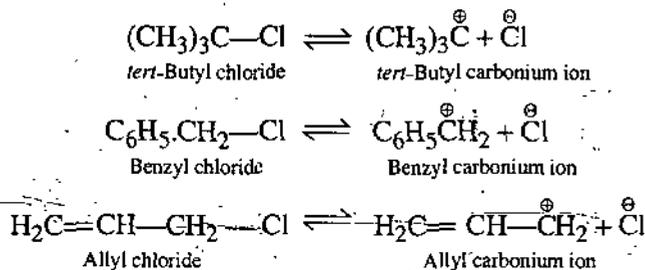
(1) All the carbonium ions are named by adding the suffix 'ium' to the name of the alkyl group present, e.g., CH_3^+ (methylium) etc.

(2) The carbonium ions are very reactive. This is due to the fact that the central positively charged carbon in them has only six electrons in the outermost shell and they have a marked tendency to complete the octet. Hence, a carbonium ion combines readily with any substance that can donate a pair of electrons.

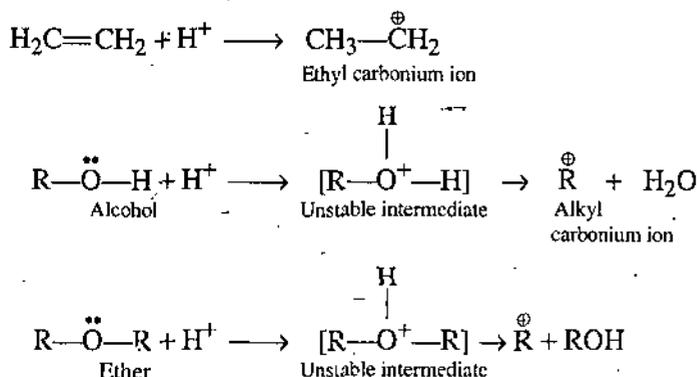
(3) Carbonium ion being deficient in electrons, is ordinarily very unstable. However, if an electron repelling group is present adjacent to positively charged carbon, the former neutralizes the positive charge.

Formation of Carbonium Ions

(i) They are formed by the ionisation of halogen compounds, *e.g.*,

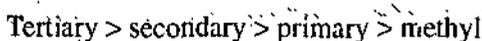


(ii) They are also formed by the addition of a proton to the π -electrons of an unsaturated compound or to the lone pair of electrons of atoms such as oxygen, nitrogen or sulphur present in a neutral molecule.



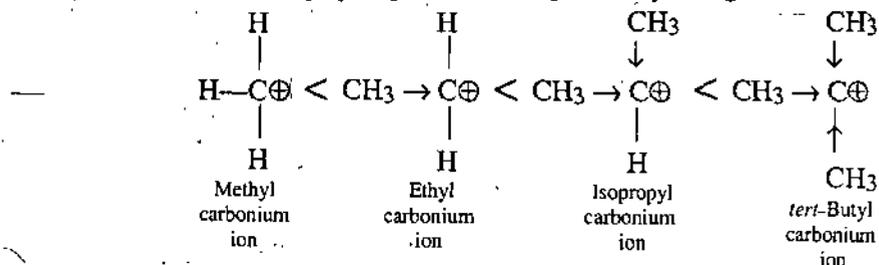
Stability of carbonium ions

The stability of carbonium ions, like free radicals, also follow the following decreasing order :



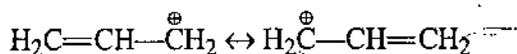
The stability of charged systems depends upon the dispersal of the charge. Any factor, therefore, that results in spreading out the positive charge of the electron-deficient carbon and distributes it over the rest of the atoms must stabilize a carbonium ion. Thus, they are stabilized inductively by electron donating substituents and rendered less stable by electron withdrawing substituents.

Alkyl group, attached to a positively charged carbon exerts an electron-releasing (positive) inductive effect and thus reduces the positive charge of the carbon atom to which it is attached. In doing so, the alkyl group itself becomes somewhat positive. This dispersal of charge stabilizes the carbonium ion. Hence, *tert*-butyl carbonium ion containing three methyl (alkyl) groups attached to positively charged carbon is most stable, while methyl carbonium ion with no alkyl group attached to positively charged carbon is least stable.



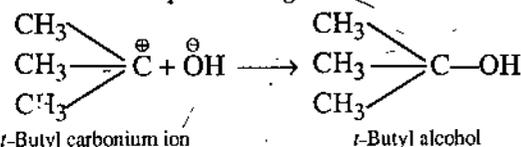
Thus, the stability of carbonium ions depends mainly upon the tendency of the attached groups to release or withdraw electrons. Stabilization is, therefore, also possible through

resonance. If the carbon atom with the positive charge is adjacent to an unsaturated system, its positive charge easily delocalises over the molecular system making it more stable than when only simple alkyl group is present.

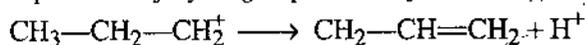


Some Important Reactions Involving Carbonium Ions

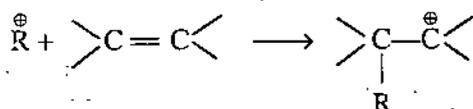
(i) Reaction with a nucleophilic reagent.



(ii) Separation of hydrogen proton to form an unsaturated molecule.

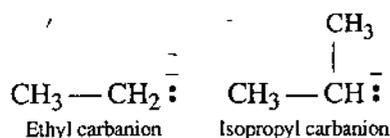


(iii) By the addition of carbonium ion to the π electrons of an unsaturated molecule.



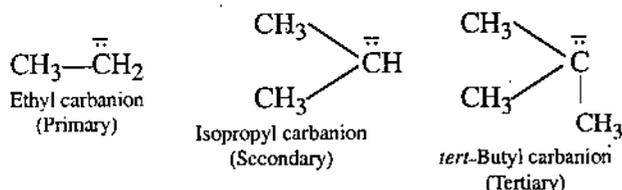
1.12. CARBANION

An ion containing a negatively charged carbon centre is called as carbanion. These ions are named by adding the word carbanion to the parent alkyl group. For example,



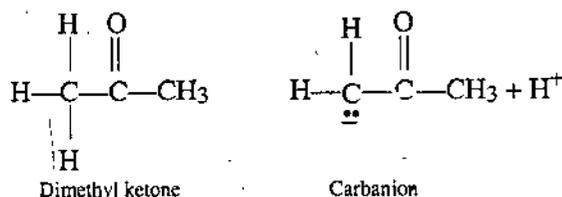
Characteristics of Carbanions

(1) Carbanions are named by writing the word carbanion after the name of the alkyl group present in them.



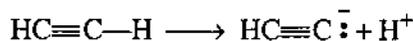
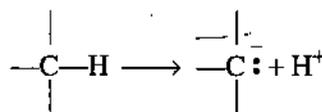
(2) Though the carbon of the carbanions contain eight electrons (complete octet) even then they are highly reactive intermediates. They readily attach with electrophilic reagents (electrophiles).

(3) In general, the carbanions are unstable, as they have negative charge on the carbon. However, the presence of some electronegative group ($>\text{C}=\text{O}$; $\text{C}\equiv\text{N}$ etc.) in the vicinity makes them stable.

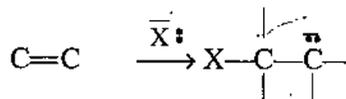
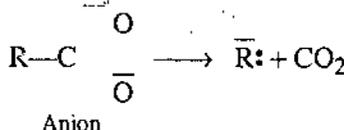


Formation of Carbanions

Organic compounds which possess a labile or acidic hydrogen have a tendency to produce carbanions. In such cases, hydrogen breaks away, as hydrogen proton bearing the lone pair of electrons on the carbon, thus producing carbanions.

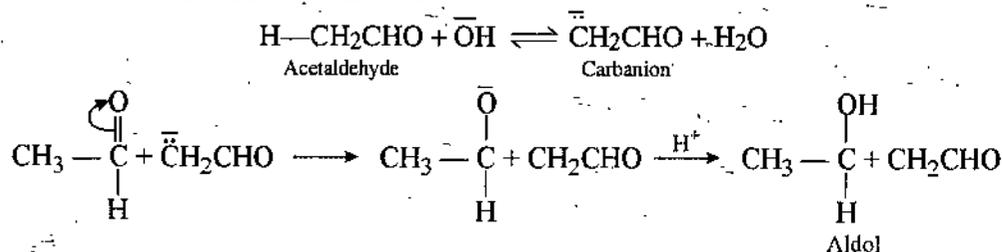


Carbanions are also formed by the decomposition of anions or addition of an anion on double bond, e.g.,



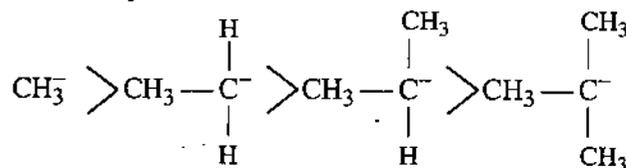
Some Important Reactions Involving Carbanions

All the reactions of reactive methylene compounds such as malonic ester, acetoacetic ester etc., proceed via the formation of carbanions. Apart from these, aldol condensation reactions, base catalysed halogenation of ketones, addition reactions of Grignard's reagents proceed via the formation of carbanions.



Stability of Carbanions

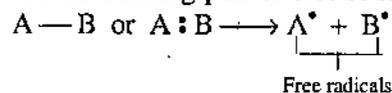
Although carbanions are electron rich but they are very reactive and are easily affected by electron deficient reagents (electrophiles). Ordinarily, carbanions are unstable because of their negative charge. They are stabilized by the presence of an adjacent electron attracting group. The stability of carbanions is in the order :



• 1.13. HOMOLYTIC AND HETEROLYTIC FISSION

[I] Homolytic fission

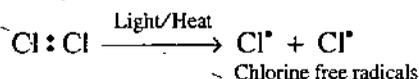
A covalent bond undergoes homolytic fission when each of two separating atoms takes away one electron with one of the bonding pair of electrons.



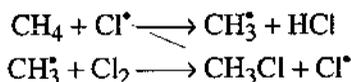
The two fragments, thus, produced carry an odd electron each and are called as *free radicals*. These are unstable and at once react with other radicals or molecules by gaining one more electron to restore the stable bonding pair.

Homolytic fission proceeds to produce free radicals by the application of energy, may be heat or light. This type of fission generally takes place in gaseous reactions and explains the substitution reactions of alkanes. Consider the reaction of methane and chlorine to form methyl chloride. Firstly, homolytic fission of Cl_2 molecules takes place in the presence of

ultraviolet light or by heat, resulting in free chlorine radicals which are highly reactive.

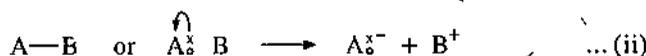
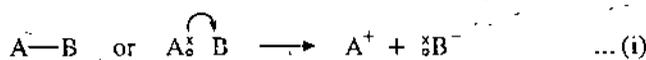


Methane then reacts with chlorine free radical to form methyl free radical (CH_3^\bullet) which then combines with chlorine molecule to form methyl chloride (CH_3Cl) and chlorine free radical.



[II] Heterolytic fission

When a covalent bond breaks in a way that both the bonding electrons are taken away by one of the two separating atoms or groups, it is said to have undergone heterolytic fission.



The curved arrow points towards the atoms or groups that takes away both the shared electrons and, therefore, becomes negatively charged leaving behind other positively charged atom or group. In general, the heterolytic bond fission yields one positive and one negative ion.

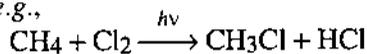
The course of heterolytic fission is determined by electronegativities of atoms or groups joined by covalent bonds. If B is more electronegative than A, then B will take away the bonding electron pair and fission will be according to course (i). If A is more electronegative than B, the fission will be according to course (ii).

Heterolytic fission is more common in organic reactions taking place in solutions. These reactions take place more readily in polar solvents like H_2O and are catalysed by the presence of ionic catalysts.

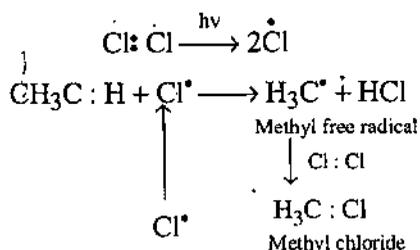
• 1.14. MECHANISM OF ORGANIC REACTIONS

[I] Free Radical Mechanism

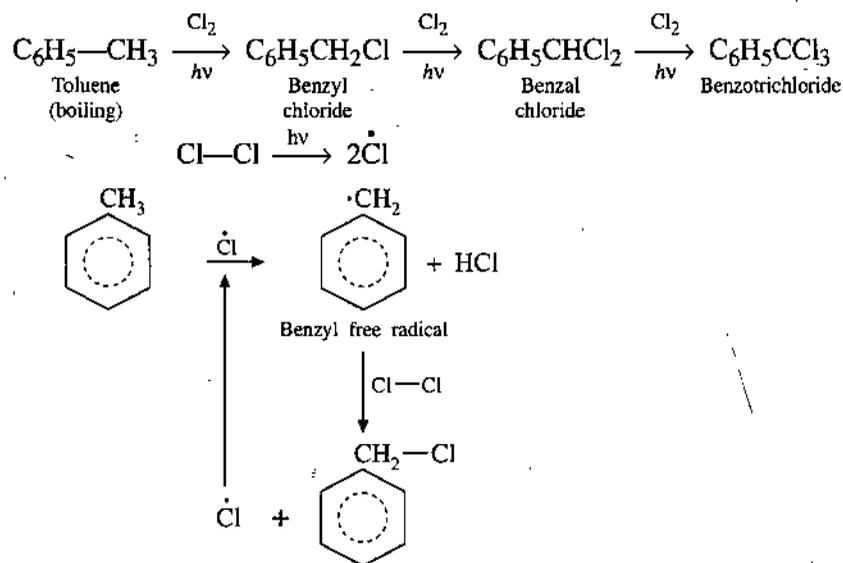
The free radical reactions are the chain reactions (once started they normally end till one of the reactants is completely consumed) and are very fast in speed. One example of free radical substitution reaction is the reaction of halogens with alkanes in presence of diffused sunlight. *e.g.*,



The mechanism of the reactions may be shown as :



Another example of free radical substitution reactions is the substitution of hydrogen atoms of the side chain present in aromatic compounds. Following reaction of toluene with chlorine occurs when chlorine is passed through boiling toluene in presence of sunlight.



[II] Ionic Mechanism

The conditions which favour heterolytic fission, *i.e.*, ions formation include :

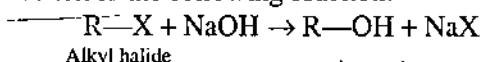
- (i) Absence of sunlight,
- (ii) Absence of peroxides,
- (iii) Absence of high temperature,
- (iv) Liquid state of reactants, and
- (v) Polar solvents.

Further, the substitution reaction may proceed by either of the following two mechanisms :

- (i) Nucleophilic or
- (ii) Electrophilic.

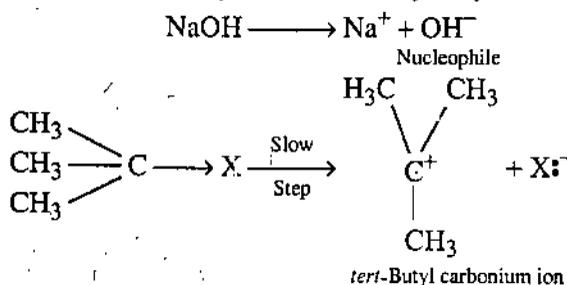
[III] Nucleophilic Substitution Reactions [S_N]

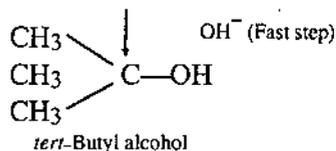
Let us consider the following reaction.



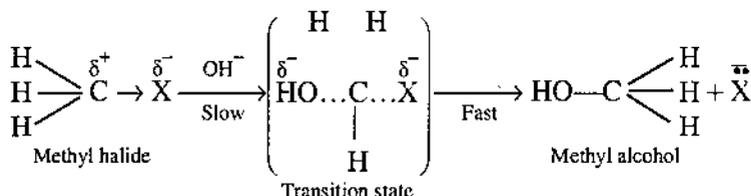
As the reaction is a substitution reaction (X is substituted by OH) and the attacking reagent is a nucleophile (OH⁻), the reaction is known as *nucleophilic substitution reaction*, and is written as S_N . Depending upon the number of molecules participating in the rate determining step, S_N reaction may also be of two types, *i.e.*, (a) S_N^1 (unimolecular) and (b) S_N^2 (bimolecular).

(a) S_N^1 (Substitution nucleophilic unimolecular) mechanism : It is a two steps mechanism, the first or the slow (rate determining) step involves the heterolytic fission of molecule R—X into R⁺ (carbonium ion) and X⁻ (anion) (rate determining step involves only one type of molecule, *i.e.*, alkyl halide, hence called unimolecular) and the second or the fast step involves the attack by OH⁻ (nucleophile) on the positively charged carbon of the carbonium ion, *e.g.*, the alkaline hydrolysis of *tert*-butyl halide.





(b) S_N^2 (Substitution nucleophilic bimolecular) mechanism : It is a one step mechanism in which the OH^- (nucleophile) attacks on the partial positively charged carbon with the simultaneous breaking of halogen atom. An unstable transition state is formed for a very short time. Since in the rate determining step two types of molecules, *i.e.*, alkyl halide and alkali are participating, it is called bimolecular, *e.g.*, alkaline hydrolysis of methyl halide.

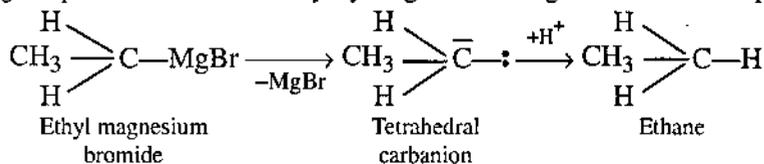


Since the attack by OH^- can take place on the positively charged carbon only from the side opposite to where halogen is attached (mainly due to steric effect and electrostatic repulsion), it always leads to inversion of configuration.

[IV] Electrophilic Substitution Reactions [S_E]

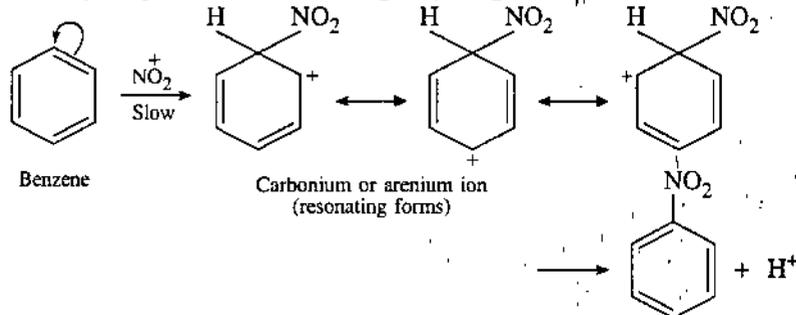
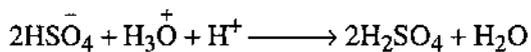
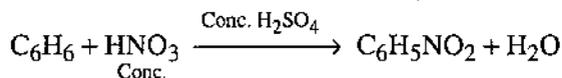
As the reaction involves substitution and an electrophile attacks first, the mechanism is known as *electrophilic substitution mechanism* and is written as S_E and similar to S_N^1 and S_N^2 it is also of two types S_E^1 (unimolecular), and S_E^2 (bimolecular).

(a) S_E^1 (Substitution electrophilic unimolecular) mechanism : The mechanism is not very common. It however, involves the formation of a carbanion as a transitory intermediate, *e.g.*, replacement of metal by hydrogen in an organometallic compound.



(b) S_E^2 (Substitution electrophilic bimolecular) mechanism : It is a more common mechanism. Aromatic substitution reactions such as *halogenation, nitration, sulphonation* and *Friedel Craft's reaction, etc.* proceed by this mechanism,

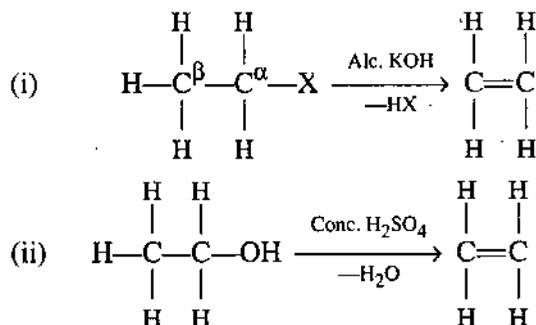
e.g.,



The first or the slow step involves the attack by an electrophile with the formation of a transitory intermediate, carbonium or arenium ion. In the second or fast step, hydrogen breaks as hydrogen proton to complete the substitution.

• 1.15. ELIMINATION REACTIONS

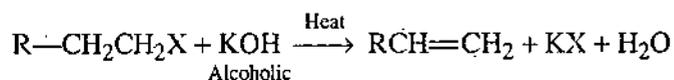
Elimination reactions are those in which two atoms or groups attached to two adjacent carbon atoms in a molecule are removed with simultaneous formation of a multiple bond between the two carbon atoms. One of the groups of atoms commonly eliminated as a proton and the other as an anion. *e.g.*,



Let us now discuss the mechanisms of the above two examples.

[I] Dehydrohalogenation of Alkyl Halides

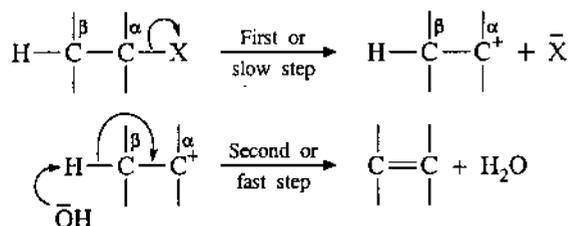
As we know, an alkyl halide undergoes dehydrohalogenation to form olefin when it is heated with alcoholic KOH.



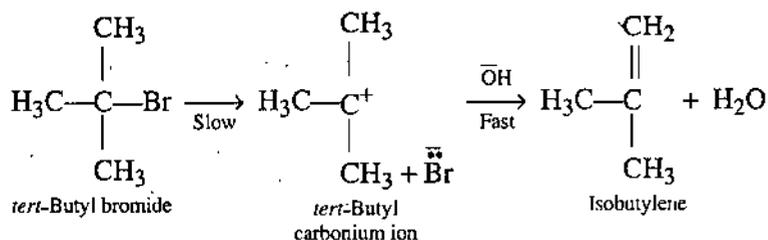
The reaction may proceed through two different mechanisms.

(a) **Two steps elimination reaction mechanism (E_1)**: The first or slow step involves the heterolytic fission of carbon-halogen bond to form a carbonium ion and halide ion.

The second or fast step involves the elimination of a proton from β -carbon atom with the help of OH^- , to produce an olefin.



Since only one molecule, *i.e.*, alkyl halide takes part in the slow or rate determining step, it is called E_1 mechanism. The mechanism is found in the case of tertiary halides as stable tertiary carbonium ions are formed, *e.g.*,



(b) **One step elimination reaction mechanism (E_2)**: This type of mechanism involves the abstraction of a proton from β -carbon atom by a base with the simultaneous loss of a halide ion from the α -carbon of the alkyl halide molecule, *e.g.*,

• 1.17. CARBENES

Carbenes also called as methylenes are short lived species and contain a carbon atom with two bonds and two electrons, e.g., $:\text{CH}_2$, $:\text{CCl}_2$. These are neutral and have the electronic structure $-\ddot{\text{C}}-$ or $-\dot{\text{C}}-$. They are electron deficient and have only six electrons in the outermost shell. They are highly reactive and act as strong electrophiles as they need a pair of electrons to complete the octet. They are Lewis acids.

Classification : The two unbonded electrons of a carbene may be either paired or unpaired. If both the electrons are paired, this is called as **singlet state**. In this state carbon atom is sp^2 hybridized. It is attached to two atoms or groups by bonded electrons and remaining one sp^2 hybridized orbital contains a lone pair of electrons. The unhybridized p -orbital remains vacant. This state has no magnetic moment.

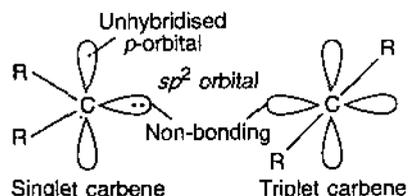
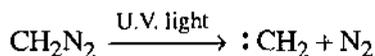
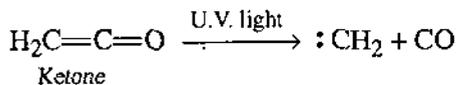


Fig. 1.17. Structure of carbene

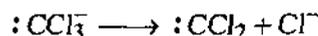
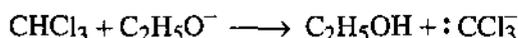
On the other hand if both the electrons are unpaired, they will have parallel spins. When placed in a magnetic field, it exists in three closely grouped energy states. Such a state is called as **triplet state**. In this state carbon atom is sp hybridized. It is attached to two atoms or groups with these hybridized orbitals. Such a carbon contains two unhybridized p -orbitals. Each of these orbitals contain one unpaired electron. In this state carbene is relatively more stable and has a permanent magnetic moment.

Formation of carbenes

(i) By the decomposition of ketone or diazo methane in the presence of ultraviolet light.

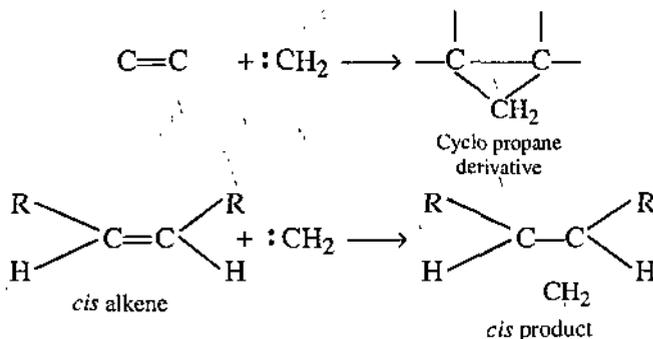


(ii) By the action of the alkoxides on CHCl_3 .

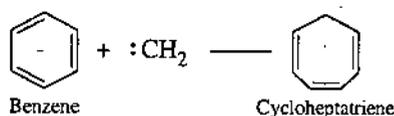


Reactions : Carbenes are highly reactive unstable compounds. They are always prepared in the presence of the compound with which they react. Some of the important reactions are :

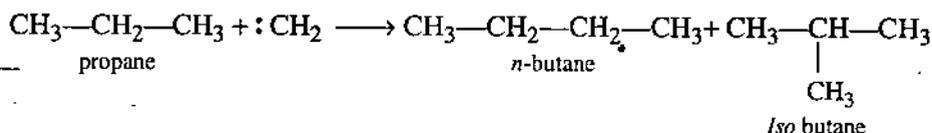
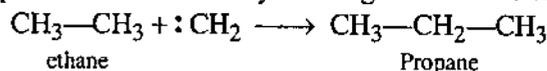
(i) **Addition to $\text{C}=\text{C}$ bonds :** Carbenes add on alkenes to form cyclo propane derivatives.



Carbenes also add to aromatic systems when ring expansion takes place.



(ii) **Addition reactions to alkanes:** Ethane adds methylene (:CH₂) to form propane and propane reacts with methylene to give *n*-butane and isobutane.



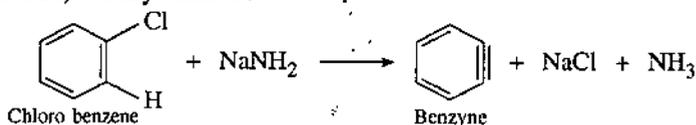
Applications: Carbenes are the reactive intermediates in a number of reactions such as Reimer Tiemann reaction, carbylamine reaction, Wittig reaction. In these reactions, :CCl₂ is formed as a reaction intermediate.

• 1.18. ARYNES OR BENZYNE, (C₆H₄)

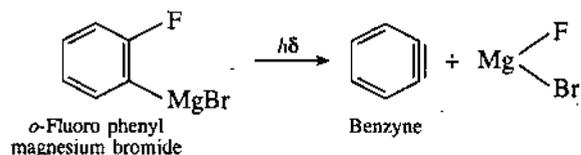
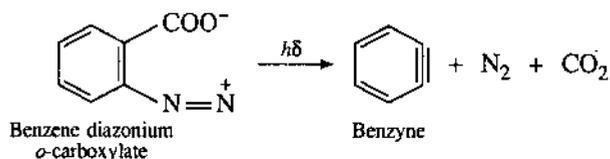
Benzyne is neutral, highly reactive intermediate in which aromatic character is not much disturbed. It is formed as an intermediate compound during nucleophilic substitution of aromatic compounds. It contains carbon-carbon triple bond which is quite different from that of acetylene.

Formation of Benzyne

(i) By the action of strong bases such as sodamide or metal alkoxide (potassium *t*-butoxide) on aryl halides.

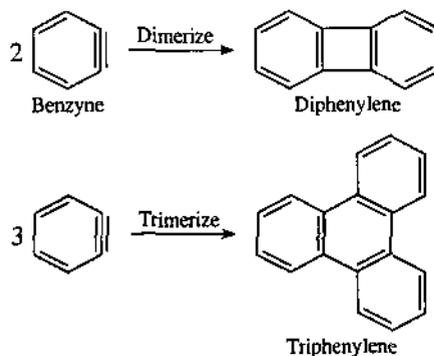


(ii) By the decomposition of benzene diazonium *o*-carboxylate or *o*-fluoro phenyl magnesium bromide

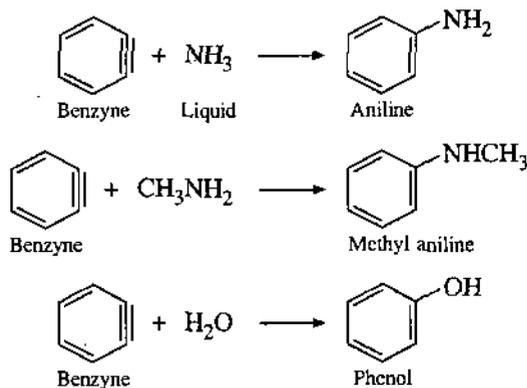


Reactions: It is very reactive compound. This is because in this compound π -bond is formed by sideways overlapping of sp^2 orbitals which is very unstable. Some of its reactions are:

(i) In the absence of any reagent, two or three molecules of benzyne react together to form diphenylene and triphenylene, respectively.



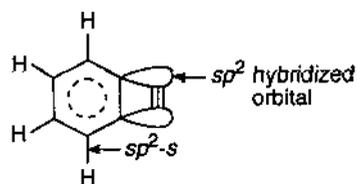
(ii) It reacts with nucleophilic reagents to form addition compounds.



(iii) It reacts with phenyl lithium to form phenyl lithium compound which is used in the synthesis.



Structure : The carbon-carbon triple bond present in benzyne is different from the triple bond of acetylene. In acetylene each carbon atom is sp -hybridized. These two sp -hybridized orbitals form σ -bonds with sp -hybridized orbital of carbon and s -orbital of hydrogen. The remaining two unhybridized p -orbitals form two π -bonds. Such a structure is not possible in benzyne due to hexagonal geometry of benzene ring. Thus, a new bond of benzyne is formed by sideways overlapping of sp^2 hybridized orbitals of two adjacent carbon atoms as shown below :



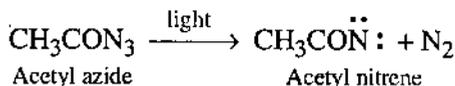
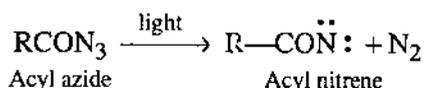
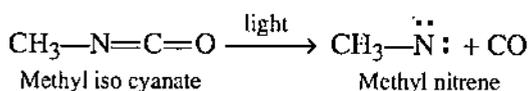
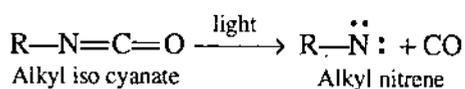
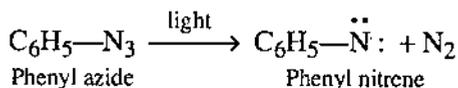
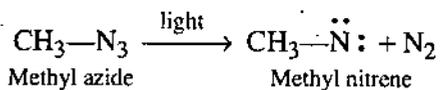
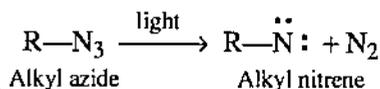
Structure of benzyne

• 1.19. NITRENES OR IMIDOGENS

Nitrenes are the organic species having the general formula, $\text{R}-\ddot{\text{N}}:$ They are similar to carbenes and contain a nitrogen atom with one bond and two non bonded electron pairs, i.e., $-\ddot{\text{N}}:$. They are electron deficient and have only six electrons in the outermost shell. They are highly reactive and act as strong electrophiles as they need a pair of electrons to

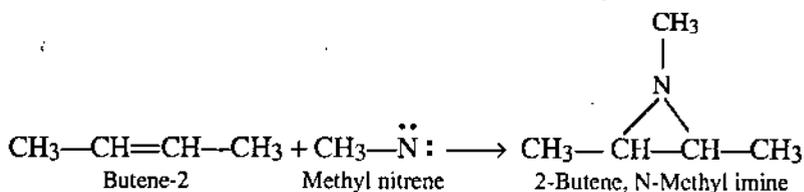
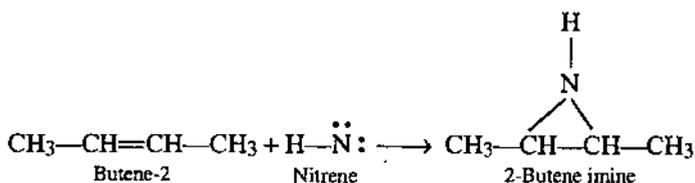
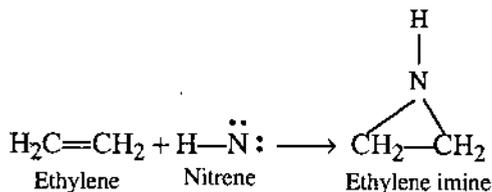
complete the octet. The parent compound nitrene, $\text{H}-\ddot{\text{N}}:$ is also known as imidogen, azene or imene. Nitrenes can exist in the singlet and triplet states. The triplet state is the ground state and most nitrenes exist in this state.

Formation of nitrenes : Alkyl and acyl nitrenes may be prepared by the decomposition of alkyl azides, alkyl iso cyanates or acyl azides in the presence of light or heat.



Reactions : Nitrenes are highly reactive unstable compounds. Some of the important reactions are :

1. Addition to $\text{C}=\text{C}$ bonds : Nitrenes add on alkenes to form cyclic products.



22. Which has least carbon-carbon bond length ?
 (a) Ethane (b) Ethene (c) Ethyne (d) Benzene
23. Which of the following bonds has the maximum bond energy ?
 (a) C — C (b) C — H (c) C = O (d) C — Q
24. Which one of the following is an electrophilic ?
 (a) NH₃ (b) BF₃ (c) H₂O (d) C₂H₅OH
25. Fill in the blanks :
 (i) Out of NH₃ and PH₃, has the largest bond length.
 (ii) The correct order of decreasing bond length amongst C — C, C = O and C ≡ C is
 (iii) Methyl amine is basic than NH₃.

ANSWERS

21. (d) 22. (c) 23. (b) 24. (b) 25. (i) NH₃ (ii) C — C > C = C > C ≡ C (iii) more



2

STEREOCHEMISTRY OF
ORGANIC COMPOUNDS

STRUCTURE

- Isomerism
- Optical Isomerism
- Enantiomers
- Racemic and Meso Forms
- Racemization
- Diastereoisomers or Diastereomers
- Resolution
- Geometrical Isomerism
- R, S, System of Nomenclature of Optical Isomers
- E, Z System of Nomenclature of Geometrical Isomers
- Summary
- Student Activity
- Test Yourself

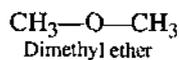
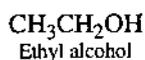
LEARNING OBJECTIVES

After going this unit you will learn :

- Structural isomerism, stereo-isomerism, functional isomerism, metamerism and tautomerism.
- Optical activity, optical isomers, *l*-form and *d*-form.
- Optical isomerism of a compound containing one stereogenic carbon atom and containing two similar stereogenic carbon atoms.
- Methods for resolution of a racemic mixture : biochemical method, salt formation method and mechanical separation.
- Geometrical isomerism of oximes and alicyclic.
- R and S configurations of lactic acid and bromo-chloro iodo-methane.

2.1. ISOMERISM

Compounds which have the same molecular formula but different physical or chemical properties are called isomers and this phenomenon is known as isomerism. For example, molecular formula C_2H_6O can represent the following two organic compounds :

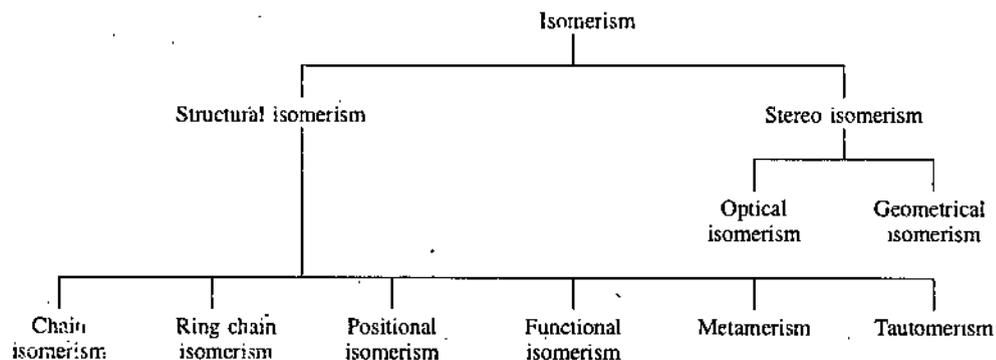


Both the compounds contain the same number of carbon, hydrogen and oxygen atoms. However, the difference in their properties must be due to the difference in the relative arrangement of atoms in the compounds. Broadly speaking isomerism is of two types :

(i) **Structural isomerism** : When the isomerism is due to the difference in the relative arrangement of atoms within the molecule without any reference to space, the phenomenon is known as *structural isomerism*. In other words, in this type of isomerism, the compounds have the same molecular formula but have different structural formulae.

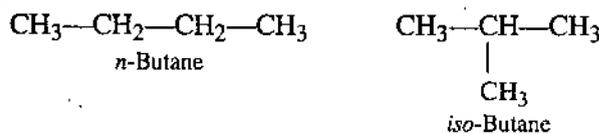
(ii) **Space isomerism or stereo-isomerism** : This isomerism is due to the different arrangement of atoms or groups in space. In other words, stereo-isomers have the same structural formulae but have different configurations.

Isomerism has been further classified as follows :

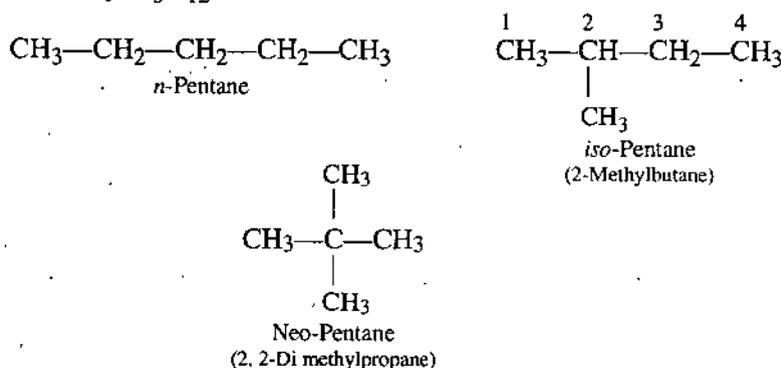


Structural isomerism

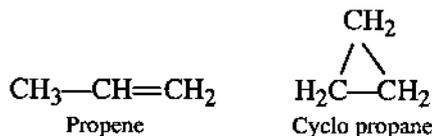
(I) Nuclear or chain isomerism : When two or more compounds have the same molecular formula but have difference in the structure of the carbon chain which may be a straight chain or branched chain, the compounds are called as *chain isomers* and the phenomenon is known as *chain isomerism*. For example, C_4H_{10} represents two chain isomers.



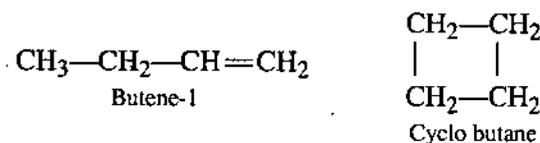
Similarly, C_5H_{12} has three chain isomers



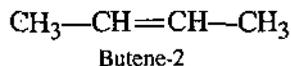
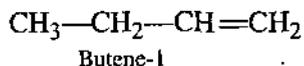
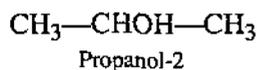
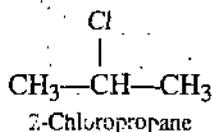
(II) Ring chain isomerism : When the compounds have the same molecular formula but one of the compounds has open chain of carbon atoms whereas other has closed chain of carbon atoms, the compounds are called as *ring chain isomers* and the phenomenon is known as *ring chain isomerism*. For example, C_3H_6 represents two ring chain isomers, viz.,



Similarly, C_4H_8 has two ring chain isomers, viz.,

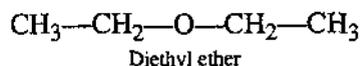
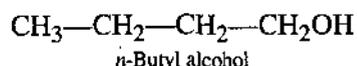


(III) Positional isomerism : When the isomers have the same carbon chain but differing in the position of the substituent atom or group such as $-\text{Cl}$, $-\text{Br}$, $-\text{I}$, $-\text{OH}$, $-\text{NO}_2$, $-\text{NH}_2$, double bond or triple bond, they are called as *positional isomers* and the phenomenon is known as *positional isomerism*. For example,

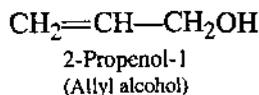
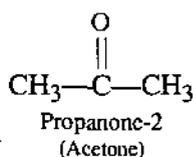
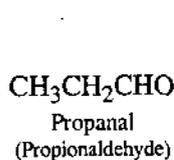


(IV) **Functional isomerism** : When the compounds have the same molecular formula but have different functional groups, the compounds are called as *functional isomers* and the phenomenon is known as *functional isomerism*. For example,

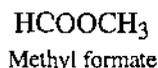
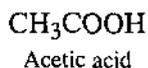
(1) C₄H₁₀O—



(2) C₃H₆O—

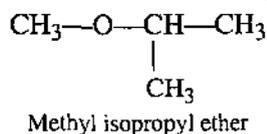
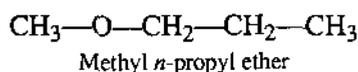
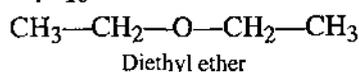


(3) C₂H₄O₂—

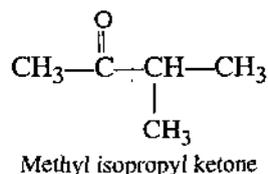
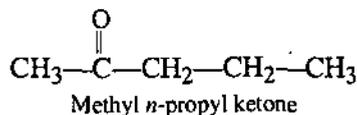
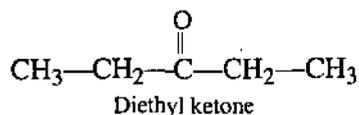


(V) **Metamerism** : When the compounds belong to the same class but have different arrangement of alkyl groups to the same functional group, the compounds are called as *metamers* and the phenomenon is known as *metamerism*. For example,

C₄H₁₀O—



C₅H₁₀O—



(VI) **Tautomerism** :

It is a special type of functional group isomerism in which a compound remains as an equilibrium mixture of two forms. These forms arise due to the migration of proton from one polyvalent atom to another with necessary rearrangement of linkages. The two forms are always in a state of dynamic equilibrium.

109° 28'. If four different atoms or groups are attached to such a carbon atom, then the following two arrangements are possible Fig. (2).

These two arrangements are not super-imposable and show mirror image relationship. Such molecules are called as chiral and this property is known as molecular chirality. Hence, the compounds containing an asymmetric or chiral carbon atom are capable of showing the phenomenon of optical isomerism. On the other hand, there are certain compounds which contain two or more asymmetric carbon atoms and yet they are optically inactive. It means that the presence of asymmetric carbon atom is not only sufficient to make the molecule optically active. Actually, the molecule as a whole should be asymmetric. **Thus, molecular asymmetry or chirality is an essential condition for the compound to show optical activity.** If the molecule contains a plane of symmetry or centre of symmetry, the molecule becomes optically inactive due to internal compensation.

A plane of symmetry is an imaginary plane which divides the molecule into two parts such that each part is the mirror image of the other. The molecules having such a plane are always optically inactive due to internal compensation.

A centre of symmetry is an imaginary point in the molecule such that if a line is drawn from any group of the molecule to this point and then extending the line to an equal distance beyond the point, it meets the mirror image of the original group. For example, trans-dimethyl diketopiperazine contains centre of symmetry and is optically inactive.

(i) Optical isomerism of a compound containing one stereogenic (asymmetric) carbon atom: The most common example of a compound containing one stereogenic

carbon is lactic acid, $\text{CH}_3\text{CH}(\text{OH})\text{COOH}$. It contains one asymmetric carbon atom and according to van't Hoff it can exist in the following two optically active forms which are related to each other as object to image. The priority order of rotating the plane of polarised light of four groups attached to an asymmetric carbon atom in lactic acid is $-\text{OH} > -\text{COOH} > -\text{CH}_3 > -\text{H}$ (refer to problem 7). Therefore,

(a) Compound I will rotate the plane of polarised light in clockwise direction and is known as *d*-form.

(b) Compound II will rotate the plane of polarised light in anticlockwise direction and is known as *l*-form.

(c) A third form results when equal amounts of *d*- and *l*-forms are mixed together. It is called as *racemic* form or *dl* mixture. It is optically inactive due to external compensation.

(ii) Optical isomerism of a compound containing two similar stereogenic carbon atoms.

The most common example of a compound containing two similar stereogenic (asymmetric) carbon atoms is tartaric acid.

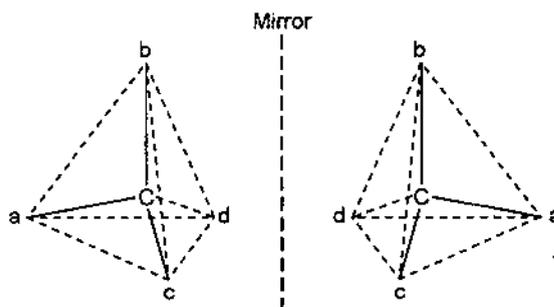
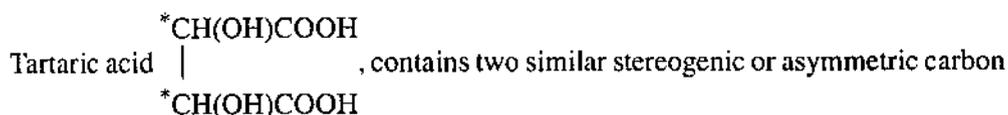


Fig. 2. Two space models due to the presence of an asymmetric carbon atom.

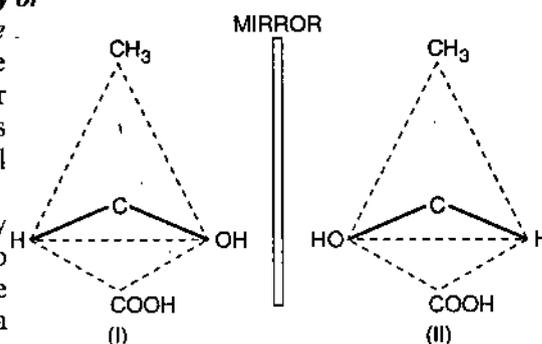
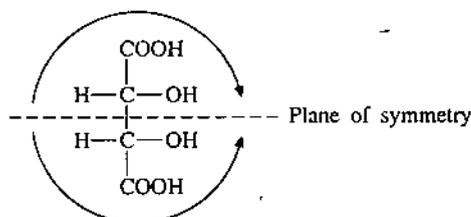
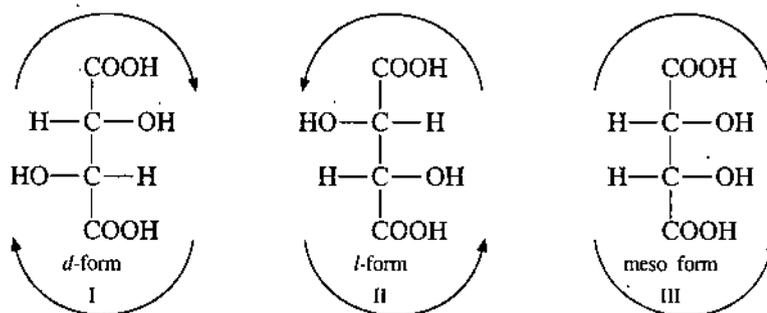


Fig. 3. *d* and *l* forms of lactic acid.



atoms, each of which is attached to four different groups, *i.e.*, —H, —OH, —COOH, —CH(OH)COOH. Due to the presence of two similar asymmetric carbon atoms, the configurations of various groups in tartaric acid can be represented in the following three ways :

(a) Compound I will rotate the plane of polarised light in clockwise direction and is known as *d*-form.

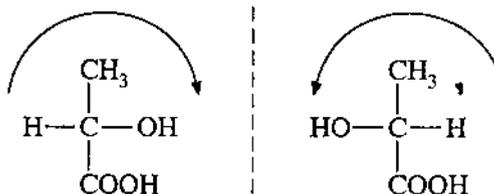
(b) Compound II will rotate the plane of polarised light in anti-clockwise direction and is known as *l*-form.

(c) Compound III will not rotate the plane of polarised light in any direction and is known as *meso* form. It is optically inactive due to internal compensation. The half of the molecule rotates the plane of polarised light in clockwise direction, whereas the remaining half equally rotates the plane of polarised light in anticlockwise direction.

(d) A fourth form results when equal amounts of *d* and *l*-forms are mixed together. It is called as *racemic* form or *dl* mixture. It is optically inactive due to external compensation. The *d*-form rotates the plane of polarised light in clockwise direction and its rotation is balanced by an equal but opposite rotation of *l*-form.

• 2.3. ENANTIOMERS

Enantiomers or enantiomorphs or antimers are the *d*- and *l*-forms of an optically active compound which are related to each other as object to image. By the *d*-form means dextrorotatory, (D-) *i.e.*, which rotates the plane of polarised light in clockwise direction and *l*-form (L-) means laevorotatory, *i.e.*, which rotates the plane of polarized light in anti-clockwise direction.



For a compound to show optical isomerism, it must contain an asymmetric carbon atom, *i.e.*, a carbon atom which is attached with four different atoms or groups. For example, lactic acid, active valeric acid etc. The enantiomers of lactic acid may be represented as follows :

Properties of Enantiomers

Enantiomers are stable compounds which differ from one another in three dimensional arrangements. They have same melting points, density, solubility, colour and reactivity. They differ only in their behaviour towards polarized light. The mixture of equal amounts of two enantiomers is called as racemic mixture. It is optically inactive.

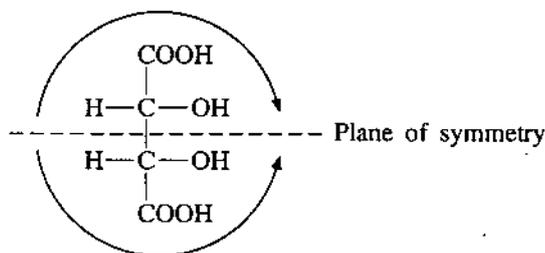
• 2.4. RACEMIC AND MESO FORMS

The compounds which contain one or more similar asymmetric carbon atoms but do not rotate the plane of polarised light are optically inactive. Such compounds are found in racemic and meso forms.

Racemic form : It is a mixture of equal amount of *d*- and *l*-forms. It is optically inactive due to external compensation. The *d*-form rotates the plane of polarised light in

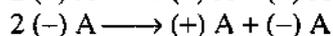
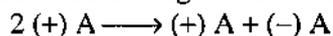
clockwise direction and its rotation is balanced by an equal but opposite rotation of *l*-form.

Meso form : It is only one compound containing two similar asymmetric carbon atoms. The compound is optically inactive as it contains plane of symmetry or centre of symmetry. The half of the molecule rotates the plane of polarised light in clockwise direction, whereas the remaining half equally rotates the plane of polarised light in anti-clockwise direction. The molecule is, thus, optically inactive due to internal compensation. For example, one of the optical isomers of the tartaric acid is its meso form.



• 2.5. RACEMIZATION

It has been observed that an optically active substance may be converted into optically inactive racemic mixture under the influence of heat, light or some suitable catalyst. For example, when a solution of *d*-tartaric acid is heated at 175°C, racemic mixture of tartaric acid is obtained. *The conversion of a d- or l-isomer into its racemic mixture is known as racemization.* This involves the change of half of the optically active compound to the isomer of opposite rotation resulting in the racemic mixture.



Racemization can be brought about in the following ways :

(i) **By heating :** Lactic acid, amyl alcohol, mandelic acid are racemised by heating.

(ii) **By heating with water :** *d*-tartaric acid is racemised by heating its aqueous solution at 175°C.

(iii) **By heating with dilute H₂SO₄ :** *d*-Valeric acid is racemised by heating with dilute H₂SO₄.

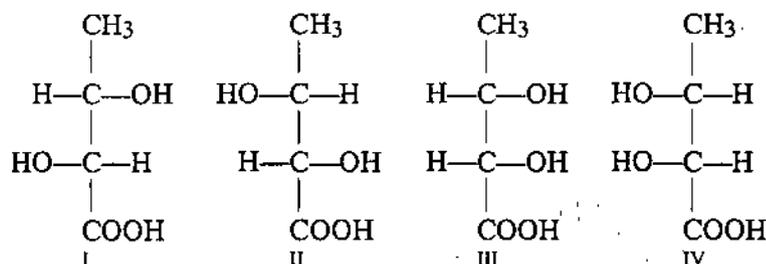
(iv) **By heating with alkali :** Lactic acid, tartaric acid and mandelic acid are racemised by the presence of alkali.

(v) **By auto racemisation :** In some cases, racemisation takes place itself in the presence of certain impurities. It is known as *auto racemisation*.

• 2.6. DIASTEREOMERS OR DIASTEREOMERS

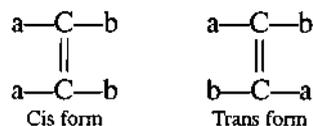
The compounds which are optical isomers but not the mirror images are called as *diastereo isomers* or *diastereomers*. For example, the compound,

$\text{CH}_3\text{CH}(\text{OH})\text{CH}(\text{OH})\text{COOH}$ has two asymmetric carbon atoms and, therefore, it can exist in the following four forms depending upon the relative arrangements of —H and —OH groups.



The forms I and II are mirror images and so are the forms III and IV. The forms I and III, II and III, II and IV, I and IV although optically active but they are not the mirror images. These are called as *diastereo isomers*.

corners gives different arrangements of atoms or groups in space provided they are different on each carbon atom. Thus, $C_2 a_2 b_2$ can be represented as :

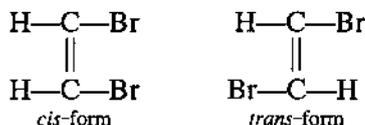


The isomerism which arises due to the different geometrical arrangements of atoms or groups about doubly bonded carbon atom is known as geometrical isomerism and the isomers are called as geometrical isomers. The isomer in which same or similar groups lie on the same side is called as *cis isomer* (Latin, *cis* = same side) and the isomer in which same or similar groups lie on the opposite sides in space is called as *trans isomer* (Latin, *trans* = across) and the phenomenon is also called as *cis-trans isomerism*.

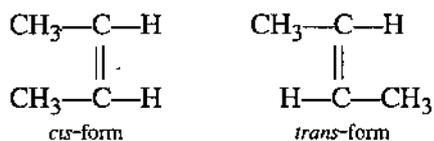
In general, all alkene compounds having the general formula $abc = cxy$ or a more simple formula $abC = Cab$ show the phenomenon of geometrical isomerism. On the other hand, the compounds of the general formula, $abC = Cxx$ will not show geometrical isomerism as one of the carbon atom contains same atoms or groups. Some examples are as follows :

Examples :

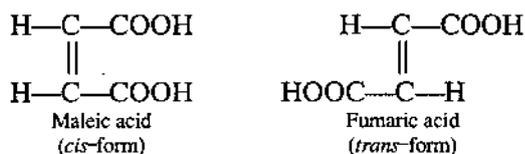
(1) 1, 2-Dibromoethene, $\begin{array}{c} CHBr \\ || \\ CHBr \end{array}$



(2) Butene-2, $CH_3-CH=CH-CH_3$



(3) Maleic and fumaric acids, $C_2H_2(COOH)_2$



Geometrical Isomerism of Oximes or $>C=N$ Compounds

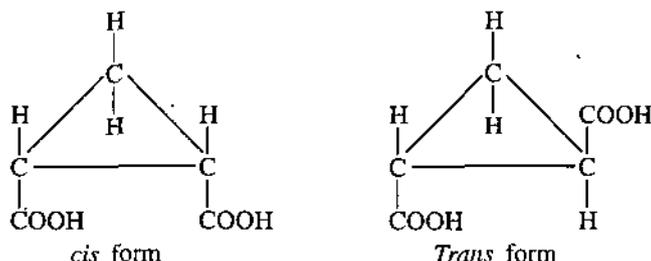
The carbon and a nitrogen atom joined by a double bond ($>C=N$) can- not easily rotate similar to two carbon atoms joined by a double bond ($>C=C<$). The positions of various groups attached to $>C=N$ are fixed in space and such compounds, therefore, show geometrical isomerism. The geometrical isomers of benzaldoxime may be represented as:



The isomer in which H and OH groups are on the same side is known as *cis* or *syn*, while the isomer in which H and OH groups are on opposite sides is known as *anti* or *trans* form.

Geometrical isomerism of Alicyclic or Ring compounds

Geometrical isomerism is also shown by ring compounds. In the ring compounds, there is no free rotation around C—C single bonds as the rotation will break the bonds as well as the ring. For example, geometrical isomers of cyclopropane dicarboxylic acid may be represented as :



Explanation of Geometrical Isomerism

According to van't Hoff and Le Bel, the four valencies of carbon atom are directed towards four corners of a regular tetrahedron, at the centre of which carbon atom is situated. The angle between any two valency bonds is $109^{\circ} 28'$. According to this theory, a compound containing two carbon atoms united by a single bond can be represented by two tetrahedra joined together corner to corner as given below for succinic acid :

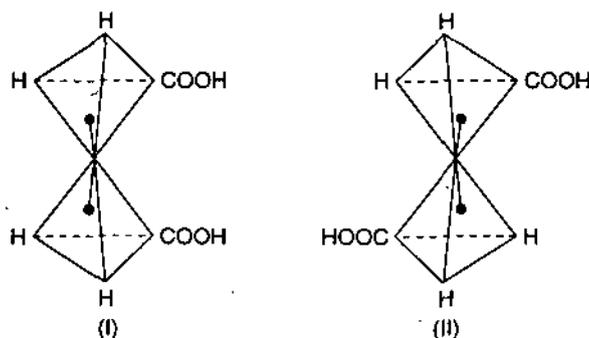


Fig. 2.4. Identical molecules of succinic acid.

If two tetrahedra were fixed rigidly to each other, the two compounds having the models I and II should be possible. In fact, there is only one succinic acid known. Therefore, it is concluded that there occurs a free rotation of carbon atoms about the single bond and there is no possibility of two space models in such cases.

If the two carbon atoms are joined by a double bond, the two tetrahedra representing them must be in contact at two common corners and their free rotation ceases. Therefore, in such compounds, the position of the groups attached to two carbon atoms are fixed relative to each other.

Thus, different geometrical arrangements of groups about the doubly bonded carbon atom now become possible. For example, tetrahedral models of maleic and fumaric acid may be represented as :

The lack of free rotation by doubly bonded carbon atoms or carbon and nitrogen atoms forms the basis of geometrical isomerism. It is confirmed by the fact that when maleic and fumaric acids are reduced to succinic acid, the isomerism disappears due to the free rotation of carbon-carbon single bond.

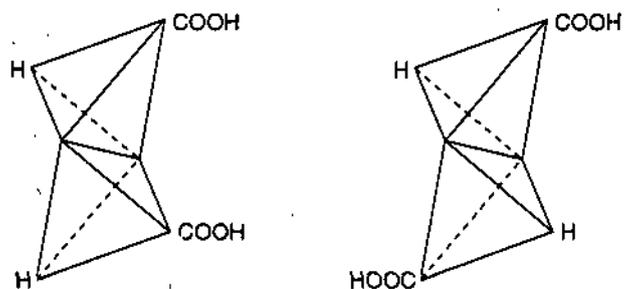
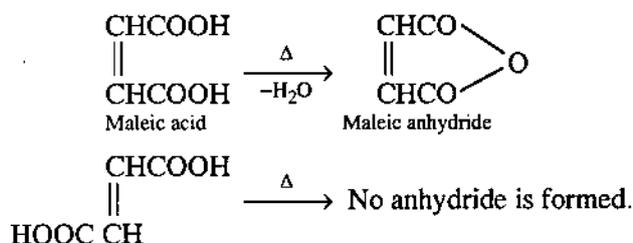


Fig. 2.5.—Tetrahedral models of maleic and fumaric acids.

Determination of Configuration of Isomers

(i) **By physical methods** : In general, it has been observed that the cis isomer has a lower melting point, a higher boiling point, a greater solubility in organic solvents, a higher density, a higher dipole moment, a higher heat of combustion and a higher ionization constant as an acid. The modern analytical techniques like X-ray analysis, infrared, ultraviolet and Raman spectra have also been used for this purpose.

(ii) **By formation of a cyclic compound** : The formation of a cyclic compound takes place easily when the two reacting groups are close to each other. Maleic acid readily forms cyclic anhydride, whereas fumaric acid does not.

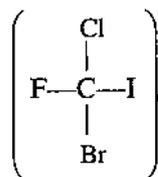


• 2.9. R, S SYSTEM OF NOMENCLATURE OF OPTICAL ISOMERS

R, S system of configuration of optical isomers was given by Cohn, Ingold and Prelog. The symbols R and S are derived from the Latin words *rectus* meaning right and *sinister* meaning left. The configuration of an optically active compound is based upon the nature of the groups attached to an asymmetric centre. The nature of the groups is determined by the priority of the groups which depends upon the following rules :

(a) The four different atoms or groups attached to an asymmetric centre are arranged in the decreasing order of priority 1, 2, 3, 4.

(b) When four different atoms are attached to an asymmetric centre, priority is given to atomic number. The atom with the highest atomic number is given the highest priority. Thus, in bromo chloro fluoro iodo methane

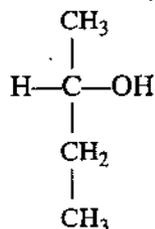


the priority sequence of four atoms is

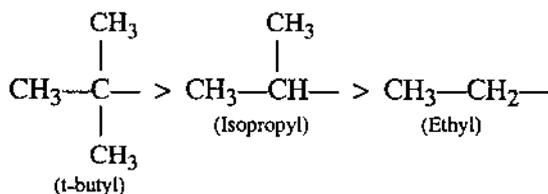
I (Z = 53), Br (Z = 35), Cl (Z = 17), F (Z = 9).

(c) If isotopes of the same element are attached to an asymmetric centre, the isotope with higher mass number is given the higher priority. For example, deuterium (${}^2\text{H}$) is given higher priority as compared to hydrogen (${}^1\text{H}$).

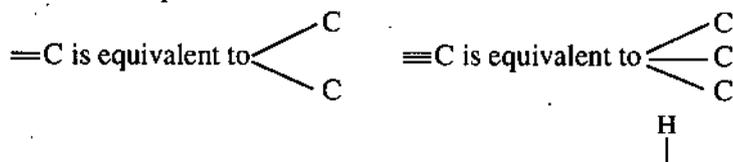
(d) If two atoms attached to an asymmetric centre are same, the priority is determined by the atomic number of next atom away from asymmetric centre.



For example, in butanol-2, ethyl group has higher priority than methyl group because in ethyl group carbon atom is attached to C, H, H whereas in methyl group carbon atom is attached to only hydrogen atom (H, H, H). Since carbon has higher atomic number than hydrogen, ethyl group has higher priority over methyl group. Similarly, the priority of *t*-butyl, isopropyl and ethyl groups is in the order :



(e) An atom attached with a double or triple bond is equivalent to two or three such atoms. For example,

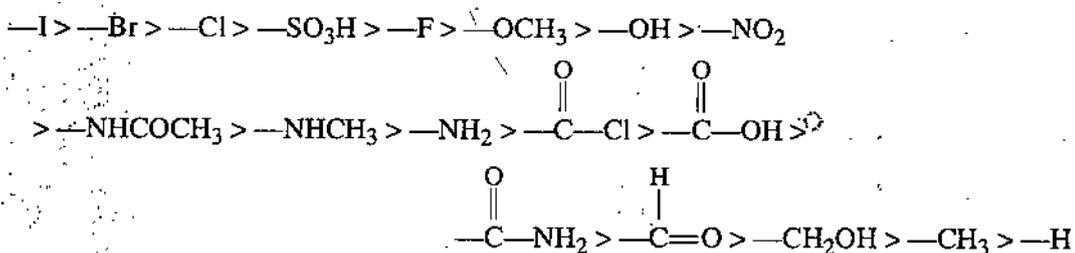


For example, out of $-\text{CHO}$ and $-\text{CH}_2\text{OH}$ groups, $-\text{C}=\text{O}$ group has higher priority

than $\begin{array}{c} \text{H} \\ | \\ -\text{C}-\text{OH} \\ | \\ \text{H} \end{array}$ group. This is because in $-\text{C}=\text{O}$ group, C is attached to O, O, H atoms

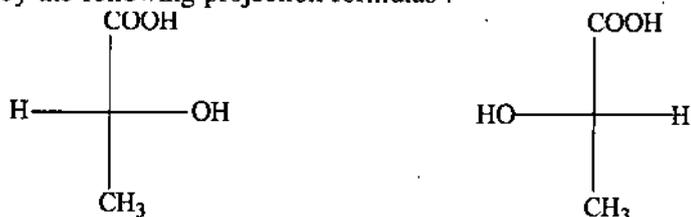
whereas, in $\begin{array}{c} \text{H} \\ | \\ -\text{C}-\text{O}-\text{H} \\ | \\ \text{H} \end{array}$, C is attached to H, H and O. The third atom in $-\text{CHO}$ is O (Z=8), while in $-\text{CH}_2\text{OH}$ it is H (Z=1).

On the basis of these rules, some common groups are given the following priority sequence in the decreasing order :



After giving priorities to four atoms or groups attached to an asymmetric centre, the molecule is now rotated so that the atom or group of lowest priority (4) is directed away from the viewer. Now the arrangement of remaining three atoms or groups is viewed in the decreasing order of their priorities. In looking so, if the eye moves in a clockwise direction, the configuration is assigned as R (Rectus, meaning right), while if the eye moves in anti-clockwise direction, the configuration is assigned as S (Sinister, meaning left)

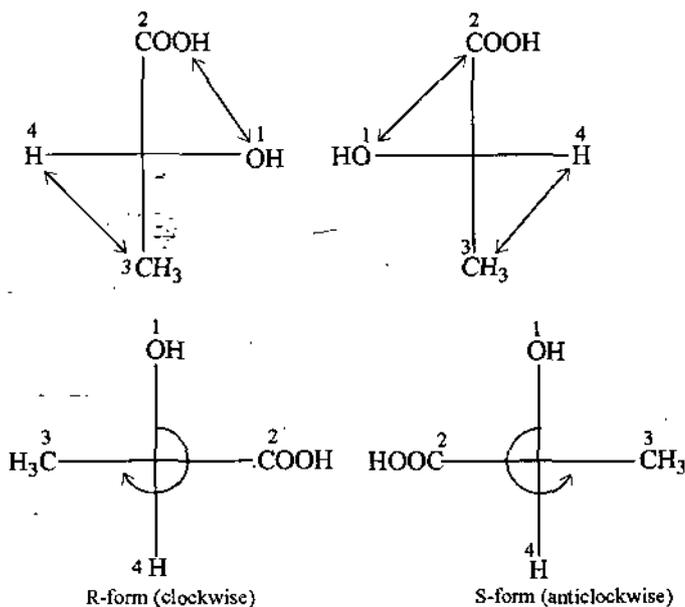
(a) **R and S Configurations of Lactic Acid, $\text{CH}_3\text{CH}(\text{OH})\text{COOH}$** : Lactic acid can be represented by the following projection formulas :



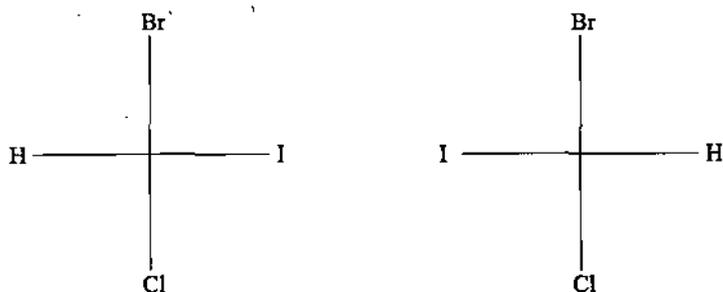
The priority order of four groups attached to an asymmetric carbon atom in lactic acid is :



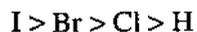
The interchange of two pairs of groups is done so as to keep the lowest priority H-atom below the vertical line. This will retain the original configuration. The interchange is represented by the double headed arrows in the following manner :



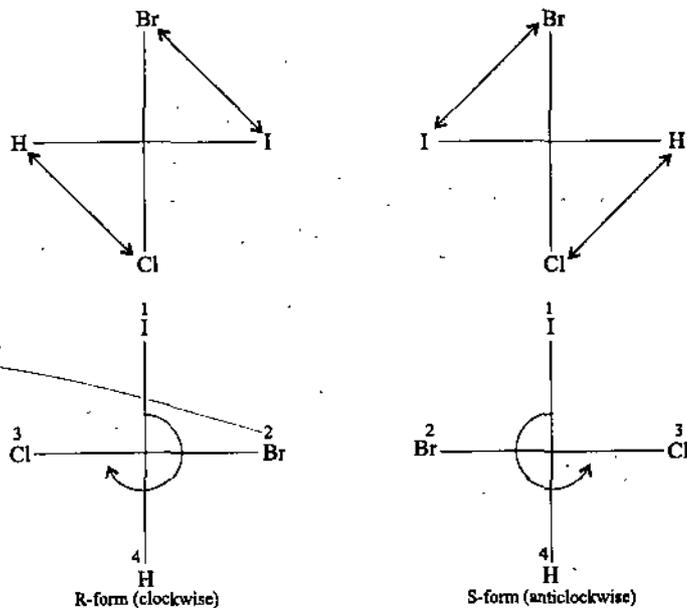
(b) **R and S configurations of bromo-chloro iodo-methane, $\text{CH}(\text{Cl})(\text{Br})(\text{I})$** : The compound can be represented by the following projection formulas :



The priority order of four atoms attached to an asymmetric carbon atom in the above compound is



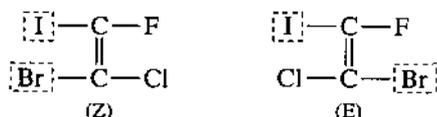
The interchange of two pairs of atoms is done so as to keep the lowest priority H-atom below the vertical line. This will retain the original configuration. The interchange is represented by the double headed arrows in the following manner :



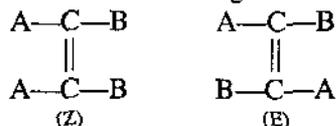
• 2.10. E, Z SYSTEM OF NOMENCLATURE OF GEOMETRICAL ISOMERS

The configuration of geometrical isomers can be represented as cis or trans. When two identical atoms or groups are on the same side of the double bond, the isomer is known as cis (Latin, *cis* = same side) and if they are on the opposite side, it is called as trans (Latin, *trans* = across). When atoms or groups attached to doubly bonded carbon atom are different, cis trans designations cannot be applied. A new system of nomenclature of geometrical isomers (E and Z) has been introduced to name such stereo isomers. This system is based on a priority system developed by Cohn, Ingold and Prelog. The symbols E and Z have been taken from the German words *Entgegen* meaning opposite and *Zusammen* meaning together. The system of nomenclature involves the following steps :

(i) The atom or group of higher priority is determined on each doubly bonded carbon atom.



(ii) If the atoms or groups of higher priority (represented by A) on each carbon atom are on the same side of the double bond, the isomer is assigned the configuration, Z. On the other hand, if the atoms or groups of higher priority on each carbon atom are on opposite sides of double bond, the isomer is assigned the configuration, E.

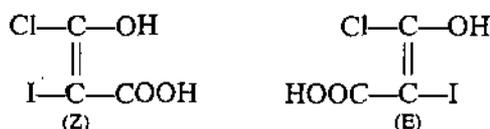


where A and B represent the atoms or groups of higher and lower priority, respectively.

(i) Consider an alkene in which doubly bonded carbon atoms are attached with the atoms F, Cl, Br and I as shown below :

Now since I (Z = 53) has higher atomic number than F (Z = 9), it is given the higher priority. Similarly, bromine (Z = 35) has higher atomic number than chlorine (Z = 17). Thus, E and Z configurations of the isomers are assigned as above.

(ii) Consider an alkene in which doubly bonded carbon atoms are attached with —Cl, —OH, —COOH and I as shown below :



For the first carbon atom Cl has higher priority than —OH group and for the second carbon atom I has higher priority than —COOH. Thus, E and Z configurations of the isomers are assigned as above.

• SUMMARY

- Compounds which have the same molecular formula but different physical and chemical properties are called **isomers** and the phenomenon is called **isomerism**.
- Isomers which have similar properties but differ in their behaviour towards polarised light are called **optical isomers** and the phenomenon is called **optical isomerism**.
- The *d*- and *l*-forms of an optically active compound which are related to each other as object to image are called **enantiomers**.
- The compounds which are not optical isomers but not the mirror images are called **diastereomers**.
- The isomerism which arises due to different geometrical arrangements of atoms or groups about doubly bonded carbon atom is called **geometrical isomerism**. The isomers are called geometrical isomers, e.g., maleic acid and fumaric acid.

• STUDENT ACTIVITY

1. State and explain optical isomerism, by taking the example of lactic acid.

2. Write a short note on racemization.

3. What are distereomers ?

4. Explain geometrical isomerism by taking the example of maleic acid and fumaric acid.

• TEST YOURSELF

Answer the following questions :

1. Explain R, S system of configuration of optical isomers with a suitable example.
2. Explain E, Z system of configuration of geometrical isomers with examples.
3. What is optical isomerism ? Explain it by taking the examples of lactic acid and tartaric acid.
4. Write a short note on enantiomers.
5. What do you understand by racemic and meso forms ?
6. Explain racemization.
7. Define diastereomers. Give example also.
8. What is geometrical isomerism ? Discuss it for maleic and fumaric acids.
9. The number of optically active isomers of lactic acid and tartaric acid are, respectively:
(a) 2, 4 (b) 2, 3 (c) 2, 2 (d) 3, 3
10. Which one of the following compounds show geometrical isomerism ?
(a) $\text{ClCH} = \text{CHBr}$ (b) $\text{CH}_2 = \text{CHBr}$ (c) $\text{Br}_2\text{C} = \text{CCl}_2$ (d) $\text{CH}_2 = \text{CHBr}_2$
11. Meso tartaric acid is optically inactive due to :
(a) Molecular symmetry (b) Molecular asymmetry
(c) External compensation (d) Two asymmetric carbon atoms
12. Fill in the blanks :
(i) Butene-2 exists in and forms.
(ii) E, Z system of nomenclature of configuration is in isomers.
(iii) A mixture of equal amounts of enantiomers is known as form.
(iv) Optically active isomers which are not mirror images are called

ANSWERS

9. (b) 10. (a) 11. (a) 12. (i) cis, trans (ii) geometrical (iii) racemic (iv) diastereomers



3

ALKYNES AND CYCLOALKANES

STRUCTURE

- Alkanes
- Cycloalkanes
- Baeyer Strain Theory
 - Summary
 - Student Activity
 - Test Yourself

LEARNING OBJECTIVES

After going this unit you will learn :

- Hydrocarbons, longest chain rule lowest sum rule and naming of side chain.
- Chain isomerism and conformational isomerism.
- General methods of preparation of alkanes, physical and chemical properties of alkanes.
- Freund's method Perkin method and Dieckmann method for preparation of cycloalkanes.
- Explanation of the relative stability of ring compounds and theory of strainless rings.

• 3.1. ALKANES

Organic compounds which contain only carbon and hydrogen are called as **hydrocarbons**. They contain two types of covalent bonds, carbon-carbon (C—C) and carbon-hydrogen (C—H). On the basis of structure, hydrocarbons may be open chain (acyclic) and closed chain (cyclic). Open chain hydrocarbons are further classified into two groups—saturated and unsaturated. The saturated hydrocarbons contain single covalent bonds between the carbon atoms, for example alkanes. Alkanes contain strong C—C and C—H covalent bonds. Therefore, this class of hydrocarbons are relatively chemically inert. Hence they are sometimes referred to as paraffins (Latin, parum affinis little affinity) The unsaturated hydrocarbons contain at least one double or triple covalent bonds between the carbon atoms, for example, alkenes (C=C) and alkynes (C≡C).

[I] IUPAC Nomenclature of Alkanes

Alkanes form a homologous series having the general formula C_nH_{2n+2} . The IUPAC name of a compound consists of two parts. The first part is prefix and second part is called as suffix. The prefix shows the longest possible chain of carbon atoms, *e.g.*,

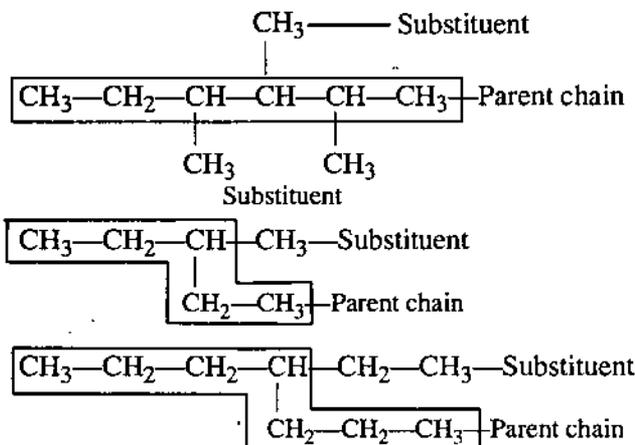
C ₁ — Meth—	C ₅ — Pent—
C ₂ — Eth—	C ₆ — Hex—
C ₃ — Prop—	C ₇ — Hept—
C ₄ — But—	C ₈ — Oct—

The suffix shows the functional group and for each functional group, there is a separate suffix. The suffix of this class of compounds is '*ane*'. Thus, IUPAC name of this class of compounds is alkane. The molecular formulae and names of some of the alkanes are :

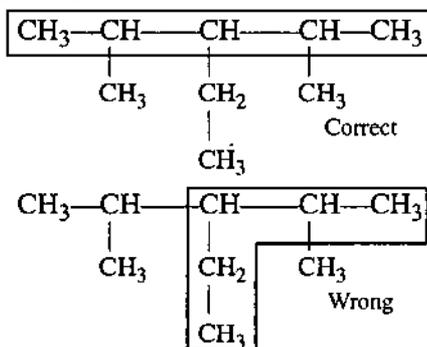
Molecular formula of the compound	Name of the compound
CH ₄	Meth + ane = Methane
C ₂ H ₆	Eth + ane = Ethane
C ₃ H ₈	Prop + ane = Propane
C ₄ H ₁₀	But + ane = Butane
C ₅ H ₁₂	Pent + ane = Pentane
C ₆ H ₁₄	Hex + ane = Hexane
C ₇ H ₁₆	Hept + ane = Heptane
C ₈ H ₁₈	Oct + ane = Octane

In addition, the following rules are used for the nomenclature of alkanes :

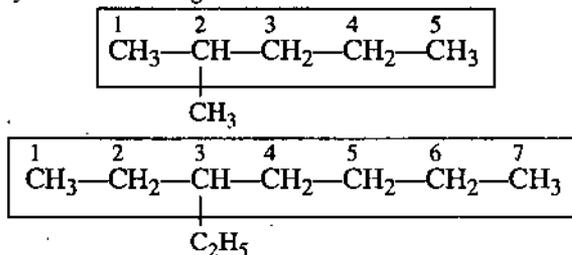
(i) **Longest chain rule :** *In the given compound, the longest continuous chain of carbon atoms is located and the compound is named as the derivative of that alkane. The continuous chain may or may not be straight. The selected chain is called as parent or main chain and it gives the name of parent hydrocarbon. The carbon atoms which are not included in the parent chain are known as side chains or substituents.*



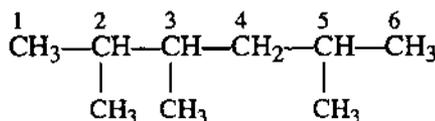
If two different chains of equal length are possible, the chain with maximum number of side chains is selected.



(ii) **Lowest number to the side chain and lowest sum rule :** *The carbon atoms of the chain are numbered from one end to the other by Arabic numbers. The numbering is done from the end which is nearest to the side chain. The positions of the side chains are indicated by the numbers given to the carbon atoms to which they are attached.*

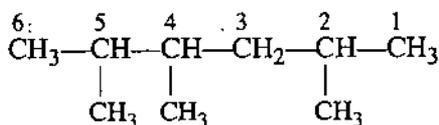


When many substituents are present, the numbering is done from the end where upon the sum of substituent positions is minimum.



$$\text{Sum of substituent positions} = 2 + 3 + 5 = 10$$

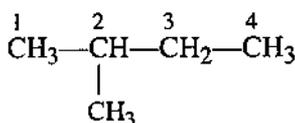
(correct)



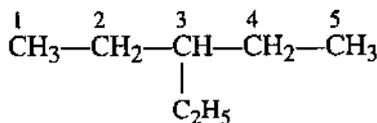
Sum of substituent positions = 2 + 4 + 5 = 11
(wrong)

(iii) Naming of substituents or side chains :

(a) When only one substituent is present in the compound : When only one substituent is present in the given compound, its name is prefixed to the name of parent alkane. The position of the substituent is also indicated by an appropriate number. This number is separated from the substituent by hyphen and no gap is left between the substituent and that of parent alkane.

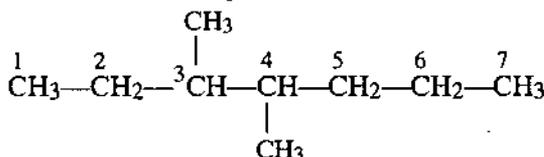


2-Methylbutane

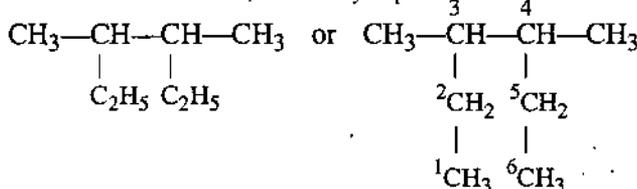


3-Ethylpentane

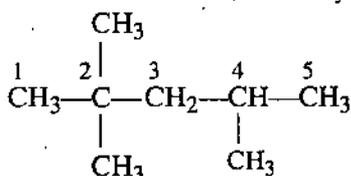
(b) When same substituent is present more than once in the compound : When same substituent is present more than once in the compound, the prefixes di, tri, tetra etc. are prefixed before the name of the substituent and their positions are written in increasing order separated by commas. For example,



3, 4-Dimethylheptane

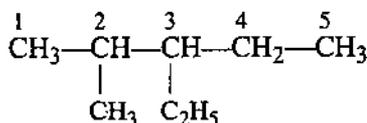


3,4-Di methyl hexane

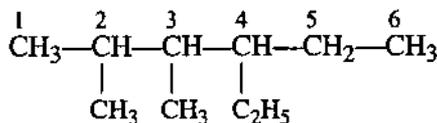


2, 2, 4-Trimethylpentane

(c) When different substituents are present in the compound : When different substituents are present in the compound, they are named in the alphabetical order along with their appropriate positions.

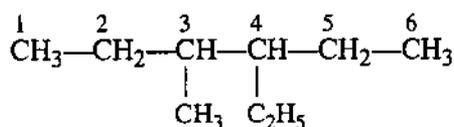


3-Ethyl-2-methylpentane



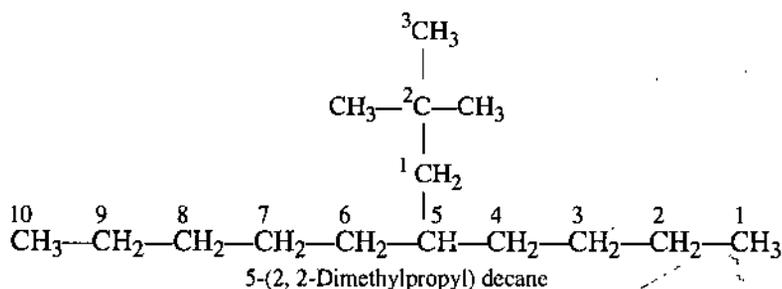
4-Ethyl-2, 3-dimethylhexane

In case different substituents are present at identical positions relative to the ends of the carbon chain, the numbering is done from the end where the alkyl group has lesser number of carbon atoms.



4-Ethyl-3-methylhexane

(d) When the substituent present itself contains branched chain : When the substituent present itself contains branched chain, it is named as substituted alkyl group. Its chain is separately numbered from the carbon atom attached to the main chain. The number representing its position in the main chain is written outside the bracket. For example,



[II] Isomerism in Alkanes

Alkanes show the following two types of isomerism :

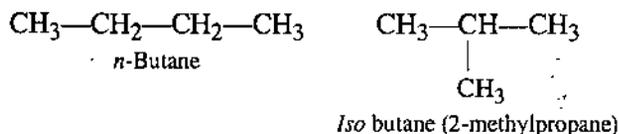
- (i) Chain isomerism
- (ii) Conformational isomerism

(i) **Chain isomerism** : This isomerism in alkanes arises due to the difference in the structure of the carbon chain which may be a straight chain or branched chain. The first three alkanes, *i.e.*, methane, ethane and propane do not show chain isomerism. The remaining alkanes show chain isomerism. The number of isomers increase with the increase in the number of carbon atoms in the homologous series as :

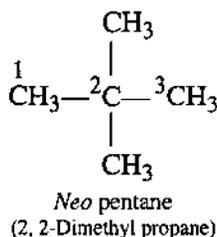
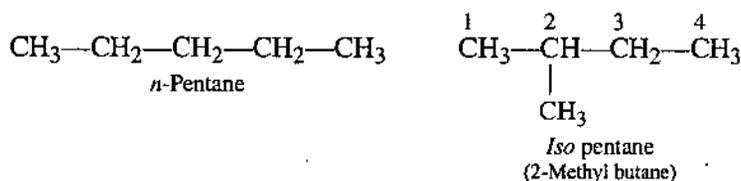
Alkane	C ₄ H ₁₀	C ₅ H ₁₂	C ₆ H ₁₄	C ₇ H ₁₆	C ₈ H ₁₈
No. of chain isomers	2	3	5	9	18

Examples :

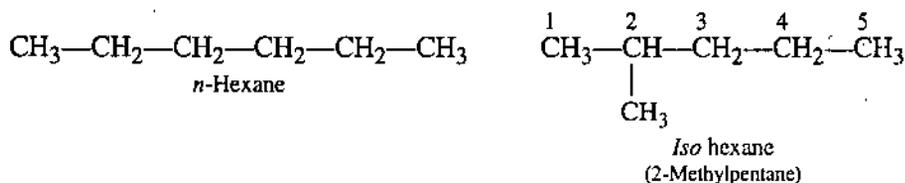
(i) C₄H₁₀ represents two chain isomers.

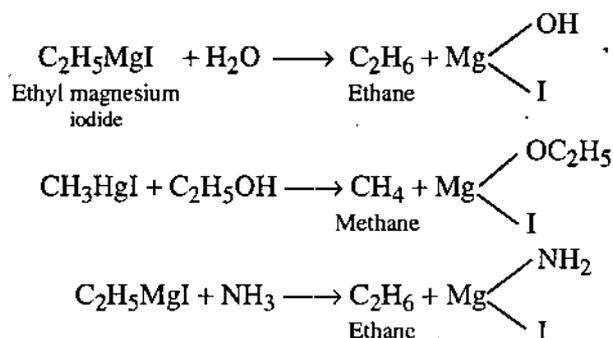


(ii) C₅H₁₂ represents three chain isomers.

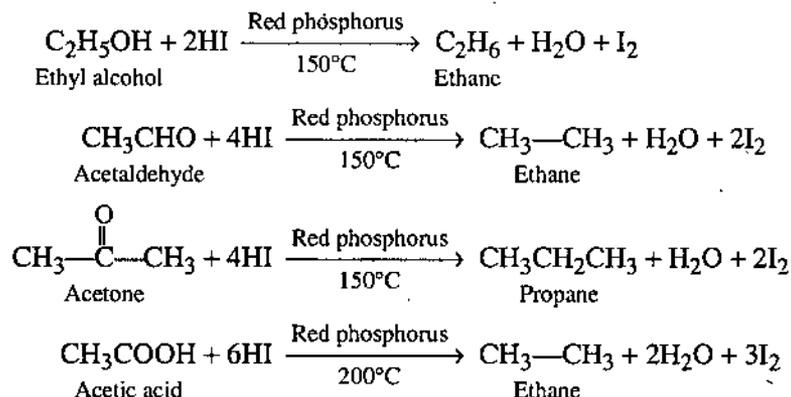


(iii) C₆H₁₄ represents five chain isomers.

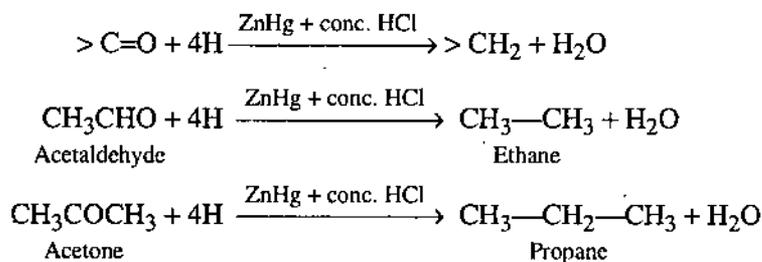




(4) By the reduction of alcohols, carbonyl compounds or fatty acids with red phosphorus and HI :

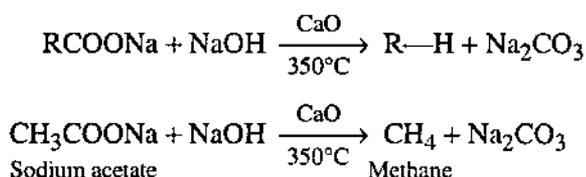


(5) By the reduction of carbonyl compounds with ZnHg and conc. HCl : The conversion of carbonyl group into methylene (>CH₂) group by the reaction with ZnHg and conc. HCl is known as **Clemmensen's reduction**.



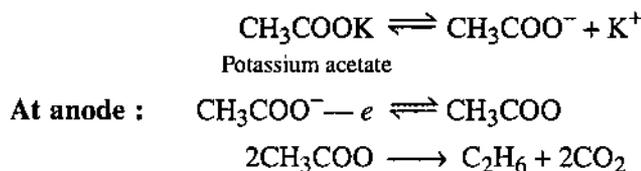
(6) From carboxylic acids :

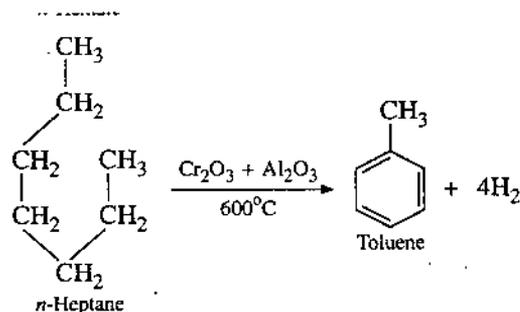
(a) *By the decarboxylation of fatty acids* : Sodium salt of a fatty acid reacts with sodalime (NaOH + CaO) at about 350°C to give alkane.



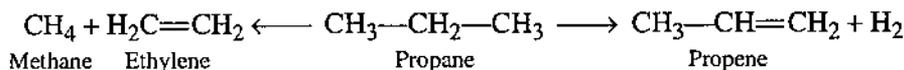
In this reaction a molecule of CO₂ is removed as carbonate from carboxylic acid and therefore, the reaction is known as **decarboxylation**.

(b) *Kolbe electrolytic method, i.e., by the electrolysis of sodium or potassium salts of fatty acids*:





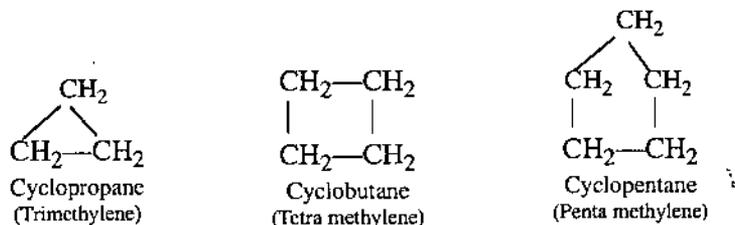
(7) **Cracking** : The thermal decomposition of alkanes in the absence of air is known as cracking. The nature of the products depends upon—(i) Temperature (ii) Pressure (iii) Catalyst (iv) Structure of alkane. For example the cracking of propane gives the following possible products :



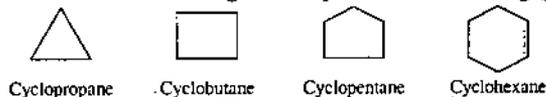
The process is particularly useful in the conversion of high boiling fractions of petroleum into low boiling gasoline.

• 3.2. CYCLOALKANES

Cycloalkanes or cycloparaffins are saturated hydrocarbons in which carbon atoms are joined by single covalent bonds to form a ring. These compounds are also called, as alicyclic compounds because of their similarity with aliphatic compounds. These compounds have the general formula C_nH_{2n} and are isomeric with alkenes. Since these compounds contain a number of methylene groups forming a closed ring, they are also called as **polymethylene compounds**. For example,

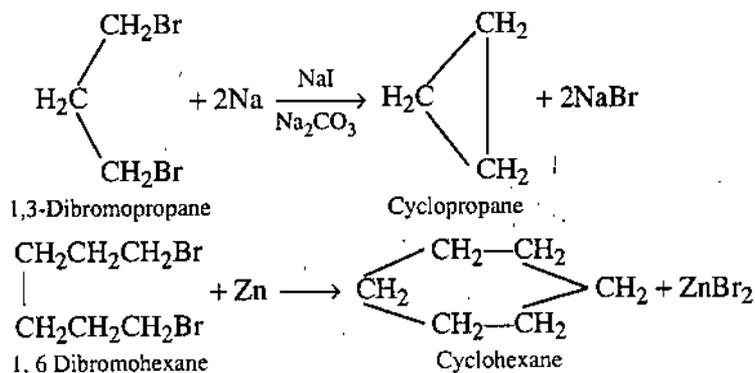


These compounds may be represented by simple geometric figures, *i.e.*, a triangle for cyclopropane, a square for cyclobutane, a pentagon for cyclopentane, a hexagon for cyclohexane etc. Each corner of these figures represents a $-\text{CH}_2$ group.

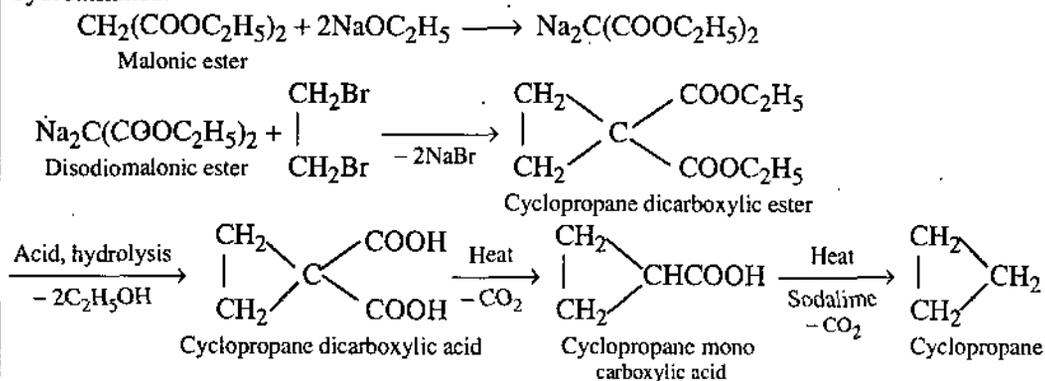


[I] General Methods of Preparation of Cycloalkanes

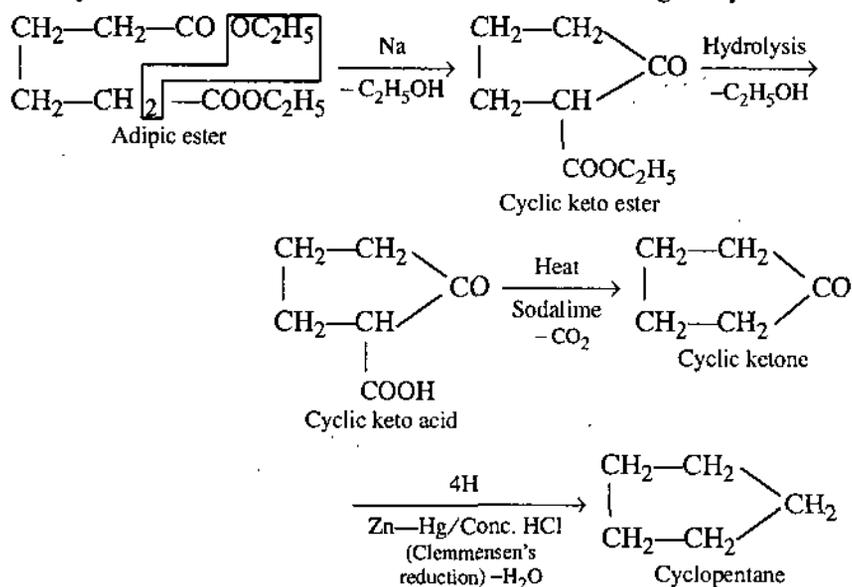
(1) **Freund's method (From ω -dihalides)** : Dichloro or dibromo alkanes having terminal halogen atoms when treated with Na or Zn in an inert solvent, *e.g.*, ether or benzene, in presence of catalyst NaI and Na_2CO_3 , produce cycloalkanes.



(2) **Perkin method** (From malonic ester) : The ω -dihalide is treated with malonic ester. Alicyclic carboxylic ester so formed is hydrolysed and decarboxylated to give cycloalkanes.



(3) **Dieckmann method** (From esters of dicarboxylic acids) : Esters of dicarboxylic acids undergo intramolecular condensation in presence of sodium or sodium alkoxides to form cyclic ketones. These on Clemmensen's reduction give cycloalkane.



[II] Physical Properties of Cycloalkanes

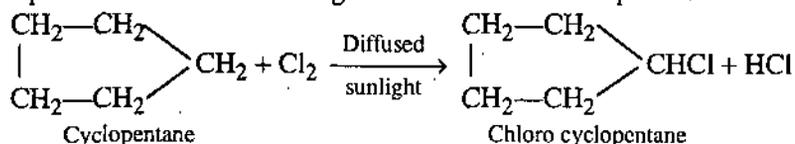
Cyclopropane is a gas, cyclobutane a liquid (b.p. 12°C). The higher members of the series are liquids, having higher boiling points and greater densities than the corresponding alkanes. They are insoluble in water but are soluble in the organic solvents like alcohol and ether.

[III] Chemical Properties of Cycloalkanes

Cycloalkanes resemble alkanes and alkenes in their chemical properties. The higher members such as cyclopentane and cyclohexane prefer to show substitution reactions like alkanes, whereas lower members such as cyclopropane and cyclobutane are less stable and show addition reactions to form open chain aliphatic compounds.

(1) Resemblance with Alkanes—Substitution Reactions :

Action with Cl_2 or Br_2 : Cyclopentane and cyclohexane react with Cl_2 or Br_2 in the presence of diffused sunlight to form substitution products.



(1) The four valencies of carbon are directed towards four corners of a regular tetrahedron. The angle between any two valency bonds is $109^{\circ}28'$.

(2) The valencies of carbon are not rigid and their directions can be changed but any such change will produce a strain and, thus, the compound will become unstable.

(3) The greater is the deviation from the normal valency angle ($109^{\circ}28'$), the greater is the strain and consequently greater is the instability of the compound.

(4) All the carbon atoms of a polymethylene ring are coplanar.

Explanation of the relative stability of ring compounds : The relative stability of different cycloalkanes can be explained by keeping in view that the greater is the deviation of valency bonds, the greater is the instability of the compounds. Baeyer calculated the angles through which each of the valency bond was deflected from its normal position in the formation of various cycloalkanes. This he called as **angle strain** which determines the relative stability of the ring compounds. For example, the C—C—C angle of cyclopropane ring is 60° because each carbon atom occupies a corner of an equilateral triangle. Thus, angle strain in cyclopropane would be $\frac{1}{2}(109^{\circ}28' - 60^{\circ}) = 24^{\circ}44'$. Similarly, the C—C—C angle of cyclobutane ring is 90° because each carbon atom occupies a corner of a square. The angle strain in cyclobutane would be $\frac{1}{2}(109^{\circ}28' - 90^{\circ}) = 9^{\circ}44'$.

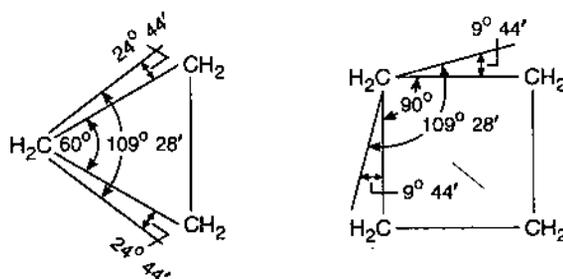


Fig. 3.3. Angle strain in cyclopropane and cyclobutane.

The following table shows the deviations from normal valency angle in different cycloalkanes. Whether the angle strain is positive or negative, its magnitude determines the extent of strain.

Name of cyclic compound	Bond angle	Angle strain
Cyclopropane,	60°	$\frac{1}{2}(109^{\circ}28' - 60^{\circ}) = +24^{\circ}44'$
Cyclobutane,	90°	$\frac{1}{2}(109^{\circ}28' - 90^{\circ}) = +9^{\circ}44'$
Cyclopentane,	108°	$\frac{1}{2}(109^{\circ}28' - 108^{\circ}) = +0^{\circ}44'$
Cyclohexane,	120°	$\frac{1}{2}(109^{\circ}28' - 120^{\circ}) = -5^{\circ}16'$

Thus, angle of strain is maximum in the case of cyclopropane and minimum in cyclopentane. On the basis of this theory, cyclopropane should be a highly strained molecule and consequently most unstable and reactive. In cyclobutane strain is less than cyclopropane and is much stable. Thus cyclobutane undergo ring open reactions only under drastic conditions. The angle strain is minimum in cyclopentane and thus does not undergo ring opening reactions.

Limitation of Baeyer Strain Theory

(1) According to this theory, cyclopentane should be more stable than cyclohexane because angle of strain is less in cyclopentane. However, observed facts are against it. Cyclopentane ring is opened on catalytic hydrogenation at 300°C but not cyclohexane.

Further, six membered ring compounds are more abundant than five membered ring compounds.

(2) This theory does not explain the stability of cyclohexane and higher members. Various natural products like muscone ($C_{16}H_{30}O$) and civetone ($C_{17}H_{30}O$) were found to be large ring compounds and were stable.

Modifications in Baeyer Strain Theory—Theory of strainless rings : Sachse suggested that rings with six or more carbon atoms are not planar but are puckered. Since carbon atoms lie in different planes, their valency bonds are not deviated from the normal valency angles and so no strain is developed in such molecules. Sachse, therefore suggested that cyclohexane exists in following two strain free forms, called as chair and boat forms.

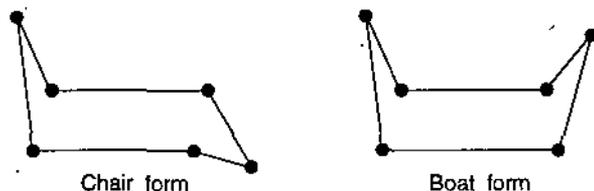


Fig. 2. Chair and boat forms of cyclohexane.

However, cyclohexane was found to exist in only one form. To explain it, Mohr (1919) suggested that these boat and chair forms continuously change into one another. Hence, they cannot be separated from each other. However, the later work by scientists clearly proved the boat and chair forms of cyclohexane. The concept of Sachse and Mohr is now known as the **theory of strainless rings**.

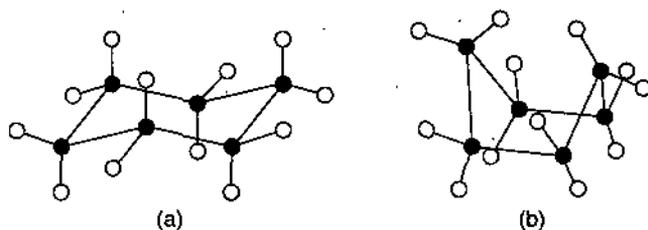


Fig. 3. Chair and boat conformations of cyclohexane.

Sachse and Mohr has given two conformations of cyclohexane showing the relative spatial disposition of hydrogen atoms in them as shown in figure. All the pairs of carbon-carbon bonds in the chair form of cyclohexane are perfectly staggered bonds, and in boat form, there are eclipsed bonds. In the chair conformation, therefore, the angle strain as well as torsional strain are absent.

The boat conformation has appreciable torsional strain and steric strain due to the crowding of C_1 and C_4 hydrogens, although it has no angle strain. The boat form should thus be much less stable than the chair form. It has been seen that the chair conformation

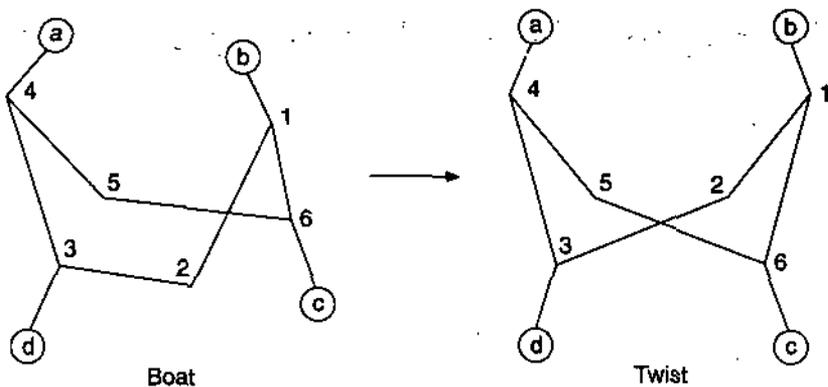


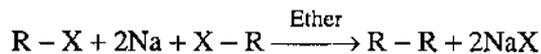
Fig. 4. Boat and twist conformations of cyclohexane.

of cyclohexane has 7.0 kcal/mole less energy (thus more stable) than the boat conformation. Besides the above conformations, cyclohexane has several other conformations as shown in Fig. 4.

This theory is also confirmed by Ruzicka, who synthesised cycloketone containing 34 carbon atoms. The stability of muscone $C_{16}H_{30}O$, civetone $C_{17}H_{30}O$ has also been explained on the basis of their multiplanar strainless ring structures.

• SUMMARY

- The general formula of alkanes is C_nH_{2n+2} .
- Only carbon and hydrogen containing compounds are called hydrocarbons.
- **Wurtz reaction** : When sodium reacts with alkyl halide in presence of ether, the reaction is called Wurtz reaction.



- The thermal decomposition of alkanes in the absence of air is known as cracking.
 - Cycloalkanes are saturated hydrocarbons in which carbon atoms are joined by single covalent bonds to form a ring.
 - Baeyer's strain theory explains the stability of higher cycloparaffins and greater reactivity of lower cycloparaffins and compounds containing double and triple bonds.
-

• STUDENT ACTIVITY

1. State and explain Baeyer's strain theory.

2. What are cycloalkanes ? Give one method of their preparation.

3. Write is chain isomerism ?

• TEST YOURSELF

Answer the following questions :

- How are alkanes prepared ? Describe their important reactions.
- Explain why alkanes are relatively unreactive ?
- What happens when ethane is treated with conc. HNO_3 at 450°C ?
- Write a note on halogenation of alkanes.
- Write a note on Wurtz reaction.
- What are cycloalkanes ? Give some examples.
- Write the preparation of cycloalkanes. Describe their important reactions.
- (a) Write a note on Baeyer's strain theory.
(b) Explain why cyclohexane is more stable than cyclopropane ?
(c) Explain why cyclobutane is more stable than cyclopropane ?
- Ethylene reacts with HI to give :
(a) Iodoethane (b) 2, 2, Diiodoethane
(c) 1, 1, diiodoethane (d) None of the above
- Which one the following reactions can be used to prepare alkanes ?
(a) Wurtz reaction (b) Wolf-Kishner reduction
(c) Kolbe's electrolysis (d) All of these
- Sodium salt of a fatty acid reacts with sodalime at about 350°C to give :
(a) alkynes (b) propane
(c) alkanes (d) none of these
- Cycloalkanes are oxidized by strong oxidising agents like conc. HNO_3 or alkaline KMnO_4 to give :
(a) tribasic acids (b) Oxalic acid
(c) carboxylic acid (d) dibasic acid
- The angle between any two valency bonds is :
(a) $24^\circ 44'$ (b) $109^\circ 28'$
(c) $9^\circ 44'$ (d) $5^\circ 16'$
- Fill in the blanks :
(i) Alkanes mainly show reactions.
(ii) The most strained cycloalkane is
(iii) The bond angle of cyclopentane is
(iv) is the molecular formula of heptane.

ANSWERS

9. (a) 10. (d) 11. (c) 12. (d) 13. (b) 14. (i) substitution (ii) cyclopropane
(iii) 108° (iv) C_7H_{16} .



4

ALKENES AND ALKYNES

STRUCTURE

- Alkenes
- Mechanism of Electrophilic Addition Reactions
- Free Radical Mechanism
- Alkynes
- Acidity of Alkanes, Alkenes and Alkynes
- Summary
- Student Activity
- Test Yourself

LEARNING OBJECTIVES

After going this unit you will learn :

- Nomenclature and isomerism of alkenes.
- General methods of preparation of alkynes; physical and chemical properties of alkenes.
- General methods of preparation of alkynes, physical and chemical properties of alkynes.

• 4.1. ALKENES

The unsaturated hydrocarbons which contain one carbon-carbon double bond, are called *olefins*. The name has emerged from olefiant (oil forming) as ethylene with chlorine forms an oily liquid, ethylene dichloride. This class has the general formula C_nH_{2n} . Ethylene, $CH_2=CH_2$ being the first member of this homologous series, the carbon-carbon double bond is, therefore, often referred to as ethylenic or olefinic double bond.

Each hydrocarbon of this homologous series has two hydrogen atoms less than the corresponding paraffin or alkane. The series is generally called as *alkylene*, *alkene* or *olefin* series.

[I] Orbital Structures

A carbon atom bonding only with three other atoms undertakes hybridisation of the s with the two p orbitals (p_x and p_y). This type of hybridisation is known as sp^2

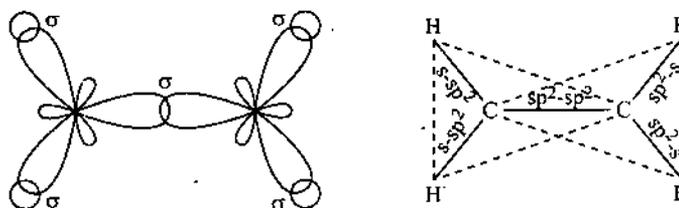
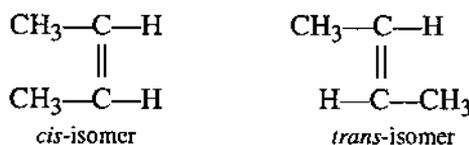


Fig. 1. Orbital picture of ethylene depicting σ -bonds only.

hybridisation. This is trigonal, *i.e.*, forms an angle of 120° with each other. The unhybridised p_z orbital with its single electron remains as such at right angles to the hybridised orbital, *e.g.*, ethylene (C_2H_4).

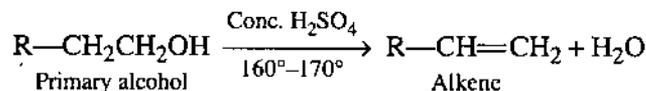
One sp^2 hybrid orbital of one carbon atom overlaps co-axially with that of another carbon atom to form a σ -MO (MO = molecular orbital) linking the two carbon atoms together. The remaining sp^2 hybrid orbitals of two different hydrogen atoms form four σ (C—H) bonds. The six atoms of an ethylene molecule thus lie on the same plane, bond

(iii) **Geometrical isomerism** : Due to the presence of double bond some alkenes also exhibit geometrical isomerism, *e.g.*, butene-2 occurs in *cis* and *trans* forms.

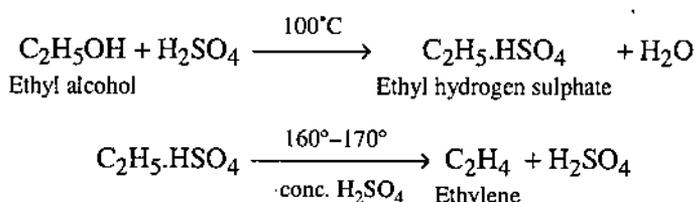


[IV] General Methods of Preparation of Alkenes

(i) **By dehydration of alcohols** : When primary alcohols are heated with conc. H_2SO_4 to $160^\circ\text{--}170^\circ\text{C}$ they lose a molecule of water forming corresponding alkene.

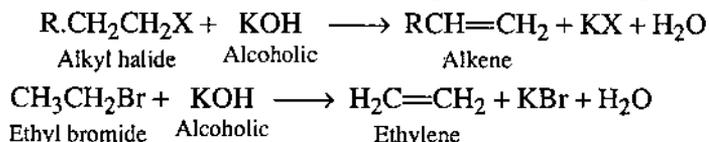


Alcohols first react with H_2SO_4 to form esters, alkyl hydrogen sulphate. These esters on heating leave a molecule of H_2SO_4 to form alkene, *e.g.*, ethyl alcohol forms ethylene.

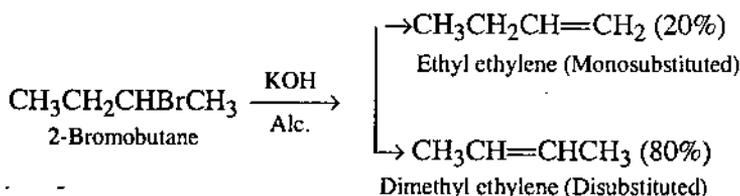


Dehydration may also be carried out, using phosphoric acid (H_3PO_4), phosphorous penta-oxide (P_2O_5), anhydrous zinc chloride (ZnCl_2) in place of conc. H_2SO_4 .

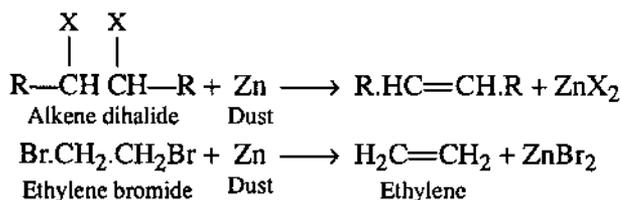
(ii) **By dehydrohalogenation of alkyl halides** : When an alkyl halide is heated with alcoholic KOH, it eliminates one molecule of hydrogen halide forming an alkene.



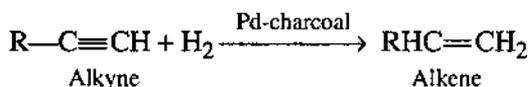
According to **Saytzeff's rule**, when two olefins are formed by dehydrohalogenation, the one which is more substituted predominates, *e.g.*,



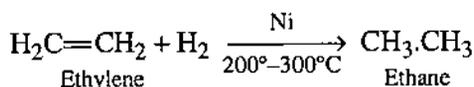
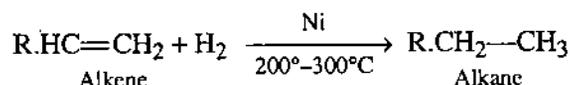
(iii) **By dehalogenation of alkene dihalides** : The method involves the heating of a methanolic solution of a dihalide with zinc dust, where two atoms of halogen from adjoining carbon atoms leave to form alkene.



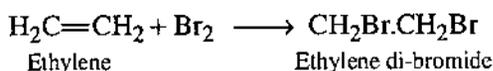
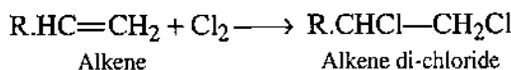
(iv) **By the partial hydrogenation of alkynes** : Partial hydrogenation of alkynes is carried out in presence of catalysts like Pd or Pt.



(a) **Addition of hydrogen** : Alkenes add on hydrogen in presence of Raney nickel (finely divided nickel) at 200°–300°C and in presence of finely divided palladium or platinum at room temperature.



(b) **Addition of halogens** : Generally, the reaction is carried out by taking the solutions of reactants in inert solvents like CCl₄, CS₂ etc. Two halogen atoms add to each double bond forming a dihalide.

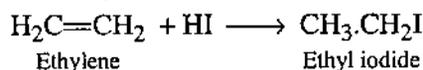


Decolorisation of 5% solution of bromine in carbon tetrachloride is used as a test for alkenes or the double bond.

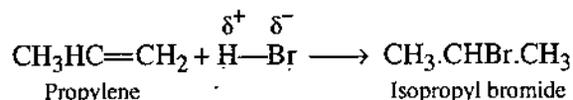
The order of reactivity amongst the halogens is :



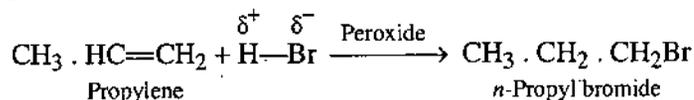
(c) **Addition of halogen acids** : Alkenes add halogen acids to form alkyl halides. The order of reactivity is HI > HBr > HCl.



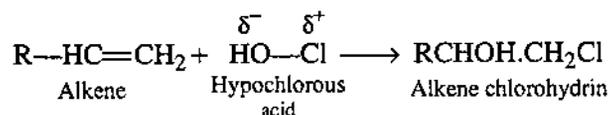
Markownikoff's rule : The rule is used to predict the reaction product of the addition of a polar molecule to an unsymmetrical olefin. It states that : *The negative part of the addendum (molecule which adds) attaches to that olefinic carbon of unsymmetrical olefin which contains the lesser number of hydrogen atoms, i.e., more substituted carbon, e.g., addition of HBr to propylene gives isopropyl bromide.*



However, when the addition of HBr is carried out in presence of a peroxide (benzoyl peroxide etc.), the addition is abnormal, i.e., anti to Markownikoff's rule, commonly referred to as **peroxide effect** or **Kharasch's effect** or **anti-Markownikoff's addition**.

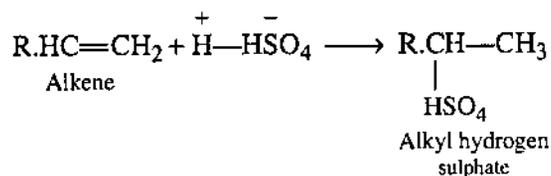


(d) **Addition of hypohalous acids** : Alkenes form alkene halohydrins with chlorine or bromine in presence of water.



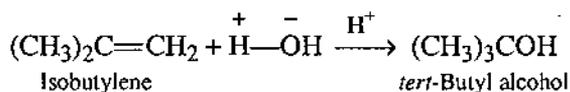
In case of unsymmetrical olefins, Markownikoff's rule is followed.

(e) **Addition of sulphuric acid** : Alkenes are absorbed by conc. H₂SO₄ to produce alkyl hydrogen sulphates.

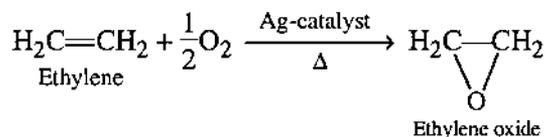


Here too, addition to unsymmetrical olefins is according to Markownikoff's rule.

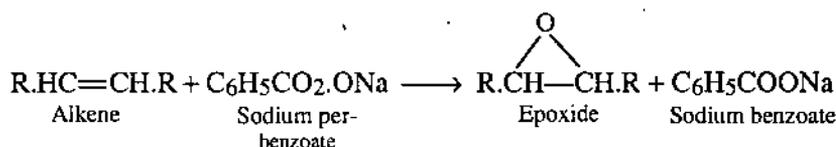
(f) **Addition of water or hydration of alkenes** : More reactive alkenes (secondary and tertiary), in presence of catalysts ($\text{H}_3\text{PO}_4/\text{SiO}_2$) or dilute acids, add on water to form alcohols, e.g., isobutylene gives *tert*-butyl alcohol in dilute acid solution.



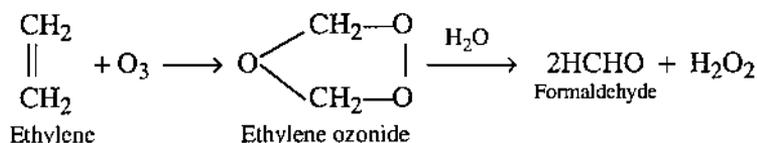
(g) **Addition of oxygen (epo-oxidation)** : Lower alkenes when mixed with air and passed under high pressure on a silver catalyst, add an atom of oxygen to give an alkene oxide or epoxide.



Epoxides are also formed when alkenes are treated with peracids (e.g., perbenzoic acid).

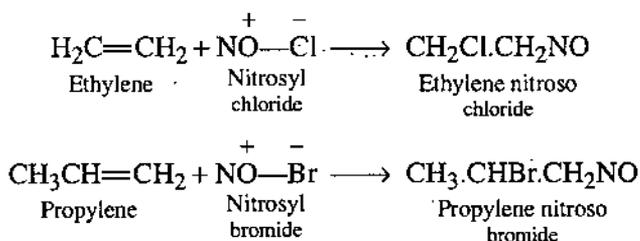


(h) **Addition of ozone** : When ozonised oxygen is passed through a solution of an alkene in organic solvents, ozonides are formed which on hydrolysis give aldehydes and ketones.



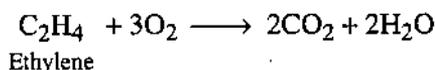
The two step process of preparing the ozonide and then hydrolysing it to get the carbonyl compound is called ozonolysis.

(i) **Addition of nitrosyl chloride or bromide** : Addition results in the formation of nitroso halides.

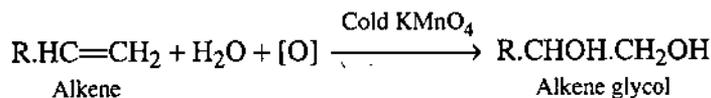


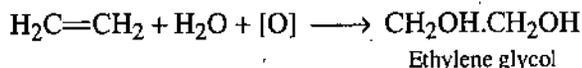
(ii) **Oxidation reactions** : Alkenes are easily oxidised, the oxidation products depend upon the nature of oxidising agent used.

(a) **Combustion** : They burn with luminous flame forming carbon dioxide and water vapours.

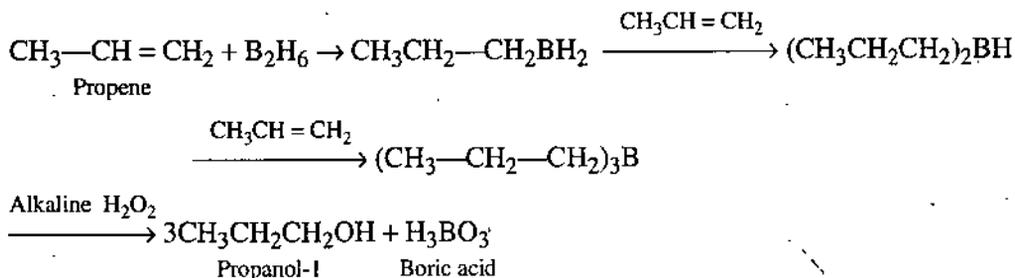


(b) **With alkaline KMnO_4** : Alkenes react with cold dilute potassium permanganate solution to form glycols. 1% Alkaline solution of KMnO_4 is known as Baeyer's reagent. It oxidises an alkene to a glycol and the permanganate solution gets decolorised. Decoloration of Baeyer's reagent is, therefore, used as a test for olefins or the double bond.

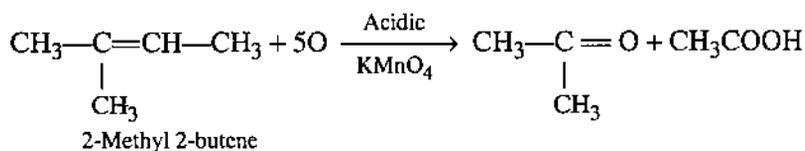
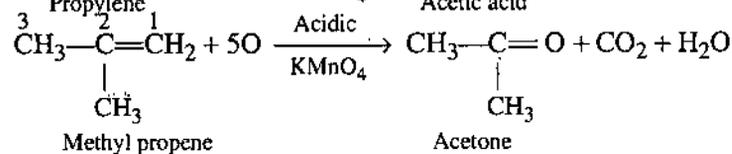
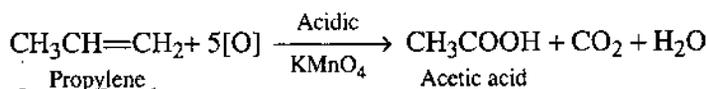
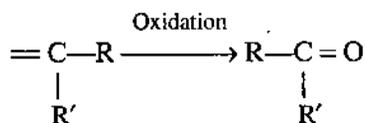
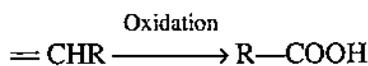
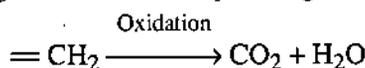




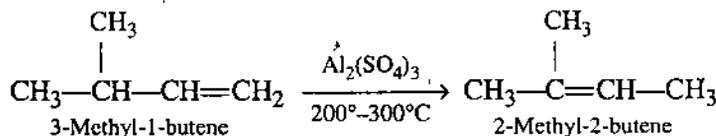
(c) **Hydroboration oxidation** : Alkenes react with diborane to form trialkyl boranes which on oxidation with alkaline H_2O_2 give alcohols.



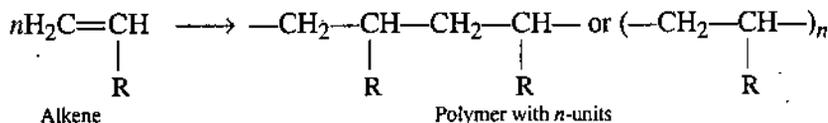
(d) **With moderate oxidising agents** : Alkenes react with mild oxidising agents which leads to breaking of double bond with the formation of aldehydes, ketones, acids and CO_2 . The oxidising agents include acid-potassium permanganate, acid-dichromate etc.



(iii) **Isomerisation** : In presence of catalyst (e.g., aluminium sulphate) or on heating to $500^\circ\text{--}700^\circ\text{C}$, isomerisation of alkene takes place.



(iv) **Polymerisation** : One of the characteristic reactions of alkenes is polymerisation in which two or more molecules of an olefin add to each other with the formation of a new compound having identical units, the new compound formed is called a *polymer*. The molecular unit which undergoes polymerisation is often referred to as a *monomer*.

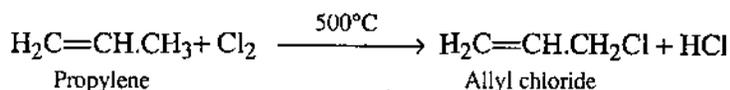
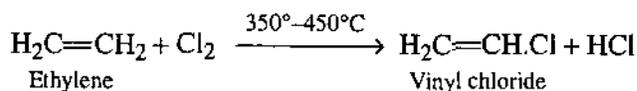


This type of polymerisation in which no atom breaks off and the alkene molecules unite together by the change in the position of double bonds is called *addition*

polymerisation. In the addition polymerisation, the polymer and the monomer have the same empirical weight but differ in molecular weights, which is normally very high in case of a polymer.

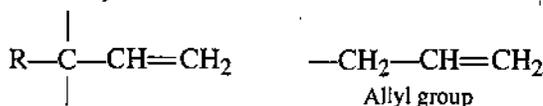
Ethylene, propylene, isobutylene and other substituted olefins polymerise to form polymers known as *plastics*, the highly useful substances.

(v) **Substitution reactions :** Under drastic conditions like high temperature or pressure, alkenes also undergo substitution reactions with chlorine or bromine. In this process, one of the allylic hydrogens is replaced by halogen atom, Allylic position is the carbon adjacent to one of the unsaturated carbon atoms. For example,



Except for ethylene, all the alkenes possess alkyl group. The carbon of the alkyl group which is directly attached to olefinic carbon is called allylic carbon.

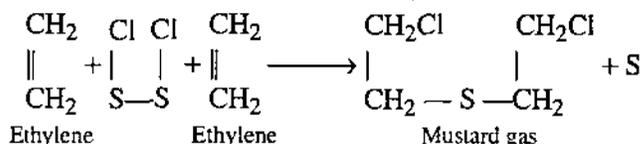
Allylic hydrogen \rightarrow H Allylic carbon



Allylic substituent \rightarrow X

Allylic halogenation proceeds through free radical mechanism.

(vi) **Action with sulphur monochloride :** Ethylene gives mustard gas



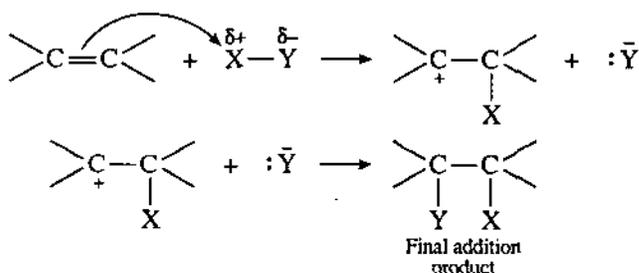
4.2. MECHANISM OF ELECTROPHILIC ADDITION REACTIONS

Addition reactions in alkenes generally proceed through ionic mechanism. In few cases, however, they may proceed through free radical mechanism.

[I] Ionic Mechanism

This is a two step mechanism. In the first step, the adding molecule (X—Y), on coming close to the π -electron, undergoes polarisation ($\text{X}^{\delta+}-\text{Y}^{\delta-}$). At the same time, the π -electron pair undergoes electromeric displacement and migrates to one of the π -bonded carbon atoms, from where it attacks the electrophilic end ($\text{X}^{\delta+}$) of the adding molecule.

This attack brings about the union of the electrophilic end to the olefinic carbon atom to which the π -electron pair had migrated, forming a carbonium ion (the product of electrophilic addition). Simultaneously, the nucleophilic portion ($:\text{Y}^-$) of the



nucleophile ($:\text{Y}^-$) is bonded to the positively charged carbon atom of the carbonium ion to produce the final compound.

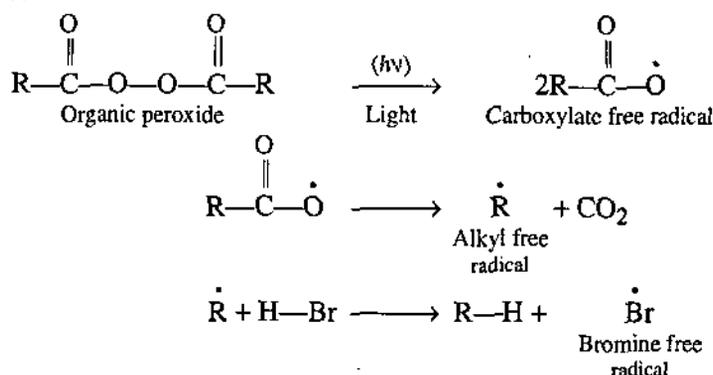
(i) **Addition of symmetrical reagents, like halogens :** In the addition of bromine, which is a symmetrical reagent, the adding bromine molecule is polarised ($\text{Br}^{\delta+}-\text{Br}^{\delta-}$) on its approach to the π -electron pair of the olefin. The π -electron pair then attacks the positive

This explains Markownikoff's rule according to which, in an addition of an unsymmetrical molecule to an unsymmetrical olefin, the negative part of the adding molecule is added to the more substituted olefinic carbon atom, i.e., the one having lesser number of hydrogen atoms.

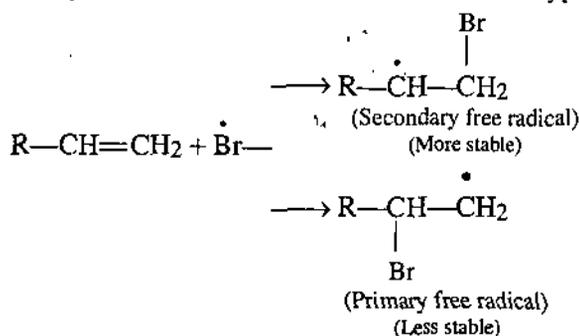
• 4.3. FREE RADICAL MECHANISM

Under certain conditions, such as the presence of organic peroxides (R—O—O—R), a homolytic breaking of the adding molecules takes place. When such a breaking occurs in case of H—Br, the addition proceeds through free radical mechanism. Addition of H—Br in unsymmetrical olefin such as propene normally proceeds through ionic mechanism according to Markownikoff's rule, but because of the homolytic breaking of H—Br due to the presence of organic peroxide, the reaction proceeds through free radical mechanism forming *n*-propyl bromide instead of isopropyl bromide. This is thus against the Markownikoff's rule. Such an effect of organic peroxides on the course of addition of H—Br is called *Kharasch peroxide effect*. It is illustrated as below :

(i) Initiation :

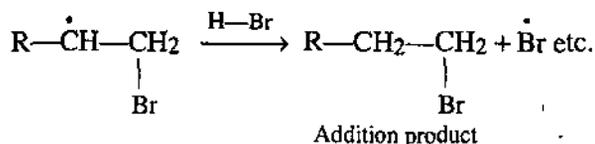


(ii) Propagation by addition : Bromine free radical now attacks the π -electrons of the olefin and may lead to the formation of two different types of free radicals.

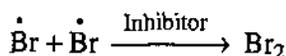


Since due to hyperconjugation, the secondary free radical is more stabilised than the primary free radical, the former is preferentially formed in the above step of the addition reaction.

Propagation further continues to finally produce the addition compound as shown below :



(iii) Termination :



• 4.4. ALKYNES

The first member of alkynes is acetylene hence the name of the series is given as acetylene series. The general molecular formula of this homologous series is $\text{C}_n\text{H}_{2n-2}$.

The members of this homologous series has two hydrogen atoms less than the corresponding member of olefin series. All members of this series have at least one triple bond. Alkadienes or dienes are isomeric with alkynes.

[I] Nomenclature of Alkynes

There are two main systems of nomenclature.

(i) **Trivial system** : Higher members of this series in this system, are named as the alkyl derivatives of acetylene.

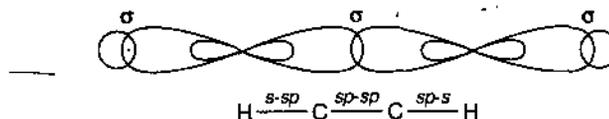
(ii) **IUPAC system** : The members of this series are named after the corresponding alkane by changing the suffix 'ane' into 'yne', hence in general they are called 'alkynes'. The rules of numbering the carbon atoms are the same as for alkenes.

The trivial and IUPAC names alongwith the formulae of few members are given below :

Formula	Corresponding paraffin	Trivial name	IUPAC name
$\text{CH}\equiv\text{CH}$	Ethane (C_2H_6)	Acetylene	Ethyne
$\text{CH}_3-\text{C}\equiv\text{CH}$	Propane (C_3H_8)	Methylacetylene	Propyne
$\text{CH}_3\text{C}\equiv\text{CCH}_3$	Butane (C_4H_{10})	Dimethylacetylene	Butyne-2
$\text{CH}_3\text{CH}_2\text{C}\equiv\text{CH}$	Butane (C_4H_{10})	Ethylacetylene	Butyne-1
$\text{CH}_3\text{CH}_2\text{CH}_2\text{C}\equiv\text{CH}$	Pentane (C_5H_{12})	<i>n</i> -Propylacetylene	Pentyne-1
$\begin{array}{c} \text{CH}_3\text{CH}-\text{C}\equiv\text{CH} \\ \\ \text{CH}_3 \end{array}$	Pentane (C_5H_{12})	Isopropylacetylene	3-Methyl butyne-1
$\text{CH}_3\text{CH}_2\text{C}\equiv\text{C}\cdot\text{CH}_3$	Pentane (C_5H_{12})	Ethylmethylacetylene	Pentyne-2

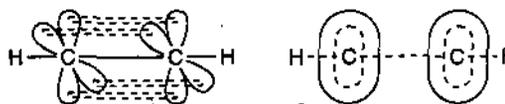
[II] Orbital Structure of Acetylene

(iii) ***sp*-hybridisation** : The mixing of an *s* and *p*-orbitals only leads to two co-linear hybrid orbitals known as *sp* hybrid orbitals. This process is called ***sp*-hybridisation**. This gives an angle of 180° . The remaining two *2p* (say $2p_y$, $2p_z$) orbitals are left undisturbed and lie perpendicular to each other, e.g., acetylene (C_2H_2).



Orbital picture of acetylene depicting σ -bonds only.

One *sp* hybrid orbital of carbon atom overlaps co-axially with that of another carbon atom to form a sigma ($\text{C}-\text{C}$) bond. The remaining 1 *sp* hybrid orbital of each of the two carbon atoms overlap with one *s*-orbital of two different hydrogen atoms to form two sigma ($\text{C}-\text{H}$) bonds. The $2p_y$ and $2p_z$ orbitals perpendicular to each other are thus left on each of the carbon atom. Thus, these form two π -bonds by sidewise overlapping and the four lobes of the two π -bonds merge to form a single electron cloud which is symmetrical (cylindrically) about the inter-nuclear axis (fig. 4.7). The π -bonds formed by relatively poorer sideways overlapping of *2p*-orbitals would be weaker than the σ -bond formed by the efficient overlapping of *sp-sp* orbitals.



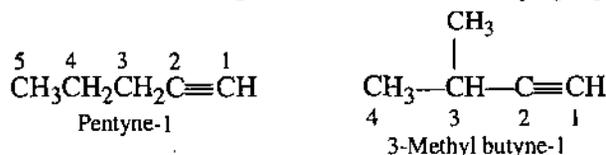
Orbital picture of acetylene depicting the formation of π -bonds.

The structure of $\text{C}\equiv\text{C}$ triple bond in higher alkynes is similar to that mentioned above in the case of acetylene.

[III] Isomerism in Alkynes

Alkynes exhibit the following three types of isomerism :

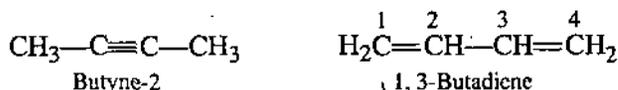
(i) **Chain isomerism** : Alkynes with same molecular formula may differ in the structures of their chains, e.g., molecular formula C_5H_8 represents :



(ii) **Position isomerism** : When alkynes possess same molecular formula but differ in the positions of triple bond, e.g., molecular formula C_4H_6 represents two alkynes. They are :

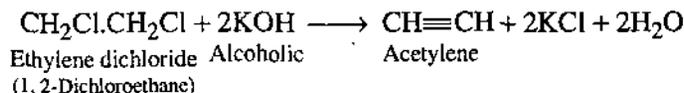


(iii) **Functional isomerism** : Alkynes show functional isomerism with alkenes, e.g.,

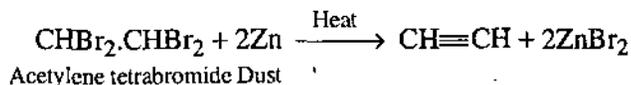


[IV] General Methods of Preparation of Alkynes

(i) **By dehydrohalogenation of alkene dihalides** : When alkene dihalides are heated with alcoholic caustic potash, alkynes are formed.

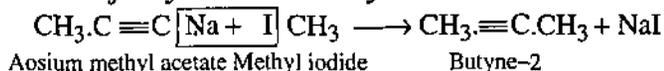


(ii) **By dehalogenation of tetrahalides** : Tetrahalides in which the halogen atoms are attached to adjacent carbon atoms (two on each C) form alkynes when heated with zinc dust.

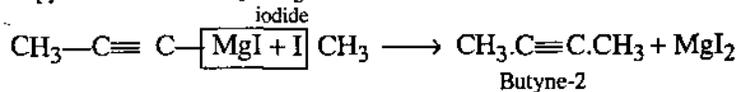
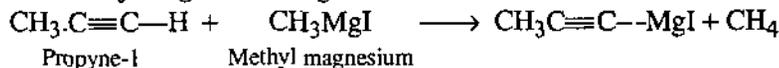


(iii) **By the alkylation of lower homologues** : Higher homologues of alkynes are obtained from lower homologues by the following methods.

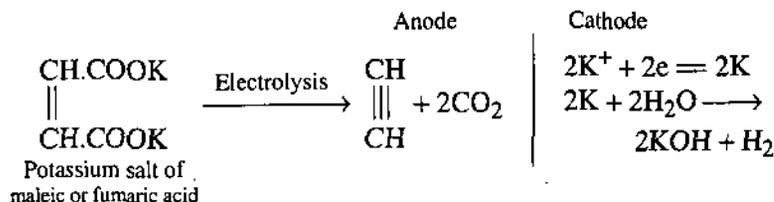
(a) **By the action of alkyl halides on alkynides.**



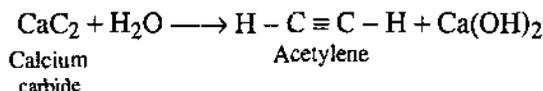
(b) **By the action of Grignard's reagents.**



(iv) **By Kolbe's electrolysis method** : The method involves the electrolysis of a concentrated aqueous solution of sodium or potassium salts of unsaturated dicarboxylic acids.



(v) **By the action of water on calcium carbide** : Calcium carbide reacts with water to give acetylene.



[V] General Physical Properties of Alkynes

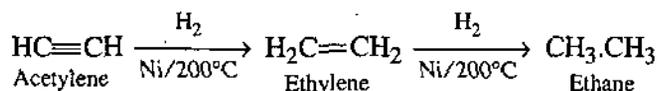
First three members are gases, the next eight are liquids and the rest are solids. All are colourless and odourless except for acetylene which possesses garlic odour due to the presence of impurities like phosphine in particular. They are almost insoluble in water but are readily soluble in organic solvents like alcohol, acetone, benzene etc. Lower members are somewhat poisonous and when inhaled cause unconsciousness.

[VI] General Chemical Properties of Alkynes

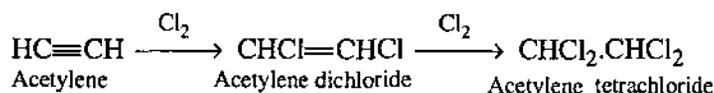
Among the alkynes, a triple bond is present which is made up of one σ and two π -bonds. It is because of these π -bonds that alkynes give addition reactions like alkenes. The mechanism of addition is the same as in alkenes, however, alkynes are more reactive than alkenes. As the first member of this series is acetylene, all the reactions are written taking acetylene as the example.

(1) Addition Reactions :

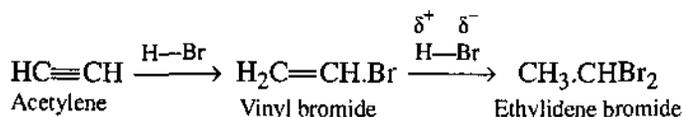
(a) **Addition of hydrogen :** Alkynes also add on hydrogen in presence of Raney nickel at $200^\circ\text{--}300^\circ\text{C}$ and in presence of finely divided palladium or platinum at room temperature. First two hydrogen atoms add to form alkenes and finally two more hydrogen atoms add to give alkanes, e.g.,



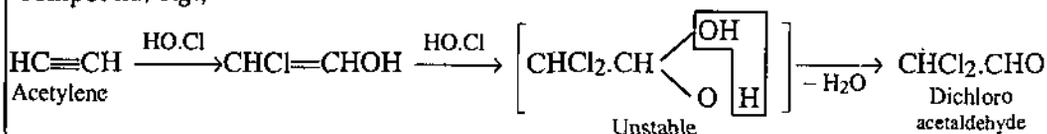
(b) **Addition of halogens :** Like hydrogen, halogens also add two atoms at a time forming first dihalides and finally tetrahalides.



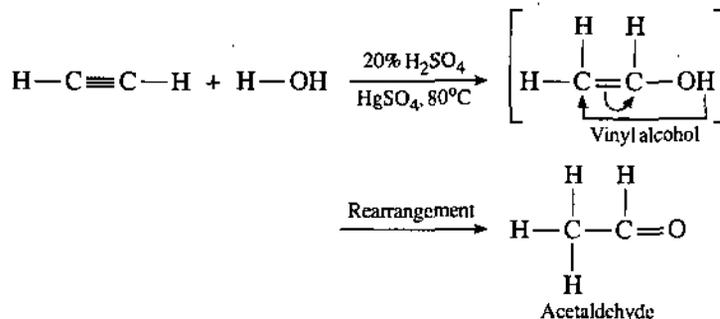
(c) **Addition of halogen acids :** First, molecule of halogen acid adds to form vinyl halide. The addition of second molecule of halogen acid follows Markownikoff's rule to form ethylidene halides.



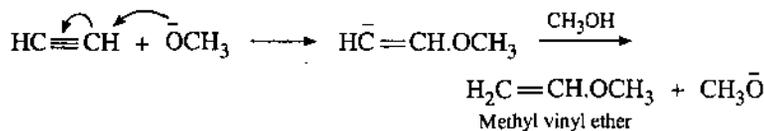
(d) **Addition of hypochlorous acid :** Again the two molecules of hypochlorous acid add with the formation of an unstable compound (with two $-\text{OH}$ groups attached to the same carbon) resulting into the loss of water molecule and formation of a carbonyl compound, e.g.,



(e) **Addition of water :** When an alkyne is passed through a dilute (20%) solution of H_2SO_4 at 80°C in presence of HgSO_4 as catalyst, addition of one molecule of water takes place resulting into the formation of a carbonyl compound.



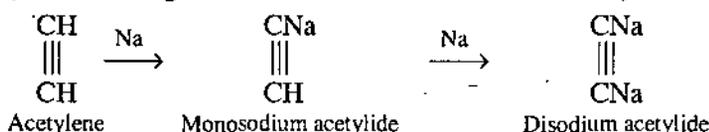
alkynes also add alcohols to form unsaturated ethers, the mechanism of the addition is believed to be nucleophilic, *i.e.*, a nucleophile adds first, *e.g.*, when acetylene is passed into methanol at 200°C in presence of potassium methoxide and under high pressure, methyl vinyl ether is obtained. The mechanism of the reaction is :



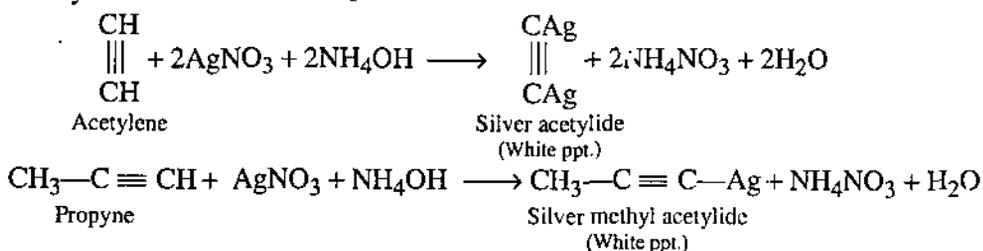
The reaction is often referred to as *vinylation*.

(5) Substitution Reactions : The hydrogen atoms of acetylene are acidic in nature, hence they are substituted by metals forming salts known as **acetylides**.

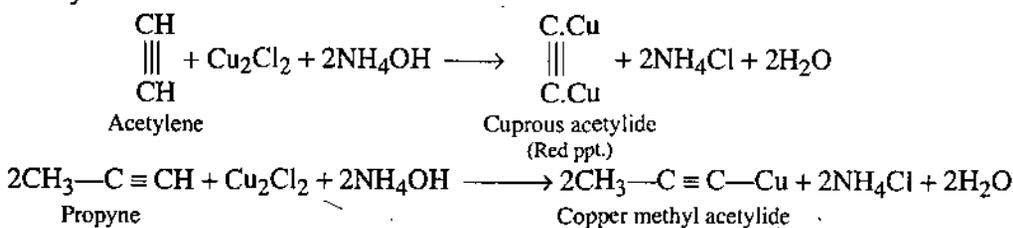
(a) When acetylene is passed over heated sodium, the hydrogen atoms are replaced one by one forming both monosodium and disodium acetylides.



(b) Acetylene and propyne when passed into an ammoniacal solution of silver nitrate (*Tollen's reagent*) gives a white precipitate of silver acetylide and silver methyl acetylide, respectively.

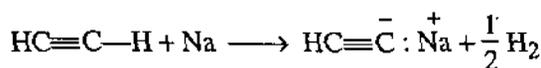


(c) Similarly, acetylene and propyne on passing into an ammoniacal solution of cuprous chloride gives a red precipitate of cuprous acetylide and copper methyl acetylide, respectively.

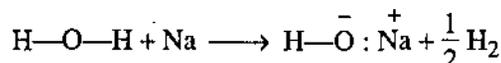


• 4.5. ACIDITY OF ALKANES, ALKENES AND ALKYNES

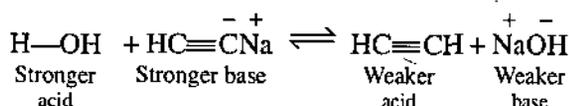
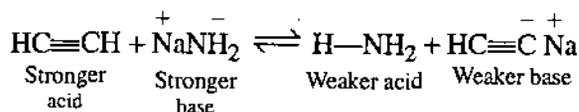
Acetylene reacts with sodium to form sodium acetylide and hydrogen gas.



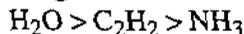
This is similar to the reaction of sodium with water.



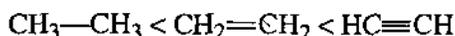
This suggests that hydrogen in acetylene is acidic in nature. It is known that a weaker acid is displaced from its salt by a stronger acid. While C_2H_2 displaces NH_3 from its salt sodamide (NaNH_2), water displaces acetylene from its salt sodium acetylide.



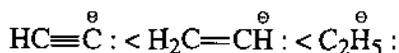
So, acetylene is a stronger acid than ammonia but weaker acid than water, *i.e.*,



Relative acidities of ethane, ethylene and acetylene : The increasing order of acidities of these hydrocarbons is :



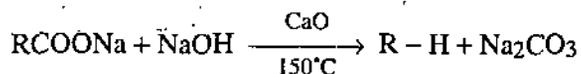
Conversely, the increasing order of basicities of anions resulting from these hydrocarbons is:



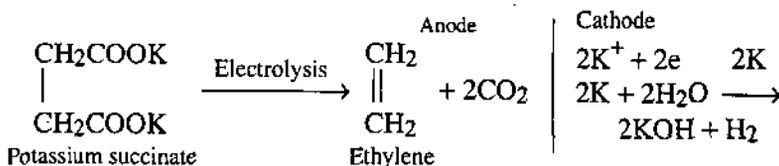
In $\text{HC}\equiv\overset{\ominus}{\text{C}} :$, $\text{CH}_2=\overset{\ominus}{\text{C}}\text{H}$ and $\text{C}_2\text{H}_5\overset{\ominus}{\text{C}} :$, the unshared pair of electrons occupies an sp , sp^2 and sp^3 orbital, respectively. As we move along sp , sp^2 and sp^3 series, the p -character of the hybrid orbital increases and the s -character decreases. An electron in an s -orbital is closer to the nucleus and is held more tightly. But an electron in a p -orbital is farther from the nucleus and is held less tightly. So, the electron pair in $\text{C}_2\text{H}_5\overset{\ominus}{\text{C}} :$ should be held most loosely and in $\text{HC}\equiv\overset{\ominus}{\text{C}}$ should be held most tightly. Therefore, the electron pair in $\text{C}_2\text{H}_5\overset{\ominus}{\text{C}}$ should be most available, while in $\text{HC}\equiv\overset{\ominus}{\text{C}}$ should be least available, for protonation. Thus, in the above series, the carbanion $\text{C}_2\text{H}_5\overset{\ominus}{\text{C}}$ should be the strongest base and $\text{HC}\equiv\overset{\ominus}{\text{C}}$ should be the weakest base. Conversely, acetylene should be most acidic, while ethane should be least acidic.

• SUMMARY

- Alkanes, alkenes and alkynes have the general $\text{C}_n\text{H}_{2n+2}$, C_nH_{2n} and $\text{C}_n\text{H}_{2n-2}$, respectively.
- Alkanes are obtained by the decarboxylation of fatty acids in presence of sodalime at 150°C .



- Kolbe's method :** The electrolysis of aqueous sodium or potassium salt solutions of saturated dicarboxylic acids to form an alkene is called Kolbe's method.



- Markownikoff's rule :** When an unsymmetrical reagent adds to an unsymmetrical double bond, the positive part of the reagent becomes attached to the double-bonded carbon atom which bears the greatest number of hydrogen atom.

- 1% alkaline solution of KMnO_4 is called **Baeyer's reagent**. Decolouration of Baeyer's reagent is a test for the presence of double or triple bond in an organic compound.
- Acetylene on ozonolysis (reaction with O_3) followed by hydrolysis gives glyoxal.

• STUDENT ACTIVITY

1. Write a note on Wurtz reaction.

2. State and explain Markownikoff's rule.

3. Write a short note on ionic mechanism.

• TEST YOURSELF

Answer the following questions :

1. How are alkenes prepared ? Describe their important reactions.
2. How is ethylene prepared in laboratory ? What happens when ethylene reacts with Br_2/CCl_4 , dil. H_2SO_4 , dilute cold KMnO_4 , conc. H_2SO_4 , O_3 and then $\text{Zn}/\text{H}_2\text{O}$.
3. Write a note on Markownikoff's rule.
4. Write a note on ozonolysis.
5. How are alkynes prepared ? Describe their important reactions.
6. What happens when acetylene is passed through ammoniacal silver nitrate solution ?
7. What happens when acetylene is passed through ammoniacal cuprous chloride solution?
8. Write a note on acidity of acetylene.
9. How will you distinguish between acetylene and ethylene ?
10. Acetylene reacts with water in presence of sulphuric acid and mercuric sulphate to give :
 (a) Acetone (b) Acetic acid (c) HCHO (d) CH_3CHO
11. When acetylene is passed through hot iron tube at 400°C , it gives :
 (a) Benzene (b) Toluene (c) Ethylene (d) Ethane

12. Baeyer's reagent is :
(a) dil. KMnO_4 (b) $\text{HCl} + \text{ZnCl}_2$ (c) Br_2 in CCl_4 (d) NH_2NH_2
13. Which is the correct order of reactivity amongst the halogens ?
(a) Iodine > Bromine < Chlorine (b) Chlorine > Iodine > Bromine
(c) Chlorine > Bromine > Iodine (d) none of these
14. Addition of ozone and hydrolysis together are called :
(a) ozonolysis (b) polymerisation
(c) isomerism (d) hybridisation
15. Fill in the blanks :
(i) In CCl_4 , the alkenes are soluble.
(ii) Butane gives a test with Baeyer's reagent.
(iii) Ozonolysis of acetylene gives
(iv) Vinyl cyanide is used in the manufacture of

ANSWERS

9. With ammoniacal AgNO_3 and cuprous chloride, acetylene gives silver mirror and red precipitate, respectively, while ethylene does not give these tests.
10. (d) 11. (a) 12. (a) 13. (c) 14. (a) 15. (i) most/highly (ii) negative (iii) glyoxal
(iv) buna-N



ARENES AND AROMATICITY

STRUCTURE

- Distinction between Aromatic and Aliphatic Hydrocarbons
- Aromaticity
- Huckel's (4n + 2) Rule
- Aromatic sextet
- Delocalisation
- Aromatic Substitution
- Orientation
- Mechanism of Electrophilic Aromatic Substitution
- Aromatic Hydrocarbons or Arenes
- Nomenclature of Benzene Derivatives
- Benzene
- Homologues of Benzene
- Xylenes
- Friedel-Crafts Reaction
 - Summary
 - Student's Activity
 - Test Yourself

LEARNING OBJECTIVES

After going this unit you will learn :

- Aromaticity, anti-aromaticity and anti-aromatic compounds.
- Cum-Brown Gibson's rule, Vorlander's rule and Hammett-illingworth's rule.
- Methods of orientation : Korner's absolute method, relative and physical methods.
- Aromatic substitutions : electrophilic, nucleophilic and free radical.
- Aryl groups aralkyl groups, Kekule's structure and orbital diagram of benzene.
- Toluene and xylene with their properties and uses.
- Formation of hydrocarbons, ketones, acid chlorides and acid amides.

4.1. DISTINCTION BETWEEN AROMATIC AND ALIPHATIC HYDROCARBONS

The distinction between aromatic and aliphatic hydrocarbons is given in the following table:

Aromatic hydrocarbons	Aliphatic hydrocarbons
1. Closed chain compounds.	1. Open chain compounds.
2. Colourless liquids or solids.	2. A few lower members are colourless gases.
3. Contain high percentage of carbon hence burn with smoky flame.	3. Contain low percentage of carbon, hence burn with non-smoky flame.
4. Except benzene, all oxidise easily.	4. Alkanes do not oxidise easily, while unsaturated hydrocarbons oxidise easily.
5. Characteristic aromatic odour.	5. No such characteristic odour.
6. Undergo electrophilic substitution reactions, e.g., halogenation, nitration, sulphonation, Friedel Craft reaction etc.	6. Do not give electrophilic substitution reactions easily.
7. Hydroxy derivatives, i.e., phenols are acidic.	7. Hydroxy derivatives, i.e., alcohols are neutral.

4.2. AROMATICITY

Aromatic compounds apparently are cyclic compounds and contain alternate single and double bonds. Although they have a high degree of unsaturation, yet they do not give the normal tests of unsaturated compounds, e.g., Baeyer's test, bromine test etc. They, generally, do not show addition reactions but they prefer to show electrophilic substitution

reactions such as nitration, halogenation, sulphonation and Friedel-Craft reaction. These compounds are very stable as is indicated by their low heat of combustion and hydrogenation. Thus, their properties are quite different from those of aliphatic and alicyclic compounds.

This unique behaviour is called as *aromaticity* or *aromatic character*. In fact aromaticity is a property of sp^2 hybridized planar rings in which p -orbitals (one on each atom) allow cyclic delocalization of π -electrons.

Conditions for Aromaticity

- (i) An aromatic compound is cyclic and planar.
- (ii) Each atom of the aromatic ring should contain p -orbital which must be parallel so that a continuous overlap is possible around the ring. Thus, each carbon atom is in sp^2 hybridized state.
- (iii) The cyclic π -molecular orbital formed by the overlapping of p -orbitals must contain $(4n + 2)$ π -electrons, where n is an integer, e.g., 0, 1, 2, 3 etc. This is known as Huckel's rule.

• 4.3. HUCKEL'S $(4n + 2)$ RULE

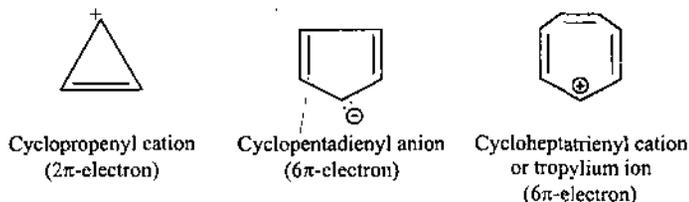
According to Huckel's rule, a cyclic compound which has $(4n + 2)$ π -electrons (where, n is an integer) should be markedly stable typical of benzenoid aromatics.

The cyclic compounds with $(4n)$ π -electrons should be even less stable than their open-chain analogues. So, cyclic compounds with $(4n)$ π -electrons are known as **anti-aromatic compounds**, and this quality is known as **anti-aromaticity**.

Evidence in Support of Huckel's Rule

(1) Benzene which is a cyclic compound having a cloud of six delocalised π electrons, is in accordance with Huckel's $(4n + 2)\pi$ rule (where $n = 1$ and 6 is a Huckel number).

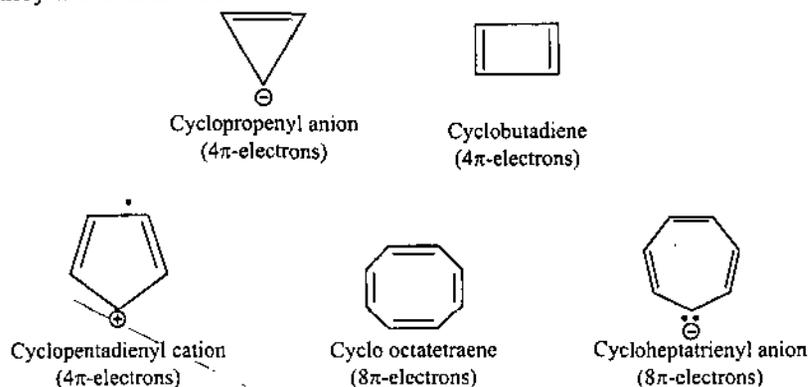
(2) Non-benzenoids as shown below also show the aromatic character, since they have a cyclic structure with 2 or 6 (both are Huckel numbers) π -electrons.



(3) Hydrocarbons like naphthalene, anthracene, etc., are *cyclic compounds* containing 10, 14, etc. π -electrons (all Huckel numbers). They should also exhibit aromatic character which they actually do.

(4) Heterocyclic compounds like furan, thiophene, pyrrole, pyridine etc., are cyclic compounds containing six π -electrons. These compounds should exhibit aromatic character which they actually do.

(5) Cyclic systems of compounds such as cyclopropenyl anion, cyclobutadiene, and cyclopentadienyl cation, cyclo octatetraene and cycloheptatrienyl anion contain 4 or 8 π -electrons. Since they follow $(4n)$ π -rule, they should not show aromatic character. Actually, they are non-aromatics.



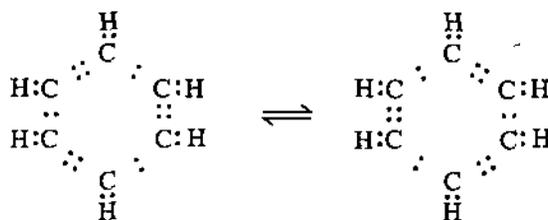
It may be noted that the Huckel number 6 is the most common number observed in aromatic systems or compounds. So, the term aromatic sextet is commonly used for these six π -electrons. Aromatic compounds (e.g., tropylium bromide C_7H_7Br ; dicyclopentadienyl iron $[(C_5H_5)^-]_2 Fe^{++}$, etc.), which contain no benzene ring are referred to as **non-benzenoid aromatic compounds**, to distinguish them from **benzenoid aromatic compounds** containing at least one benzene ring.

Benzene, which is a flat molecule with six carbons provides the *aromatic sextet* and bond angles which exactly match the trigonal angle of 120° . It is thus a 'perfect' aromatic compound. Other aromatic compounds with Huckel numbers 2, 10, 14, etc. no doubt have stability characteristics of aromatic systems, but their rings are too small or too large to accommodate perfectly the trigonally hybridised atoms. The stability of these non-benzenoid aromatics is reduced by angle strain and/or poor overlap of *p*-orbitals. It is, thus important to note that the stability of an aromatic compound or system is not always of the same order. Therefore,

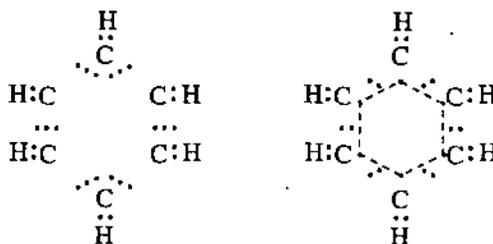
"An aromatic compound is not only a cyclic compound containing clouds of delocalised π -electrons above and below the plane of the molecule, but it must also have a π cloud containing a total of $(4n + 2)$ π -electrons." The presence of a benzene ring is not an absolute condition for a compound to show aromaticity or aromatic behaviour.

• 4.4. AROMATIC SEXTET

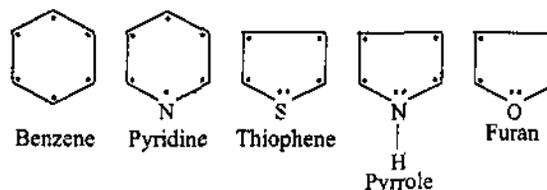
On the basis of electronic theory, the Kekule's structures of benzene can be represented as :



According to J.J. Thomson, the C—C bond in benzene molecule depicted by a three electron bond is as follows :

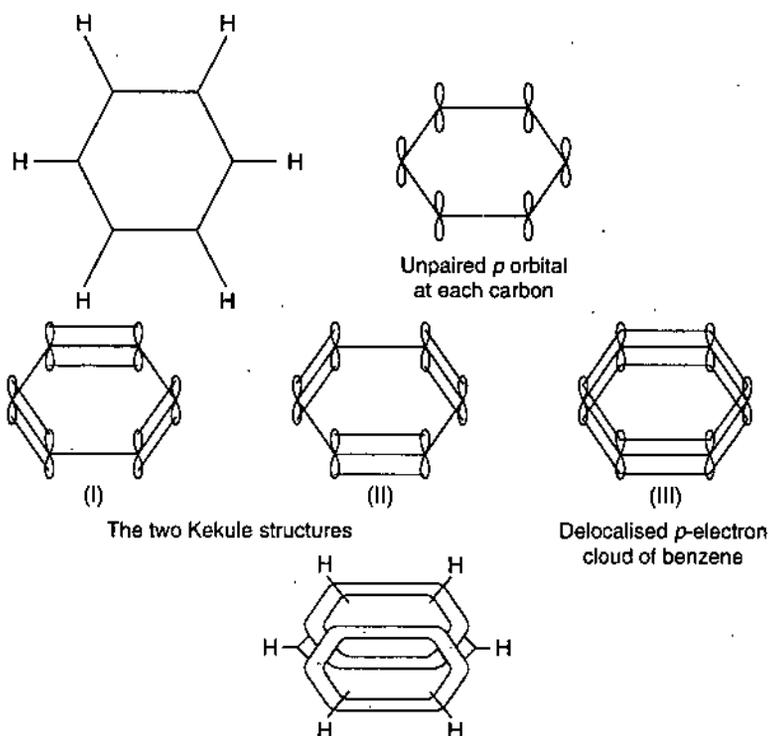
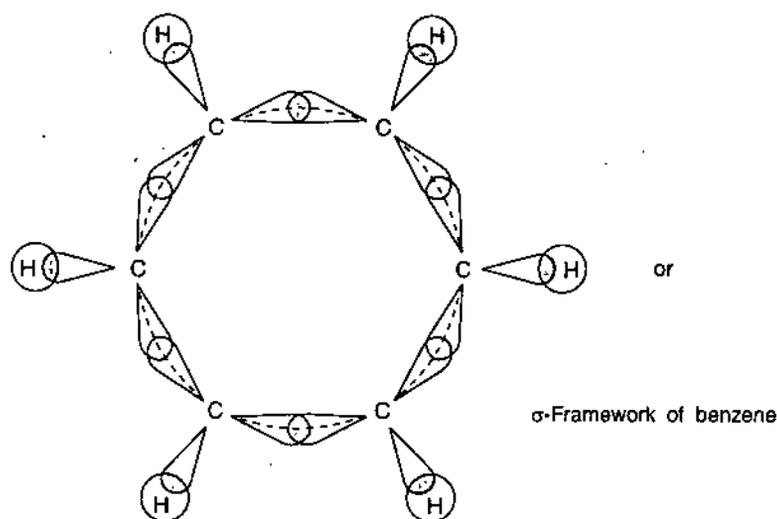


However, Ingold (1928) and Huckel (1931) suggested that each C—C bond in benzene molecule can be represented by 2 electrons and the remaining 6 electrons (1 electron on each carbon atom) form a sextet, known as **aromatic sextet**. The aromatic properties in the molecule are due to the presence of this aromatic sextet. Therefore, due to aromatic sextet, heterocyclic compounds like pyridine, thiophene, pyrrole, furan etc. exhibit aromatic properties.



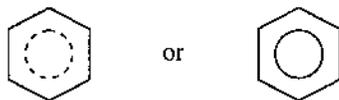
• 4.5. DELOCALISATION

Consider the benzene molecule. Usually, a carbon involved in the double bond formation is in sp^2 hybridized state, as found in Kekule's structure of benzene. The three



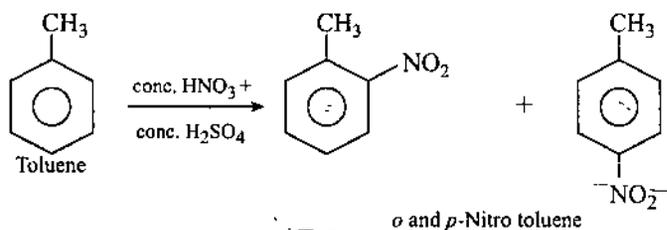
hybrid orbitals of each such carbon atom are in the same plane and form two σ bonds with two other such carbons on either side by coaxial overlap of hybrid orbitals and on σ bond with s -orbital of hydrogen. The usual valency angle among the sp^2 hybrid orbitals is 120° which is also the observed bond angle in benzene. This gives rise to a total of 12 σ bonds and carbon skeleton acquires a hexagonal shape with all the C and H atoms in the same plane. At each of the sp^2 hybridised carbon atoms there is still an unhybridised p -orbital that lies perpendicular to the plane of the three hybrid orbitals. The sidewise or parallel overlap of these p -orbitals with those on adjacent carbon atoms results in the formation of π bonds as shown in two Kekule's structures shown above. Since p -orbital at any carbon atom can overlap with either of the p -orbitals on the carbon at its left or right and the probability of both types of overlapping being equal, this results in the continuous **overlapping** or **delocalisation** as shown in structure III. This leads to the formation of two continuous or delocalised π -electron clouds; one above and the other below the plane of the hexagon of 6 carbon atoms—sandwiching the hexagon between them. The six π electrons are delocalised over all the six carbon atoms and the molecular orbital is polycentric. The energy of these six delocalised π -electrons is less than those pairs of localised or isolated π -electrons and so the molecule is stabilised. **The difference of energy due to which the molecule is stabilised is known as delocalisation energy.**

Since the π -electrons are delocalised and form electron clouds on either side of the plane of carbon atoms, benzene will thus act as a source of electrons. To show the delocalisation of 6π -electrons benzene is represented by drawing a dotted or continuous inscribed circle as shown below.

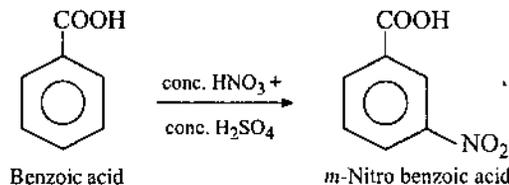


• 4.6. AROMATIC SUBSTITUTION

When a mono substituted derivative of benzene is converted into a di-substituted derivative, the product is either a mixture of ortho and para derivatives or it is a meta derivative. Thus, when toluene is nitrated, the $-\text{NO}_2$ group enters the ortho and para positions and a mixture of ortho and para nitro toluenes is obtained.



But when benzoic acid is nitrated, the $-\text{NO}_2$ group enters in the meta position and *m*-nitro benzoic acid is obtained.



From the above, it is clear that the group already present in the benzene ring is responsible for the position taken by incoming group. This is known as *directive influence of groups in aromatic substitution*.

It has also been observed that *o*- and *p*-directive groups possess activating effect on the substituent reactions, whereas meta directive groups deactivate the whole ring so that further substitution becomes difficult.

Certain empirical rules have been given to explain the nature of the groups already present in the ring. These are :

(1) **Cum-Brown-Gibson's rule (1892)** : According to this rule, "If the substituent *X* already present in the benzene ring forms a compound *HX* with hydrogen which can be directly oxidised to *HXO*, then *X* is *meta*-directing group, otherwise it is *ortho* and *para* directing."

Group X	HX	HXO	Oxidation	Directive influence
$-\text{CH}_3$	CH_4	CH_3OH	Difficult	<i>o</i> -, <i>p</i> -
$-\text{OH}$	H_2O	H_2O_2	Difficult	<i>o</i> -, <i>p</i> -
$-\text{NH}_2$	NH_3	NH_2OH	Difficult	<i>o</i> -, <i>p</i> -
$-\text{NO}_2$	HNO_2	HNO_3	Easy	<i>m</i> -
$-\text{COOH}$	H.COOH	H_2CO_3	Easy	<i>m</i> -
$-\text{SO}_3\text{H}$	H_2SO_3	H_2SO_4	Easy	<i>m</i> -
$-\text{Cl}$	HCl	HOCl	Difficult	<i>o</i> -, <i>p</i> -
$-\text{CHO}$	HCHO	HCOOH	Easy	<i>m</i> -

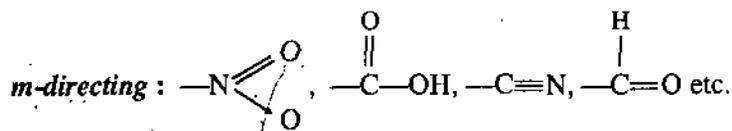
Objections : The main objection against the rule was that the word 'direct oxidation' was vague. For example, $-\text{CN}$ forms HCN which is oxidised to HCNO but not easily and so it should be *o*-, *p*-directing but actually it is *m*-directing. This rule is

silent about the orientation of a trisubstituted product formed from a disubstituted product containing two different groups. This rule also does not give the proportions of ortho and para-isomers.

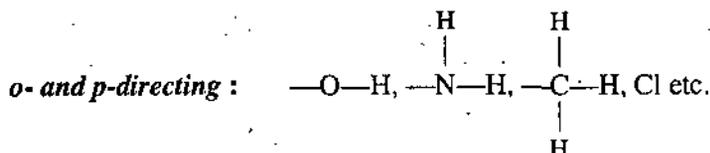
(2) **Vorlander's rule (1902)** : According to this rule,

Unsaturated groups are meta directing, whereas saturated groups are ortho and para directing.

(i) **Unsaturated groups** :



(ii) **Saturated groups or atoms** :



Objections : This rule had exceptions, e.g., in cinnamic acid $\text{C}_6\text{H}_5\text{CH}=\text{CH}.\text{COOH}$, the group $-\text{CH}=\text{CH}.\text{COOH}$ is unsaturated but it is *o*-, *p*-directing.

(3) **Hammett-illingworth's rule (1930)** : According to this rule, in the benzene derivative $\text{C}_6\text{H}_5\text{XY}$,

(a) If Y belongs to a higher group in the periodic table than X, the group already present is meta directing.

(b) If Y belongs to a lower group in the periodic table than X, the group already present is ortho and para directing.

(c) If X and Y belong to the same group in the periodic table and Y has lower atomic weight than X, the group already present is meta directing.

(d) If there is no Y, the group already present is ortho and para directing.

Group	X and its group	Y and its group	Directive influence
$-\text{NO}_2$	N (Group V)	O (Group VI)	<i>m</i> -directing
$-\text{NH}_2$	N (Group V)	H (Group I)	<i>o</i> -, <i>p</i> -directing
$-\text{CH}_3$	C (Group IV)	H (Group I)	<i>o</i> -, <i>p</i> -directing
$-\text{CN}$	C (Group IV)	N (Group V)	<i>m</i> -directing
$-\text{OH}$	O (Group VI)	H (Group I)	<i>o</i> -, <i>p</i> -directing
$-\text{COOH}$	C (Group IV)	O (Group VI)	<i>m</i> -directing
$-\text{SO}_3\text{H}$	S (Group VI)	O (Group VI)	<i>m</i> -directing
Cl	Cl (At. wt. = 32)	O (At. wt. = 16)	<i>o</i> -, <i>p</i> -directing

(4) **Modern view** : According to modern view, the directive influence and the activating or deactivating effect of substituents on the benzene ring can be accounted for in terms of the mechanism of aromatic substitution and electron displacement effect of the substituent already present.

Introduction of a Third Substituent into the Benzene Ring

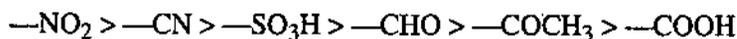
When a third group enters the benzene ring, its position is ascertained by the nature of the two substituents already present in it.

(a) If the two substituents already present have the same directive influence, then directive influence will be in the following order.

o- and *p*-directing substituents :



m-directing substituents :

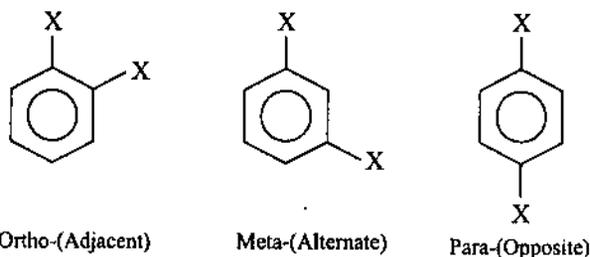


(b) When the two substituents already present have different directive influence, then the influence of *o*- and *p*-directing groups predominates. In case the influence of the two substituents reinforces each other, the third substituent will enter almost entirely in reinforced position.

• 4.7. ORIENTATION

The process by which the positions of two different substituents with respect to each other in the unknown benzene derivative are determined is known as orientation.

For di-substitution products, there are three different positions, viz., ortho (*o*-), meta (*m*-) and para (*p*-), as shown below :



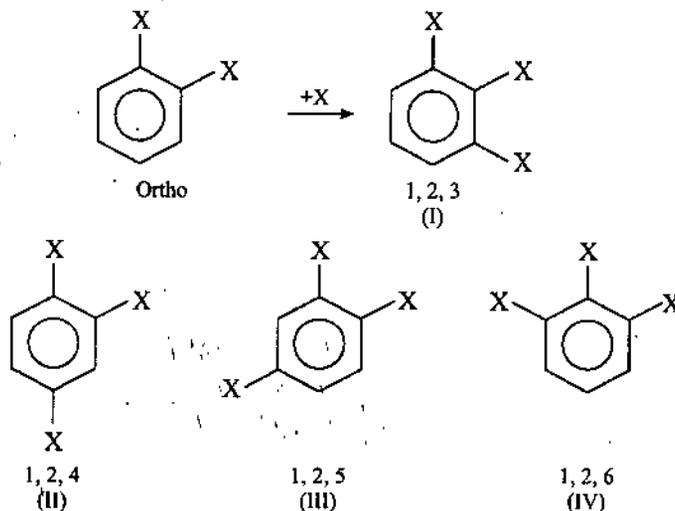
Methods of Orientation

There are three methods for finding orientation :

- (a) Korner's absolute method (b) Relative method
(c) Physical methods.

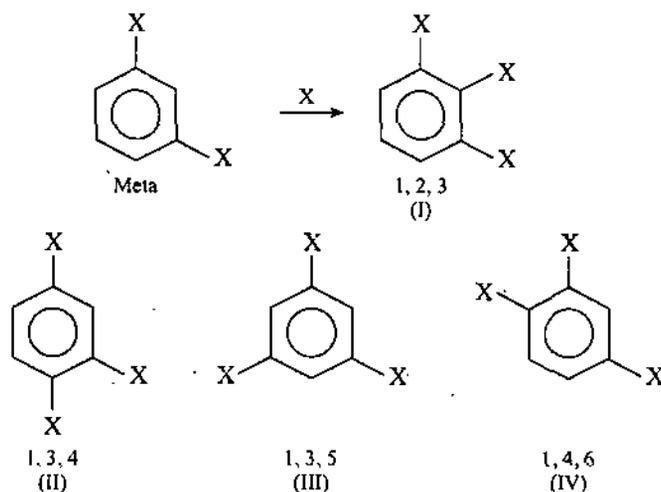
(1) **Korner's absolute method (1874)** : In this method, the given disubstitution compound is converted into the *tri*-substitution product. From the number of *tri*-substitution products formed, it is possible to say whether the original di-substitution compound is *ortho*-, *meta*- or *para*.

(i) With an *ortho* compound, the possible *tri*-substitution products are :



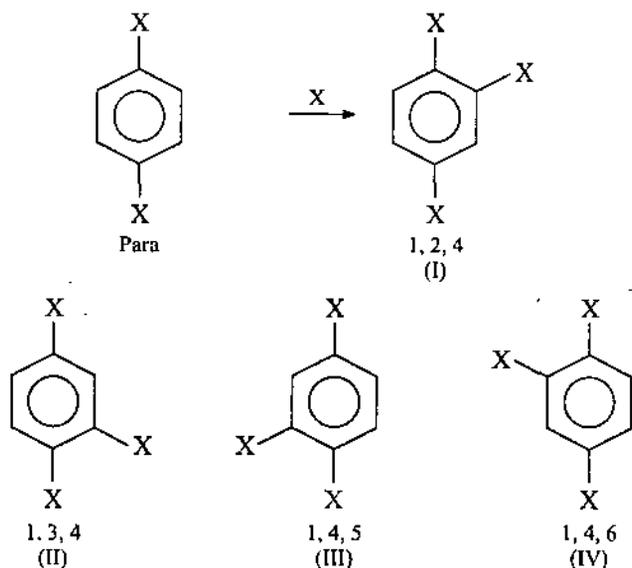
I and IV are similar and II and III are similar. So, there are only two di-substitution products formed by the *ortho*-compound.

(ii) With a *meta*-compound, the possible *tri*-substitution products are :



II and IV are similar. So, the meta-compound gives three different *tri*-substitution products.

(iii) With a para-compound, the possible *tri*-substitution products are :



Here, all the four products are similar. So, a para-compound gives only one *tri*-substitution product. Therefore,

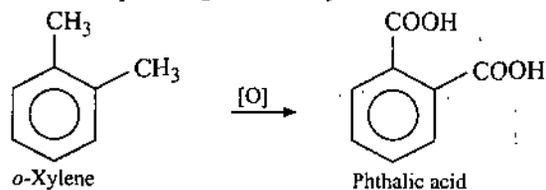
(i) If two *tri*-substitution products are formed, the original compound is *ortho*.

(ii) If three *tri*-substitution products are formed, the original compound is *meta*.

(iii) If only one *tri*-substitution product is formed, the original compound is *para*.

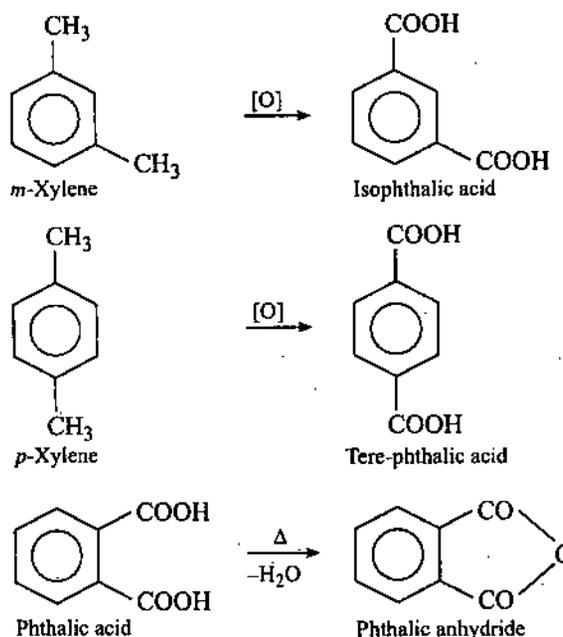
(2) Relative method : In this method, the relative position of the substituents in any unknown compound is determined indirectly by studying its properties. Alternately, the compound under study is converted into or synthesised from another compound of previously known orientation.

For example, there are three xylenes, viz., *o*-xylene, *m*-xylene and *p*-xylene. On oxidation, they form the corresponding dicarboxylic acids as follows :

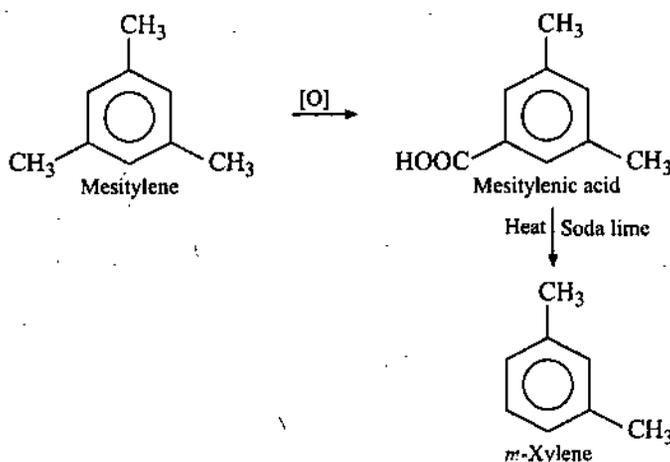


On strong heating, phthalic acid gives only anhydride, but not the other two.

(i) So, that particular xylene which on oxidation and heating gives anhydride, must be *o*-xylene.



(ii) *m*-Xylene can be obtained from an other compound called mesitylene, whose structure is known as follows :

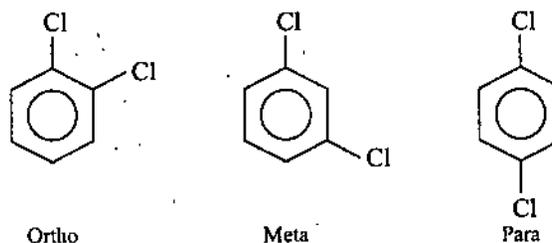


So, that xylene which resembles the xylene obtained from mesitylene, must be *m*-xylene.

(iii) The remaining xylene must automatically be *p*-xylene.

(3) **Physical methods** : At present, the position of different substituents on the benzene ring can be easily ascertained by physical methods, *e.g.*, dipole moment, IR spectrum, nuclear magnetic resonance etc.

In certain cases, where the two substituents are either atoms or simple groups, measurement of dipole moment of the compound helps in orientation. For example, the observed dipole moment of C—Cl bond (in chlorobenzene) is 1.55 D. By using this value,



we can calculate the dipole moments of three chlorobenzenes (*o*-, *m*- and *p*-). By comparing the calculated values with the observed ones, we can decide the orientation of the given dichlorobenzene.

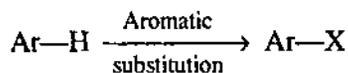
Dipole moment—

Calculated : 2.68 D 1.55 D 0.0 D

Observed : 2.32 D 1.48 D 0.0 D

• 4.8. MECHANISM OF ELECTROPHILIC AROMATIC SUBSTITUTION

The most important characteristic reactions of aromatic hydrocarbons are those in which the hydrogen of the aromatic ring is substituted by an atom or group X.



There are three possible ways of aromatic substitution :

(i) Electrophilic (S_E)

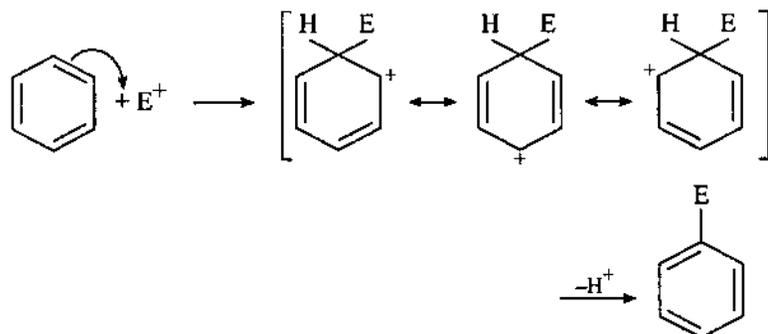
(ii) Nucleophilic (S_N)

(iii) Free radical (S_R)

Benzene ring contains 6π -electrons in a delocalised state, therefore, it serves as a source of π -electrons. Therefore, benzene readily undergoes electrophilic substitution, *i.e.*, it easily reacts with electron deficient substituents, *i.e.*, electrophiles (E^+).

[I] General Mechanism of Electrophilic Substitution

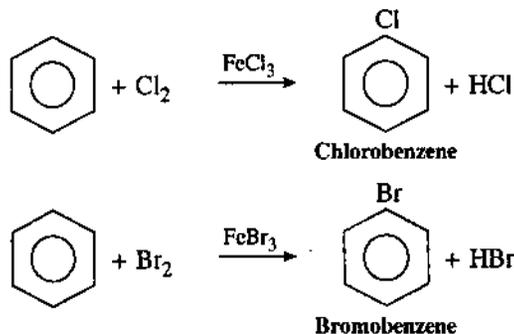
The benzene ring with its π -electrons behaves as an electron rich system. The electrons in the π -clouds are readily available to form new bonds with electron deficient species, the electrophile (E^+). Electrophilic substitution in benzene ring is believed to be a bimolecular (S_E^2) reaction, involving the formation of an unstable intermediate carbonium ion, which in presence of a proton acceptor, say HSO_4^- , etc., readily loses a proton forming the stable substitution product.



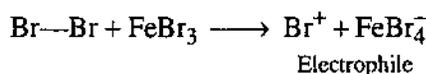
[where, E^+ is an electrophile and may be X^+ (Cl^+ , Br^+ or I^+) in halogenation, SO_3H^+ or SO_3 in sulphonation, NO_2^+ in nitration and R^+ and R.CO^+ in Friedel-Crafts reaction].

[II] Electrophilic Substitution Reactions of Aromatic Hydrocarbons

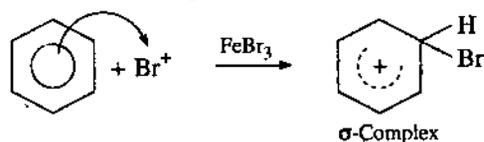
(1) **Halogenation :** (a) Benzene reacts with chlorine or bromine in presence of AlCl_3 , FeCl_3 or FeBr_3 (Lewis acid) as catalyst. The substitution in the ring occurs and a proton is lost as HCl or HBr .



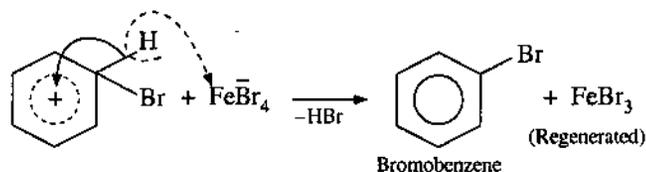
Mechanism : (i) Generation of the electrophile Br^+ .



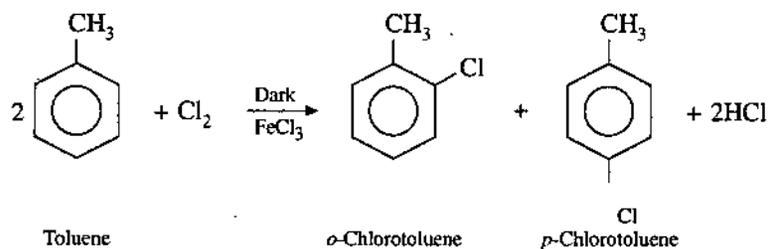
(ii) Formation of σ -complex.



(iii) Elimination of a proton.



(b) Halogenation of toluene : (i) When toluene is treated with chlorine or bromine in dark and in presence of FeCl_3 , FeBr_3 (Lewis acid) as catalyst, it undergoes halogenation in the ring in *o*- and *p*-chlorination.

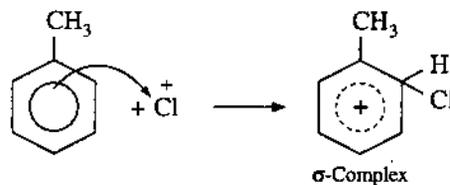


Mechanism : The mechanism of formation of *o*- and *p*- chlorination, bromination, product is the same as described for benzene. Thus, *o*-chlorotoluene is produced by the following steps :

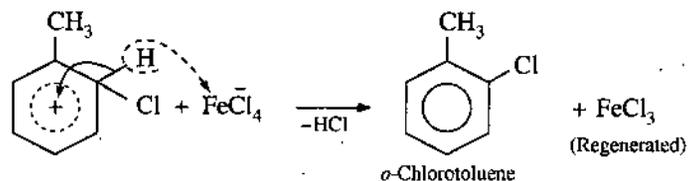
(i) Generation of electrophile Cl^+ .



(ii) Formation of σ -complex.

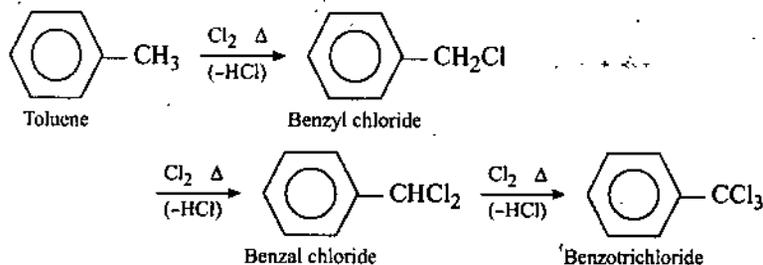


(iii) The para isomer is also produced by similar steps.

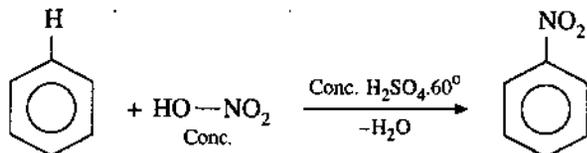


(b) When Cl_2 or Br_2 is passed into boiling toluene, it attacks the side-chain and the hydrogen atoms of the methyl group are successively replaced.

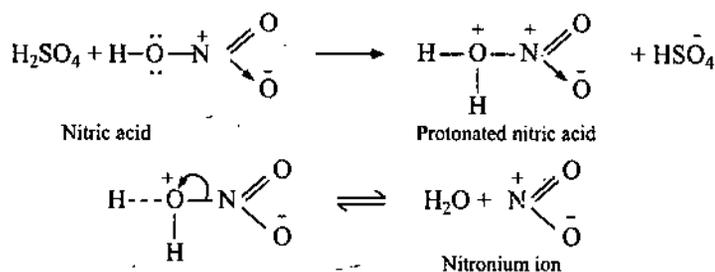
The substitution in side-chain is favoured by sunlight or UV-light and the mechanism resembles the halogenation of alkanes.



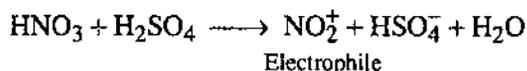
2. Nitration : (a) Benzene reacts with nitric acid in presence of sulphuric acid to form nitrobenzene.



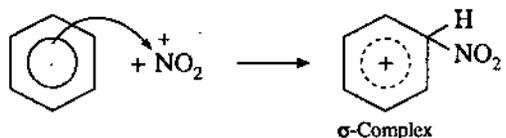
Mechanism : (i) Generation of the electrophile nitronium ion by the protonation of concentrated nitric acid by sulphuric acid.



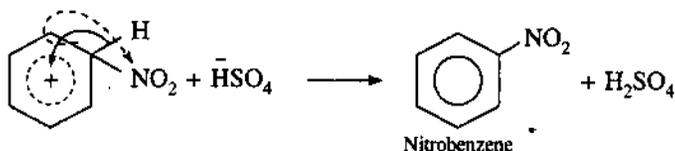
The overall reaction is :



(ii) Formation of σ -complex or stable resonance hybrid.

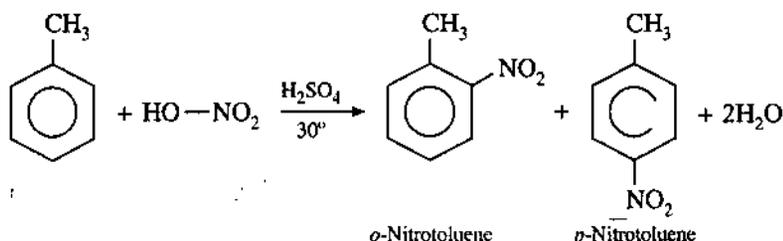


(iii) Elimination of proton from the σ -complex.

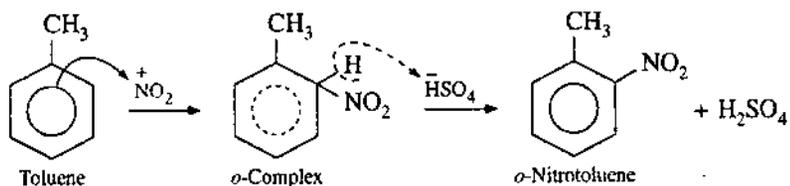


At higher temperature and on prolonged treatment with nitrating mixture, di- and tri-nitrobenzenes can be obtained. The incoming nitro group occupies the meta position relative to the previous one and the mechanism is the same as mentioned above.

(b) Toluene when treated with concentrated nitric acid and sulphuric acid gives *o*- and *p*-nitrotoluene.

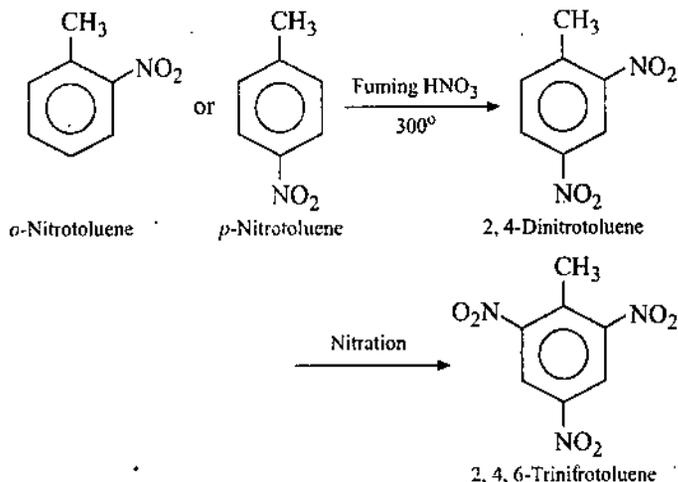


The mechanism of the reaction remains the same as for benzene. However, the electrophile is attached to electron-rich positions (ortho and para).

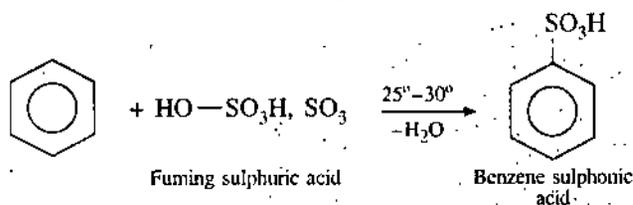


Nitration of toluene is easier than benzene, because CH_3 is an electron-releasing group and makes the π ring system electron rich.

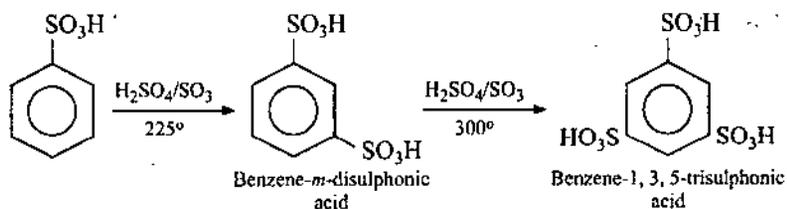
2, 4, 6-Tri nitrotoluene (TNT) can be obtained by further nitration of toluene in presence of fuming HNO_3 .



(3) Sulphonation : (a) Benzene may be sulphonated by treating it with concentrated sulphuric acid or fuming sulphuric acid ($\text{H}_2\text{SO}_4 \cdot \text{SO}_3$).

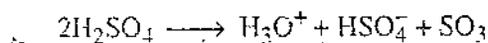


At higher temperature, two or three sulphonic groups ($-\text{SO}_3\text{H}$) can be introduced in the ring.

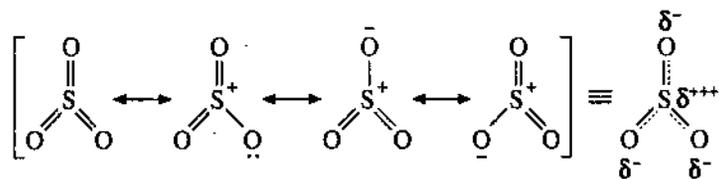


Mechanism : Sulphonation of benzene to give benzene sulphonic acid follows the following steps :

(i) generation of the electrophile.

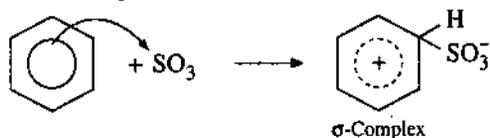


Although SO_3 is a neutral molecule, its sulphur atom carries a positive charge due to the resonance of the molecule.

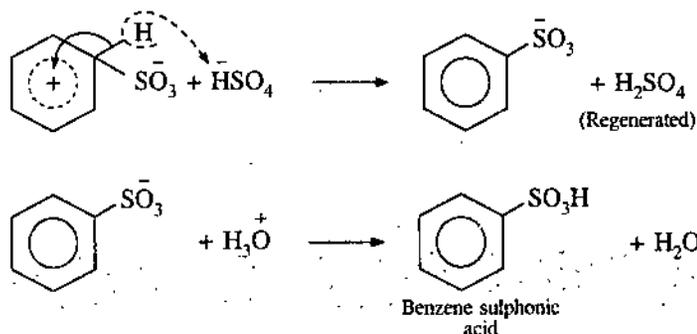


Therefore, SO_3 acts as an electrophile.

(ii) Formation of σ -complex.

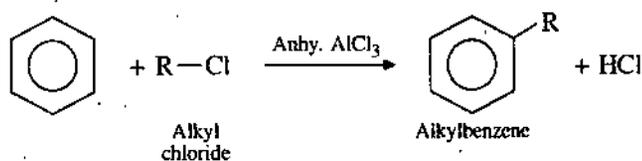


(iii) Elimination of a proton (H^+).

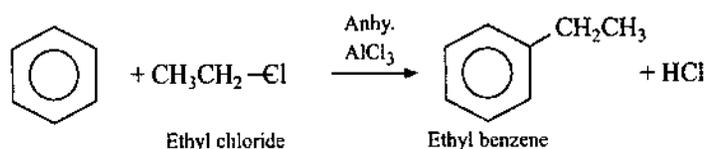
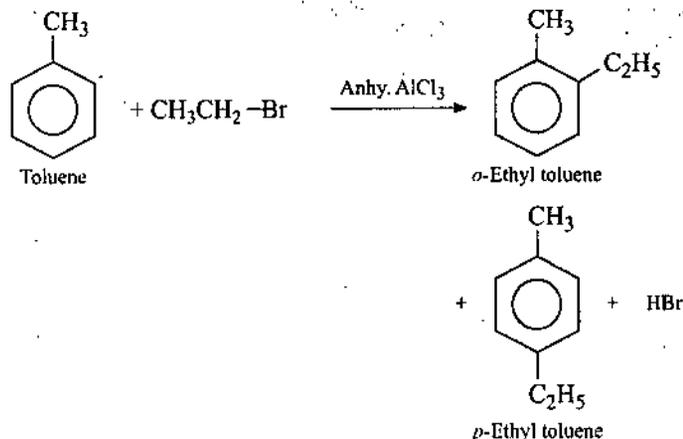


Di- and tri-sulphonation also shows the same mechanism.

(4) Alkylation: This reaction consists in introducing an alkyl group in the benzene ring for the synthesis of alkyl benzenes. For example, when benzene reacts with an alkyl halide (RCl or RBr) in presence of anhydrous AlCl_3 (catalyst), one of the hydrogen atoms of the ring is substituted by an alkyl group R .

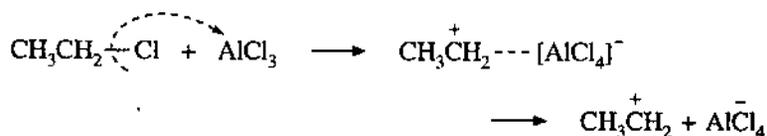


The alkylating agent used in Friedel-Crafts alkylation is an alkyl halide. The catalyst used may be AlCl_3 , BF_3 , FeCl_3 , HF (Lewis acids) etc. Some examples showing the reaction to form arenes are :

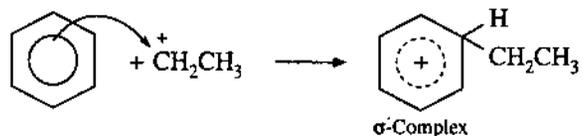


Mechanism : Friedel-Crafts alkylation proceeds according to the following steps.

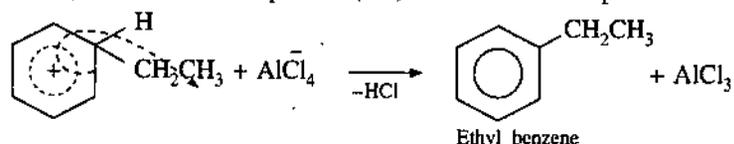
(i) Generation of the electrophile which, in this case, is a carbonium ion.



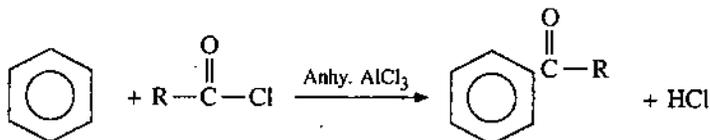
(ii) Formation of the σ -complex.



(iii) Elimination of proton (H^+) from the σ -complex.



(5) Acylation : This reaction consists of introducing an acyl group (RCO—) in the aromatic ring in presence of anhydrous AlCl_3 , BF_3 , FeCl_3 (Lewis acid) as catalysts.

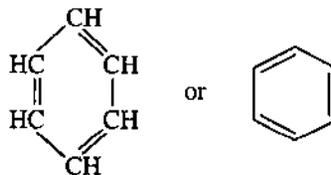


The mechanism of Friedel-Crafts acylation is also an electrophilic substitution reaction and follows the same mechanism as observed in Friedel-Crafts alkylation.

• 4.9. AROMATIC HYDROCARBONS OR ARENES

[1] Introduction

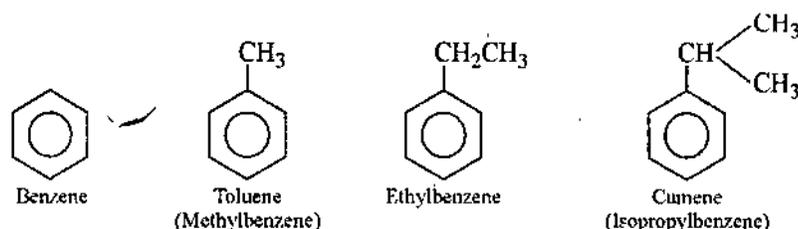
Many organic compounds which were obtained from natural sources, *e.g.*, resins, balsams, aromatic oils, etc. and had a characteristic odour, were classified as **aromatic** (Greek : *aroma* = odour) **compounds**. Early distinction between aliphatic and aromatic compounds were arbitrary, but later on distinction was done on the basis of structures. At present, the term aromatic represents benzene and its derivatives. Benzene, C_6H_6 , is represented by a closed chain of 6—C atoms with alternate single and double bonds and each carbon carrying an H-atom. Benzene is, therefore, shown as :



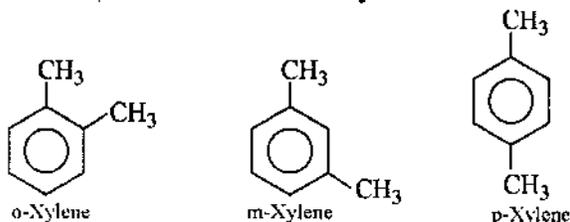
Aromatic compounds containing at least one benzene ring are also referred to as benzenoid compounds.

• 4.10. NOMENCLATURE OF BENZENE DERIVATIVES

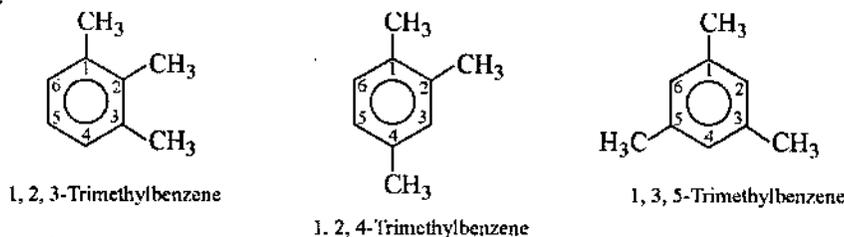
Benzene and its homologues are frequently called by the common names which are accepted by the IUPAC system. The homologues of benzene having a single alkyl group are called alkylbenzenes. These are made of a benzene ring to which is attached the alkyl group. The alkyl group bonded to a ring carbon is designated as the side chain.



Dimethyl benzenes have the common name **xylene**. The three isomeric xylenes are:

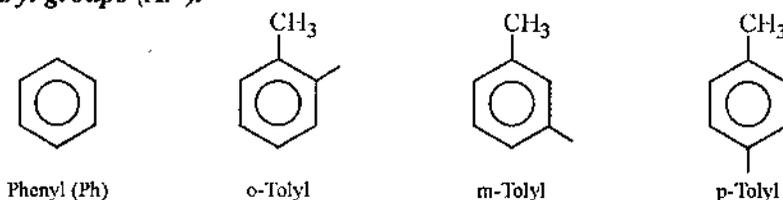


Trimethylbenzenes are invariably given systematic names, the positions of CH_3 -groups are shown by numbers. The three isomeric trimethylbenzenes are named as follows :



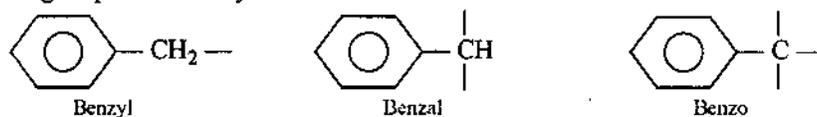
[I] Aryl Groups

The groups which result from arenes by dropping an H atom of the benzene ring are named as **aryl groups (Ar-)**.



[II] Aralkyl Groups

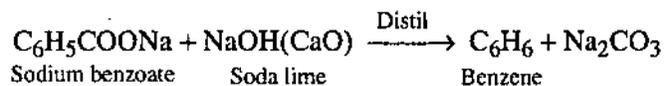
The groups derived by removal of H atom from the side chain are called aralkyl groups. The groups formed by toluene are as follows :



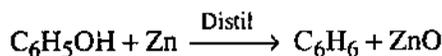
• 4.11. BENZENE

[I] Methods of Preparation

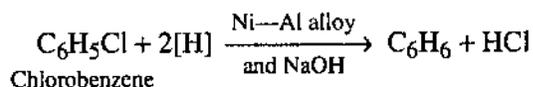
(i) **Laboratory method** : Benzene is prepared in laboratory by the distillation of a mixture of sodium benzoate and soda lime.



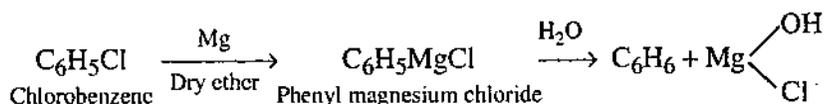
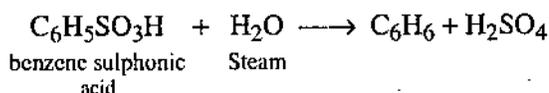
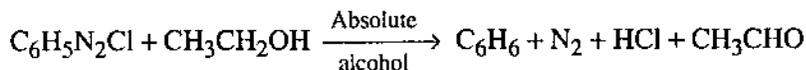
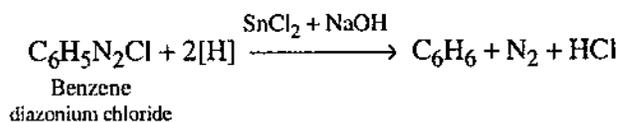
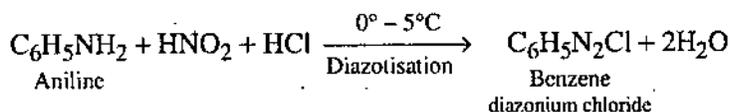
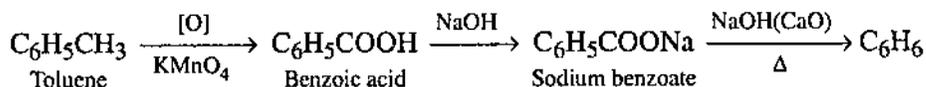
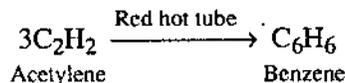
Experiment : A mixture of 20 g of sodium benzoate and 30 g of soda lime is taken in a round-bottom flask fitted with a thermometer and a delivery tube attached to a water condenser. On heating, benzene is formed and is collected in a receiver along with water. Benzene is then separated using a separating funnel. It is then dried over anhydrous calcium chloride and finally obtained in pure form by distillation.

(ii) **From derivatives of benzene :**(a) **From phenol :** By distillation with zinc dust.(b) **From chlorobenzene :** There are two methods :

(i) By its reduction with Ni—Al alloy and NaOH.



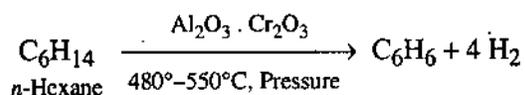
(ii) By first preparing Grignard's reagent and then hydrolysing it.

(c) **From benzene sulphonic acid :** By its hydrolysis with superheated steam.(d) **From aniline or benzene diazonium chloride :** Aniline on diazotisation forms benzene diazonium chloride which is then reduced to benzene by SnCl₂ and NaOH or absolute alcohol.(e) **From homologues of benzene :** Monoalkyl benzenes, on oxidation with KMnO₄, form benzoic acid which is then decarboxylated by heating with soda lime (*See laboratory method*), e.g.,(iii) **Synthesis :** Benzene is synthesised by passing acetylene through red hot tube.(iv) **Manufacture :** Benzene is manufactured :(a) **From coal tar :** When dehydrated coal tar is subjected to fractional distillation, we get several fractions. Benzene is mainly present in light oil fraction (80–170°C). Light oil fraction is first washed with concentrated sulphuric acid in order to remove the basic impurities such as aniline, pyridine, etc. The lower sulphuric acid layer is removed and the upper layer is treated with dilute sodium hydroxide which dissolves the acidic impurities present, such as phenol. Now the upper layer is separated from the lower alkali layer and is washed with water, dried and subjected to fractional distillation. Following fractions are then collected.

Fraction	Temp. range	Main constituents
(a) 90% Benzol	80°–110°C	Benzene, toluene
(b) 50% Benzol	110°–140°C	Toluene, xylenes
(c) Solvent naphtha	140°–170°C	Mesitylene, cumene

The 90% benzol so obtained is again subjected to fractional distillation. A fraction is collected between 80°–85°C which mainly contains benzene along with small quantities of toluene and thiophene. This fraction is now chilled in freezing mixture when benzene along with traces of thiophene solidifies. It is separated from the remaining liquid-mother liquor. The benzene so obtained is 99.5% pure but still contains about 0.5% thiophene as impurity. The traces of thiophene are finally removed by washing this benzene several times with concentrated sulphuric acid. Washing is continued till the benzene does not give a blue colour with isatin (*Indophenin test for thiophene*). Benzene so obtained is washed with water, dried and fractionally distilled to obtain 100% pure form at 80°C.

(b) *From petroleum* : *n*-Hexane, obtained from petroleum, is passed over oxides of chromium, vanadium or molybdenum carried on an alumina support at a temperature 480°–550°C, under pressure. The reaction involves dehydrogenation, cyclisation and isomerisation.



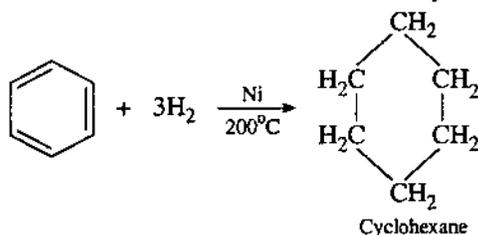
[II] Properties of Benzene

Physical : Benzene is a colourless, volatile liquid with characteristic odour. It is highly inflammable and burns with sooty flame. It is immiscible and lighter than water but miscible in organic solvents. Benzene itself is a good solvent for fats, resins, rubber etc. Its boiling point is 80°C and freezing point is 5.5°C.

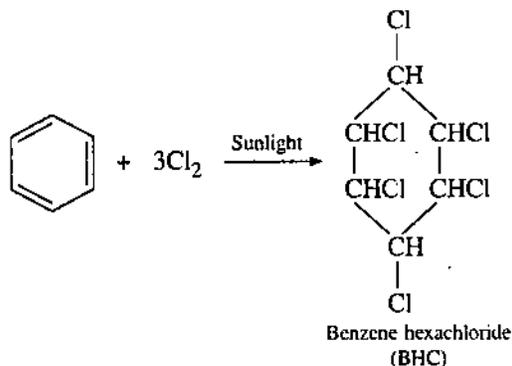
Chemical : In spite of the presence of three double bonds benzene prefers to undergo substitution reactions rather than addition reactions. This is because in benzene π -electrons are delocalized due to resonance and become inactive for addition reactions. However, it shows only few addition reactions.

(1) Addition Reactions

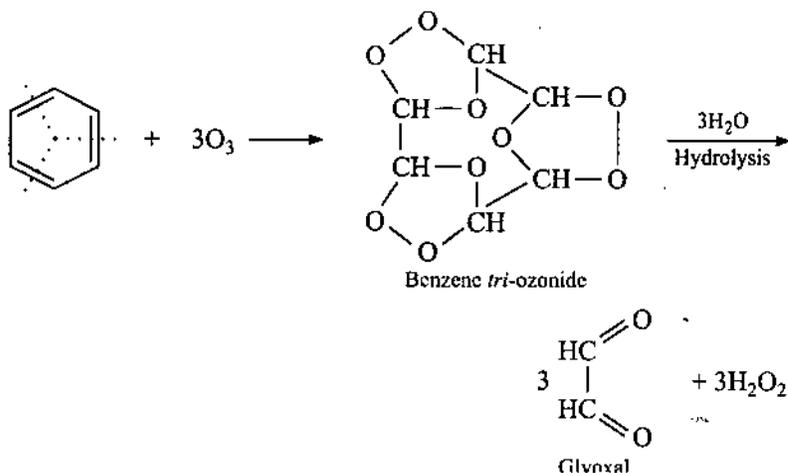
(a) **Addition of hydrogen** : When benzene vapours and hydrogen mixture under pressure are passed over nickel heated to 200°C, cyclohexane is formed.



(b) **Addition of halogen** : In the presence of sunlight, chlorine and bromine add to benzene to form benzene hexachloride (BHC) or benzene hexabromide, respectively.

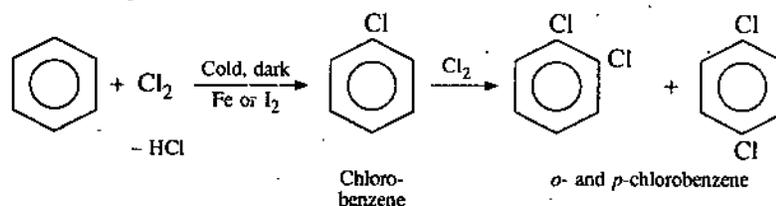


(c) **Addition of ozone :** Benzene reacts with ozone to form benzene triozonide. This on hydrolysis gives three molecules of glyoxal, thus, showing the presence of three double bonds.

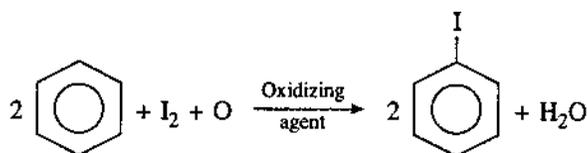


(2) Substitution Reactions

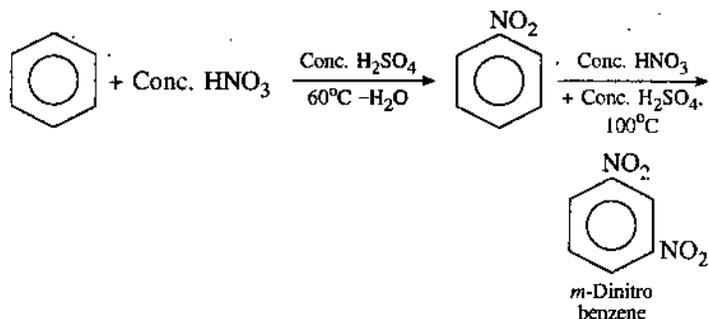
(a) **Halogenation :** The phenomenon of replacement of one or more hydrogen atoms from benzene nucleus by halogen atom is known as *halogenation*. Thus, benzene reacts with chlorine in presence of halogen carriers Fe or I₂ and in cold dark to form chlorosubstitution products.



Bromine reacts similarly but with iodine the reaction is reversible. In order to make the reaction reversible, the reaction is carried out in the presence of an oxidizing agent like conc. HNO₃, HgO or HIO₃.

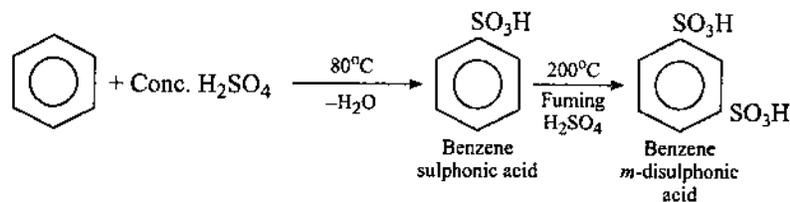


(b) **Nitration :** The phenomenon of replacement of one or more hydrogen atoms from benzene nucleus by nitro group is known as *nitration*. Thus, benzene reacts with a mixture of conc. HNO₃ and conc. H₂SO₄ at 60°C to give nitrobenzene whereas at 100°C it gives meta dinitro benzene.

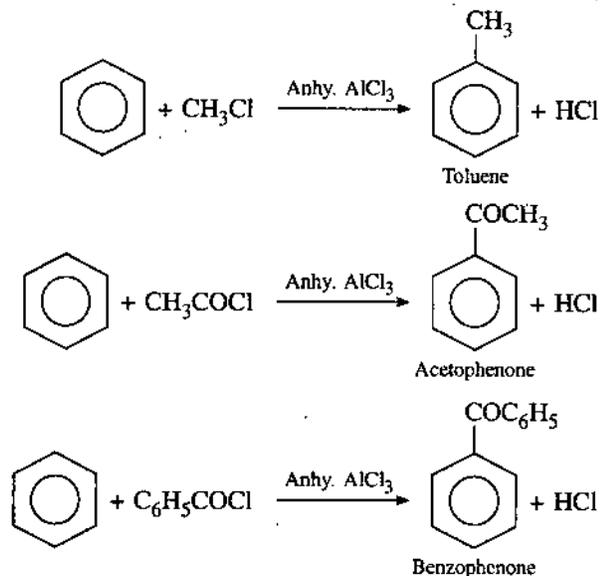


(c) **Sulphonation :** The phenomenon of replacement of one or more hydrogen atoms from benzene nucleus by —SO₃H group is known as *sulphonation*. Thus, benzene reacts

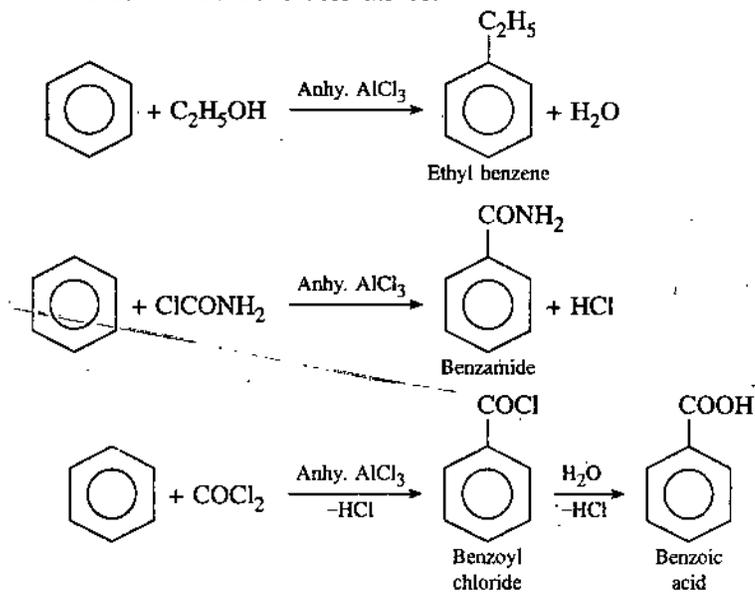
with conc. H_2SO_4 at 80°C to form benzene sulphonic acid. If fuming sulphuric acid is used, the reaction takes place further and benzene *m*-disulphonic acid is formed at 200°C .



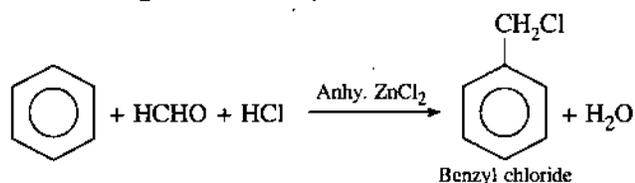
(d) Friedel-Craft's reaction : The reaction involves the introduction of an alkyl or acyl group into the benzene nucleus in the presence of anhydrous AlCl_3 as catalyst.



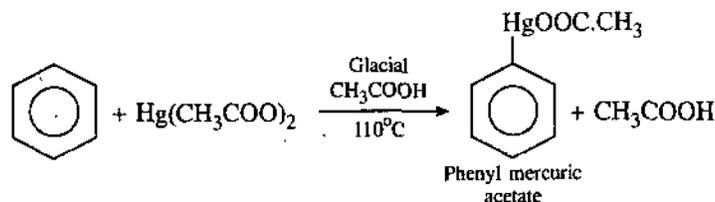
Benzene also shows the following reactions in the presence of anhydrous AlCl_3 to form a number of benzene derivatives.



(e) Chloromethylation : Benzene reacts with HCHO and conc. HCl in the presence of anhydrous ZnCl_2 to form benzyl chloride.

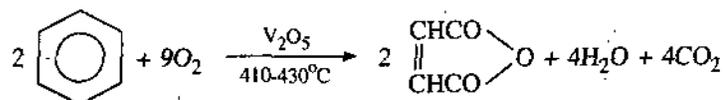


(f) **Mercuration** : Benzene reacts with mercuric acetate in glacial CH_3COOH at 110°C to form phenyl mercuric acetate.



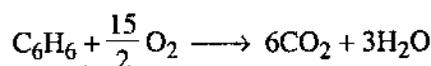
(3) Catalytic Oxidation

Benzene is not easily oxidized. However, passing of benzene and air over heated V_2O_5 at $410\text{--}430^\circ\text{C}$ results in the formation of maleic anhydride.



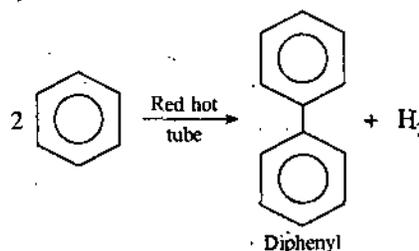
(4) Combustion

On combustion, benzene gives CO_2 and H_2O .



(5) Formation of Diphenyl

When vapours of benzene are passed through red hot tube, it forms diphenyl.



[III] Uses of Benzene

Benzene is used :

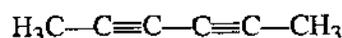
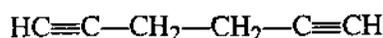
- (i) As a solvent for oils, fats, resins, rubber, etc. both in laboratory and industries.
- (ii) In preparation of trinitrobenzene (an explosive), BHC (an insecticide) etc.
- (iii) As a solvent in drycleaning, and
- (iv) Along with petrol and alcohol, as a fuel in motor cars.

[IV] Constitution of Benzene

(1) **Molecular formula** : Analysis and molecular weight determination shows that benzene has a molecular formula C_6H_6 .

(2) **Open chain structure not possible** : Benzene cannot be an open chain saturated hydrocarbon (alkane) since it has 8—H atoms less than required (general molecular formula for alkanes is $\text{C}_n\text{H}_{2n+2}$, hence H-atoms needed are 14, i.e., C_6H_{14}).

Hence, it can be an unsaturated open chain hydrocarbon. Theoretically, the following structures may be written with the molecular formula C_6H_6 .



But the possibility of benzene having an unsaturated open chain structure was also ruled out due to the following reasons :

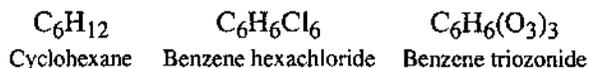
- (i) All the above unsaturated would require 8—H atoms to get saturated while, in practice, benzene requires only 6—H atoms.

(ii) Benzene does not decolorise bromine water or alkaline KMnO_4 like unsaturated open chain hydrocarbons.

(iii) Unlike unsaturated hydrocarbons, benzene undergoes substitution reactions rather easily.

(iv) Benzene, unlike unsaturated open chain hydrocarbons, does not add halogen acids, hypohalous acids, etc.

However, benzene shows addition reactions under suitable conditions. It adds on 6—H and 6—Cl atoms and also three ozone molecules.



All the above points led to the conclusion that benzene, no doubt was an unsaturated compound with three double bonds and had a typical type of unsaturation which was different from open chain compounds.

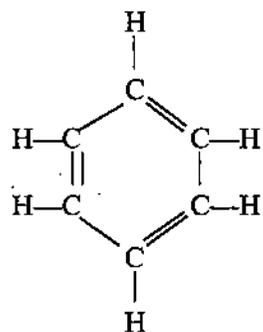
(3) **Ring structure possible :** The idea that benzene had a ring structure, was originated from the following evidences in its favour.

(i) Benzene forms only one monosubstituted product clearly showing that all the 6—H atoms of benzene are identical.

(ii) Disubstituted benzene occur in three isomeric forms, a fact which cannot be explained by open chain structure.

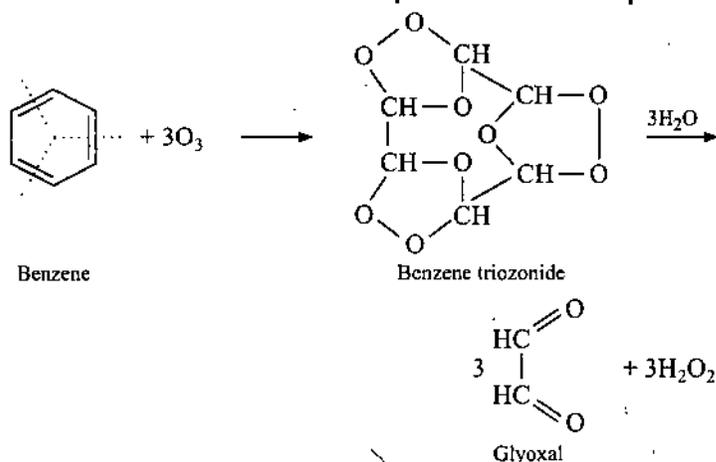
(iii) Benzene, on hydrogenation, forms a cyclic compound, *i.e.*, cyclohexane.

(4) **Kekule's structure :** Kekule, a German chemist, in 1865, gave the first ring structure of benzene with alternate single and double bonds.



Evidences in support of Kekule's structure. Following facts gave support to Kekule's structure:

(i) Under suitable conditions benzene combines with three molecules of hydrogen and chlorine to form cyclohexane (C_6H_{12}) and benzene hexachloride ($\text{C}_6\text{H}_6\text{Cl}_6$), respectively. This showed the presence of three double bonds in the benzene ring. Further, on ozonolysis, benzene formed three molecules of glyoxal and this further proved that the three double bonds in benzene are present in alternate positions.



(ii) It can explain the formation of one monosubstituted and three isomeric disubstituted products.

(iii) It explains the synthesis of benzene from acetylene.

(iv) Formation of three molecules of glyoxal by ozonolysis of benzene, can be explained by this structure.

(v) Physico-chemical methods like X-ray analysis, IR, Raman spectra, etc. also favour this type of structure.

Objections against Kekule's structure : There were two main objections raised against Kekule's structure.

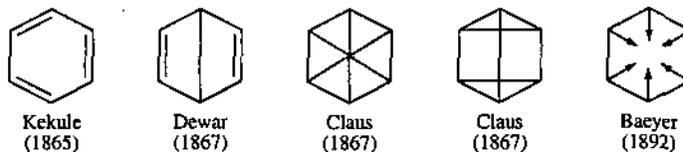
(i) It admits the formation of two ortho disubstitution products for similar substituents. Thus, the two *o*-dibromobenzenes possible would be :



However, actually one *o*-dibromobenzene is known.

(ii) Benzene with three double bonds should be highly unstable (reactive) while, in practice, it was found to be a very stable compound.

Various chemists, from time to time suggested different cyclic structures for benzene, but sooner or later, all of them were discarded.

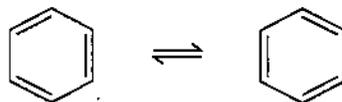


Kekule, on the other hand, proposed a **dynamic structure** in 1874, in order to overcome the objections raised against his earlier proposed structure.

(5) Modern view : According to the modern view, the structure of benzene can be explained by both *valency bond theory* and *molecular orbital theory*.

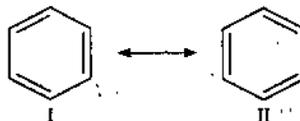
(i) **By valency bond theory :** Again there are two theories by which the structure of benzene can be explained.

(a) **Resonance theory :** The theory was put forward by Pauling (1933). According to this theory, 'benzene cannot be represented by a single structure but it is a resonance hybrid of the following structures' :



Explanation of the unusual properties of benzene : The unusual properties of benzene like heat of combustion, bond length, stability can be readily explained on the basis of resonance structure.

(i) **Stability :** A resonance hybrid is always more stable than any of the contributing structures. The resonance hybrid of benzene would thus be more stable than either of the following structures I and II contributing to it:



We know that benzene molecule is more stable than these structures by 35–37 kcal mole⁻¹. The difference in energy contents of benzene molecule and structure I or II (*i.e.*, 35–37 kcal mole⁻¹) is known as *resonance energy* of benzene molecule.

(ii) **Bond lengths :** The resonance hybrid of benzene has no true carbon-carbon double and single bonds. All the carbon-carbon bonds in benzene are expected to be nearly equal, and their length lies between that of a single and a double bond. This is actually seen to be so.

(iii) **Number of isomers :** As all the carbon-carbon bonds in the resonance hybrid of benzene are equivalent, 1, 2 and 1, 6 positions are thus identical. Therefore, three and only three disubstitution products of benzene should actually exist.

(iv) **Chemical properties :** In the aromatic substitution reactions of benzene, the tendency is to preserve the resonance stabilised benzene ring system by substitution, in spite of the presence of carbon-carbon double bonds in I and II. Addition of one molecule of hydrogen to form cyclohexadiene requires 5–4 kcal of energy. Thus, cyclohexadiene is less stable than benzene. It is, therefore, clear to understand that benzene prefers not to undergo addition to cyclohexadiene stage. It undergoes substitution reactions in which the stable benzene ring is retained.

(b) **Aromatic Sextet theory :** According to this theory, 'benzene has six electrons more than necessary to link together the six carbon and the six hydrogen atoms. These six electrons, one being contributed by each carbon, form a closed group or sextet'. It is this sextet which is responsible for the aromatic character of benzene, hence is called **aromatic sextet**, and the theory as **aromatic sextet theory**.

[V] Orbital Diagram of Benzene

A carbon atom, through trigonal or sp^2 hybridisation can form three covalent bonds lying in one plane and having a bond angle of 120° . On arranging the six carbon atoms and six hydrogen atoms of benzene, there is maximum overlapping of these orbitals, as shown in fig. 1(a). Each bond orbital is cylindrically symmetrical about the line joining

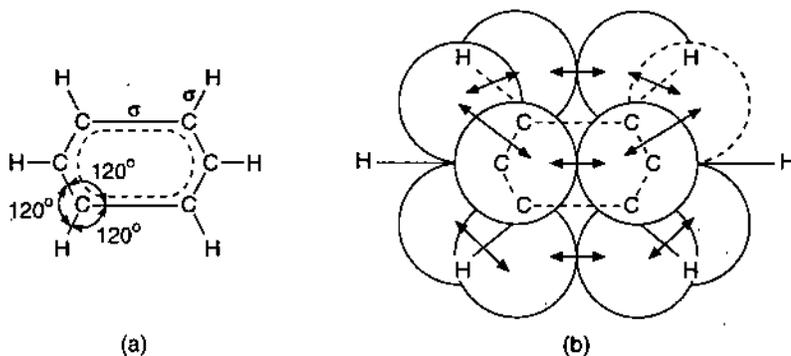


Fig. 1

the atomic nuclei. The twelve bonds are termed as sigma (σ) bonds. It thus follows from the orbital approach that benzene should be a symmetrical and flat molecule with all bond angles of 120° , as confirmed by X-ray and electron diffraction studies.

However, a fourth orbital (p -orbital) of each carbon atom has remained unused so far. This p -orbital consists of two equal lobes, one lying above and the other below the plane of the ring.

These p -orbitals of each carbon atom overlap sideways to the similar p -orbitals of two C-atoms to which it is bonded. Thus, the six electrons are paired to give additional π -bonds [Fig. 1(b)]. Due to this, we have two continuous hexagonal electron clouds, one lying above and the other below the plane of the atoms as shown in figure (2).

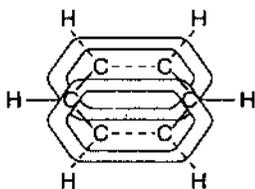


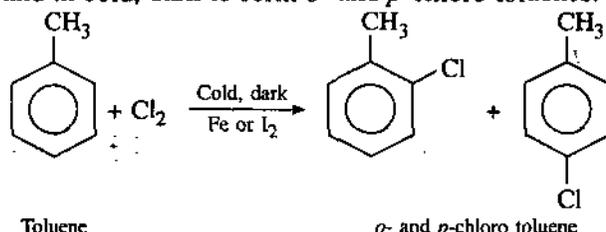
Fig. 2

[II] Properties of Toluene

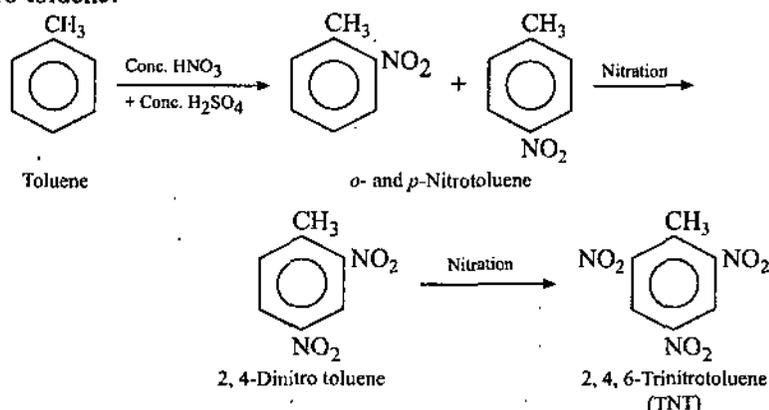
Physical : Toluene is a colourless, mobile liquid with b.p. 110°C and sp. gr. 0.67 at 20°C . It possesses a characteristic odour and is immiscible with water but miscible with alcohol, ether etc.

Chemical :**(I) Reactions due to benzene nucleus**

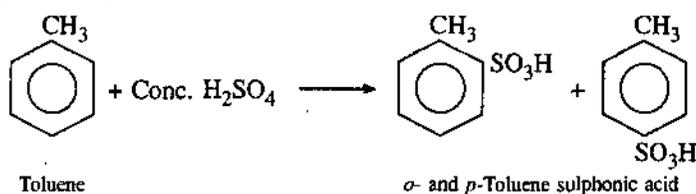
(a) Halogenation : Toluene reacts with Cl_2 in the presence of halogen carriers like Fe or I_2 and in cold, dark to form *o*- and *p*-chloro toluenes.



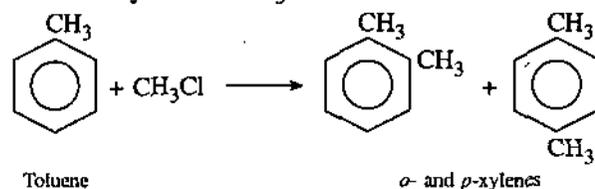
(b) Nitration : Toluene reacts with a mixture of conc. HNO_3 and conc. H_2SO_4 to form *o*- and *p*-nitro toluenes which, on further nitration in presence of fuming HNO_3 , give 2, 4, 6 trinitro toluene.



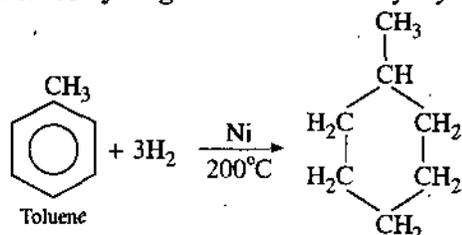
(c) Sulphonation : Toluene reacts with conc. H_2SO_4 to form *o*- and *p*-toluene sulphonic acids.



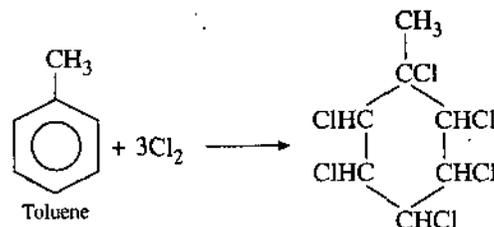
(d) Friedel-Craft Reaction : Forms a mixture of *o*- and *p*-xylenes with CH_3Cl in the presence of anhydrous AlCl_3 .

**(II) Addition Reactions**

(a) Addition of hydrogen : Forms methyl cyclohexane.

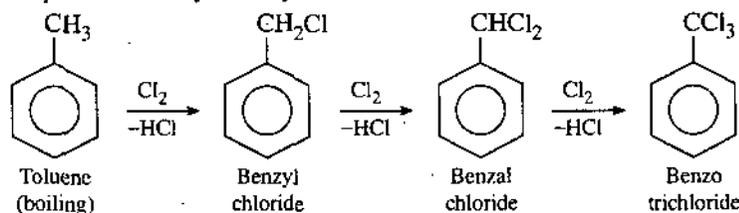


(b) **Addition of halogen :** In the presence of sunlight, chlorine and bromine add to toluene to form toluene hexachloride or toluene hexabromide, respectively.



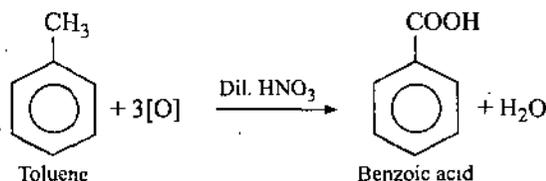
(III) Reactions due to methyl group

(a) **Halogenation :** When Cl_2 is passed through boiling toluene in the presence of sunlight, substitution in the side chain takes place and hydrogen atoms of $-\text{CH}_3$ group are replaced one by one by Cl atoms.

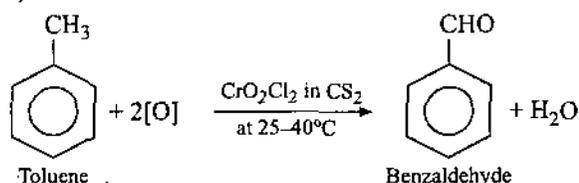


(b) Oxidation :

(i) Toluene is oxidized to benzoic acid by strong oxidizing agents like dilute HNO_3 , KMnO_4 etc.



(ii) With mild oxidizing agents like chromyl chloride, it is oxidized to benzaldehyde. (*Etard reaction*)



[III] Uses of Toluene

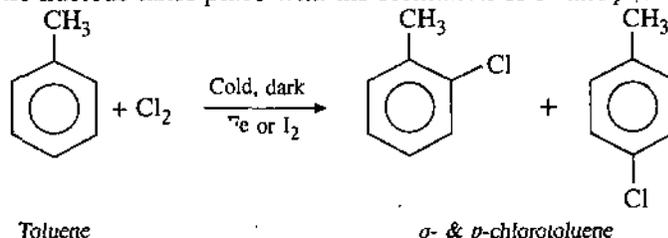
Toluene is used :

- (i) For drycleaning.
- (ii) As a solvent for lacquers.
- (iii) In the manufacture of certain dyes, drugs and explosives.

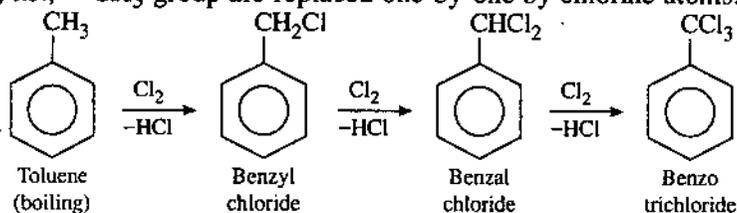
[IV] Reactions of Chlorine with Toluene and Distinction of Products

Chlorine reacts with toluene and may replace the nuclear hydrogen atoms or hydrogen atoms of the side chain under different experimental conditions.

(i) **Nuclear substitution :** Chlorine reacts with toluene in presence of halogen carriers, e.g., Fe or I_2 and in cold and dark when the substitution of hydrogen atoms of benzene nucleus takes place with the formation of *o*- and *p*-chloro toluenes.

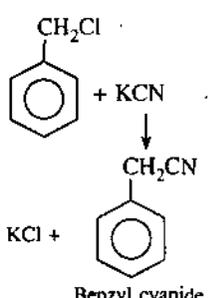
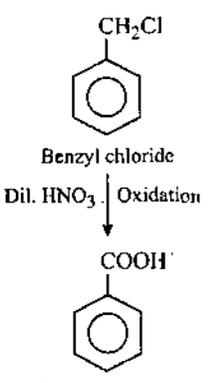


(ii) **Side chain substitution** : When chlorine is passed through boiling toluene in presence of sunlight, substitution in the side chain takes place and hydrogen atoms of the side chain, i.e., $-\text{CH}_3$ group are replaced one-by-one by chlorine atoms.



The nuclear or side chain substitution can be ascertained only after identifying the products on the basis of certain chemical reactions.

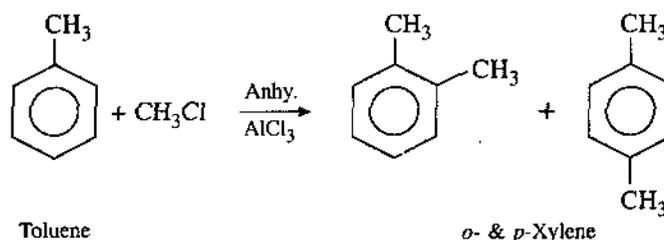
S. No.	Property	<i>o</i> - and <i>p</i> -Chloro toluenes	Benzyl chloride
1.	Smell	Not unpleasant	Unpleasant
2.	Substitution of chlorine atom	Chlorine atom is firmly attached to the benzene nucleus hence it cannot be easily replaced.	Chlorine atom is not firmly attached to the benzene nucleus and hence it can be easily replaced.
	(i) Reaction with alcoholic AgNO_3	—	A white ppt. of AgCl is obtained.
	(ii) Reaction with NH_3	—	Benzyl amine is formed.
	(iii) Reaction with KOH	—	Benzyl alcohol is formed.

(iv) Reaction with KCN	—	Benzyl cyanide is formed. 
3. Oxidation by dil. HNO ₃	$ \begin{array}{c} \text{CH}_3 \\ \diagup \\ \text{C}_6\text{H}_4 \\ \diagdown \\ \text{Cl} \end{array} \xrightarrow[\text{oxidation}]{\text{Dil. HNO}_3} \begin{array}{c} \text{COOH} \\ \diagup \\ \text{C}_6\text{H}_4 \\ \diagdown \\ \text{Cl} \end{array} $ <i>o</i> - and <i>p</i> -chloro benzoic acid	Benzoic acid is formed. 

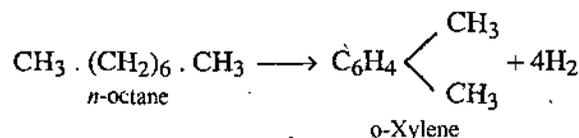
• 4.13. XYLENE

[I] Methods of Preparation

1. **From toluene** : When toluene is treated with methyl chloride in presence of anhydrous AlCl₃ *o*- and *p*-xylenes are obtained (Friedel-Crafts alkylation).



(ii) **Manufacture** : Xylenes are manufactured along with benzene and toluene by hydroforming of C₆—C₈ fractions of petroleum naphtha. For example, *o*-xylene is obtained from *n*-octane as follows :

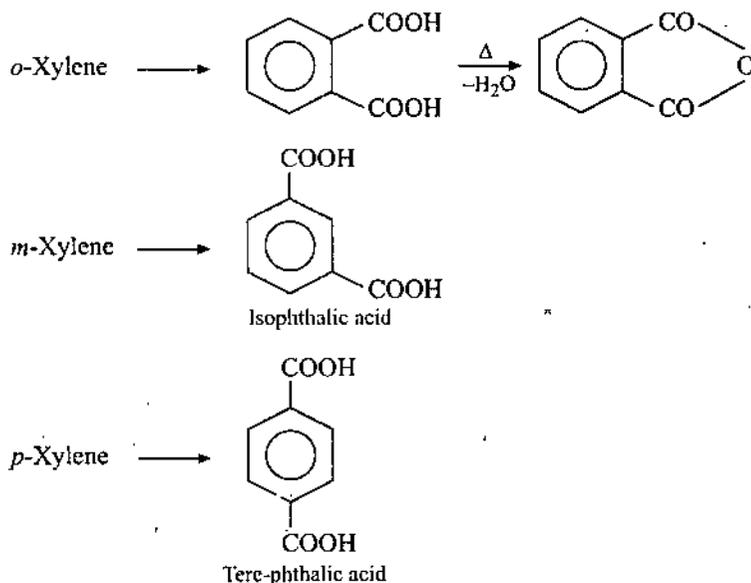


The individual xylenes are isolated from the resulting mixture by fractional distillation.

[II] Properties

Xylenes are colourless liquids, insoluble in water but soluble in alcohol and ether. Their boiling points are, *o*-xylene 144°C, *m*-xylene 139°C, *p*-xylene = 138°C.

Xylenes undergo electrophilic substitution in the ring much in same manner as toluene. On oxidation with KMnO₄ or K₂Cr₂O₇, they form the corresponding dicarboxylic acids.

**[III] Uses**

- (i) A mixture of xylenes (xylol) is used as a solvent and diluent for lacquers.
- (ii) Their amino derivatives are used in the manufacture of dyes.
- (iii) o -Xylene is the raw material for the manufacture of phthalic anhydride.

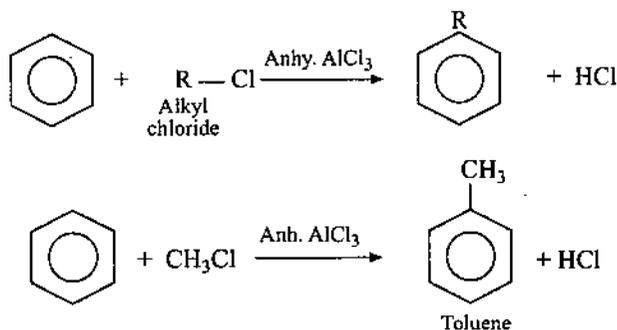
• 4.14. FRIEDEL-CRAFT'S REACTION**(1) Friedel-Craft's Reaction**

The reaction was discovered by C. Friedel and J.M. Crafts in 1877. It includes the alkylation or acylation of aromatic compounds by means of an alkyl halide or acyl halide in presence of anhydrous aluminium chloride.

This important reaction can be divided into two general types :

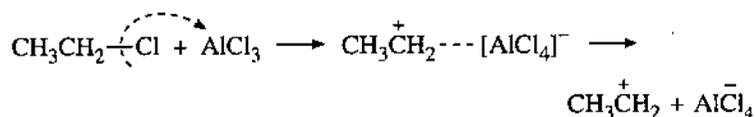
- (i) Friedel-Craft's alkylation and
- (ii) Friedel-Craft's acylation.

(1) Friedel-Craft's alkylation : This reaction consists in introducing an alkyl group in the benzene ring for the synthesis of alkylbenzenes. For example, when benzene reacts with an alkyl halide (RCl or RBr) in presence of anhydrous AlCl_3 (catalyst), one of the hydrogen atoms of the ring is substituted by alkyl group, R.

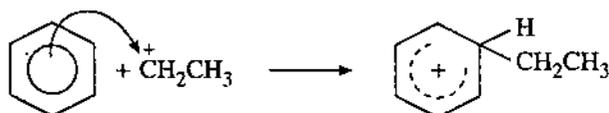


Mechanism : Friedel-Craft's alkylation proceeds in the following steps :

- (i) Generation of the electrophile which, in this case, is a carbonium ion.



- (ii) Formation of the σ -complex.



(iii) Elimination of proton (H^+) from the σ -complex.



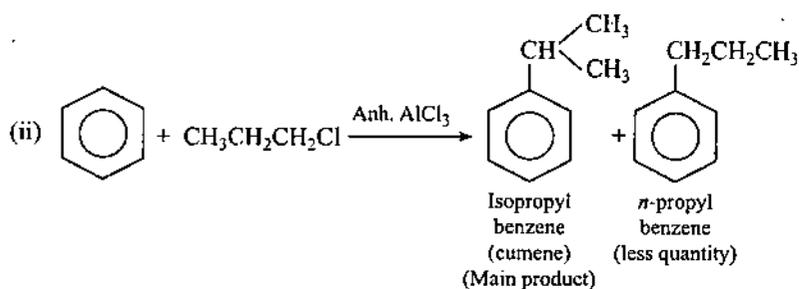
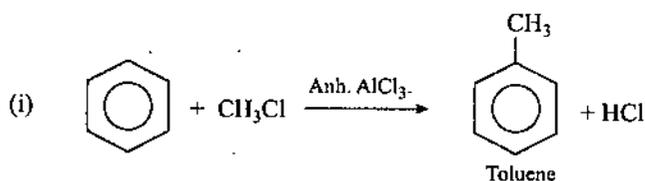
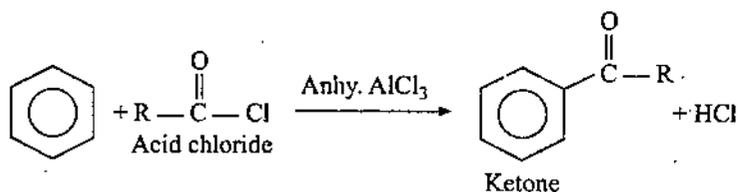
(2) **Friedel-Craft's acylation** : This reaction consists in introducing an acyl group ($\text{RCO}-$) in the aromatic ring in presence of anhydrous AlCl_3 .

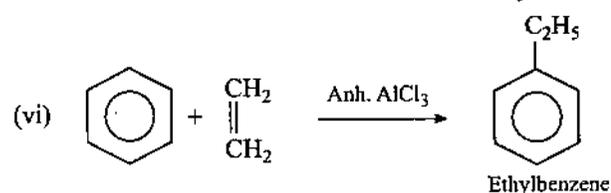
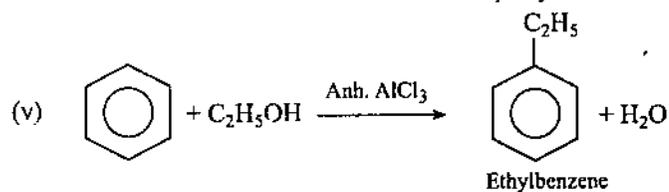
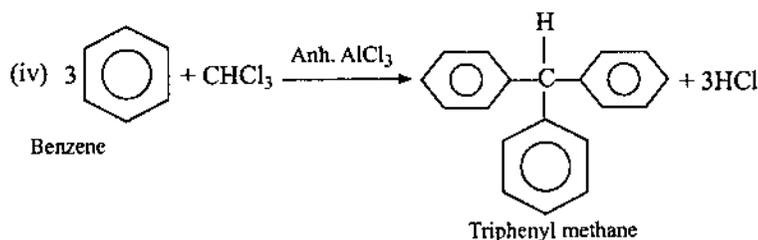
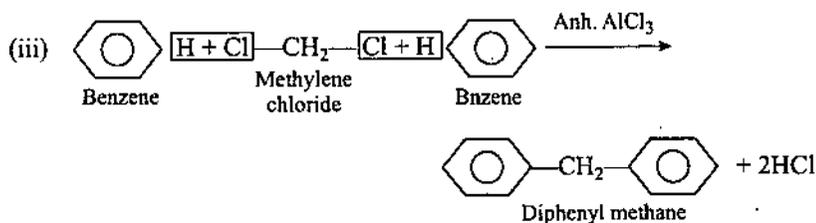
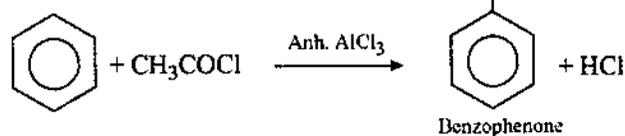
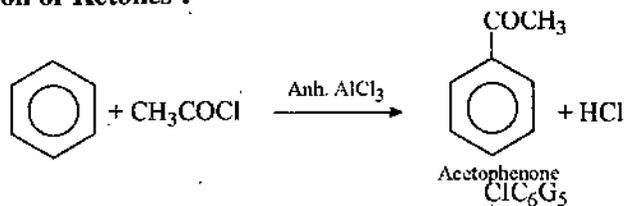
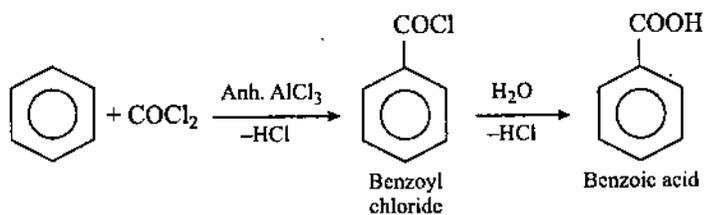
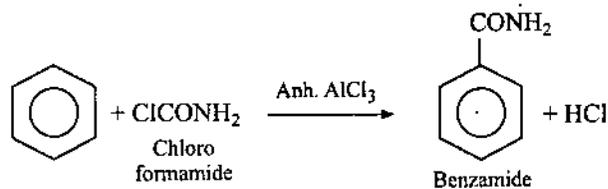
The mechanism of Friedel-Crafts acylation is also an electrophilic substitution reaction and follows the same mechanism as observed in Friedel-Craft's alkylation.

Now a days Friedel Craft reaction is a general reaction taking place between an aromatic hydrocarbon and aliphatic reagent which may be a halogen derivative, an acid chloride, an alcohol or an alkene. Other less effective catalysts such as FeCl_3 , SnCl_4 , ZnCl_2 or BF_3 may also be used in place of anhydrous AlCl_3 .

Applications

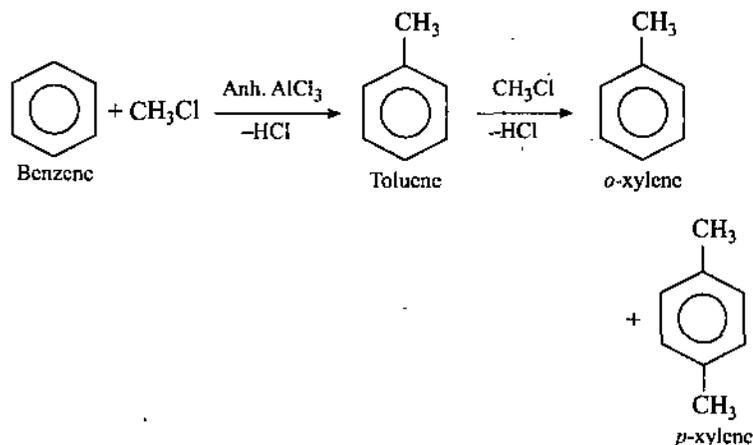
(a) **Formation of hydrocarbons** :



**(b) Formation of Ketones :****(c) Formation of acid chlorides and carboxylic acids :****(d) Formation of acid amides :**

Limitations

(i) The reaction cannot be stopped at the desired stage and sometimes over alkylation takes place.

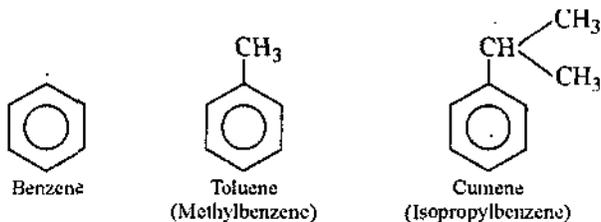


(ii) The presence of a negative group, *e.g.*, —NO₂ group in the aromatic ring hinders the reaction.

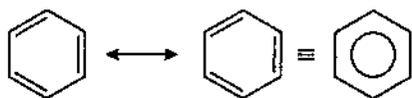
(iii) It is difficult to introduce *n*-propyl and *n*-butyl group in the benzene ring.

SUMMARY

- Aromatic hydrocarbons have high percentage of carbon and all compounds except benzene oxidise easily.
- Aliphatic hydrocarbons have low percentage of carbons, alkanes do not oxidise easily, unsaturated hydrocarbons oxidise easily.
- The unique property of aromatic compounds is called aromaticity.
- **Huckel's (4*n* + 2) rule** : A cyclic compound which has (4*n* + 2) π electrons (where *n* = an integer) should be markedly stable, typical of benzenoid aromatics.
- Cyclic compounds which have (4*n*) π electrons are called anti-aromatic compounds and this quality is known as anti-aromaticity.
- A group already present in the benzene ring is responsible for the position taken by the incoming group during substitution. This is known as directive influence of groups in aromatic substitution. It is governed by three rules, namely Cum-Brown-Gibson's rule, Vorlander's rule and Hammett-Ingold rule.
- The process by which the positions of two different substituents with respect to each other in the unknown benzene derivative are determined is known as orientation.
- Benzene and its homologues are frequently called by common names which are accepted by the IUPAC system. The homologues of benzene having a single alkyl group are called alkyl benzenes. These are made of a benzene ring to which is attached the alkyl group. The alkyl group bonded to a ring carbon is designated as the side chain.



- Benzene adds three moles of hydrogen in the presence of nickel (catalyst) to form cyclohexane. This confirms the cyclic structure of benzene and shows the presence of three carbon-carbon double bonds.
- Benzene is actually a resonance hybrid of various possible alternative structures.



- A double headed arrow (\leftrightarrow) between the resonance structures is used to represent the resonance hybrid.

STUDENT ACTIVITY

1. Mention three distinctions between aliphatic and aromatic hydrocarbons.

2. Write a short note on aromaticity.

3. What is aromatic sextet ?

4. What is orientation ?

5. Discuss the mechanism of halogenation of toluene.

6. Discuss the orbital diagram of benzene.

7. Describe the preparation of toluene.

8. Write a note on Friedel-Craft's alkylation process.

• TEST YOURSELF

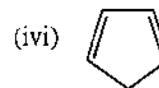
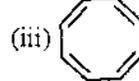
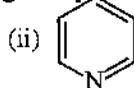
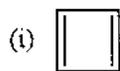
Answer the following questions :

- Discuss the molecular structure of benzene.
- Write a note on aromaticity.
- What is Huckel rule ? Write the structure of two compounds that follow this rule.
- Explain why pyridine is aromatic ?
- What happens when sodium benzoate is heated with soda-lime ?
- How is benzene prepared ?
- Describe the important reactions of benzene.
- What happens when benzene is treated with acetyl chloride in the presence of AlCl_3 ?
- What happens when benzene is treated with methyl chloride in the presence of AlCl_3 ?
- Explain why benzene undergoes electrophilic substitution reaction, whereas alkanes undergo addition reactions ?
- Give the mechanism of chlorination of benzene.
- Give the mechanism of bromination of benzene.
- Give the mechanism of nitration of benzene.
- Give the mechanism of sulphonation of benzene.
- Give the general mechanism of electrophilic aromatic substitution.
- Describe the mechanism of Friedel-Craft's alkylation of benzene.
- Mention the mechanism of Friedel-Crafts acylation of benzene.
- Write a note on Friedel-Crafts reaction.
- What are Xylenes ? Describe their preparation and properties.
- Describe any four distinctions between aromatic and aliphatic hydrocarbons.
- Write a note on aromatic sextet.
- Write a note on delocalisation.
- What do you understand by orientation ? Discuss it in di- and tri-substituted products of benzene.
- What is meant by directive influence of groups in aromatic substitution ? Discuss the rules used to determine the type of substitution.
- Discuss the structure of benzene.
- Describe the methods of preparation and important reactions of toluene.
- Using the directive influence of groups, describe the products formed by :
 - Nitration of ethylbenzene, phenol, benzoic acid, toluene, acetophenone, benzaldehyde and nitrobenzene.
 - Chlorination of nitrobenzene and benzene sulphonic acid.
 - Bromination of aniline, phenol, nitrobenzene, ethylbenzene and benzene sulphonic acid.
 - Sulphonation of toluene, benzoic acid, benzaldehyde and nitrobenzene.
- Explain why nitro group ($-\text{NO}_2$) is a meta director ?
- Classify the following as *ortho*-, *para* or *meta*- directing in an aromatic nitration reaction.

(a) $-\text{CH}_3$	(b) $-\text{NH}_2$	(c) $-\text{NO}_2$	(d) $-\text{OCH}_3$
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- Explain why toluene is more readily nitrated than benzene ?
- Which of the following compounds undergoes nitration most readily ?

(i) Benzene	(ii) Toluene	(iii) Nitrobenzene	(iv) Benzoic acid.
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- The C—C bond length in benzene is :
 - greater than the C—C bond length in ethane
 - shorter than the C—C bond length in ethylene
 - same as that of C—C bond length in ethylene
 - intermediate between C—C and length in ethane and C—C bond length in ethylene

33. Which of the following compounds is aromatic ?



34. Which of the following statements are false about benzene ?

- (i) It is a planar molecule with bond angle 120°
- (ii) It is immiscible with water forming the lower layer
- (iii) It can be converted into cyclohexane by hydrogenation at 200°C in the presence of Ni as catalyst.
- (iv) It reacts with ethyl chloride in the presence of aluminium chloride to form ethylbenzene

35. Which statement about the structure of benzene is not true ?

- (i) The two Kekule structures of benzene are in equilibrium
- (ii) The carbon-carbon bond lengths in benzene are greater than the carbon-carbon double bonds in aliphatic compounds
- (iii) The molecular geometry of benzene is best described as planar
- (iv) The stability of benzene ring is much greater than the stability of 1, 3, 5-cycloheptatriene

36. The carbon atoms in a benzene ring are :

- (i) sp hybridised
- (ii) sp^3 hybridised
- (iii) sp^2 hybridised
- (iv) None of these

37. Characteristic reactions of aromatic hydrocarbons are initiated by :

- (i) nucleophiles
- (ii) electrophiles
- (iii) free radicals
- (iv) unchanged molecules

38. Toluene undergoes oxidation to give :

- (i) Benzyl alcohol
- (ii) Quinone
- (iii) Benzaldehyde
- (iv) Benzoic acid

39. Benzene undergoes substitution reaction more easily than addition reaction because :

- (i) it has a cyclic structure
- (ii) it has double bond
- (iii) it has six hydrogen atoms
- (iv) there is delocalisation of electrons

40. Benzene reacts with conc. HNO_3 in the presence of conc. H_2SO_4 to give nitrobenzene. This reaction is an example of :

- (i) electrophilic addition
- (ii) nucleophilic addition
- (iii) electrophilic substitution
- (iv) nucleophilic substitution

41. Which of the following agents is used in order to make benzene react with conc. HNO_3 to give nitrobenzene ?

- (i) FeCl_3 catalyst
- (ii) conc. H_2SO_4
- (iii) Lindlar's catalyst
- (iv) ultraviolet light

42. Which of the following agents is used in order to make benzene react with bromine to form bromobenzene ?

- (i) ultraviolet light
- (ii) nickel catalyst
- (iii) Al_2O_3 catalyst
- (iv) Fe catalyst

43. In the Friedel-Crafts acetylation of an aromatic ring, the role of AlCl_3 is to :

- (i) form a $\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}^+$ ion
- (ii) function as a Lewis base
- (iii) chlorinate the aromatic ring
- (iv) withdraw electrons from the aromatic ring

44. In chlorination of benzene, FeCl_3 is used to generate :

- (i) Cl^-
- (ii) Cl^+
- (iii) Cl_2
- (iv) HCl

45. Fill in the blanks :

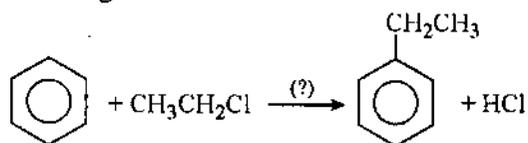
- (i) Benzene reacts with H_2 at 150°C and 30 atm in the presence of Ni catalyst to form
- (ii) Benzene reacts with benzoyl chloride in the presence of anhydrous AlCl_3 to form

(iii) Benzene reacts with propene in the presence of H_2SO_4 catalyst to give

(iv) Ozonolysis of benzene forms

(v) Gammexane is

(vi) Consider the following reaction :



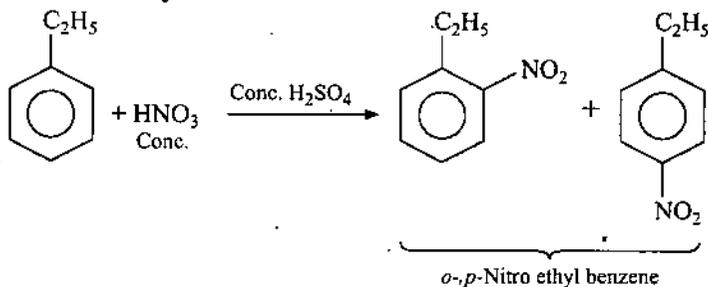
The catalyst used to complete the above reaction is

(vii) Oxidation of toluene with chromyl chloride gives benzaldehyde. This reaction is known as reaction.

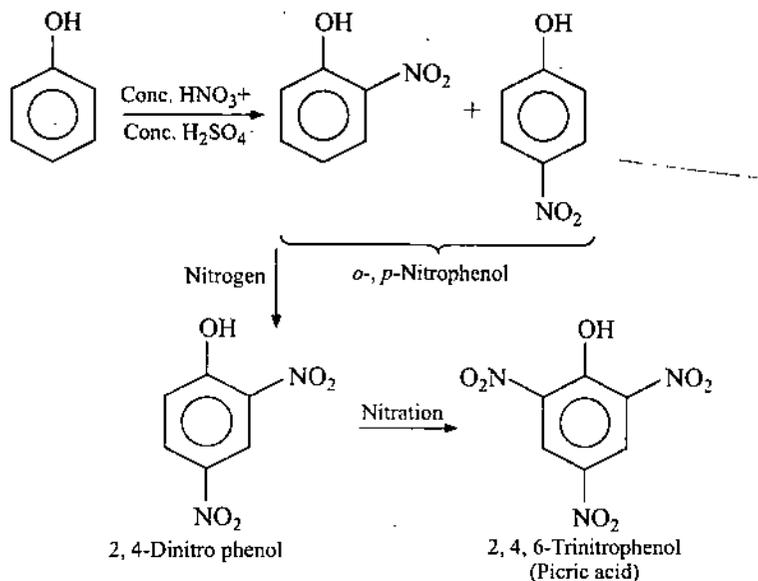
ANSWERS

5. benzene is formed 8. acetophenone is formed 9. toluene is formed

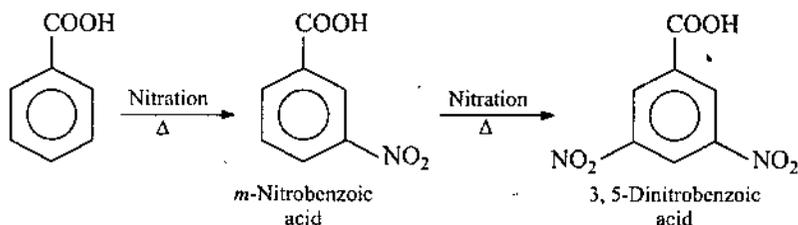
27. (a) Nitration of ethyl benzene

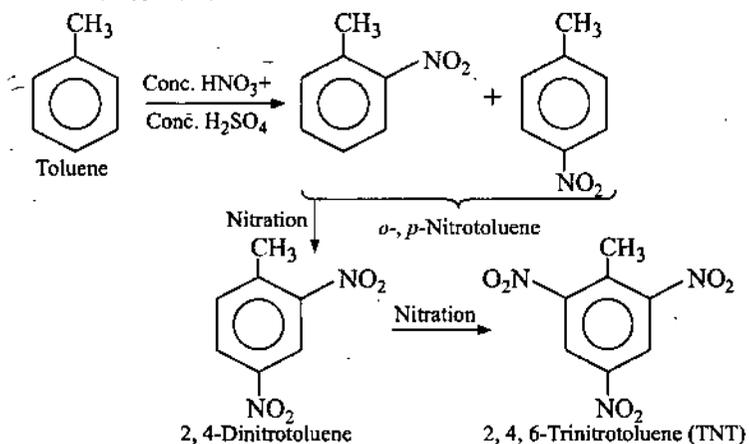
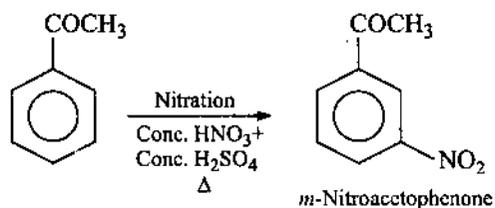
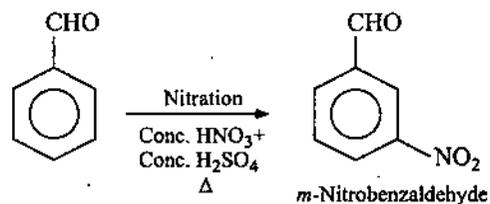
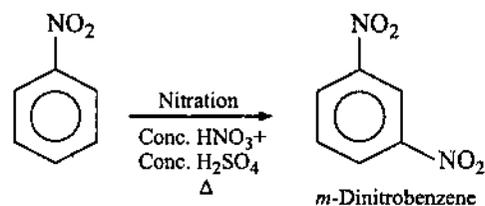
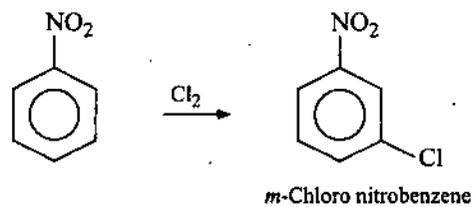
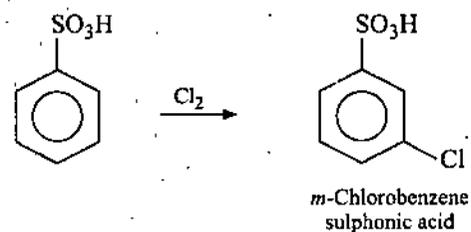


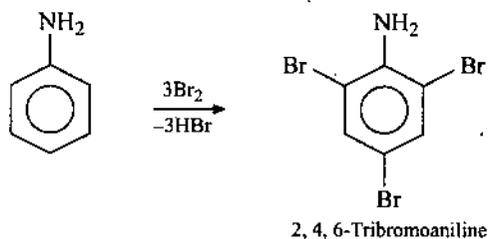
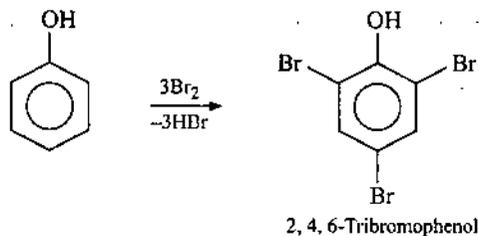
(b) Nitration of phenol



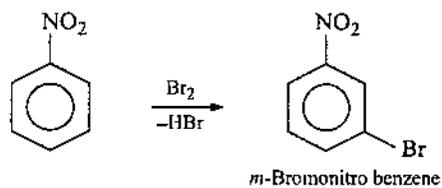
(c) Nitration of benzoic acid



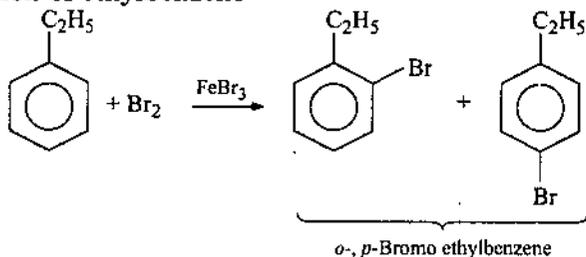
(d) Nitration of toluene**(e) Nitration of acetophenone****(f) Nitration of benzaldehyde****(g) Nitration of nitrobenzene****(ii) (a) Chlorination of nitrobenzene****(b) Chlorination of benzene sulphonic acid**

(iii) (a) Bromination of aniline (by Br₂ water)(b) Bromination of phenol (by Br₂ water)

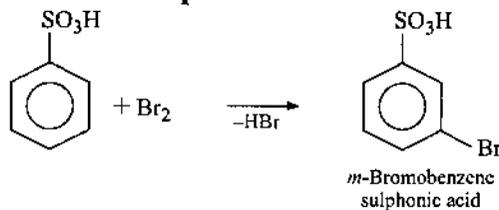
(c) Bromination of nitrobenzene



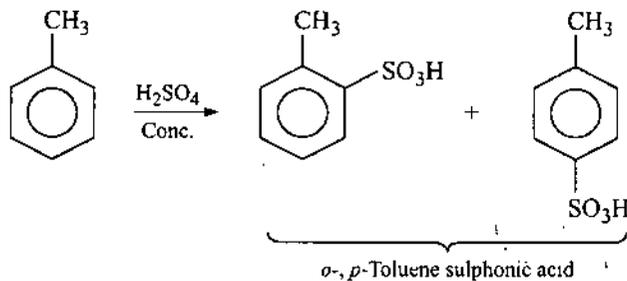
(d) Bromination of ethylbenzene

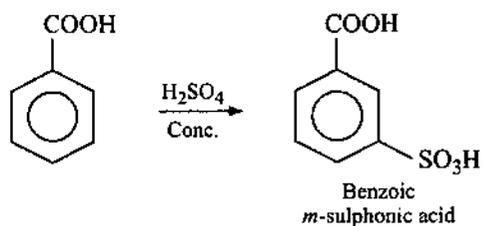
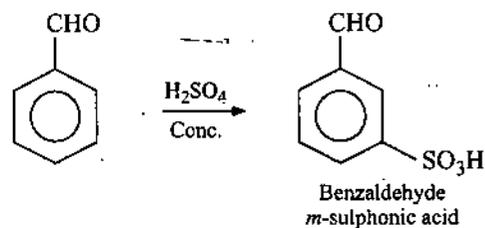
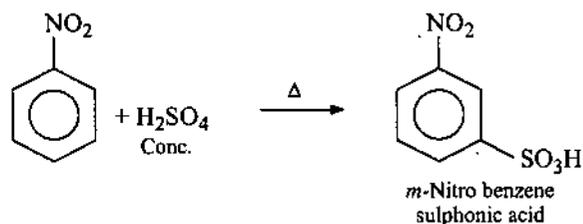


(e) Bromination of benzene sulphonic acid



(iv) (a) Sulphonation of toluene



(b) Sulphonation of benzoic acid**(c) Sulphonation of benzaldehyde****(d) Sulphonation of nitrobenzene**

29. (a), (b) and (d) are *o*- and *p*-directing, while (c) is *m*-directing.

31. (ii), 32. (iv), 33. (ii), 34. (ii), 35. (i), 36. (iii), 37. (ii), 38. (iv),

39. (iv), 40. (iii), 41. (ii), 42. (iv), 43. (i), 44. (ii)

45. (i) cyclohexane (ii) benzophenone (iii) cumene (iv) glyoxal
 (v) hexachlorocyclohexane (vi) n-hexane (vii) Etard's



6

ARYL HALIDES

STRUCTURE

- Aromatic Halogen Compounds
- Aryl Halides
- Chlorobenzene
- Dichlorobenzene
- Benzyl Chloride
- Benzal Chloride
- Benzene Hexachloride (Gammexane), BHC
- DDT
- Isomers of C_7H_7Cl , Their Preparation, Distinction and Hydrolysis
- Explanation of Facts
- Distinction between *p*-Bromotoluene and Benzyl Bromide
- Distinction between Benzyl Chloride and Benzal Chloride
- Summary
- Student Activity
- Test Yourself

LEARNING OBJECTIVES

After going this unit you will learn :

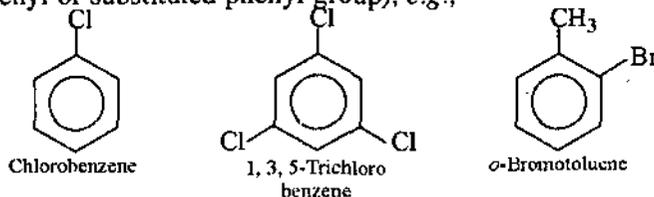
- Wurtz-Fittig reaction and Ullmann reaction.
- Formation of Grignard reagents and aryllithiums.
- Reactions involving the aromatic ring.
- Methods of preparation of chlorobenzene and dichlorobenzene with their properties and uses.
- Methods of preparation of benzal chloride and benzyl chloride with their properties and uses.

5.1. AROMATIC HALOGEN COMPOUNDS

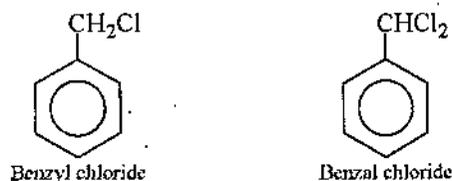
Introduction

Aromatic halogen compounds are of two types :

(1) **Aryl halides** : These are nucleus substituted aromatic halogen compounds in which the halogen atom is directly attached to the aromatic nucleus. The general formula is ArX (Ar = phenyl or substituted phenyl group), *e.g.*,



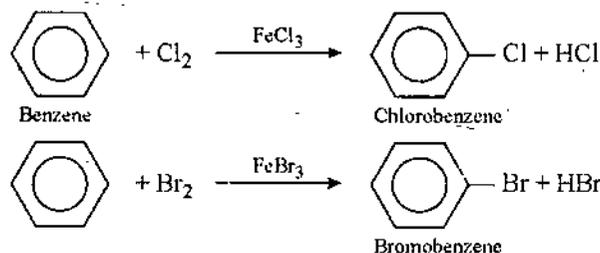
(2) **Aralkyl halides** : These are side chain substituted aromatic halogen compounds in which one or more hydrogen atoms in the alkyl side chain are replaced by halogen atoms, *e.g.*,



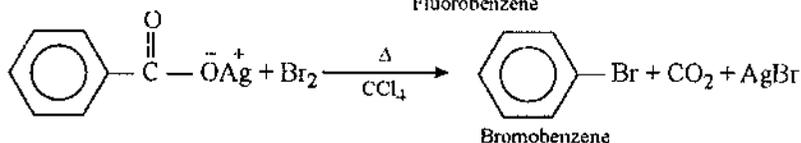
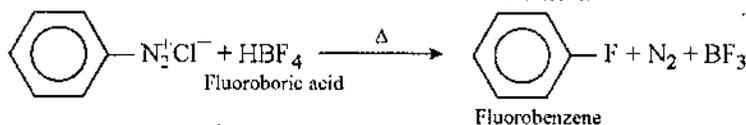
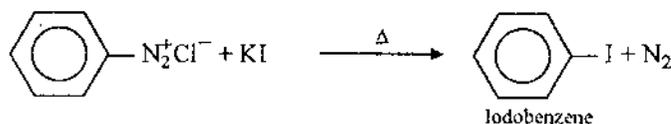
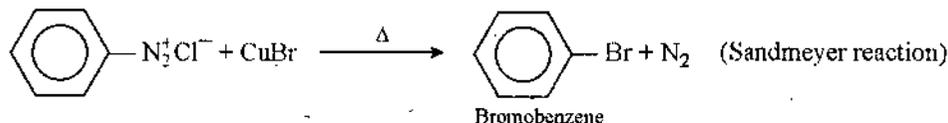
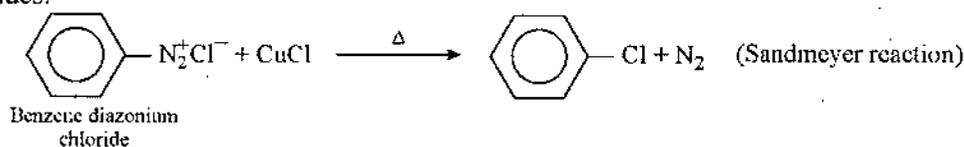
• 5.2. ARYL HALIDES

[I] Methods of Preparation

(1) **By direct halogenation** : Aryl chlorides and aryl bromides are prepared from benzene by reaction with chlorine or bromine in the presence of a catalyst such as FeCl_3 , FeBr_3 or AlCl_3 .



(2) **By decomposition of diazonium salts** : Aryl halides can be prepared most satisfactorily by the decomposition of aryl diazonium salts in the presence of suitable metal halides.



(3) **From silver salts of carboxylic acids** : The silver salt of carboxylic acids when heated with bromine, easily decarboxylates to form aryl bromide.

[II] Physical Properties :

- (1) Aryl halides are colourless oils or crystalline solids having an agreeable odour.
- (2) They are insoluble in water but soluble in organic solvents such as ethanol; diethyl ether etc.
- (3) Their boiling points, melting points and densities rise gradually as one passes from fluoro to iodo compounds.
- (4) They have density greater than one.

[III] Chemical Properties

The molecule of aryl halide is made of :

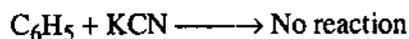
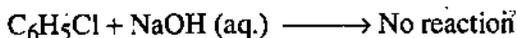
- (a) An aromatic ring
- (b) One or more halogen atoms directly bonded to the ring.

Therefore, the reactions of aryl halides are due to the aromatic ring and the halogen atoms.

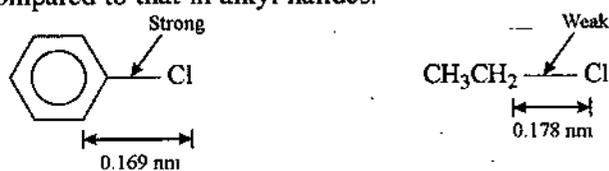
REACTIONS INVOLVING THE HALOGEN ATOMS

(1) **Nucleophilic displacement reactions** : Unlike alkyl halides, aryl halides do not undergo nucleophilic displacement reactions easily. The halogen bonded to the ring cannot

be replaced by OH, NH₂, CN by reaction with aqueous NaOH, ethanolic ammonia or potassium cyanide. Thus,

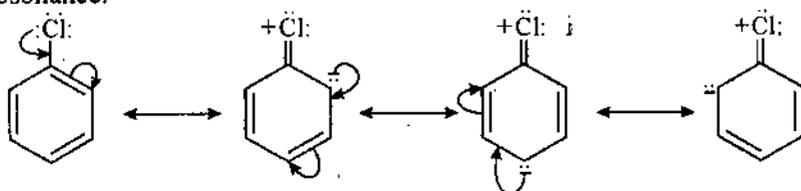


The reason for this unusual lack of reactivity is that C—X bond in aryl halides is short and strong compared to that in alkyl halides.



This is so because :

(i) The carbon-chloric bond in chlorobenzene has some double bond character as a result of resonance.

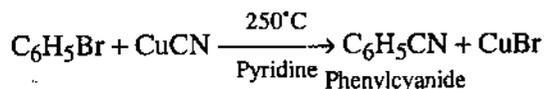
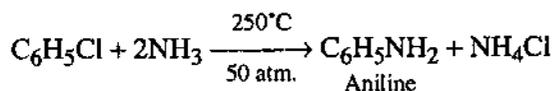
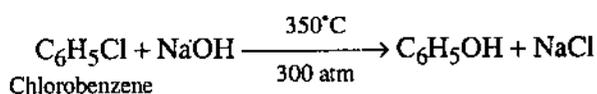


(ii) The orbitals of the carbon atom in C—Cl bond of aryl chloride are sp^2 hybridised, while those in alkyl chloride are sp^3 hybridised. Therefore, the carbon-chlorine bond in aryl chloride has more s character and is stronger than the one in alkyl chloride.

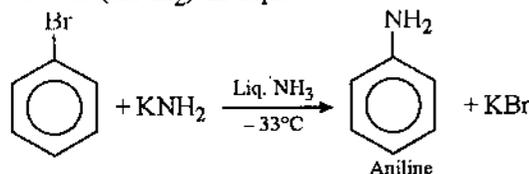
Another reason for the low reactivity of aryl halides in nucleophilic displacement reactions is that the aromatic ring is a centre of high electron density because of the π electrons. Therefore a nucleophile is discouraged from attacking the ring carbon bearing halogen.

In the light of the above facts, the nucleophilic displacement of halogen of aryl halides can occur either under drastic conditions or by the presence of electron withdrawing groups on the aromatic ring.

(a) **Under drastic conditions** : The halogens of aryl halides can be displaced by OH, NH₂ or CN with suitable nucleophilic reagents at high temperature and pressure.

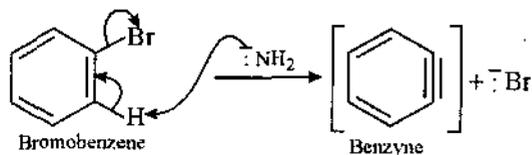


With strong bases such as NaNH₂ or KNH₂ : Aryl halides react with sodium amide (NaNH₂) or potassium amide (KNH₂) in liquid ammonia to form the respective anilines.

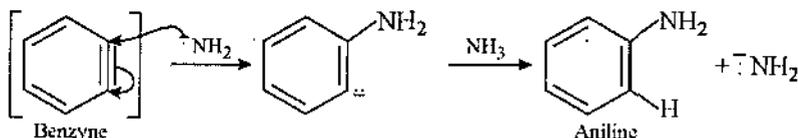


Mechanism : Following elimination addition mechanism is involved :

Step 1: Elimination Step : A benzyne is formed through removal of H^+ by NH_2^- and loss of Br^- .

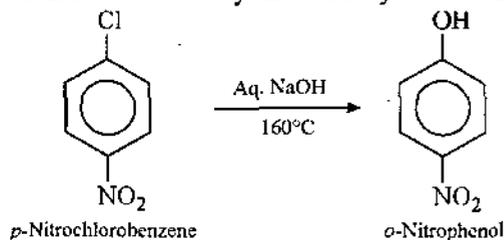


Step 2. Addition step : A carbanion is formed by nucleophilic addition of NH_2^- to benzyne. The carbanion abstracts a proton from the solvent (NH_3) to give the substitution product.

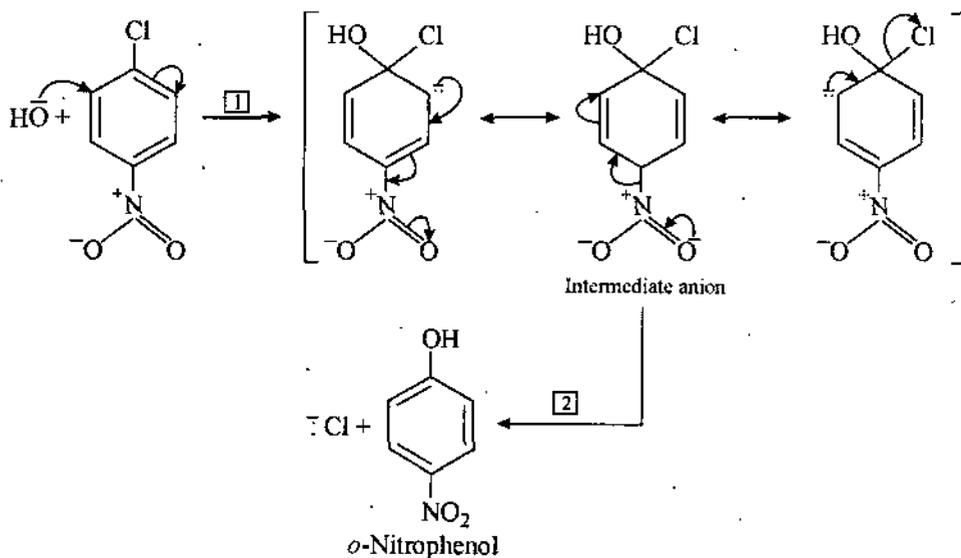


The above elimination addition mechanism is called **benzyne mechanism**.

(b) By presence of ring activating substituents : Aryl halides which have electron withdrawing groups such as NO_2 or CN in *ortho* or *para* position to the halogen, undergo nucleophilic substitution reactions relatively more easily. For example,

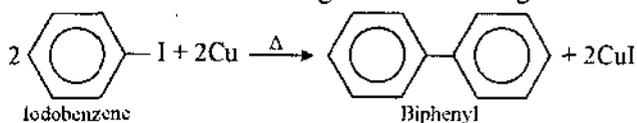


The greater the number of such *ortho* and *para* substituents, the more rapid the reaction and less vigorous the conditions required. The mechanism of the above reaction is given below :

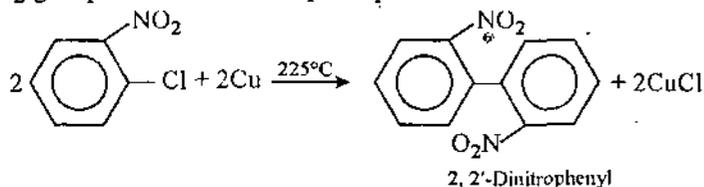


It should be noticed that it involves the formation of a carbanion as a result of nucleophilic attack by OH^- . The anionic intermediate is stabilised by resonance. Subsequent loss of chloride ion gives the substitution product.

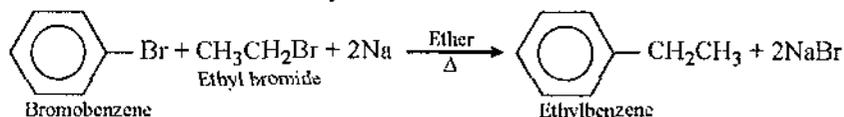
(2) Ullmann reaction : Aryl iodides and bromides when heated with copper form biaryl compounds in which two benzene rings are bonded together.



Aryl chlorides also participate in Ullman reaction if the Cl atom is activated by the presence of NO₂ group in the *ortho* and *para* positions.

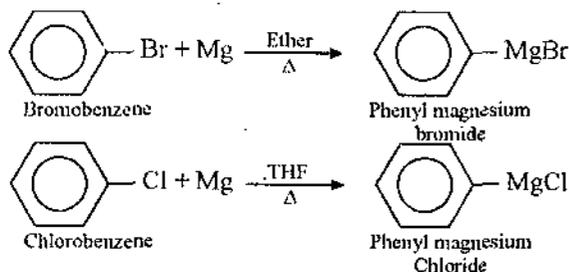


(3) **Wurtz-Fittig reaction** : Aryl halides couple with alkyl halides when heated with sodium in ether solution, to form alkylobenzenes.

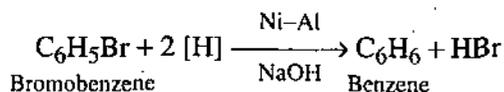


The above reaction is known as Wurtz-Fittig reaction, which is used for the synthesis of some alkylobenzenes, although the yield is poor.

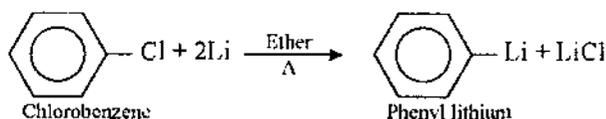
(4) **Formation of Grignard reagents** : Aryl bromides and aryl iodides form Grignard reagents in the usual manner. Aryl chlorides do so by using tetrahydrofuran (THF) in place of ether.



(5) **Reduction** : When reduced with nickel aluminium alloy in the presence of sodium hydroxide, aryl halides give corresponding arenes.



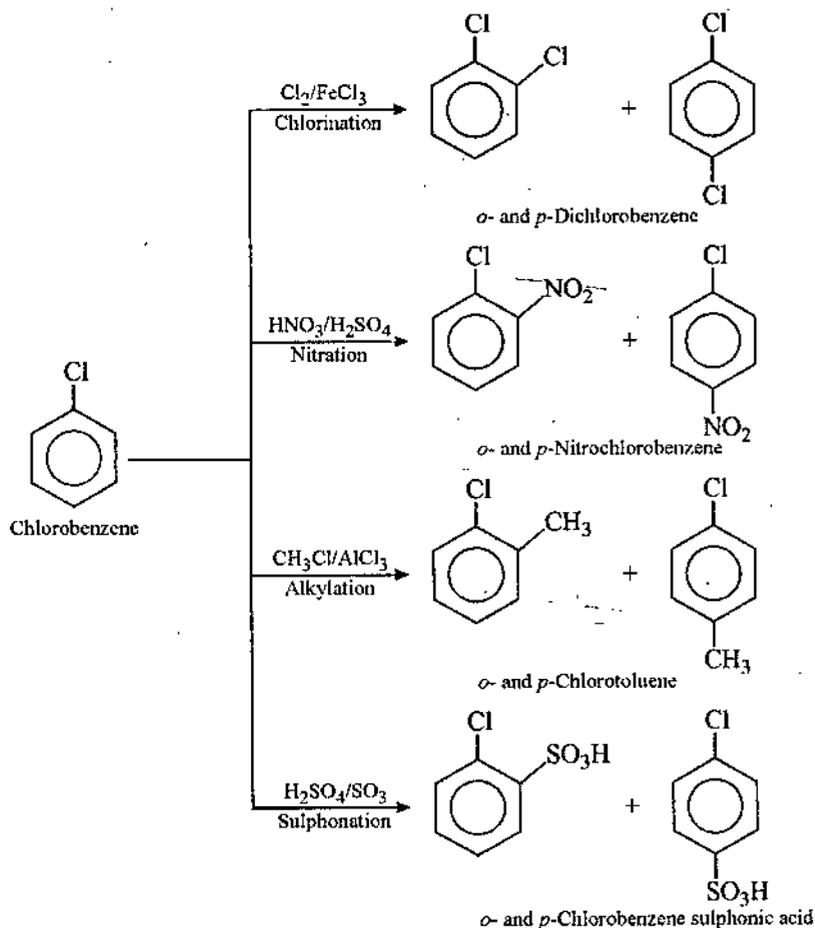
(6) **Formation of aryllithiums** : Aryl bromide react with lithium metal in ether to give aryllithiums:



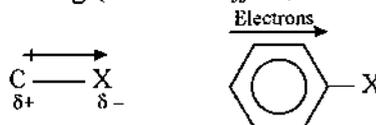
Aryllithiums give the same reactions as the Grignard reagents and are more reactive. They are now frequently used in synthesis.

REACTIONS INVOLVING THE AROMATIC RING

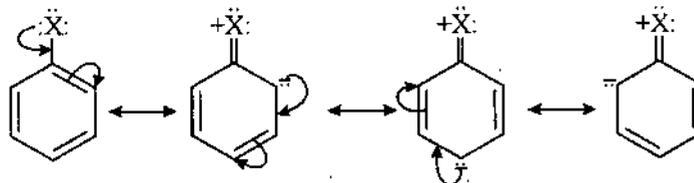
(7) **Electrophilic aromatic substitution reaction** : Aryl halides undergo the typical electrophilic aromatic substitution reactions though less readily than benzene, in *ortho* and *para* positions. The halogen atom is different from other *ortho-para* directing substituents (OH, NH₂), which makes the electrophilic substitution easy. The electrophilic substitution reactions of aryl halides are shown by taking the example of chlorobenzene.



Explanation : The halogen atom in aryl halides is highly electronegative relative to carbons and so C—Cl bond is polarised. This makes the carbon atom positive and it pulls out electrons from the benzene ring (*Inductive effect*).



On the other hand, the resonance effect causes the shift of electrons from the halogen to the ring.

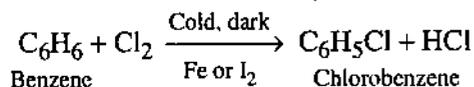


Of the two opposing effects, the inductive effect outweighs the resonance effect. So, the net result is the decrease of electron density in the benzene ring which is deactivated to electrophilic (E^+) attack. Therefore, the electrophilic substitution in the ring occurs with more difficulty than in benzene itself, and at *ortho* and *para* positions, which are relatively electron rich.

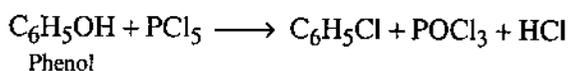
• 5.3. CHLOROBENZENE

[I] Methods of Preparation

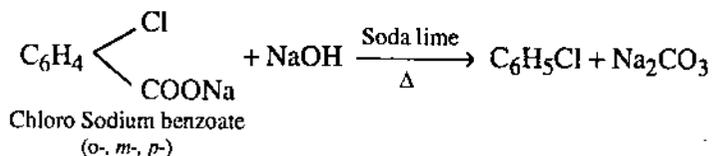
(i) **Laboratory method :** By passing chlorine in benzene, in cold, dark and in presence of a halogen carrier like I_2 , Fe, AlCl_3 etc.



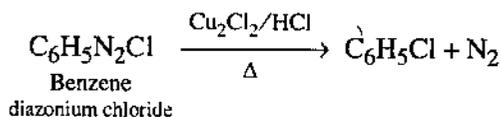
(ii) **From phenol** : By treating phenol with phosphorous pentachloride.



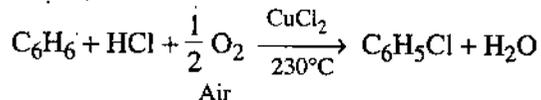
(iii) **From chlorobenzoic acids** : By heating their sodium salts with sodalime.



(iv) **By Sandmeyer's reaction** : Benzene diazonium chloride is heated with cuprous chloride and hydrochloric acid.



(v) **Manufacture** : In industries, it is prepared by passing a mixture of benzene vapours, air and hydrogen chloride gas over CuCl_2 or I_2 at 230°C . The method is known as *Raschig's process*.



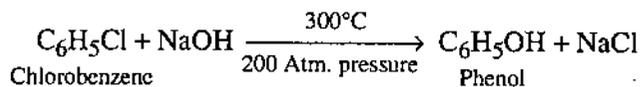
[II] Physical Properties

Chlorobenzene is a colourless liquid with a pleasant odour. It is immiscible with water, but miscible with organic solvents. Its b.p. is 132°C . The density of chlorobenzene is 1.162 g ml^{-1} .

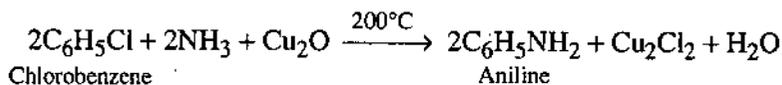
[III] Chemical Properties :

(1) **Due to chlorine atom** : The replacement of chlorine, unlike alkyl halides, is difficult owing to somewhat double bond character in C—Cl bond.

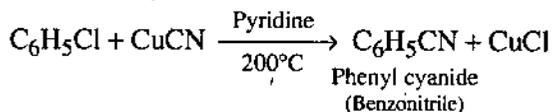
(i) **Action of NaOH** : When heated to 300°C under 200 atmospheric pressure, phenol is formed.



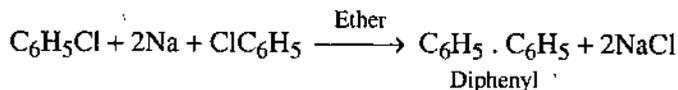
(ii) **Action of ammonia** : When heated with aq. NH_3 to 200°C in the presence of Cu_2O , aniline is formed.



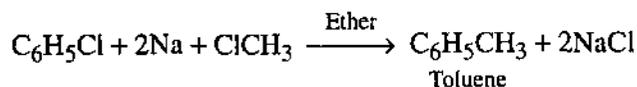
(iii) **Action of CuCN** : When heated with CuCN to 200°C in the presence of pyridine, phenyl cyanide is formed.



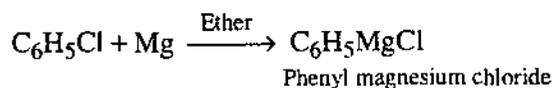
(iv) **Fittig reaction** : When treated with sodium in dry ether, it forms diphenyl.



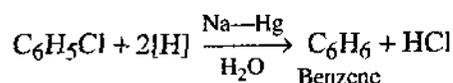
(v) **Wurtz-Fittig reaction** : Forms toluene.



(vi) **Action of Magnesium** : When treated with magnesium in dry ether, phenyl magnesium chloride (Grignard's reagent) is formed.

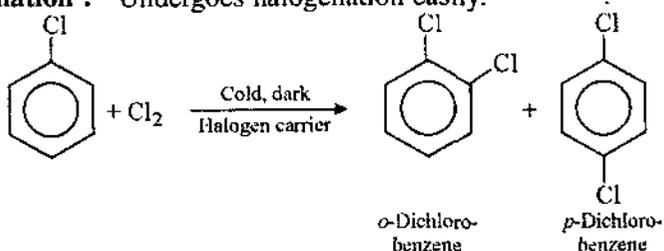


(vii) **Reduction** : When treated with Na—Hg and water, chlorobenzene forms benzene.

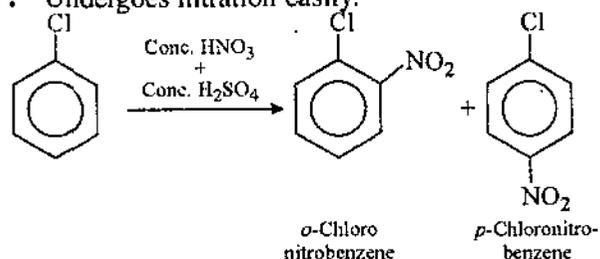


[II] Due to benzene nucleus

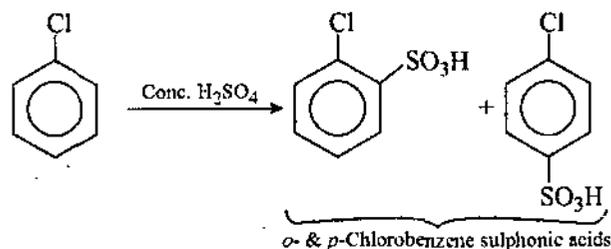
(i) **Halogenation** : Undergoes halogenation easily.



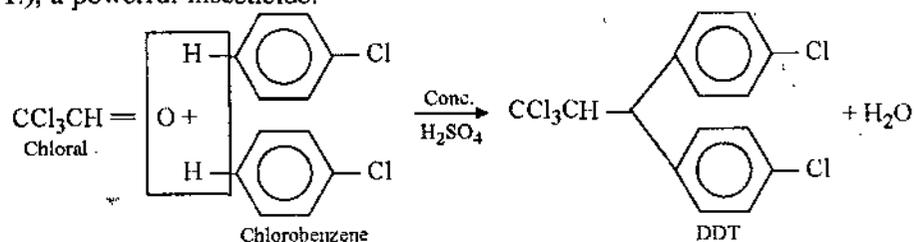
(ii) **Nitration** : Undergoes nitration easily.



(iii) **Sulphonation** : Forms mixture of *ortho*- and *para*-chlorobenzene sulphonic acids.



(iv) **Reaction with chloral** : Forms *p-p'*-dichloro diphenyl tri-chloroethane (D.D.T.), a powerful insecticide.



[III] Uses

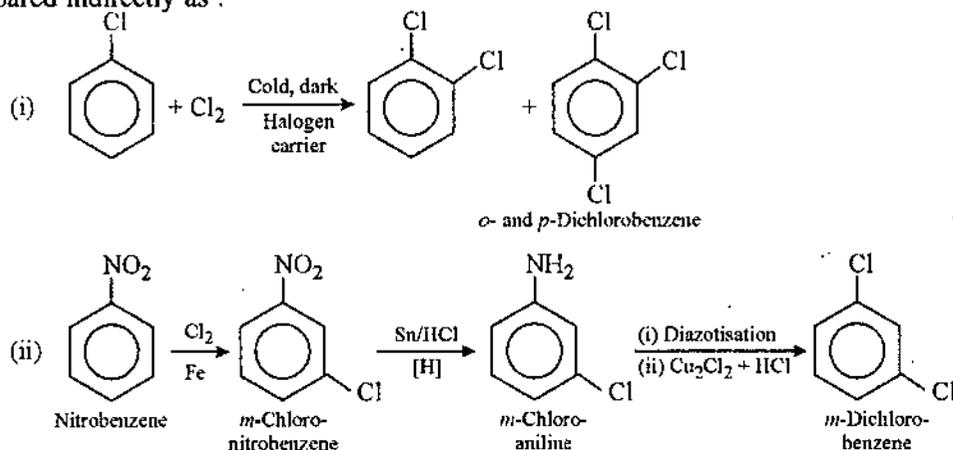
Chlorobenzene is used :

- (i) In the preparation of D.D.T., an insecticide.
- (ii) In the manufacture of phenol and aniline.

• 5.4. DICHLOROBENZENE

[I] Method of Preparation

There are three isomeric dichlorobenzenes, out of which *ortho*- and *para*-isomers can be prepared by further chlorination of chlorobenzene. The *meta*-isomer is, however, prepared indirectly as :



[II] Properties

Ortho- and *meta*-dichlorobenzenes are colourless liquids boiling at 80°C and 173°C, respectively. *p*-Dichlorobenzene is a colourless, solid and melts at 52°C (b.p. 175°C). They resemble chlorobenzene in their properties.

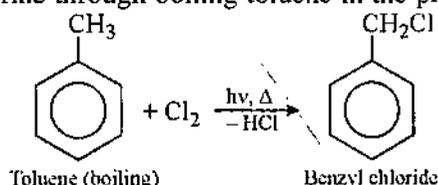
[III] Uses

Dichlorobenzene is used as a solvent for fats and also for cleaning metals like nickel and copper, as it dissolves oxides of non-ferrous metals. *p*-Dichlorobenzene finds use as a larvicide for cloth moth.

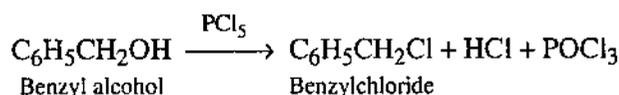
• 5.5. BENZYL CHLORIDE

[I] Preparation

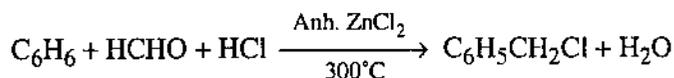
(1) Benzyl chloride can be prepared in laboratory and on large scale by passing calculated amount of chlorine through boiling toluene in the presence of sunlight.



(2) Benzyl chloride can be prepared by the action of PCl₅ or thionyl chloride on benzyl alcohol.



(3) Benzyl chloride can be obtained by chloromethylation of benzene.



[II] Physical Properties

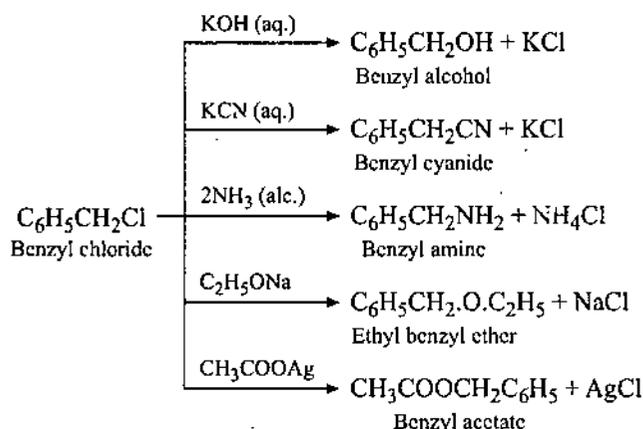
Benzyl chloride is a colourless heavy liquid, B.P. = 179°C. It possesses a pungent smell and is insoluble in water, but soluble in various organic solvents.

[IV] Chemical Properties

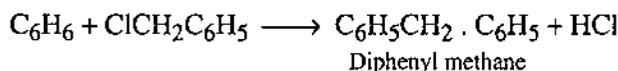
Benzyl chloride resembles alkyl halides and is reactive both in S_N¹ and S_N² reactions. The reactivity is due to the formation of resonance stabilised benzyl carbonium ion. Besides

nucleophilic substitution at side chain, benzyl chloride undergoes Friedel-Craft's reaction, Wurtz-Fittig reaction and also electrophilic substitution reactions like halogenation, sulphonation, nitration etc. Some of the important reactions of benzyl chloride are mentioned below.

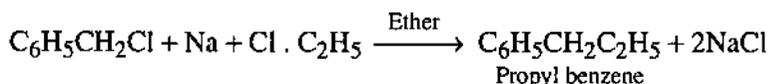
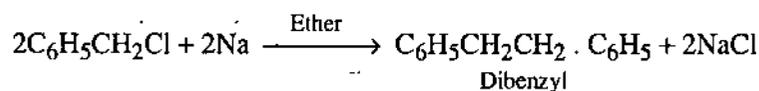
(1) **Nucleophilic substitution reactions** : These reactions are similar to alkyl halides.



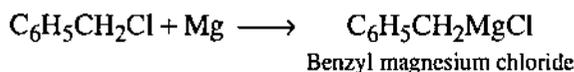
(2) **Friedel-Craft's reaction** : Benzyl chloride can replace alkyl halides in Friedel-Craft's alkylation reaction to form higher hydrocarbons.



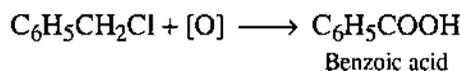
(3) **Wurtz-Fittig or Fittig reaction** : Benzyl chloride reacts with alkyl halides (Wurtz-Fittig) or aryl halides (Fittig) in presence of metallic sodium in dry ether.



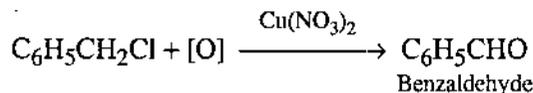
(4) **Formation of Grignard reagent** : When heated with dry Mg powder in dry ether, benzyl chloride forms Grignard reagent.



(5) **Oxidation** : (a) When oxidised with HNO_3 , the side chain along with the halogen is changed into $-\text{COOH}$ group.



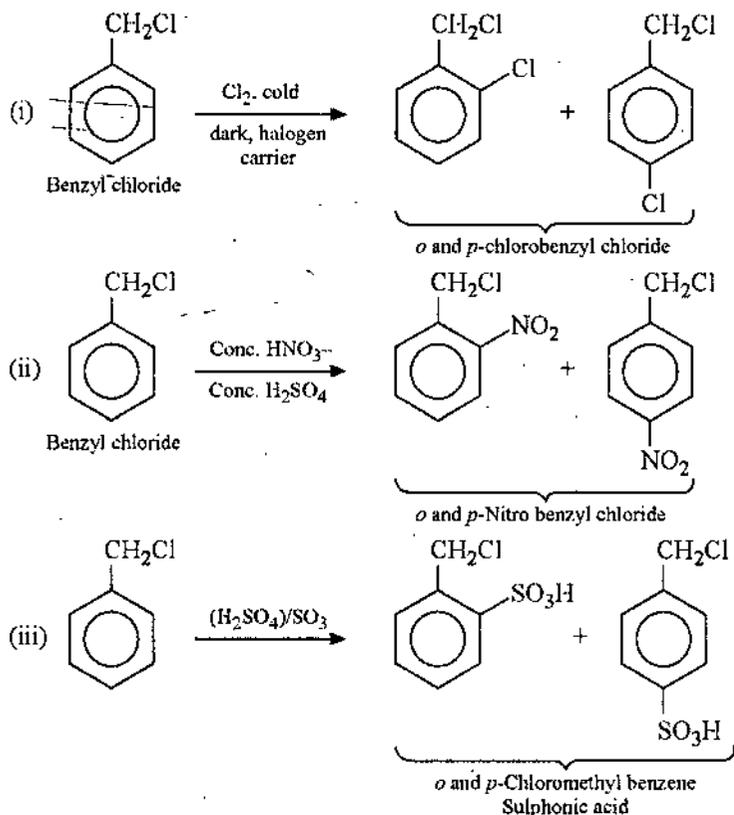
(b) With mild oxidising agents like cupric nitrate, benzyl chloride forms benzaldehyde.



(6) **Reduction** : When reduced with nascent hydrogen, benzyl chloride forms toluene.



(7) **Nuclear electrophilic substitution reactions** : Benzyl chloride undergoes halogenation, nitration, sulphonation, alkylation etc. forming *ortho*- and *para*-isomers.

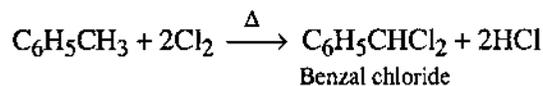
**[IV] Uses**

Benzyl chloride is used in the manufacture of benzoic acid, benzyl amine, benzaldehyde etc. It is an important laboratory reagent for introducing the benzyl group in organic compounds.

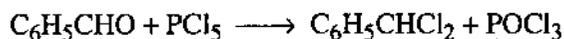
• 5.6. BENZYL CHLORIDE**[I] Preparation**

Benzyl chloride may be prepared :

(i) by passing calculated amount of chlorine into boiling toluene.



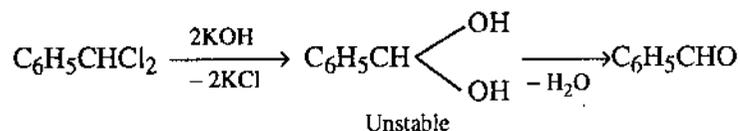
(ii) by the action of phosphorus pentachloride on benzaldehyde.

**[II] Physical Properties**

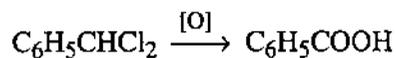
Benzyl chloride is a colourless liquid, B.P. 207°C. It is not lachrymatory.

[III] Chemical Properties

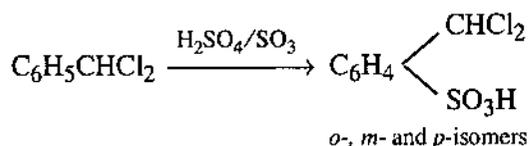
1. **Hydrolysis** : Like other gem-dihalides, benzyl chloride is hydrolysed with aqueous alkali, forming benzaldehyde.



2. **Oxidation** : Benzyl chloride is oxidised to benzoic acid.



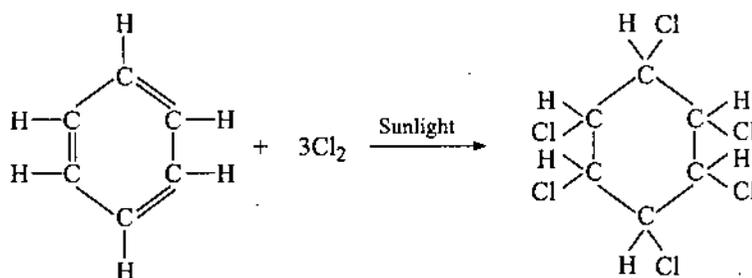
3. **Nuclear substitution reactions** : Benzyl chloride shows nitration, sulphonation, halogenation, alkylation etc. forming all the three isomers, i.e., *o*-, *m*- and *p*-isomers.

**[IV] Uses**

Benzal chloride is used in the preparation of benzaldehyde.

• 5.7. BENZENE HEXACHLORIDE (GAMMEXANE), BHC

Chemically, gammexane or 666 is the γ -isomer of 1, 2, 3, 4, 5, 6 hexachlorocyclohexane. It is obtained by heating benzene with chlorine in presence of sunlight.

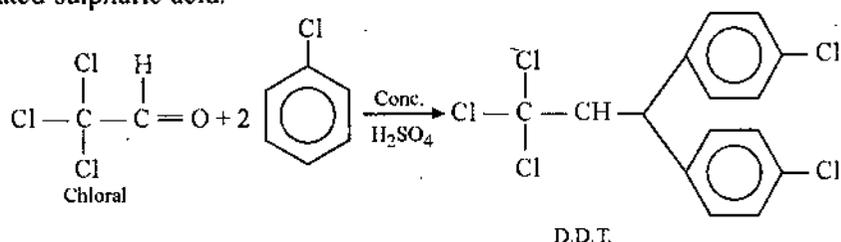


Due to the difference in the arrangement of hydrogen and chlorine atoms on opposite sides of the ring, it can exist in eight stereo-isomeric forms. One form, known as γ -isomer is a powerful insecticide and is more powerful than D.D.T. However, γ -isomer exists to an extent of 12–14% out of all isomeric forms.

Gammexane is used as a powerful insecticide.

• 5.8. DDT [2, 2'-BIS-(4-CHLOROPHENYL)-1, 1, 1-TRICHLOROETHANE OR *p*, *p*'-DICHLORO DIPHENYL TRICHLOROETHANE]

DDT is prepared by the condensation of chlorobenzene with chloral in presence of concentrated sulphuric acid.

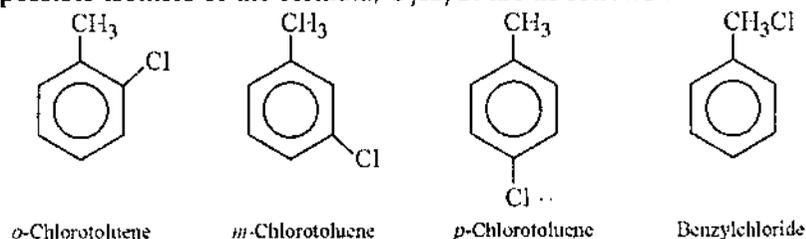


DDT is practically insoluble in water, moderately soluble in hydroxylic and polar solvents and in petroleum oils. It is readily soluble in most aromatic and chlorinated solvents.

DDT is an effective insecticide, particularly for mosquitoes, flies and crop pests.

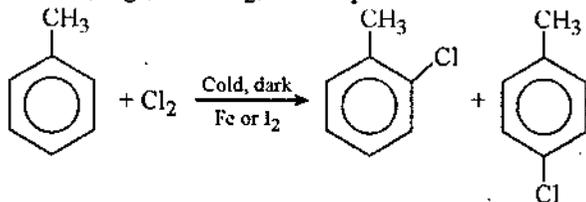
• 5.9. ISOMERS OF C₇H₇Cl, THEIR PREPARATION, DISTINCTION AND HYDROLYSIS

The possible isomers of the formula, C₇H₇Cl are as follows :



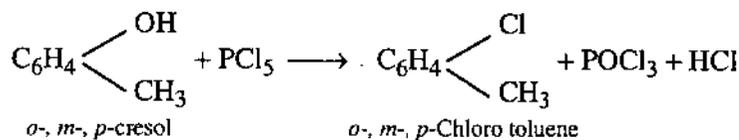
[I] Preparation of *o*, *m*, *p*-Chlorotoluenes

(i) **From toluene** : By passing chlorine gas through toluene in cold, dark and in the presence of halogen carrier, *e.g.*, Fe or I₂, *o*- and *p*-chloro toluenes are obtained.

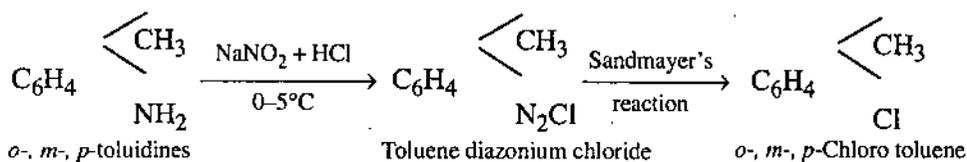


m-Chlorotoluene cannot be obtained by this method.

(ii) **From *o*, *m*, *p*-cresol** : By the action of PCl₅ on cresols.



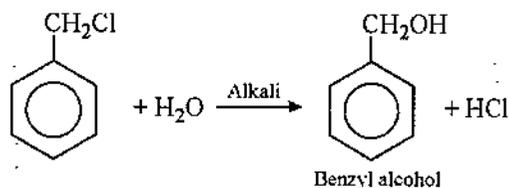
(iii) **From *o*, *m*, *p*-toluidines** :

**[II] Preparation of Benzyl Chloride**

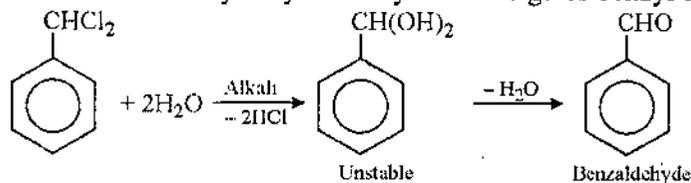
Please refer to preceding article.

[III] Distinction Between Chlorotoluenes and Benzyl Chloride :

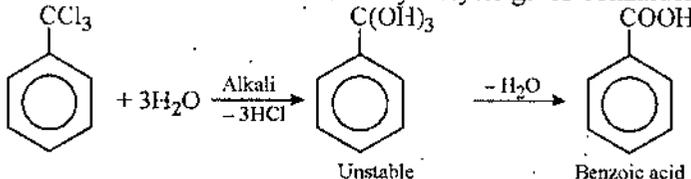
Please refer to preceding article.

[IV] Hydrolysis

(i) **Benzyl chloride** : On hydrolysis benzyl chloride gives benzyl alcohol.



(ii) **Benzal chloride** : Benzal chloride on hydrolysis gives benzaldehyde.

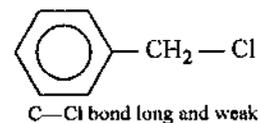
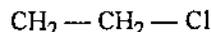
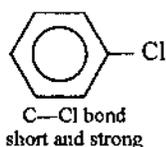


(iii) **Benzotrichloride** : Benzotrichloride on hydrolysis gives benzoic acid.

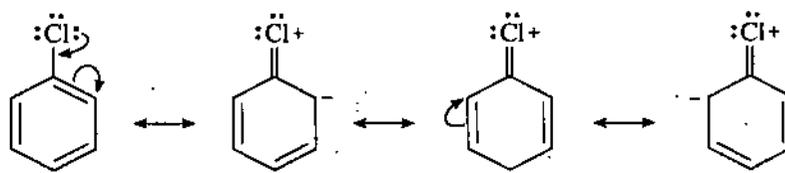
• 5.10. EXPLANATION OF FACTS

(1) *Chlorobenzene is not reactive like ethyl chloride but benzylchloride is as reactive as ethyl chloride.*

Chlorobenzene is not reactive like ethyl chloride or benzyl chloride. This is because C—Cl bond in chloro benzene is short and strong as compared to C—Cl bond in ethyl



chloride or benzyl chloride.



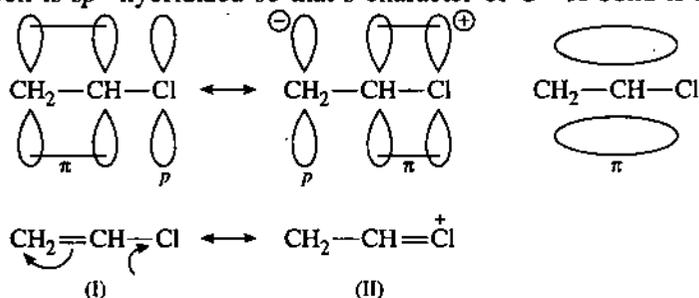
(i) In chlorobenzene, C—Cl bond has some double bond character as a result of resonance.

(ii) In chlorobenzene carbon atom of C—Cl bond is sp^2 hybridized, whereas in ethyl chloride or benzyl chloride carbon atom of C—Cl bond is sp^3 hybridized. Therefore, C—Cl bond in chlorobenzene has more s -character than in ethyl chloride or benzyl chloride. As a result in chlorobenzene chlorine atom is strongly bound to the benzene nucleus.

(iii) Another reason for the low reactivity of chlorobenzene is that the electron density of benzene nucleus is high due to the presence of π -electrons. Hence, nucleophilic reagents normally do not attack carbon atom attached to chlorine.

(2) *Vinyl halides are aliphatic halogen compounds but the reactivity of halogen in them is more like that of the halogen in aryl halides.*

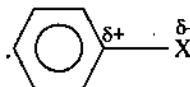
Vinyl halides are aliphatic halogen compounds but the reactivity of halogen in them is more like that of the halogen in aryl halides. This is because in both compounds halogen containing carbon is sp^2 hybridized so that s -character of C—X bond is much more. In



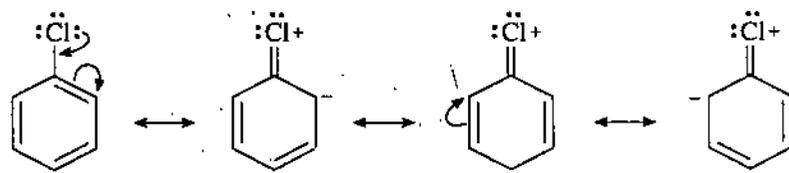
both these compounds halogen atom is strongly bound to the carbon and hence is less reactive.

(3) *Halogen atom is o- and p-directing and yet it is deactivating.*

The halogen atom in aromatic halides is more electronegative than carbon. Hence, shared pair of electron between carbon and halogen will be attracted more towards the



halogen atom. As a result, carbon atom becomes positively charged and it attracts the electrons of benzene ring (inductive effect).



On the other hand, electrons are shifted from halogen atom to benzene due to resonance.

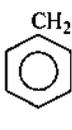
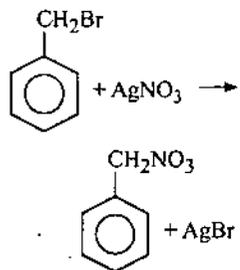
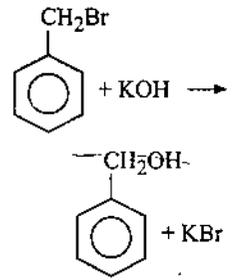
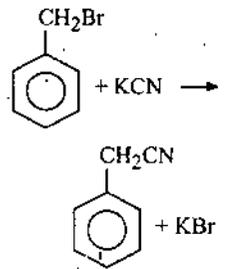
Of the two opposing effects, inductive effect overweighs the resonance effect. As a result, the electron density of benzene ring is decreased and it is deactivated for electrophilic

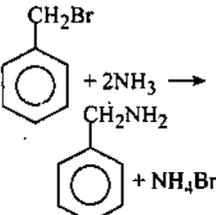
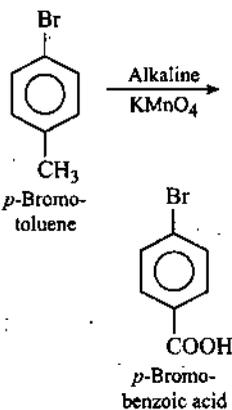
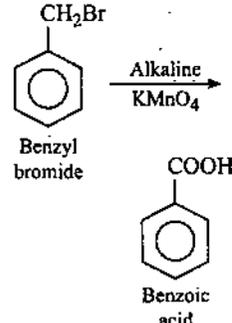
substitution. Hence, in chlorobenzene electrophilic substitution takes place with more difficulty than in benzene.

(4) Further chlorination of chlorobenzene to dichlorobenzene shall be easier or more difficult.

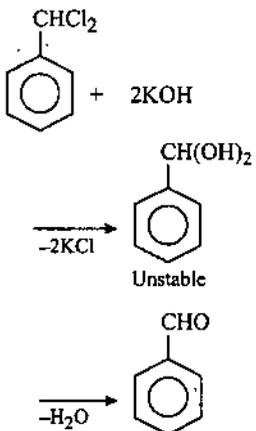
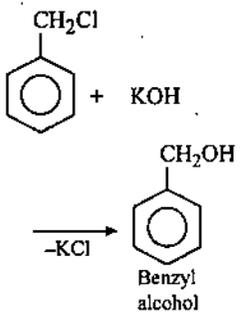
Further chlorination of chlorobenzene to dichlorobenzene shall be difficult. This is because the chlorine atom is deactivator although it is *o*- and *p*-directing. It, therefore, decreases the reactivity of benzene nucleus so that electrophilic substitution in chlorobenzene takes place with difficulty.

5.11. DISTINCTION BETWEEN *p*-BROMOTOLUENE AND BENZYL BROMIDE

Property	<i>p</i> -Bromotoluene 	Benzyl bromide, 
1. Smell	Not unpleasant	Unpleasant
2. Replacement of bromine atom.	Bromine atom is firmly attached to the benzene nucleus, hence it cannot be easily replaced.	Bromine atom is not firmly attached to the benzene nucleus, hence it can be easily replaced.
(i) Action with alcoholic AgNO ₃	—	A yellow precipitate of AgBr is obtained. 
(ii) Action with KOH	—	Benzyl alcohol is formed. 
(iii) Action with KCN	—	Benzyl cyanide is formed. 

Property	<i>p</i> -Bromotoluene 	Benzyl bromide, 
(iv) Action with NH ₃	—	Benzylamine is formed. 
3. Oxidation by alkaline KMnO ₄	<i>p</i> -Bromobenzoic acid is formed. 	Benzoic acid is formed. 

• 5.12. DISTINCTION BETWEEN BENZAL CHLORIDE AND BENZYL CHLORIDE

Property	Benzal chloride, 	Benzyl chloride, 
(i) Boiling point	207°C	179°C
(ii) Action with KOH	Benzaldehyde is formed. 	Benzyl alcohol is formed. 

2. Mention two methods of preparation of chlorobenzene.

3. Write a note on DDT.

4. Write the isomers of the molecular formula C_7H_7Cl .

5. Mention two differences between benzyl chloride and benzal chloride.

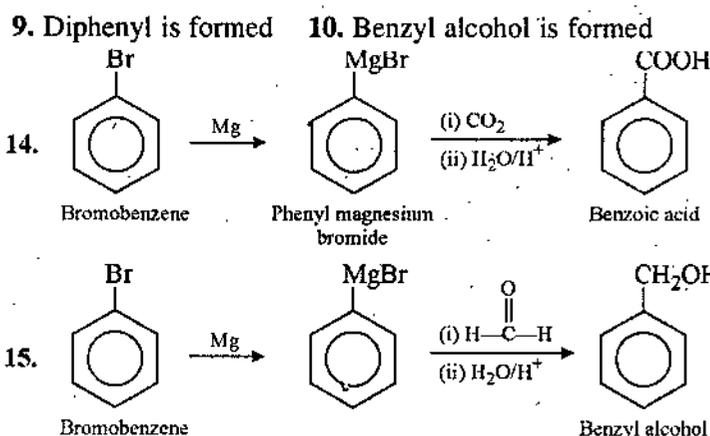
• TEST YOURSELF

Answer the following questions :

- Write a note on Ullmann reaction.
- Write a note on Wurtz-Fittig reaction.
- What are aryl halides ? How are they prepared ?
- Describe some important reactions of aryl halides.
- How is chlorobenzene prepared ?
- Describe important chemical reactions of chlorobenzene involving aromatic ring.
- How is benzyl chloride prepared ?
- What happens when benzyl chloride, benzal chloride and benzotrichloride are hydrolysed ?
- What happens when iodobenzene is heated with copper powder ?
- What happens when benzyl chloride is treated with aqueous NaOH ?
- Explain why chlorobenzene is less reactive than benzyl chloride ?
- How are chlorobenzene and benzyl chloride distinguished ?
- How will you synthesise DDT from chlorobenzene ?
- How will you synthesise benzoic acid from bromobenzene ?
- How will you prepare benzyl alcohol from bromobenzene ?
- Mention the isomers of formula C_7H_7Cl . Describe methods of their preparation.
- Write the formula of BHC.
- Write the uses of BHC and DDT.
- Explain why further chlorination of chlorobenzene to dichlorobenzene shall be easier or more difficult ?
- The directive influence of $-CHO$ group is :
(i) ortho (ii) meta (iii) para (iv) ortho and para
- Benzene undergoes substitution reaction by which mechanism ?
(i) S_N^1 (ii) S_N^2
(iii) S_E^1 (iv) S_E^2
- The ion responsible for nitration is :
(i) NO_3^- (ii) NO_2^-
(iii) NO_2^+ (iv) NO^+
- Which of the following fractions of coal tar gives benzene on fractional distillation ?
(i) Light oil (ii) Middle oil
(iii) Heavy oil (iv) Green oil
- The ozonolysis of benzene gives :
(i) Acetic acid (ii) Benzene triozonide
(iii) Glyoxal (iv) Formaldehyde
- Cresol on distillation with zinc dust gives :
(i) Toluene (ii) Benzene
(iii) Phenol (iv) Chlorobenzene
- TNT is obtained from :
(i) Benzene (ii) Toluene
(iii) Chloro benzene (iv) Nitro benzene
- Chlorination of toluene in the presence of heat and light gives :
(i) Benzoyl chloride (ii) *o*- and *p*-chlorotoluene
(iii) Benzyl chloride (iv) *m*-chloro toluene
- Cumene is :
(i) Ethyl benzene (ii) Phenyl ethylene
(iii) Isopropyl benzene (iv) *n*-propyl benzene
- Styrene is :
(i) Vinyl benzene (ii) Ethyl benzene (iii) Isopropyl benzene (iv) *o*-xylene

30. *o*-xylene on oxidation with KMnO_4 gives :
- (i) Benzene (ii) Benzoic acid
(iii) Phthalic acid (iv) Terephthalic acid
31. Chloro benzene is manufactured by :
- (i) Dows process (ii) Raschig's process
(iii) Friedel-Craft reaction (iv) Sandmayer's reaction
32. D.D.T. is obtained by the condensation of chloral with :
- (i) Chloro benzene (ii) Toluene
(iii) Aniline (iv) Acetaldehyde
33. Chloro benzene reacts with sodium in the presence of ether to form diphenyl. The reaction is called as :
- (i) Wurtz reaction (ii) Fittig reaction
(iii) Wurtz Fittig reaction (iv) Ullmann reaction
34. Ullmann reaction is used for the preparation of :
- (i) Iodobenzene (ii) Diphenyl
(iii) Toluene (iv) Benzene
35. Which of the following alkyl halides is most reactive ?
- (i) $\text{R}-\text{F}$ (ii) $\text{R}-\text{Cl}$
(iii) $\text{R}-\text{Br}$ (iv) $\text{R}-\text{I}$
36. Fill in the blanks :
- (i) The directive influence of nitro group is
- (ii) Benzene was discovered by
- (iii) In benzene each carbon atom is hybridized.
- (iv) The chemical name of D.D.T. is
- (v) The catalyst used in Friedel Craft reaction is
- (vi) Benzene reacts with acetyl chloride in the presence of anhydrous AlCl_3 to give
- (vii) Toluene on oxidation by CrO_2Cl_2 in CS_2 at $25-40^\circ\text{C}$ gives
- (viii) The hydrolysis of benzoyl chloride gives

ANSWERS



20. (ii) 21. (iv) 22. (iii) 23. (i) 24. (iii) 25. (i) 26. (ii), 27. (iii) 28. (iii)
29. (i) 30. (iii) 31. (ii) 32. (i) 33. (ii) 34. (ii) 35. (iv)
36. (i) meta (ii) Faraday (iii) sp^2 (iv) *p*, *p'*-dichlorodiphenyl trichloroethane
(v) Anhy. AlCl_3 (vi) Acetophenone (vii) benzaldehyde (viii) benzoic acid.



7

ARYL ALDEHYDES AND KETONES

STRUCTURE

- Aryl Aldehydes
- Aryl Ketones
- Benzaldehyde
- Salicylaldehyde
- Acetophenone
- Benzophenone
- Distinction Between Benzaldehyde and Acetophenone
- Explanation of Facts
- Comparison of Aromatic Aldehydes and Aliphatic Aldehydes
 - Summary
 - Student Activity
 - Test Yourself

LEARNING OBJECTIVES

After going this unit you will learn :

- General methods of preparation of aryl aldehydes : By oxidation of primary alcohols, Stephen's method.
- Specific methods of preparation of aryl aldehydes : Etard's reaction, Sommelet's reaction, Riemer-Tiemann reaction Gattermann-Koch reaction.
- Reactions of carbonyl group.
- Iodoform reaction and reactions due to benzene nucleus.
- Claisen-Schmidt condensation, Benzoin condensation and condensation with phenol and dimethyl aniline.
- Conversion of benzaldehyde into different compounds.

6.1. ARYL ALDEHYDES

Aryl aldehydes are of two types :

(i) Those in which the aldehydic group (—CHO) is attached to aromatic nucleus directly, e.g., benzaldehyde (C₆H₅CHO). These are important compounds.

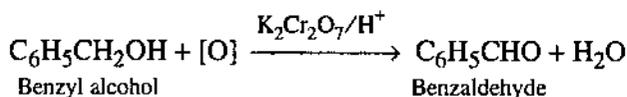
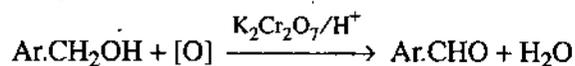
(ii) Those in which the aldehydic group is attached to the side chain of the aromatic nucleus, e.g., phenyl acetaldehyde (C₆H₅CH₂, CHO).

General Methods of Preparation

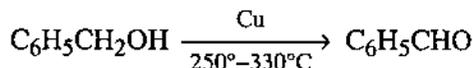
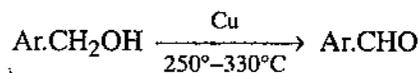
[A] Methods of Preparation Similar to Those of Aliphatic Aldehydes

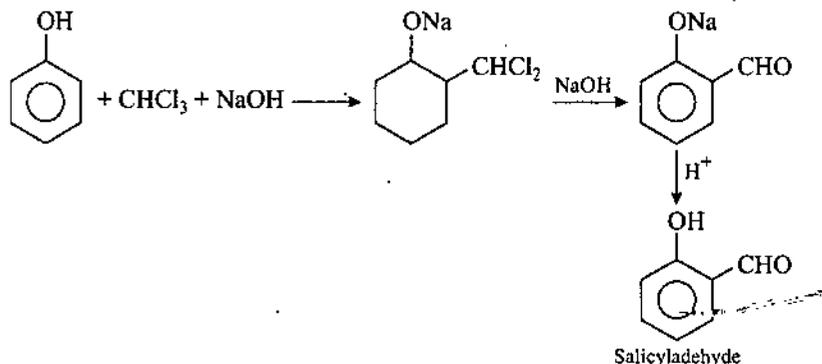
(1) Oxidation of primary alcohols :

(a) Primary alcohols when oxidised with acidic K₂Cr₂O₇ or nitric acid give aldehydes.

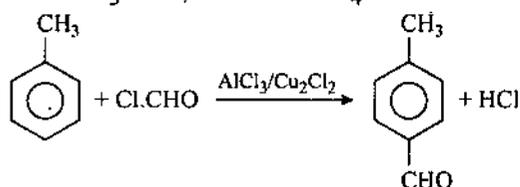
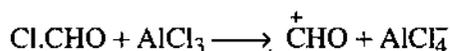


(b) By catalytic dehydrogenation of primary alcohols.

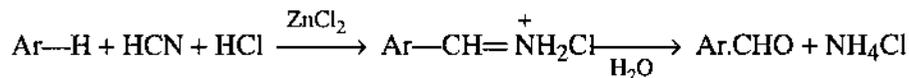




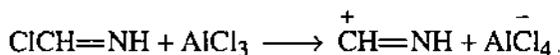
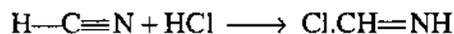
(4) **Gattermann-Koch reaction** : Homologues of benzaldehyde are obtained by the action of carbon monoxide and hydrogen chloride on toluene etc. in presence of catalysts like anhydrous aluminium chloride and Cu_2Cl_2 . This reaction proceeds via the intermediate formation of formyl chloride ($\text{Cl}\cdot\text{CHO}$). It then undergoes Friedel-Craft's reaction with aromatic substrate in which $\text{H}-\text{C}=\text{O}$ is the attacking nucleophile.



(5) **Gattermann aldehyde synthesis** : It is a Friedel-Craft's type reaction in which the aromatic substrate is treated with a mixture of hydrogen cyanide and HCl , in presence of anhydrous AlCl_3 or zinc chloride.

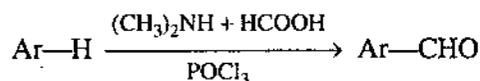


It is an electrophilic substitution reaction and the electrophile ($\text{CH}=\overset{+}{\text{N}}\text{H}$) is the attacking reagent.

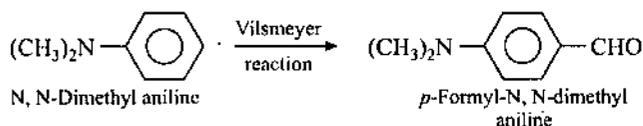


This method is chiefly used on phenols or activated substrates.

(6) **Vilsmeier reaction** : It consists in treating a suitable aromatic compound with a mixture of secondary amine and formic acid, in presence of phosphorous oxychloride.



This method is applicable to only the most reactive aromatic compounds, e.g., *N,N*-dimethylaniline.



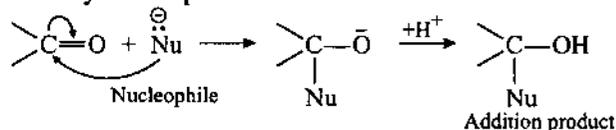
[II] General Physical Properties

Aromatic aldehydes are usually colourless liquids or solids with a characteristic pleasant odour. They are insoluble in water, but soluble in alcohol, ether and other organic solvents. They are generally steam distilled.

[III] General Chemical Properties

Aromatic aldehydes like aliphatic aldehydes contain a carbonyl group which provides a site for nucleophilic addition reactions because of :

- (i) The polar nature of carbonyl group. The carbonyl carbon becomes electron deficient and can be attacked by a nucleophile.
- (ii) The ability of carbonyl oxygen to accommodate negative charge.
- (iii) The coplanar arrangement of atoms or groups around the carbonyl carbon which makes it open to attack by nucleophiles.

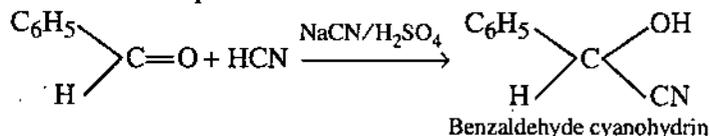


Further, due to the presence of *m*-directing and deactivating carbonyl group, the aromatic aldehydes undergo electrophilic substitution reactions at *m*-position with respect to carbonyl group.

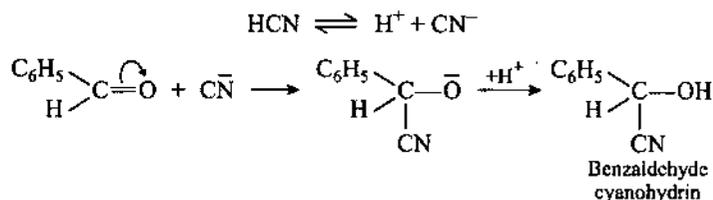
Effect of aryl group on the reactivity of the carbonyl group : The electron withdrawing inductive effect of the aryl group may increase the electron deficiency at carbonyl carbon and thus facilitate nucleophilic attack at the carbonyl carbon. The electron releasing through resonance by the benzene ring decreases the electron deficiency at carbonyl carbon and so deactivates the carbonyl group towards nucleophilic attack. The resonance effect outweighs the inductive effect and this causes net deactivation of carbonyl group in aromatic aldehydes towards nucleophilic attack.

Reactions of Carbonyl Group**[A] Reactions Similar to Aliphatic Aldehydes**

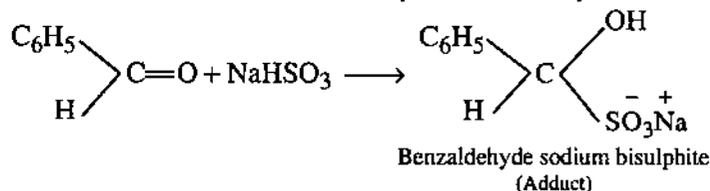
(i) **Addition of hydrogen cyanide :** Aldehydes when treated with aqueous sodium cyanide and sulphuric acid, add on a molecule of HCN to the carbonyl group to form cyanohydrin—an addition compound.



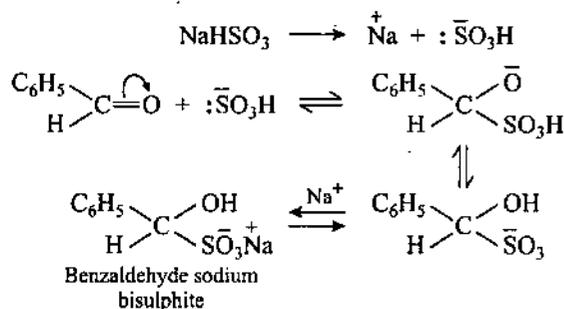
Mechanism :



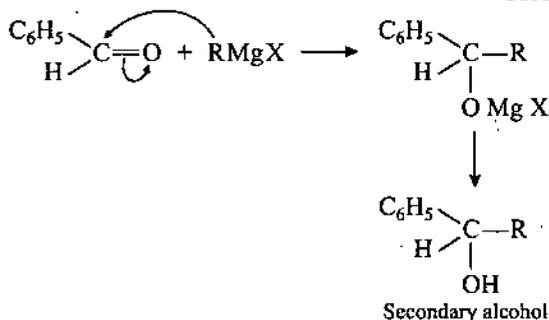
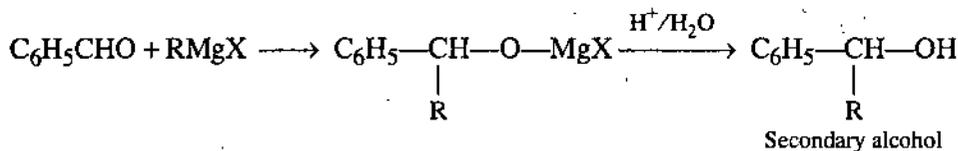
(ii) **Addition of sodium bisulphite :** Benzaldehyde and other aldehydes when treated with a saturated solution of sodium bisulphite form a crystalline adduct.



Mechanism :



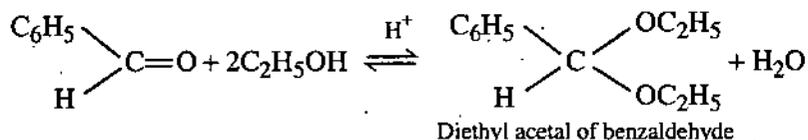
(iii) **Addition of Grignard reagents :** Grignard reagents add to the carbonyl group of aldehydes to form secondary-alcohols.



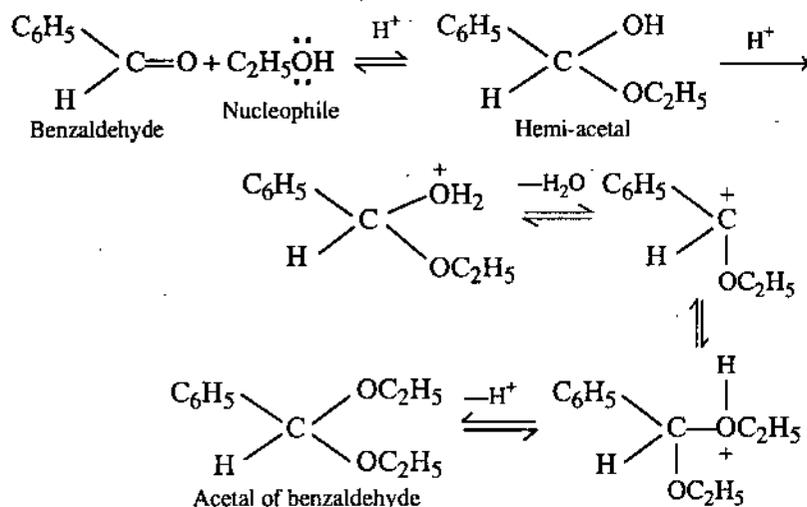
Mechanism :

(R may be alkyl or aryl group).

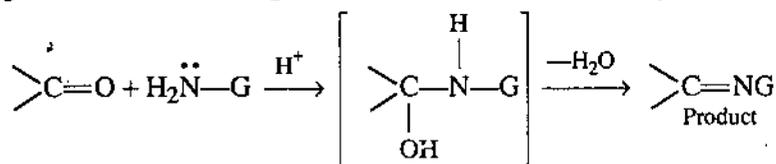
(iv) **Addition of alcohols :** Alcohols add to the carbonyl group of aldehydes to form hemi-acetals and then form acetals in presence of an anhydrous acid.



Mechanism :

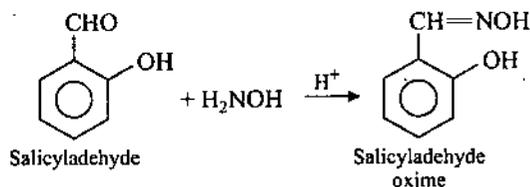
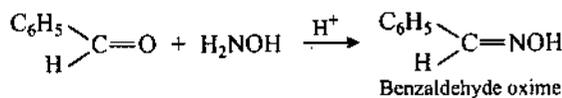


(v) **Reaction with derivatives of ammonia :** Most aromatic aldehydes react with derivatives of ammonia, e.g., hydroxylamine, hydrazine, phenyl hydrazine, semi-carbazide etc. to form unstable addition compounds. These compounds lose a water molecule to form carbon-nitrogen double bond. The general nature of the reaction is given as follows :

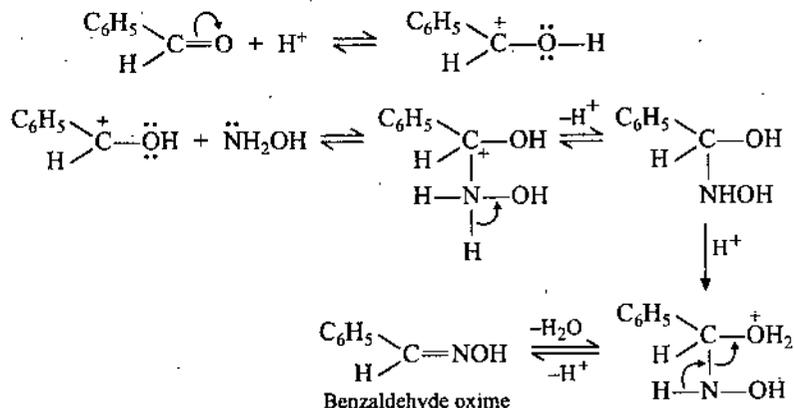


where G is OH, NH₂, C₆H₅NH, NH₂CONH, etc.

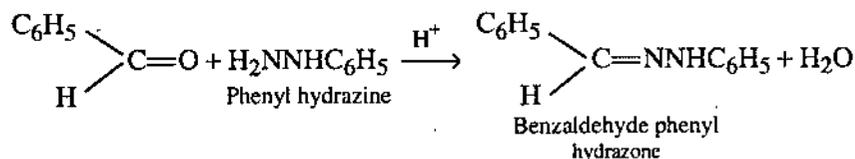
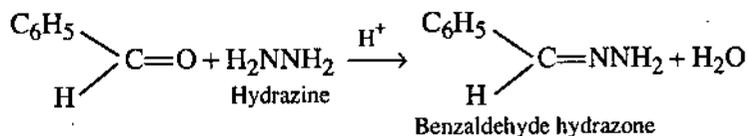
(a) **Reaction with hydroxyl amine :** Aromatic aldehydes react with hydroxyl amine in presence of a mineral acid to yield the corresponding oxime.



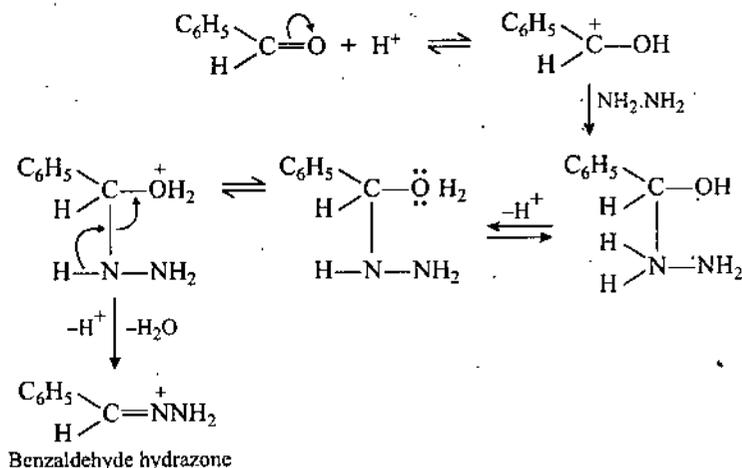
Mechanism :



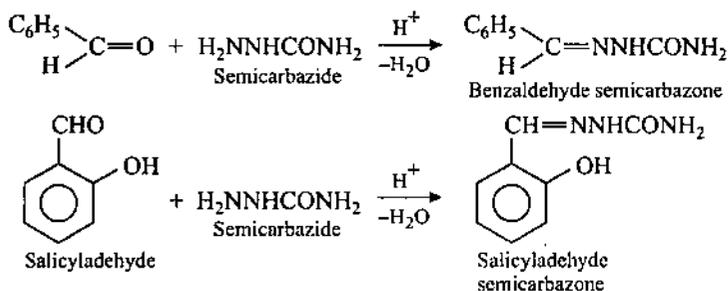
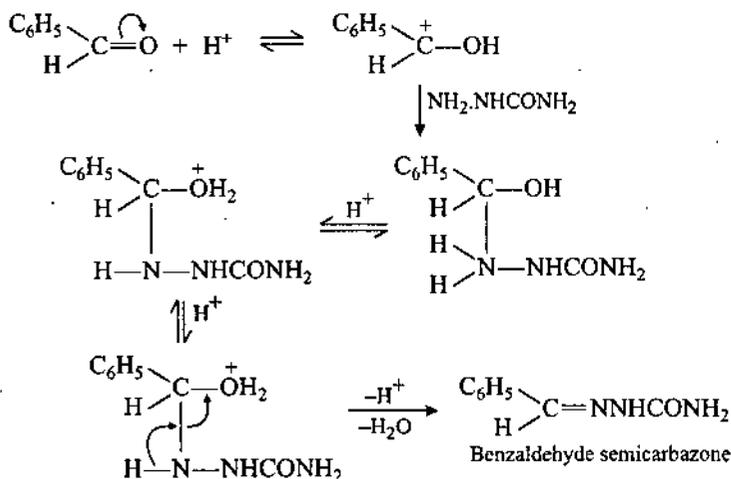
(b) Reaction with hydrazine and phenyl hydrazine : Aromatic aldehydes react with hydrazine and phenyl hydrazine in presence of a mineral acid to form the corresponding hydrazone and phenyl hydrazone, respectively.



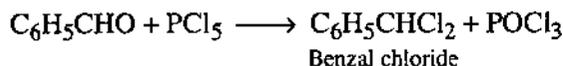
Mechanism :



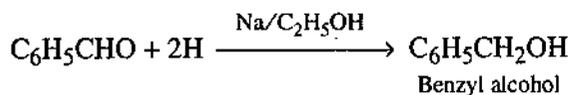
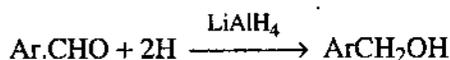
(c) Reaction with semicarbazide : Aromatic aldehydes react with semicarbazide in presence of mineral acid to form the corresponding semicarbazone.

**Mechanism :**

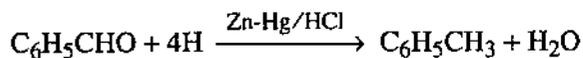
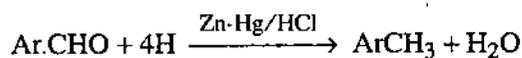
(vi) **Action of phosphorus pentachloride :** Aromatic aldehydes react with PCl_5 to form benzal chloride derivatives.



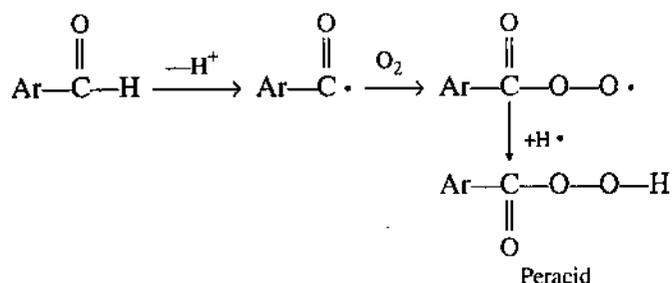
(vii) **Reduction :** Aromatic aldehydes when reduced by Na and ethyl alcohol, LiAlH_4 , NaBH_4 or by catalytic hydrogenation (H_2/Ni) form alcohols.

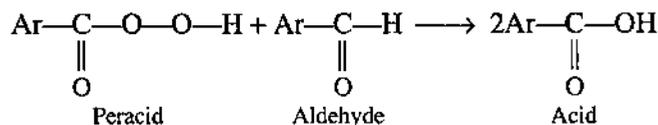


Aromatic aldehydes on reduction with amalgamated zinc and HCl, form hydrocarbons (*Clemmensen's reduction*).

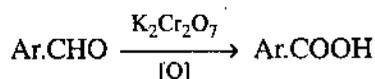


(viii) **Oxidation :** Aromatic aldehydes can be easily oxidised into corresponding acids by oxidising reagents or even on exposure to air.

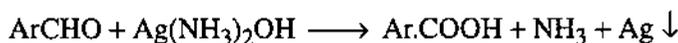




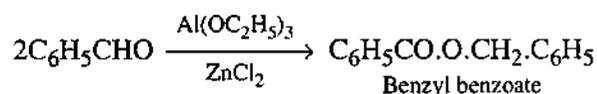
Reagents like $\text{K}_2\text{Cr}_2\text{O}_7$, KMnO_4 in neutral, acidic or alkaline media oxidise aldehydes to acids.



They also reduce ammoniacal silver nitrate solution (Tollen's reagent) to metallic silver, but does not reduce Fehling's solution. This shows that aromatic aldehydes are less susceptible to oxidation than aliphatic aldehydes.

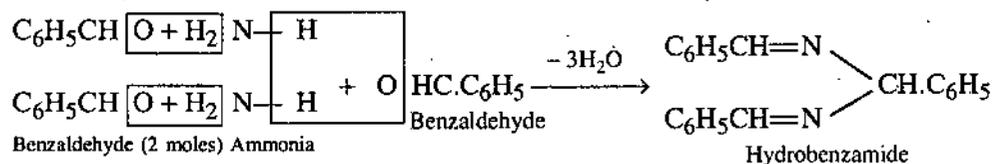


(ix) **Tishchenko reaction** : Aromatic aldehydes when treated with aluminium ethoxide in presence of anhydrous AlCl_3 or ZnCl_2 , form esters.

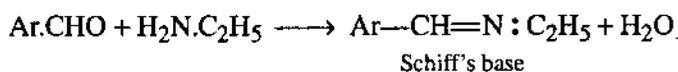
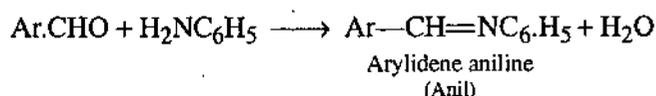


[B] Reactions Different from Aliphatic Aldehydes

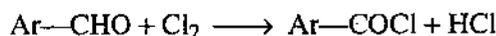
(i) **Action of ammonia** : Aromatic aldehydes do not form aldehyde ammonia like aliphatic aldehydes, but form a condensation product.



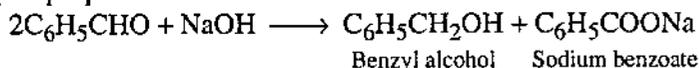
(ii) **Reaction with amines** : Aromatic aldehydes condense with aliphatic and aromatic primary amines to yield *imino derivatives*, called *Schiff's bases*.



(iii) **Action of chlorine** : Aromatic aldehydes react with chlorine in the absence of a halogen carrier to form acid chlorides. This is due to the absence of hydrogen at α -carbon atom.

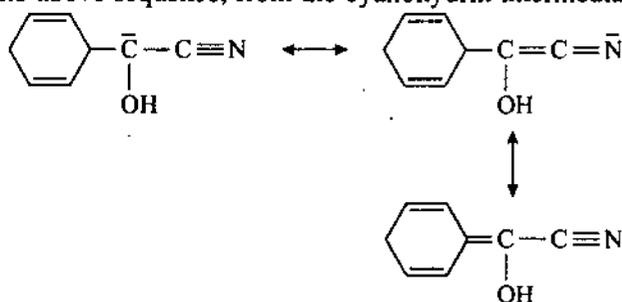


(iv) **Cannizzaro's reaction** : Benzaldehyde and other aliphatic and aromatic aldehydes which do not contain any α -hydrogen atom react with sodium hydroxide solution and give equal proportions of an acid and alcohol.

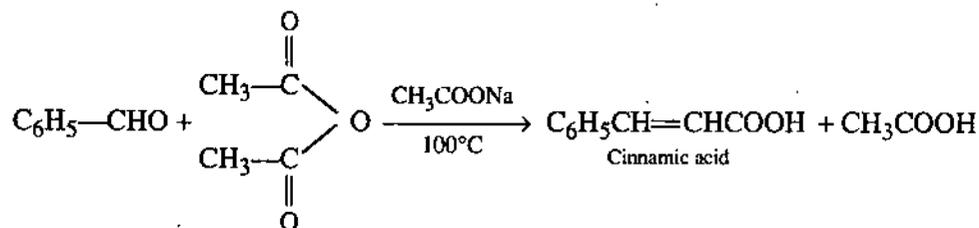


Mechanism : The mechanism can be represented as follows. In this reaction, one molecule of aldehyde acts as a hydride donor and the other acts as a hydride acceptor.

It is observed that the carbanion intermediate is resonance stabilised and is obtained preferentially, in the above sequence, from the cyanohydrin intermediate.

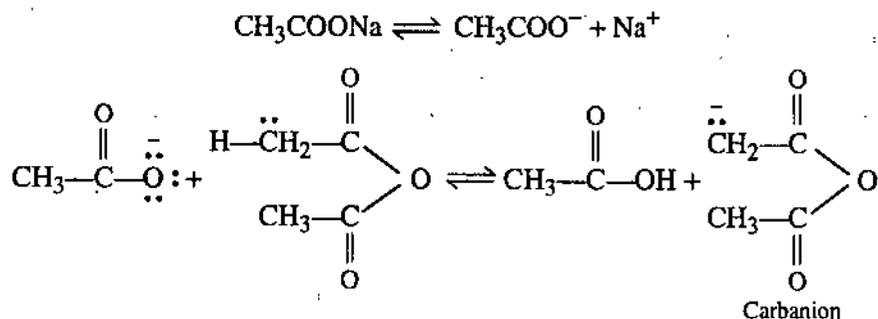


(ii) **Perkin's reaction** : When aromatic aldehydes are heated with acetic anhydride, containing α -hydrogen atoms, in presence of bases like sodium salts of same acid from which anhydride is derived, condensation occurs and α, β -unsaturated acid is formed.

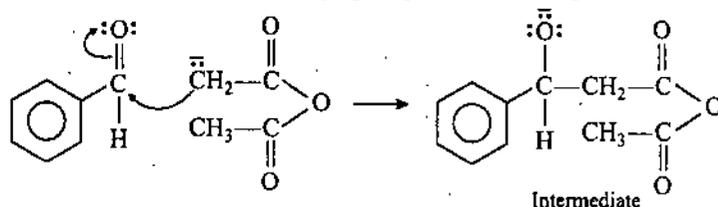


The above condensation between aromatic aldehyde and aliphatic anhydride is known as Perkin's reaction.

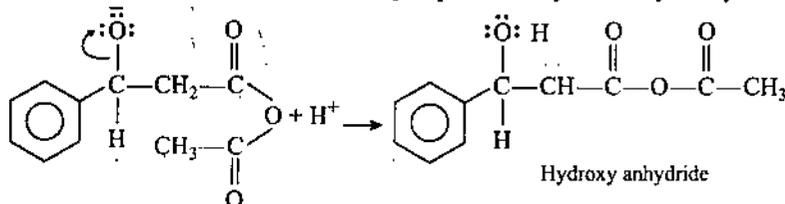
Mechanism : (a) The acetate ion (from sodium acetate) acts as a base and helps in the abstraction of α -hydrogen from aliphatic anhydride to yield a carbanion.



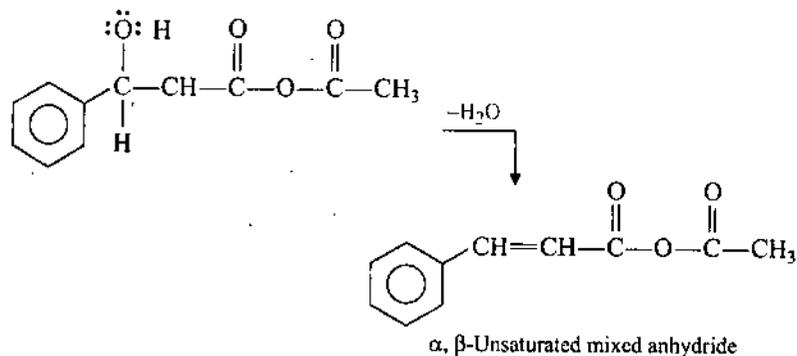
(b) The carbanion attacks the carbonyl group of benzaldehyde to form an intermediate.



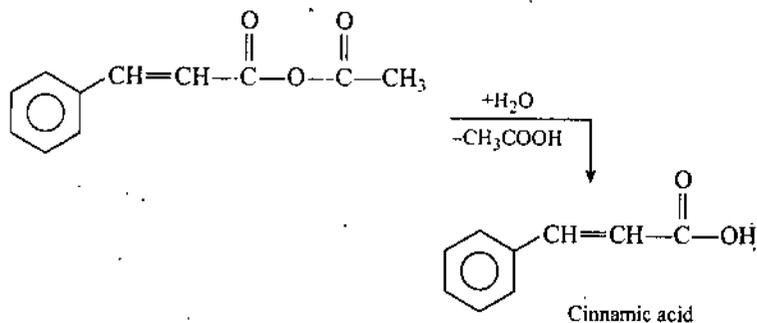
(c) The intermediate is now attacked by a proton to yield a hydroxy anhydride.



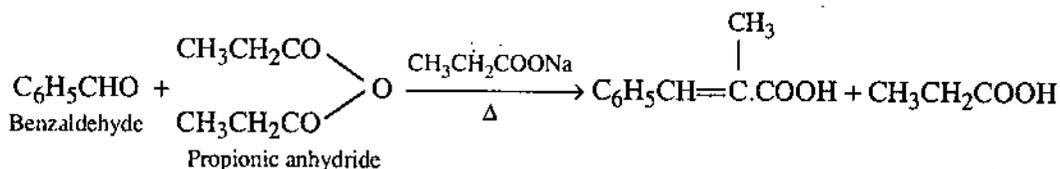
(d) The internal proton transfer occurs which leads to the elimination of water to yield α, β -unsaturated mixed anhydride.



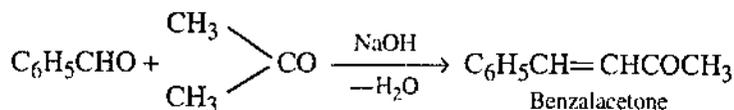
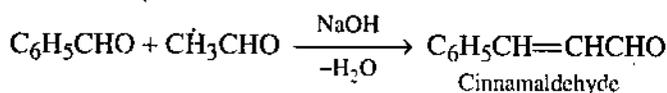
(e) The anhydride on hydrolysis gives cinnamic acid, an unsaturated acid.



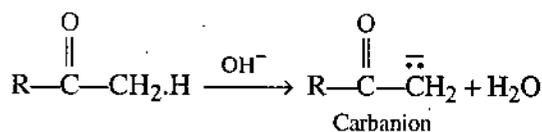
When benzaldehyde reacts with propionic anhydride in presence of sodium propionate, we get α -methyl cinnamic acid.



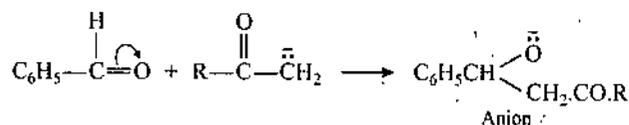
(iii) **Claisen reaction or Claisen-Schmidt reaction** : Aromatic aldehydes react with aliphatic aldehydes or ketones having α -hydrogen atoms in presence of dilute alkali to form condensation products. This reaction is called *Claisen reaction* or *Claisen-Schmidt reaction*.



Mechanism : (i) The base OH^- abstracts a proton from the α -position of the carbonyl group to yield a carbanion.

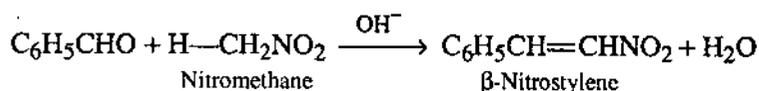


(ii) The carbanion induces the electromeric shift in the carbonyl group of benzaldehyde and combines with it to give an anion.

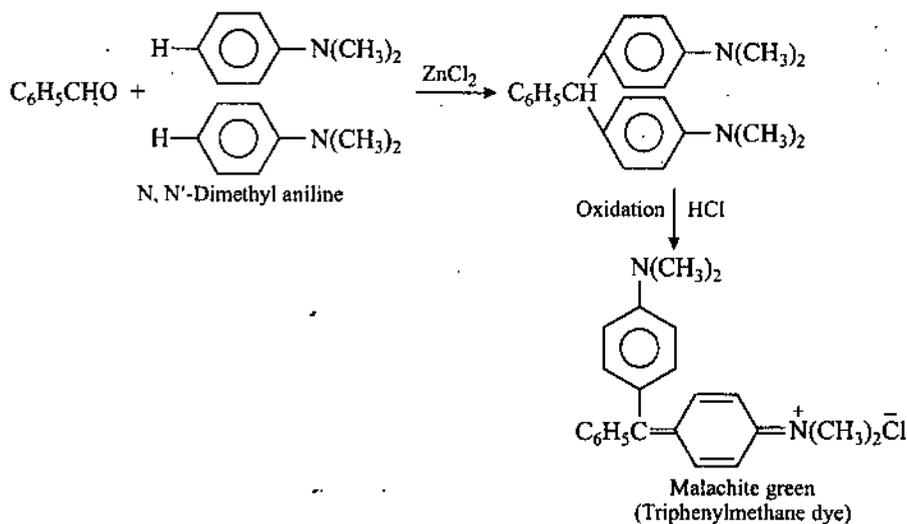


(iii) The anion accepts a proton to form an addition product which in the presence of a base undergoes dehydration to form α, β -unsaturated compound.

(vii) **Condensation with aliphatic and aromatic nitro compounds :** Aromatic aldehydes condense with nitro compounds in presence of a base.



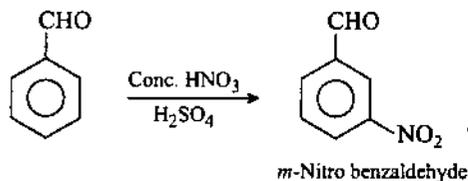
(viii) **Condensation with tertiary amines :** Aromatic aldehydes condense with aromatic tertiary amines in presence of a dehydrating reagent to form dyes of triphenylmethane series.



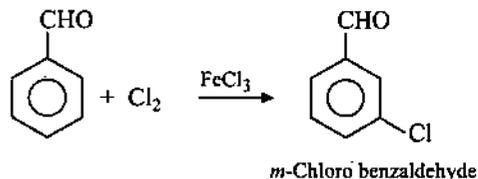
[D] Reactions of Benzene Nucleus

Aromatic aldehydes undergo typical electrophilic substitution reactions of the benzene ring, e.g., nitration, halogenation, sulphonation etc. The —CHO group is a deactivating and *m*-directing group, so the incoming substituent occupies the *m*-position.

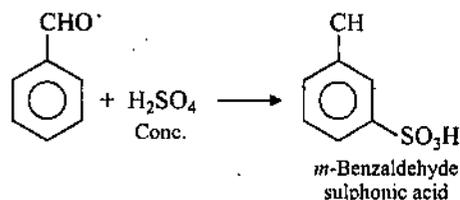
(i) **Nitration :** With conc. HNO_3 in presence of sulphuric acid, aromatic aldehydes give *m*-nitro derivative.



(ii) **Halogenation :** Aromatic aldehydes react with halogens in dark and in presence of halogen carrier to give *m*-derivative.



(iii) **Sulphonation :** Aromatic aldehydes react with conc. H_2SO_4 to form *m*-derivative.



• 6.2. ARYL KETONES

Aromatic of aryl ketones may be of the following two types :

(1) Those having carbonyl group linked directly to the benzene ring. These are further divided into two groups.

(a) Ketones containing two aromatic radicals linked to the carbonyl group, *e.g.*, benzophenone $C_6H_5.CO.C_6H_5$. They are called pure aromatic ketones or diaryl ketones.

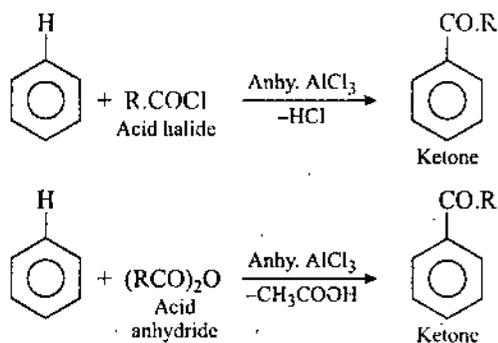
(b) Ketones containing one aromatic and one aliphatic residue linked to the carbonyl group, *e.g.*, acetophenone ($C_6H_5.CO.CH_3$). These are known as mixed or aliphatic-aromatic or arylalkyl ketones.

(2) Those having carbonyl group attached to the side chain of the benzene ring, *e.g.*, phenyl acetone ($C_6H_5.CH_2COCH_3$).

[I] Methods of Preparation

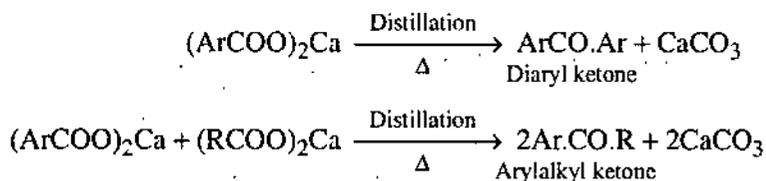
In general, aromatic ketones can be prepared by the general methods used for the formation of aromatic aldehydes. Some of the methods are mentioned below :

(1) **Friedel Craft's reaction** : Aromatic compounds like hydrocarbons when treated with an acid halide or acid anhydride in presence of anhydrous aluminium chloride form aromatic ketones.

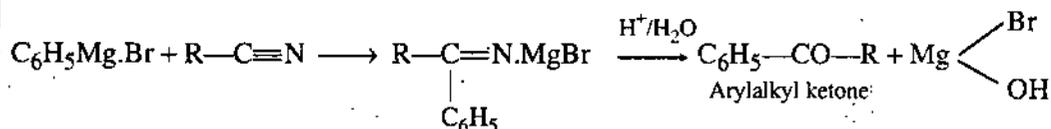


where R may be an alkyl or aryl group.

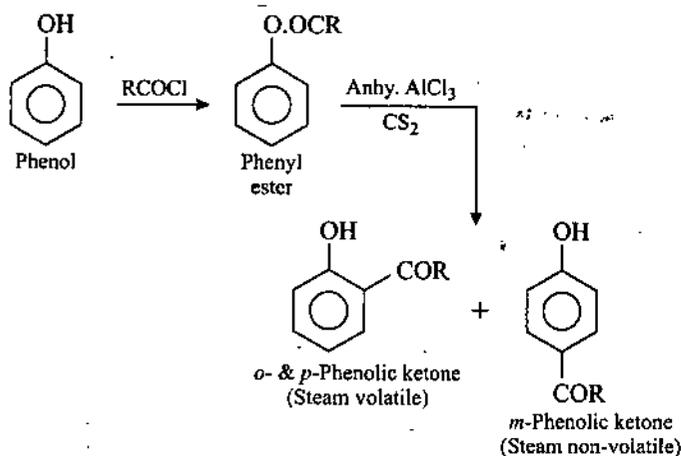
(2) **Distillation of calcium salts of the acids** : Diaryl or arylalkyl ketones can also be prepared by the distillation of calcium salts of aromatic acid alone or a mixture of calcium salts of aromatic and aliphatic acids.



(3) **From Grignard's reagents** : Grignard's reagents when reacted with nitriles or esters form ketones.



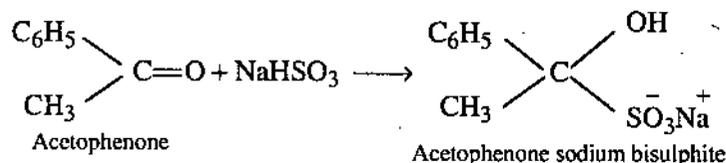
(4) **Fries' rearrangement** : On heating phenyl esters or esters of phenols with anhydrous AlCl_3 , the former undergoes an intermolecular rearrangement in which the migration of the acyl group occurs from phenolic oxygen to *o*- or *p*-positions of the nucleus with respect to hydroxyl groups and finally we get phenolic ketones.

**[II] Properties**

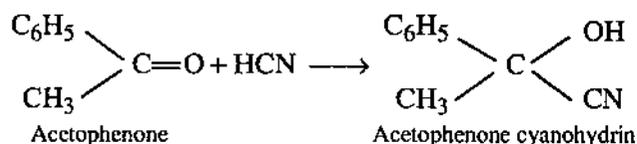
Aromatic ketones resemble aromatic aldehydes in their physical and chemical properties. The important reactions of aromatic ketones can be discussed by taking the example of acetophenone.

[A] Addition Reactions

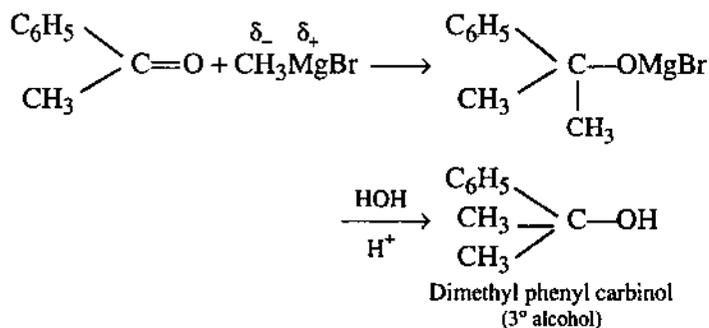
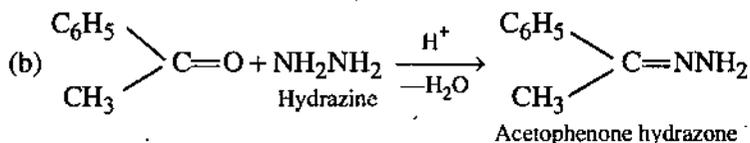
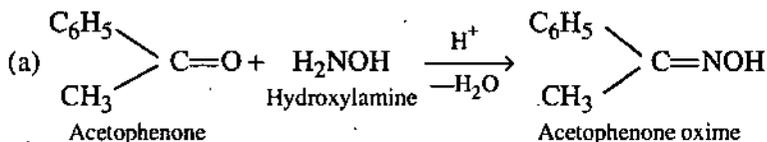
(i) **With sodium bisulphite :** Forms a crystalline addition adduct.



(ii) **With hydrocyanic acid :** Forms the corresponding cyanohydrin.



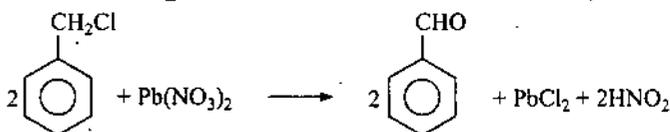
(iii) **With Grignard's reagent :** Forms an addition product which on acid hydrolysis gives a tertiary alcohol.

**[B] Reactions with Ammonia Derivatives**

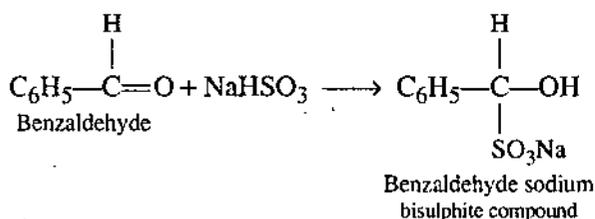
• 6.3. BENZALDEHYDE

[I] Laboratory Preparation

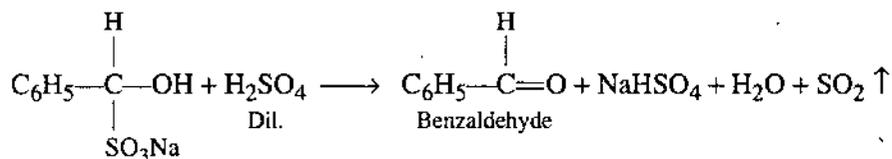
(i) In the laboratory, benzaldehyde is obtained by boiling benzyl chloride with aqueous $\text{Pb}(\text{NO}_3)_2$ or $\text{Cu}(\text{NO}_3)_2$ solution in the presence of CO_2 . By this method, 40% yield of benzaldehyde is obtained. CO_2 checks the oxidation of benzaldehyde into benzoic acid.



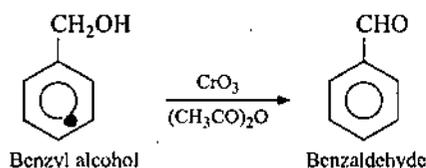
In actual practice, 10 g of benzyl chloride, 8 g of $\text{Pb}(\text{NO}_3)_2$ and 50 ml of water are taken in a round bottom flask. The flask is fitted with a reflux condenser and the solution is boiled for about six hours. The flask is now cooled and benzaldehyde is extracted with ether. The resulting solution is treated with saturated solution of sodium bisulphite when crystalline sodium bisulphite compound is obtained.



This compound is decomposed by dil. H_2SO_4 and benzaldehyde so obtained is again extracted with ether. Ether is removed by distillation and benzaldehyde is again distilled so as to obtain it in the pure form.

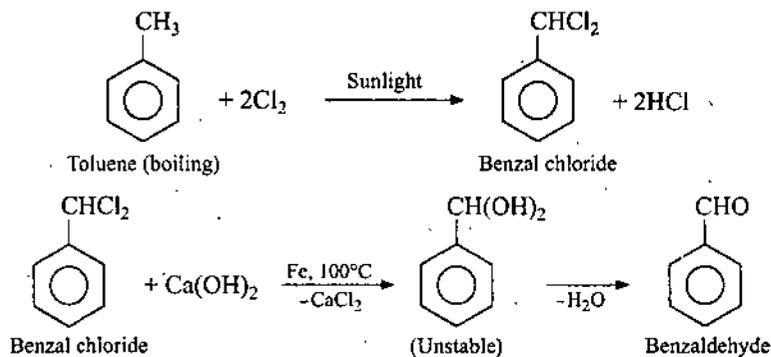


(ii) The better yield of benzaldehyde (about 90%) is obtained by the oxidation of benzyl alcohol with chromic anhydride in the presence of acetic anhydride.

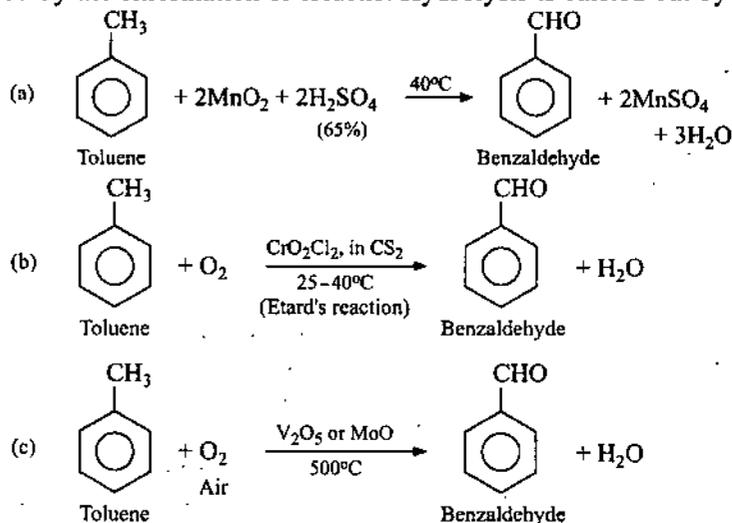


[II] Manufacture

(i) On large scale, benzaldehyde is obtained by the hydrolysis of benzal chloride obtained by the chlorination of toluene. Hydrolysis is carried out by $\text{Ca}(\text{OH})_2$ at 100°C in the presence of iron powder.

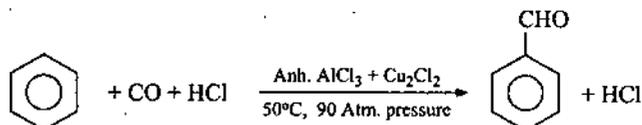


(i) On large scale, benzaldehyde is obtained by the hydrolysis of benzal chloride obtained by the chlorination of toluene. Hydrolysis is carried out by $\text{Ca}(\text{OH})_2$ at 100°C in

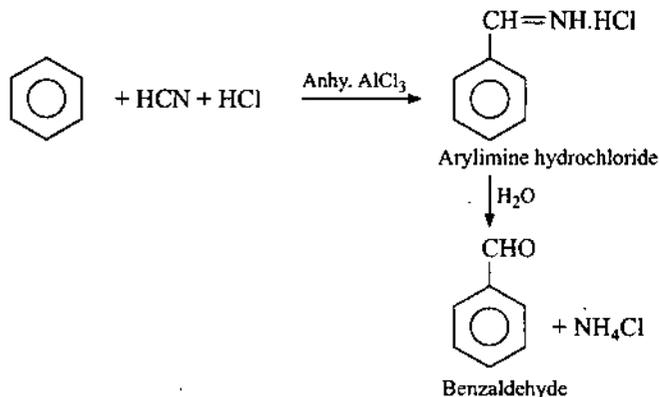


the presence of iron powder.

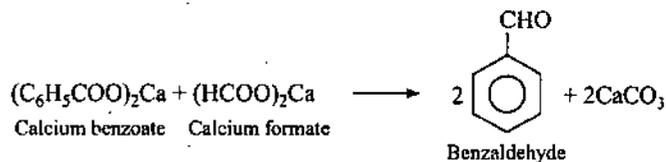
(ii) On a large scale; it is also prepared by the oxidation of toluene by different oxidizing agents.



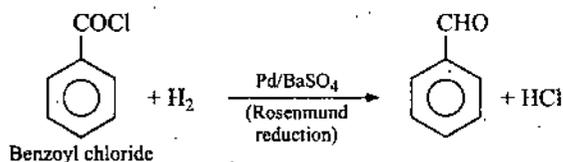
[III] Other Methods



(i) From benzene



(a) By Gattermann-Koch reaction :

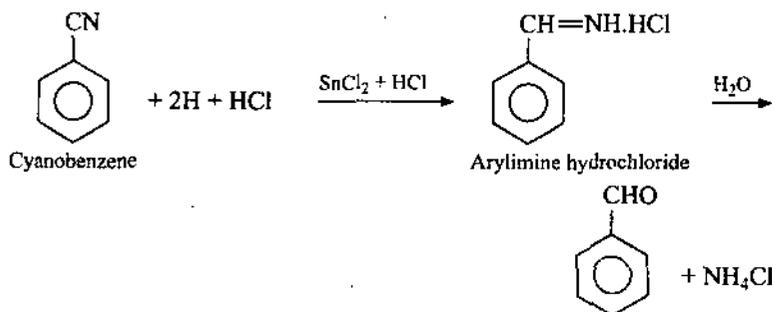


(b) By Gattermann aldehyde synthesis :

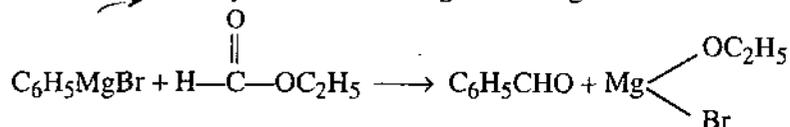
(ii) By dry distillation of calcium benzoate and calcium formate

(iii) By the catalytic reduction of benzoyl chloride.

(iv) **Stephens method** : By the hydrolysis of arylimine hydrochloride obtained by



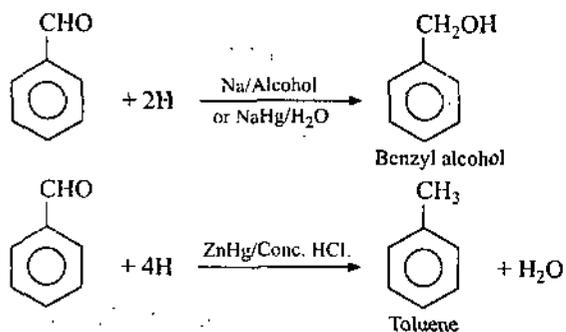
(v) By the reaction of ethyl formate on Grignard's reagent.



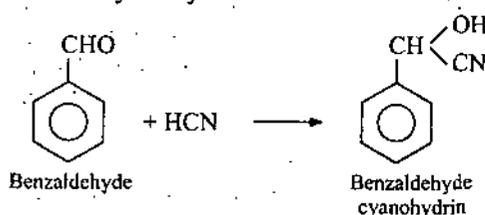
[IV] Properties

(1) Resemblance with Aliphatic Aldehydes

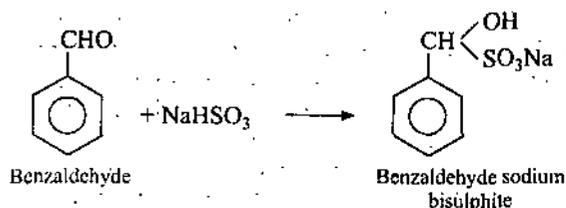
(i) **Reduction** : Benzaldehyde on reduction with different reducing agents gives different products.



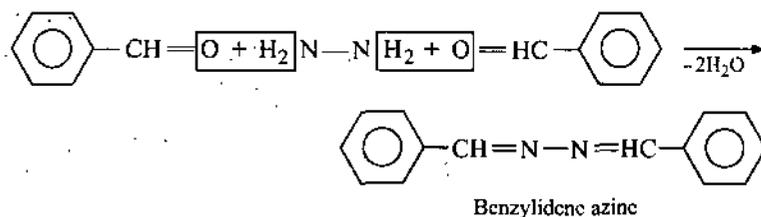
(ii) **Action with HCN** : Cyanohydrin is formed.



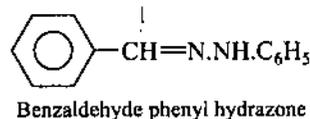
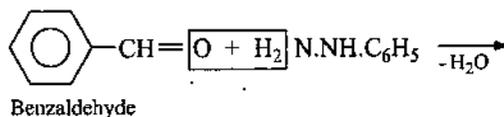
(iii) **Action with sodium bisulphite** : Crystalline sodium bisulphite compound is formed.



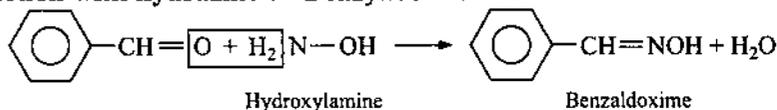
(iv) **Action with hydrazine** : Benzylidene azine is formed.



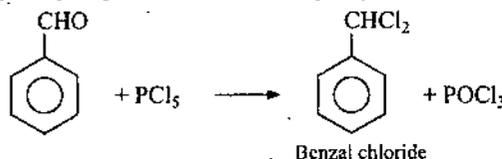
(v) **Action with phenyl hydrazine** : Phenyl hydrazone is formed.



(iv) Action with hydrazine : Benzylidene azine is formed.



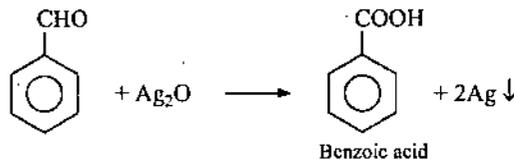
(v) Action with phenyl hydrazine : Phenyl hydrazone is formed.



(vi) Action with hydroxylamine : Benzaldoxime is formed.

(vii) Action with PCl_5 : Benzal chloride is formed.

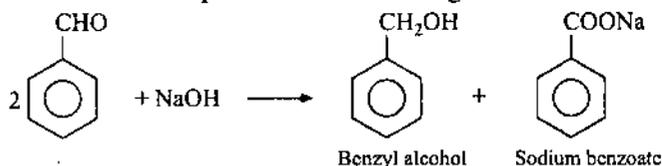
(viii) Action with Schiff's reagent : Benzaldehyde gives pink colour with Schiff's reagent.



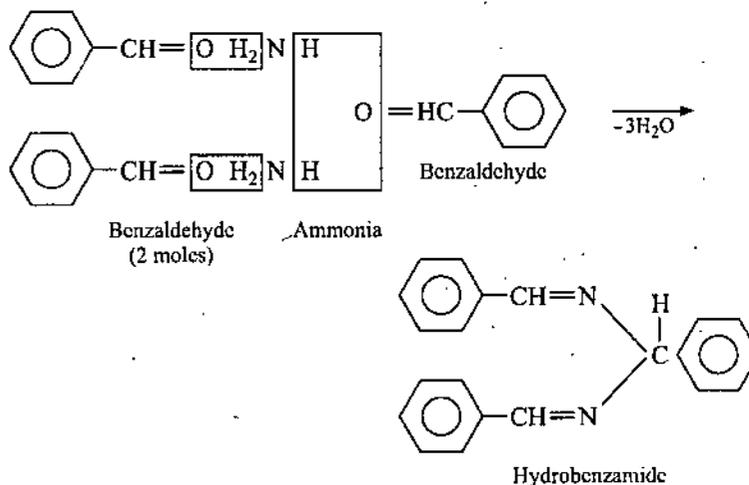
(ix) Action with Tollen's reagent : Benzaldehyde reduces Tollen's reagent to give silver mirror.

(2) Difference from Aliphatic Aldehydes

(i) Action with Fehlings' solution : Benzaldehyde does not reduce Fehling's solution. This is because NaOH present in the Fehling's solution converts benzaldehyde



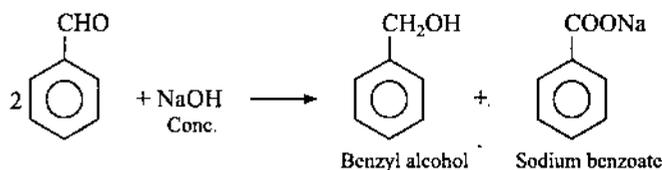
into benzyl alcohol and sodium benzoate. Both these compounds do not have reducing



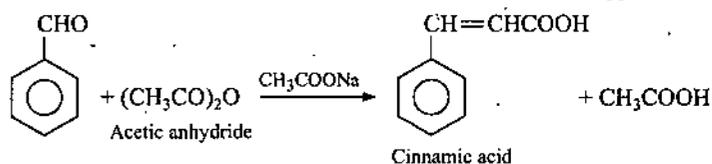
properties.

(ii) Action with NH_3 : Hydrobenzamide is formed.

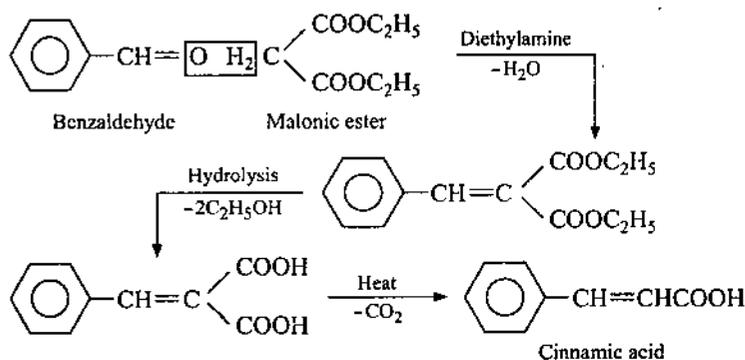
(iii) Action with conc. alkalis (Cannizzaro's reaction) : On reaction with conc.



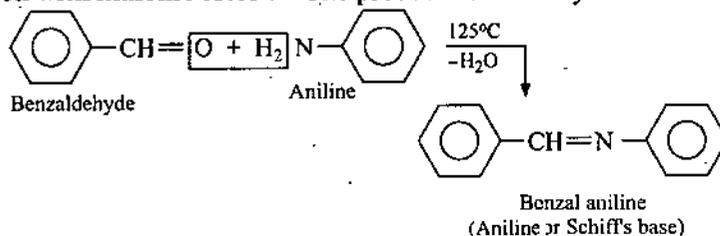
NaOH, one molecule of benzaldehyde is reduced to benzyl alcohol, whereas other molecule is oxidized to sodium benzoate. This reaction is known as *Cannizzaro's reaction*.



(iv) **Perkin's reaction :** It reacts with acetic anhydride and sodium acetate to form cinnamic acid.

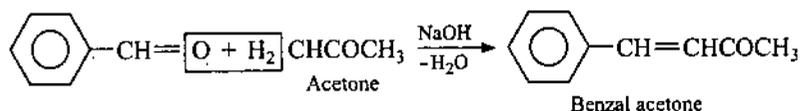
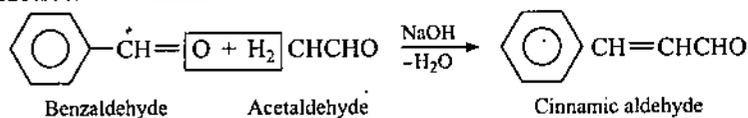


(v) **Action with malonic ester :** The product obtained by the action of malonic ester

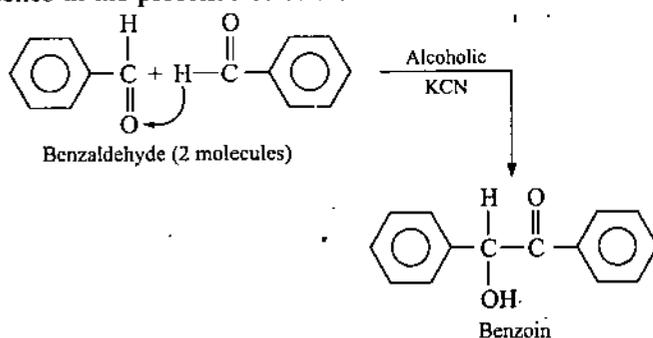


on benzaldehyde, on hydrolysis and heating gives cinnamic acid.

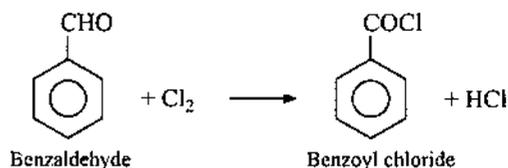
(vi) **Action with aniline :** Aniline or Schiff's base is formed.



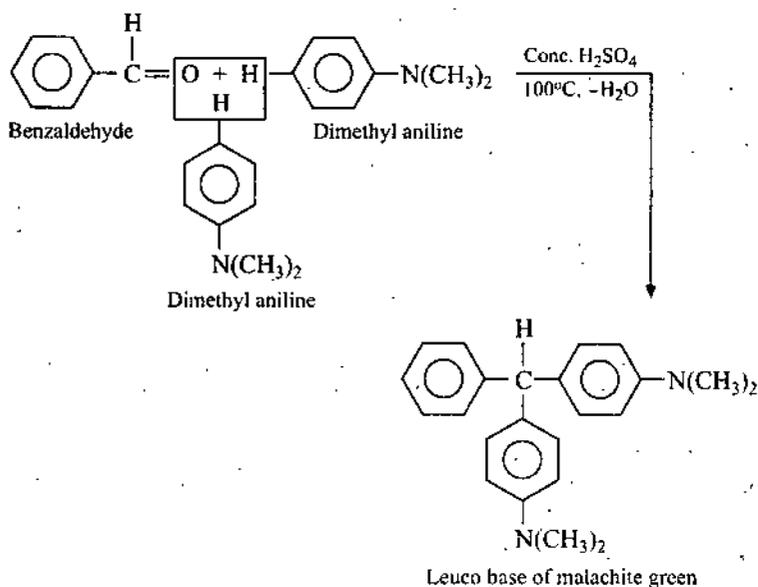
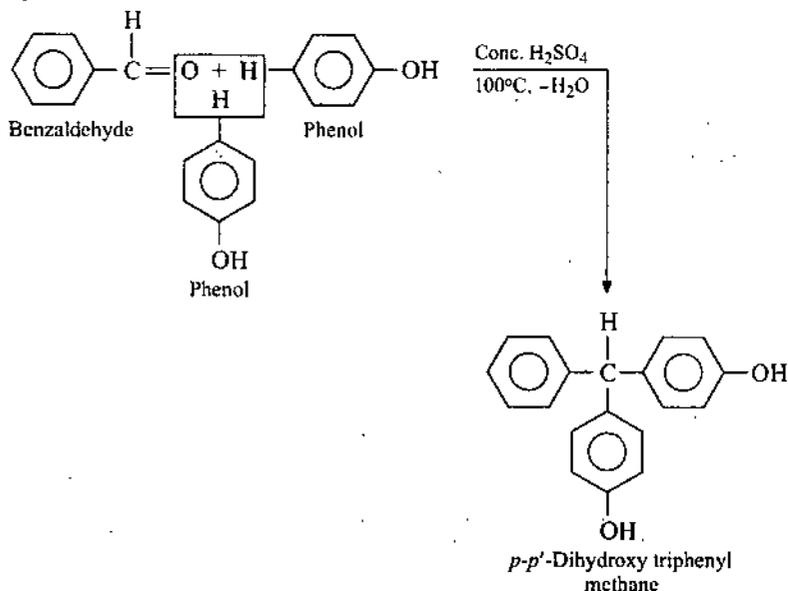
(vii) **Claisen-Schmidt condensation :** Benzaldehyde condenses with aliphatic aldehydes or ketones in the presence of dilute alkali.



(ix) **Action with Cl_2** : On passing Cl_2 through boiling solution of benzaldehyde, benzoyl chloride is formed.

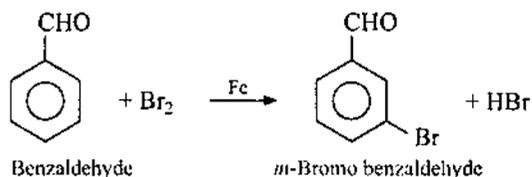


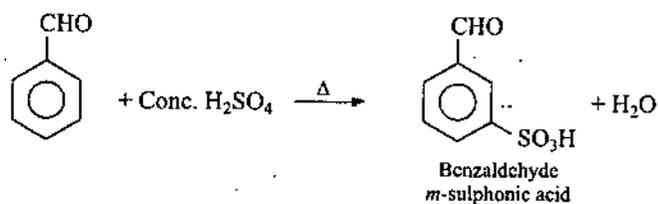
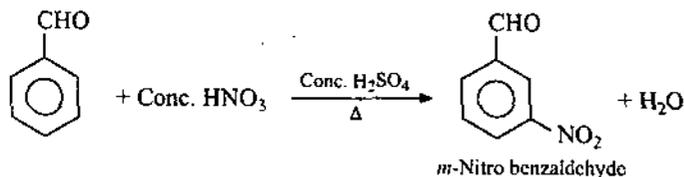
(x) **Condensation with phenol and dimethyl aniline** : Benzaldehyde condenses with phenol or dimethyl aniline in the presence of conc. H_2SO_4 or anhydrous ZnCl_2 to form triphenyl methane derivatives.



(xi) **Reactions due to benzene nucleus** : The directive influence of $-\text{CHO}$ group is meta directing. Hence, benzaldehyde can be halogenated, sulphonated and nitrated to give meta substituted derivatives.

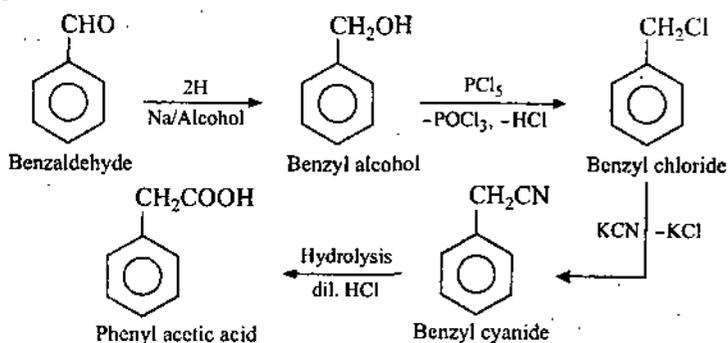
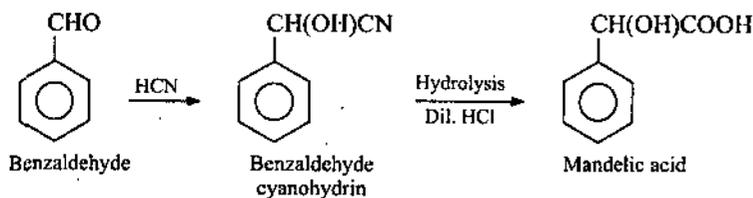
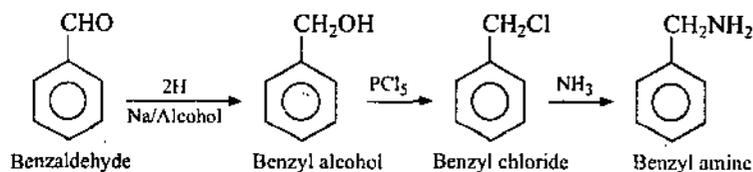
(a) **Halogenation** :

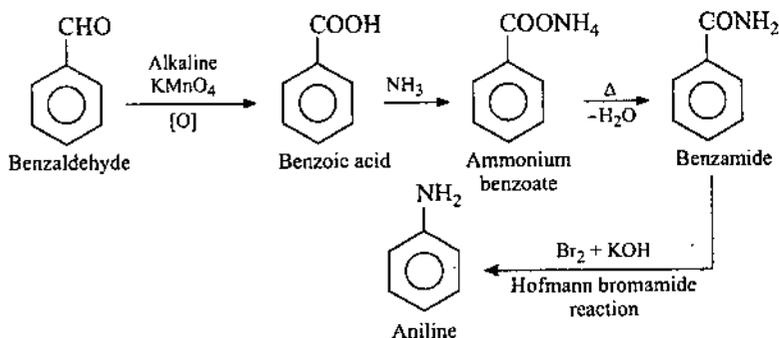


(b) Sulphonation :**(c) Nitration :****[V] Uses**

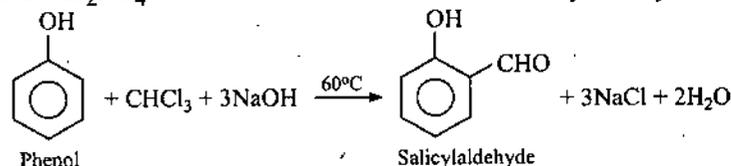
Benzaldehyde is used :

- (i) In the preparation of perfumes.
- (ii) In the preparation of important compounds such as benzoic acid, cinnamic aldehyde and cinnamic acid.
- (iii) In the manufacture of malachite green dye.

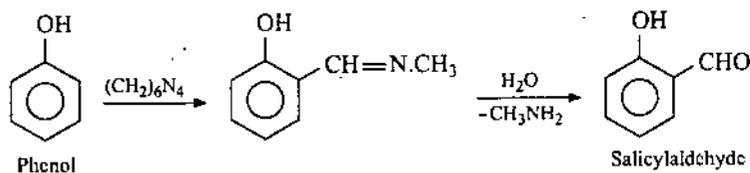
[VI] Conversion of Benzaldehyde into Different Compounds**(i) Phenyl acetic acid****(ii) Mandelic acid****(iii) Benzyl amine**

(iv) Aniline**• 6.4. SALICYLALDEHYDE****[I] Preparation**

(i) Phenol is treated with CHCl_3 and NaOH at 60°C and the resulting product is acidified with dil. H_2SO_4 and then steam distilled when salicylaldehyde is obtained.



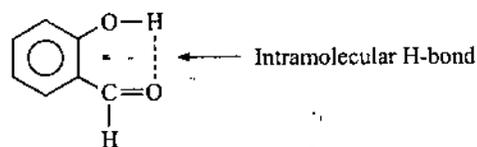
(ii) Phenol is heated with hexamethylene tetramine, glycerol and boric acid. The resulting product is acidified with dil. H_2SO_4 and then steam distilled when salicylaldehyde is obtained.

**[II] Physical Properties**

Salicylaldehyde is a colourless, sweet smelling oily liquid, boiling point 197°C . It is soluble in water and organic solvents.

[III] Chemical Properties

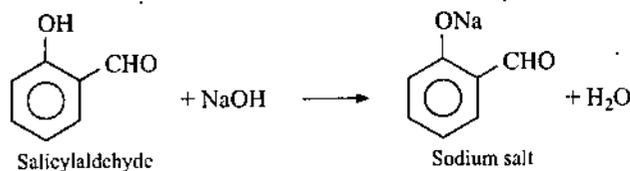
Salicylaldehyde shows the general reactions of $-\text{OH}$ and $-\text{CHO}$ groups although $-\text{OH}$ group is less reactive due to the formation of intramolecular hydrogen bonds.



Due to the formation of intramolecular H-bonds, Salicylaldehyde is steam volatile and its boiling point is less than *p*-hydroxy benzaldehyde.

(1) Reactions Due to $-\text{OH}$ Group

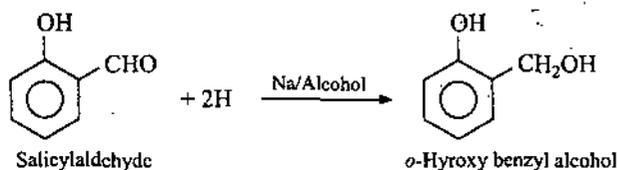
(i) **Action with NaOH :** Salicylaldehyde gives sodium salt.



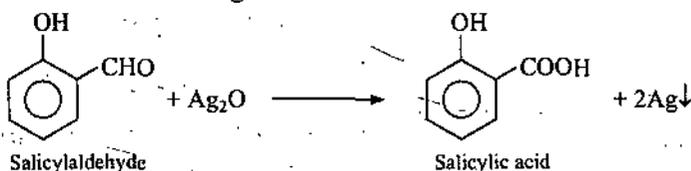
(ii) **Action with 1% FeCl_3 solution :** Salicylaldehyde gives violet solution.

(2) Reactions Due to $-\text{CHO}$ Group

(i) **Reduction :** Salicylaldehyde gives alcohol.

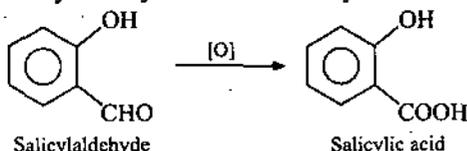


(ii) Action with Tollen's reagent : Silver mirror is formed.

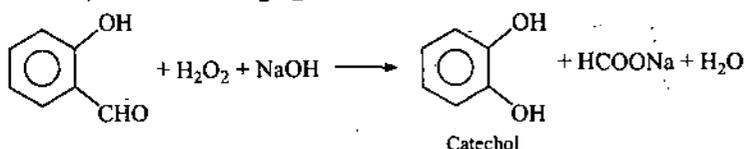


Salicylaldehyde does not reduce Fehling's solution or Schiff's reagent.

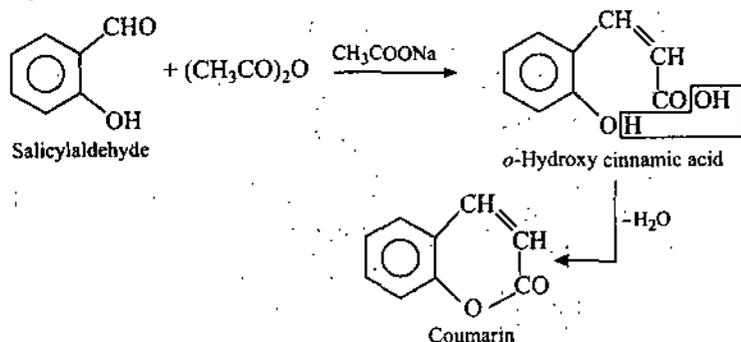
(iii) Oxidation : Salicylaldehyde is oxidised by air to form salicylic acid.



On oxidation with alkaline H₂O₂, catechol is formed.



(iv) Action with acetic anhydride and sodium acetate : Salicylaldehyde reacts with acetic anhydride and sodium acetate to form coumarin (*Perkin's reaction*).



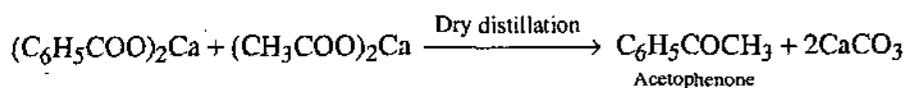
[IV] Uses

Salicylaldehyde is used in the preparation of some dyes and synthetic perfume, coumarin.

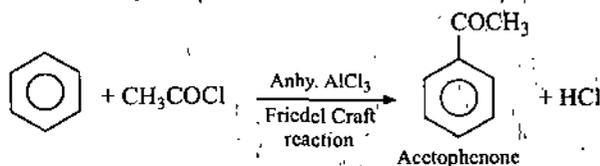
• 6.5. ACETOPHENONE

[I] Preparation

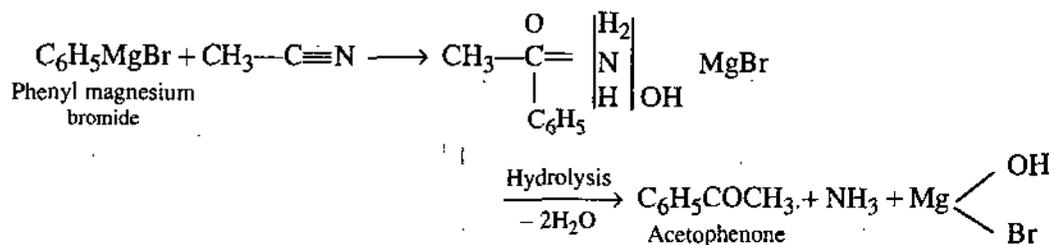
(i) By dry distillation of mixture of calcium benzoate and calcium acetate.



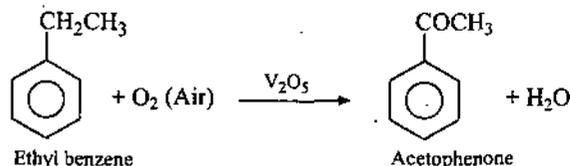
(ii) By the action of acetyl chloride on benzene in the presence of anhydrous AlCl₃.



(iii) From Grignard's reagent :



(iv) On a large scale, acetophenone is prepared by the catalytic oxidation of ethyl benzene by air.



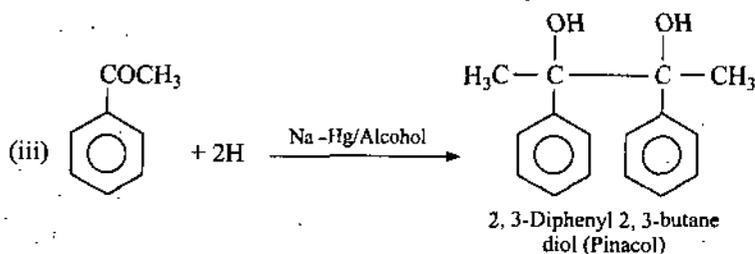
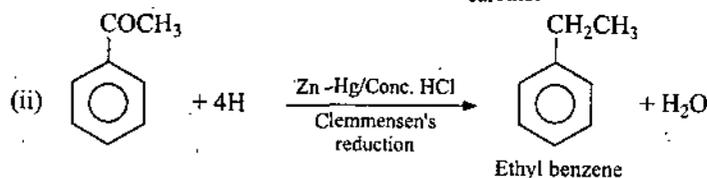
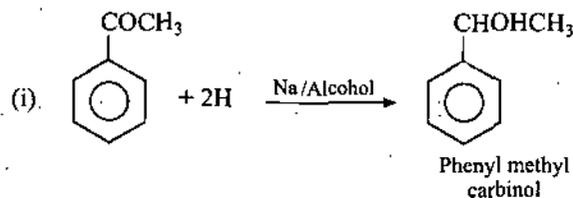
[II] Properties

Physical : Acetophenone is a colourless liquid, boiling point = 202°C. It is less soluble in water but is soluble in organic solvents such as alcohol and ether.

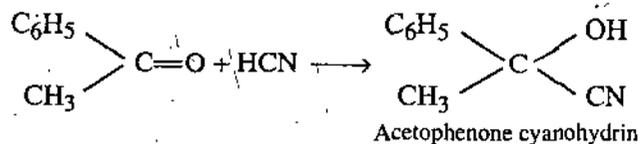
[III] Chemical Properties

(I) Resemblance with Aliphatic Ketones

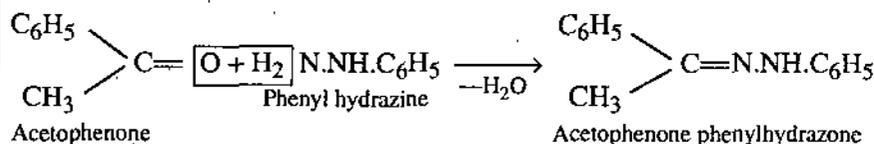
(i) **Reduction :** Different reducing agents give different products.

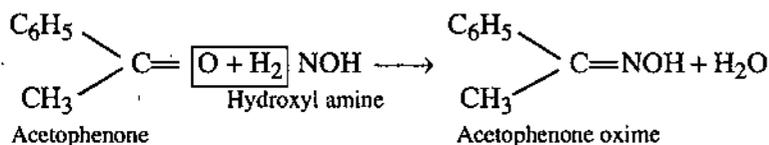


(ii) **Action with HCN :** Acetophenone cyanohydrin is formed.

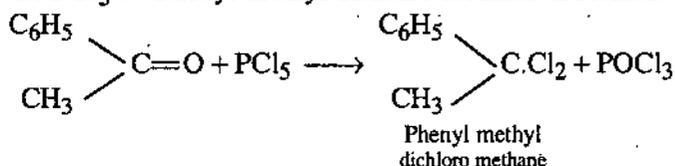


(iii) **Condensation reactions :** Acetophenone reacts with phenyl hydrazine and hydroxylamine to form phenylhydrazone and oxime.

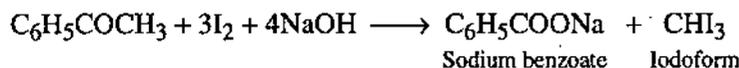




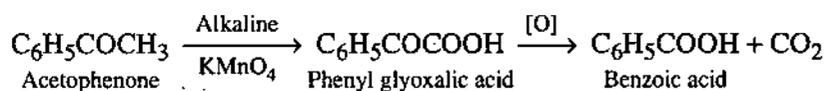
(iv) **Action with PCl_5** : Phenyl methyl dichloro methane is formed.



(v) **Iodoform reaction** : On heating with I_2 and NaOH , acetophenone gives iodoform.



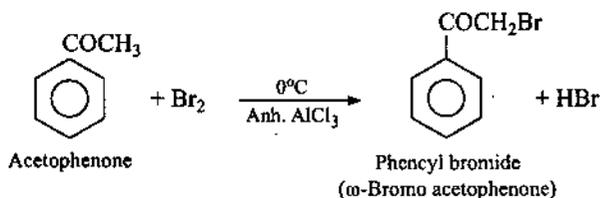
(vi) **Oxidation** : On oxidation with alkaline KMnO_4 phenyl glyoxalic acid is first formed which then oxidises to benzoic acid.



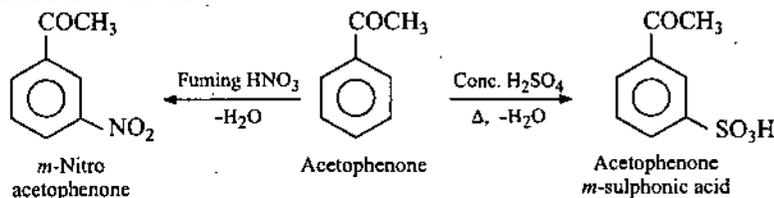
(2) Differences from Aliphatic Ketones

(i) Acetophenone does not react with NaHSO_3 .

(ii) Acetophenone reacts with ethereal solution of Br_2 at 0°C in the presence of anhydrous AlCl_3 to form phenyl bromide.



(iii) **Reactions due to benzene nucleus** : The directive influence of $-\text{COCH}_3$ group is meta directing. Hence, acetophenone can be nitrated and sulphonated to form meta-substituted derivatives.



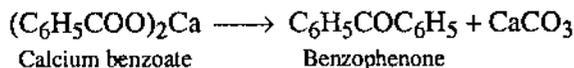
[IV] Uses

Acetophenone is used as a solvent, in making perfumes and in making sleep producing drug.

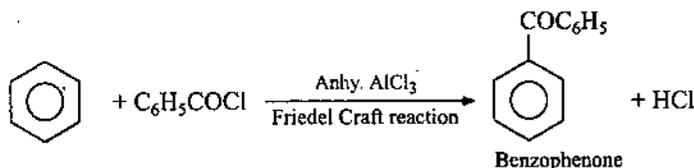
• 6.6. BENZOPHENONE

[I] Preparation

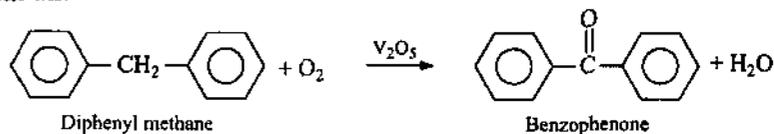
(i) By the dry distillation of calcium benzoate.



(ii) By the action of benzoyl chloride on benzene in the presence of anhydrous AlCl_3 .



(iii) On a large scale, benzophenone is prepared by the catalytic oxidation of diphenyl methane with air.



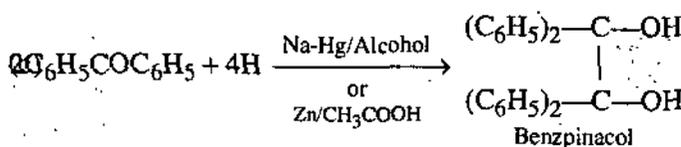
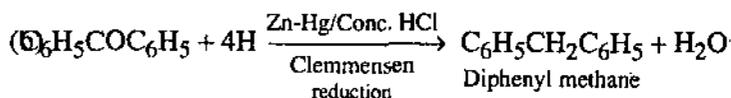
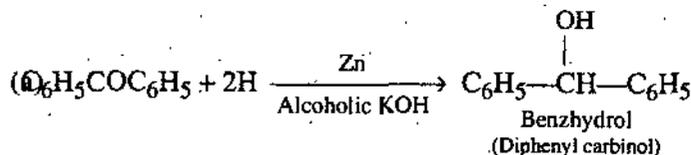
[II] Physical Properties

Benzophenone is a colourless, crystalline solid which is found in two forms. The more stable form melts at 49°C and less stable form melts at 26°C. It is insoluble in water but is soluble in organic solvents like alcohol and ether.

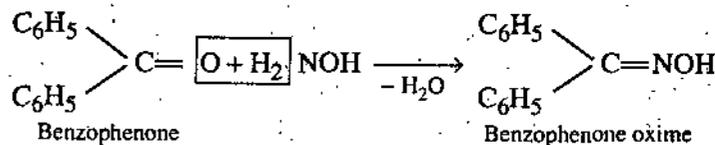
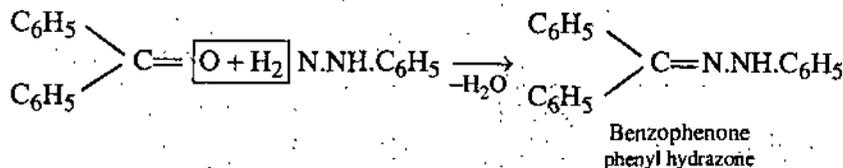
[III] Chemical Properties

(1) Resemblance with Acetophenone

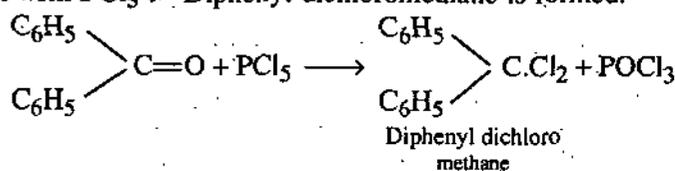
(i) **Reduction** : Different reducing agents give different products.



(ii) **Condensation reactions** : Benzophenone reacts with phenyl hydrazine and hydroxylamine to form phenyl hydrazone and oxime.

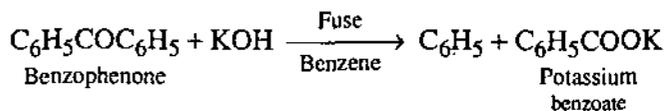


(iii) **Action with PCl₅** : Diphenyl dichloromethane is formed.



(2) Differences from Acetophenone

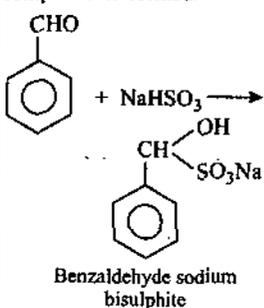
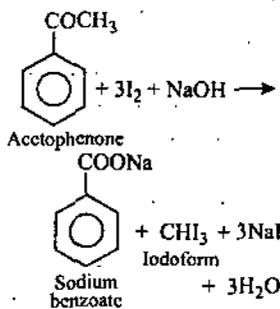
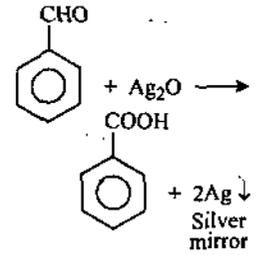
- (i) Benzophenone does not react with HCN.
- (ii) Benzophenone is decomposed by solid caustic potash to form benzene and potassium benzoate.



[IV] Uses

Benzophenone is used in the preparation of triphenyl methane dyes.

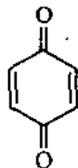
6.7. DISTINCTION BETWEEN BENZALDEHYDE AND ACETOPHENONE

Property	Benzaldehyde	Acetophenone
1. Smell	Smell of bitter almonds	No such smell
2. B. Pt.	179°C	202°C
3. Action with sodium bisulphite	Crystalline sodium bisulphite compound is formed.  Benzaldehyde sodium bisulphite	No reaction.
4. Action with I ₂ and NaOH	No reaction.	A yellow precipitate of iodoform is formed.  Acetophenone Sodium benzoate Iodoform
5. Action with Tollen's reagent.	Silver mirror is formed.  Silver mirror	No reaction.
6. Action with alkaline sodium nitroprusside	No reaction.	Red coloured solution is formed which becomes blue on adding CH ₃ COOH

6.8. EXPLANATION OF FACTS

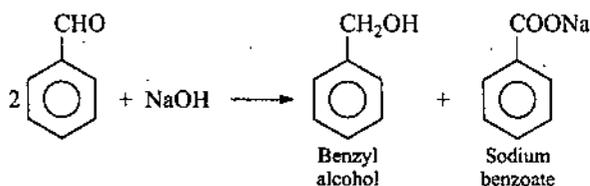
(a) *p*-Benzoquinone is not an aromatic compound

p-Benzoquinone is not an aromatic compound. According to Hückel's rule, for a cyclic compound to be aromatic, it should have $(4n + 2)\pi$ electrons, where n is an integer say 0, 1, 2, 3 etc, i.e., aromatic compound should have 2, 6, 10 or 14 π -electrons. In *p*-benzoquinone molecule, 8 π -electrons are present. Hence, it is not an aromatic compound.



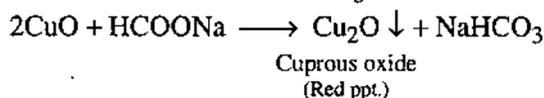
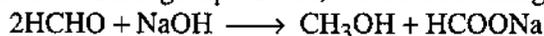
(b) Benzaldehyde does not give Fehling's test, while formaldehyde gives Fehling's test although both have aldehydic group.

Benzaldehyde does not give Fehling's test. This is because NaOH present in the Fehling's solution converts benzaldehyde into benzyl alcohol and sodium benzoate. (Cannizzaro's reaction). Both these compounds do not have reducing properties.



Formaldehyde is also converted into methyl alcohol and sodium formate by NaOH present in the Fehling's solution. Out of these compounds sodium formate

$\text{H}-\overset{\text{O}}{\parallel}{\text{C}}-\text{ONa}$ contains $-\text{CHO}$ group. Hence, it reduces Fehling's solution.



6.9. COMPARISON OF AROMATIC ALDEHYDES AND ALIPHATIC ALDEHYDES

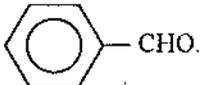
[I] Similarities

- Both give positive Tollen's test.
- Both respond to Schiff's test.
- Both are reduced to corresponding primary alcohols.
- Both give acetals with alcohols.
- Both can be prepared by similar methods, e.g., oxidation of primary alcohols.
- Both form cyanohydrins, sodium bisulphite adducts, oximes, carbazones, semicarbazones, hydrazones etc.
- Both form gem-dichlorides with PCl_5 .
- Both react with Grignard's reagent to form secondary alcohol, except HCHO which gives a primary alcohol.

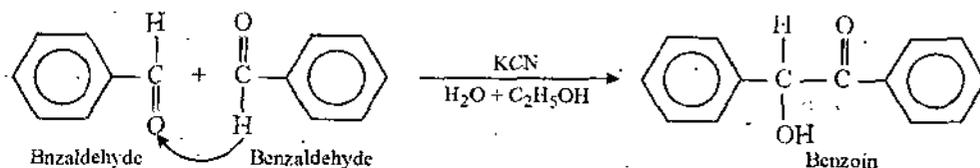
[II] Differences

Aromatic aldehydes	Aliphatic aldehydes
1. Certain specific methods of preparation are used.	—
2. Do not reduce Fehling's solution or do so with difficulty.	Reduce Fehling's solution.
3. Schiff's bases derived from aromatic aldehydes are stable and are used in organic syntheses.	Schiff's bases derived from aliphatic aldehydes are too unstable.
4. Undergo electrophilic substitution reactions, e.g., nitration, halogenation etc.	Do not undergo electrophilic substitution reactions.
5. Do not undergo polymerisation.	Undergo polymerisation in presence of acids.
6. They show Perkin reaction, benzoin condensation, Knoevenagel reactions.	Do not show such reactions.
7. They do not undergo aldol condensation, however, they show crossed aldol condensation with carbonyl compounds having α -hydrogen atom.	Unsubstituted aldehydes except HCHO, show aldol condensation.
8. Undergo Cannizzaro's reaction.	Except HCHO, show Cannizzaro's reaction.

SUMMARY

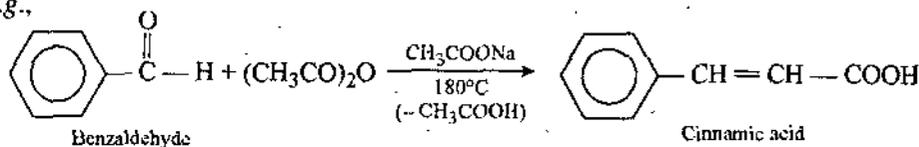
- Aromatic aldehydes are compounds in which the $-\text{CHO}$ group is attached directly to an aromatic ring, e.g., benzaldehyde,  $\text{C}_6\text{H}_5-\text{CHO}$.

- Cannizzaro's reaction involves the treatment of an aldehyde (without an α -hydrogen) with conc. NaOH or KOH. The aldehyde undergoes an oxidation reduction.
- Benzoin condensation involves the treatment of an aromatic aldehyde with aqueous KCN or NaCN. The products are α -hydroxy ketones.

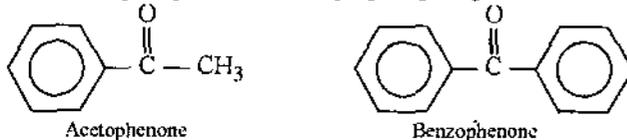


- Perkin reaction involves the treatment of an aromatic aldehyde with anhydride of an aliphatic acid and the sodium salt of that acid. Products are α, β -unsaturated acids.

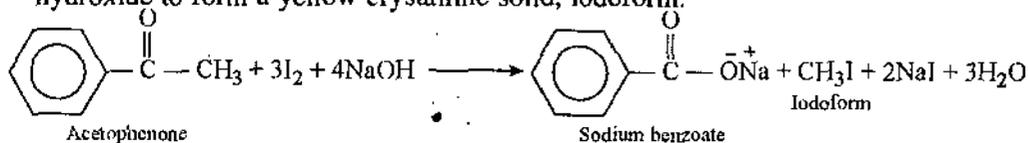
e.g.,



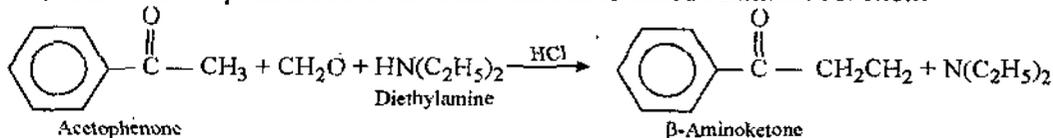
- Aromatic ketones are compounds in which a carbonyl group is attached to either two aryl groups or one aryl group and one alkyl group, e.g.,



- Acetophenone is a methyl ketone and reacts with iodine in the presence of sodium hydroxide to form a yellow crystalline solid, iodoform.



- Acetophenone reacts with HCHO and ammonia or a primary amine or a secondary amine to form β -amino ketones. This reaction is called **Mannich reaction**.



All aromatic ketones containing α -hydrogen give this reaction. The products of Mannich reaction are known as **Mannich bases**.

STUDENT ACTIVITY

- How will you distinguish between benzaldehyde and acetophenone ?

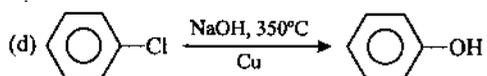
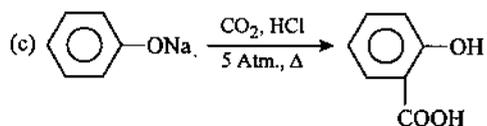
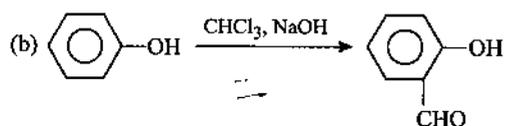
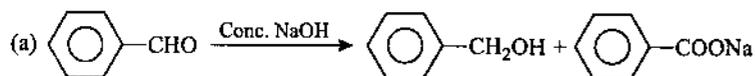
• TEST YOURSELF

Answer the following questions :

1. Describe the general methods of preparation of aromatic aldehydes.
2. Mention the general properties of aromatic aldehydes.
3. Mention the general methods of preparation of aromatic ketones.
4. Describe the general properties of aromatic ketones.
5. Mention the preparation and properties of benzaldehyde.
6. Give the preparation of acetophenone.
7. Give the preparation of benzophenone.
8. What happens when ?
 - (i) Benzaldehyde is heated with concentrated NaOH solution.
 - (ii) Benzaldehyde is heated with alcoholic KCN solution.
 - (iii) Benzaldehyde is heated with acetic anhydride in the presence of sodium acetate at 180°C.
9. How will you distinguish between benzaldehyde and acetophenone ?
10. How will you distinguish between benzaldehyde and acetaldehyde ?
11. How will you distinguish between acetophenone and benzophenone ?
12. Write a note on Cannizzaro reaction.
13. Write a note on Perkin reaction.
14. Write a note on Beckmann rearrangement.
15. Write a note on benzoin condensation.
16. Give the mechanism of Cannizzaro reaction.
17. Write the mechanism of Perkin reaction.
18. Write the mechanism of benzoin condensation.
19. How will you synthesise benzoin from benzaldehyde ?
20. How will you synthesise cinnamic acid from benzaldehyde ?
21. How will you synthesise salicylaldehyde from phenol ?
22. How will you obtain benzaldehyde from benzene ?
23. How will you obtain benzene from benzaldehyde ?
24. How will you obtain ethylbenzene from acetophenone ?
25. In which of the following types of reactions are the carbonyl compounds and alkenes similar in behaviour ?
 - (a) Hydrogenation
 - (b) Elimination
 - (c) Nucleophilic addition
 - (d) Electrophilic addition
 - (e) Nucleophilic substitution
26. When compound X is hydrolysed, the product formed reacts with phenyl hydrazine but does not reduce ammoniacal silver nitrate. The possible structure for X is :
 - (a) $\text{CH}_3\text{CHClCH}_2\text{Cl}$
 - (b) $\text{CH}_3\text{CH}_2\text{CHCl}_2$
 - (c) $\text{CH}_3\text{CCl}_2\text{CH}_3$
 - (d) $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$
27. Benzaldehyde reacts with PCl_5 to give :
 - (a) Benzal chloride
 - (b) Benzyl chloride
 - (c) Chlorobenzene
 - (d) Benzoyl chloride
28. Which of the following gives a silver mirror with an ammoniacal solution of AgNO_3 :
 - (a) Benzal chloride
 - (b) Benzaldehyde

- (c) Benzene
 (d) Benzyl alcohol
29. Phenol gives salicylaldehyde on heating with CHCl_3 and NaOH . It is known as :
 (a) Cannizzaro reaction
 (b) Benzoin condensation
 (c) Reimer Tiemann reaction
 (d) Claisen reaction

30. Which one of the following is Cannizzaro's reaction?

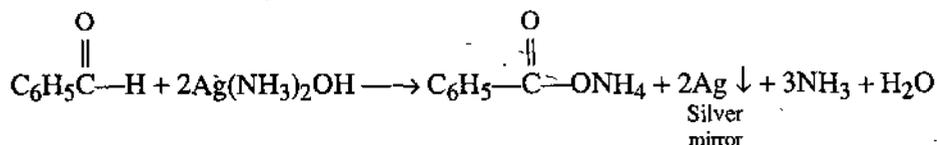
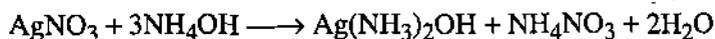


31. Aldehydes may be distinguished from ketones by using :
 (a) Fehling's solution (b) Conc. H_2SO_4
 (c) Pyrogallol (d) Grignard's reagent
32. Which one of the following does not turn Schiff's reagent to pink?
 (a) HCHO (b) $\text{C}_6\text{H}_5\text{CHO}$
 (c) $(\text{CH}_3)_2\text{CO}$ (d) CH_3CHO
33. Calcium acetate on heating gives :
 (a) Acetic anhydride (b) Acetone
 (c) Acetaldehyde (d) Ethyl alcohol
34. Alcohols react with aldehydes to form :
 (a) Acetals (b) Hemi-acetals
 (c) Acid (d) Ketone
35. Acetone undergoes reduction with hydrazine in presence of NaOH to give propane. This reaction is known as :
 (a) Clemmensen's reduction (b) Wolff-Kishner reduction
 (c) Rosenmund reduction (d) Reformatsky reaction
36. Fill in the Blanks
 (i) Perkin's reaction converts an aromatic aldehyde into an
 (ii) Benzaldehyde reacts with hydrazine in presence of acid to form
 (iii) In benzoin condensation, two molecules of benzaldehyde condense in presence of
 (iv) The reaction between an aldehyde and saturated solution of sodium bisulphite is a test of
 (v) When benzaldehyde is treated with aqueous solution of NaOH , and are formed.
 (vi) Acetophenone does not reduce
 (vii) In acetophenone, the $-\text{COCH}_3$ group present on the ring directs the new substituent into in electrophilic substitution reactions.
 (viii) In the reaction between benzene and chlorine, acts as an electrophile.
 (ix) All ketones containing group respond to iodoform test.
 (x) Acetophenone reacts with hydrazine to form the corresponding

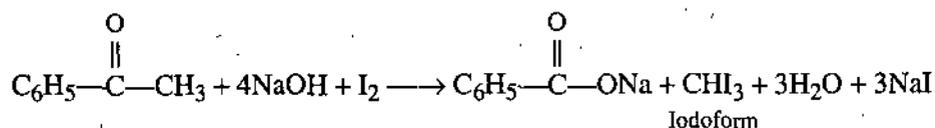
ANSWERS

9. The following tests are used :

(i) **Tollen's test** : Benzaldehyde forms silver mirror with ammoniacal silver nitrate solution (Tollen's reagent). Acetophenone does not react :

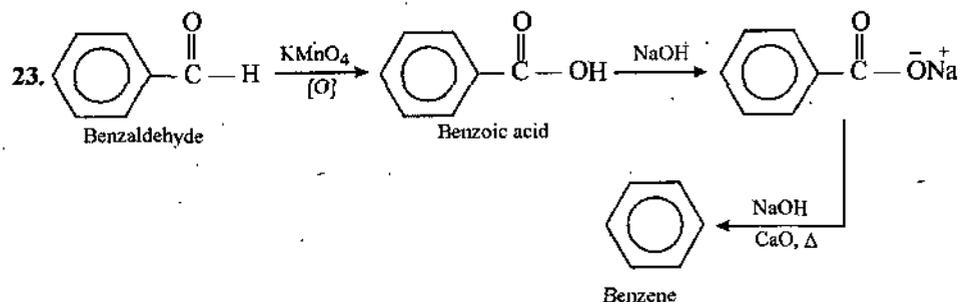
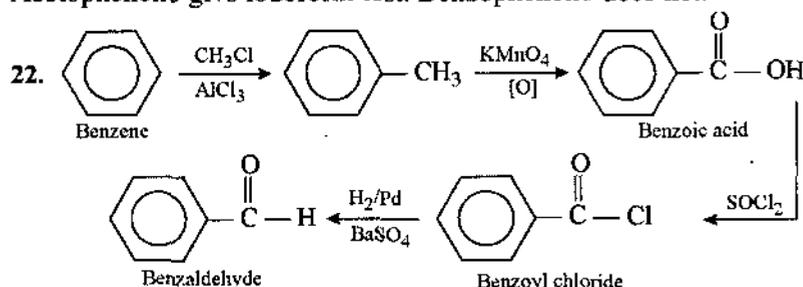


(ii) **Iodoform test** : Acetophenone forms yellow precipitate of iodoform with alkaline solution of iodine. Benzaldehyde does not react.



10. Acetaldehyde gives Fehling's test and iodoform test. Benzaldehyde does not.

11. Acetophenone gives iodoform test. Benzophenone does not.



25. (a) 26. (c) 27. (b) 28. (b) 29. (c) 30. (a) 31. (a) 32. (c) 33. (b)

34. (a) 35. (b)

36. Fill in the Blanks :

- | | |
|-------------------------------------|--|
| (i) Unsaturated acid | (ii) Benzaldehyde hydrazone |
| (iii) Potassium cyanide | (iv) Carbonyl group |
| (v) Benzyl alcohol, sodium benzoate | (vi) Fehling solution |
| (vii) Meta position | (viii) $\text{CH}_3-\overset{\oplus}{\text{C}}=\text{O}$ |
| (ix) $\text{CH}_3\text{CO}-$ | (ix) Hydrazone |

