

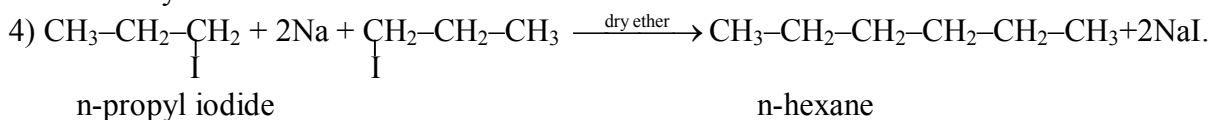
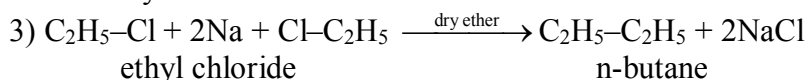
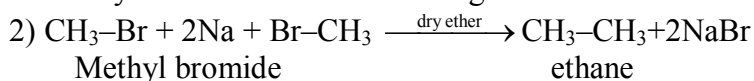
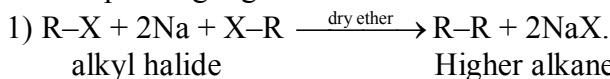


**Subject: Halogen Derivatives -1**

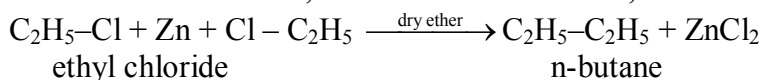
### III) Wurtz's Reaction:

**Reaction with sodium metal (Formation of higher alkanes).**

When alkyl halides react with sodium metal in the presence of dry ether as a medium, corresponding higher alkanes are formed. This reaction is called Wurtz Reaction.

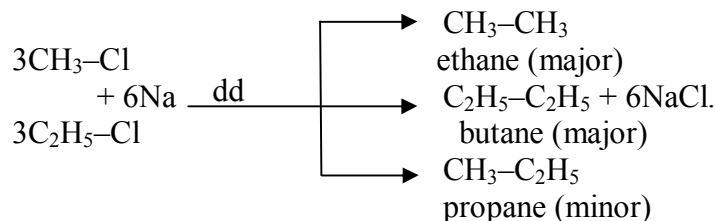


**2)** In the Wurtz's reaction, instead of sodium metal, metallic zinc may also be used.



3) Wurtz's reaction is suitable for preparing higher alkanes containing even number of carbon atoms.

4) In the Wurtz's reaction if two different alkyl halides react with sodium metal then mixture of three higher alkanes along with sodium halide is formed. However, identical molecular react rapidly. Therefore, alkanes with even number of carbon atoms are the major products.

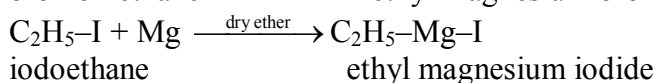
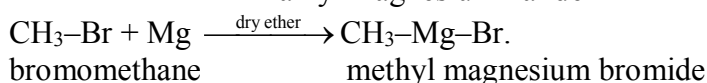
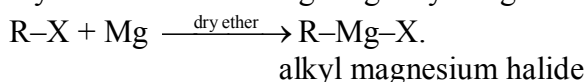


#### IV) Reaction with Magnesium metal (Formation of Grignard Reagent):

Grignard's Reagent are defined as organometallic compounds of magnesium metal having the general formula  $R-Mg-X$ .

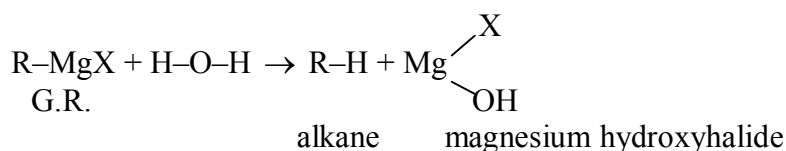
\* A compound in which metal is bonded to carbon atom is called **organometallic**.

**Preparation of Grignard's reagent:** Alkyl halides react with magnesium metal in the presence of dry ether as a medium giving alkyl magnesium halides called as Grignard's reagent.



- \* In Grignard's reagent the bond between magnesium and carbon is polar covalent bond while bond between Mg and halogen is ionic bond.  

$$\text{R}^{\delta-} - \text{Mg}^{\delta+} \cdots \text{X}$$
- \* Grignard's Reagent are called synthetic reagents, because starting from them, almost all organic compounds can be synthesized (prepared).
- \* Grignard's Reagent are highly reactive. They may be decomposed by moisture in air producing alkane.



Therefore, Grignard's Reagent are never stored in solid pure state. But they are stored in the form of their solution in dry ether.

### Optical Isomerism

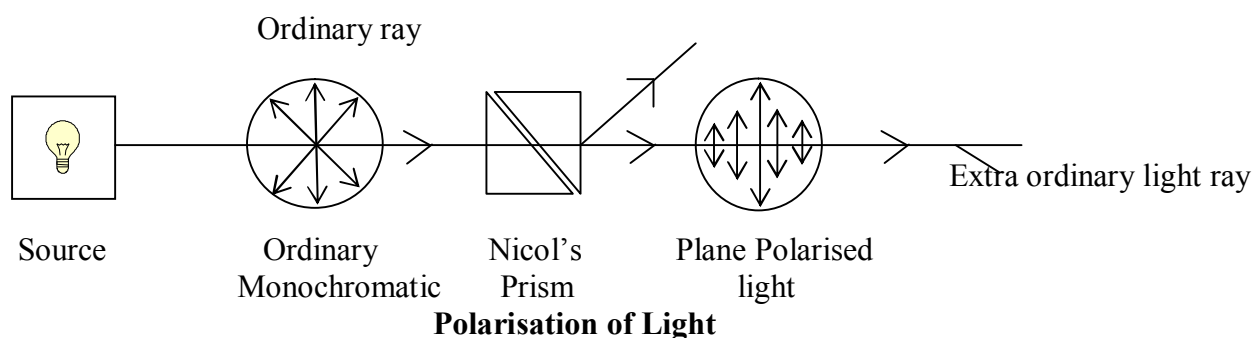
#### Definition:-

- 1) **Optical isomerism:** It is a phenomenon in which compounds have same molecular formula. Same structural formula also. But they have different configuration of atoms or groups due to which they differ in their optical activities such two compounds are called **optical isomers** or **enantiomers** or **enantiomorphs**.

- 2) **Monochromatic light:** Light having single colour or single wavelength is called **Monochromatic light**.

- 3) **Plane Polarised light:** The light having vibrations of waves in a single plane is called **plane polarized light**.

Ordinary monochromatic light has the vibrations in several planes which are perpendicular to the line of propagation (beam of light). When this ordinary monochromatic light passed through Nicol prism (polarizer), it splits into two rays such as extra-ordinary ray and ordinary ray. In the extra-ordinary ray light waves are vibrating in single plane and it is called as plane polarized light. The process is known as **polarization of light**.



- \* **Nicol's Prism:-** It consists of two prisms of Iceland spar or calcite which is chemically  $\text{CaCO}_3$ . Two prisms are joined (cemented) by using an adhesive called Canada balsum.
- 4) **Optical activity:-** Certain compounds have the ability to rotate plane of the plane polarized light either in the clockwise direction or in the anticlockwise direction, through a definite

angle. This property is called optical activity and the compounds are called optically active compounds.

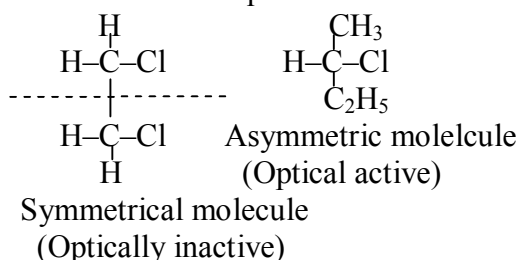
Ex. Glucose, lactic acid, Turpentine, sec. butyl chloride.

- 5) **Angle of Rotation:** The angle through which the plane of the plane polarized light is turned is called **angle of rotation**. It is denoted by  $\alpha$ . Rotation in the clockwise direction (right side) is considered to be positive ( $\alpha = +ve$ ). The rotation of the plane in anticlockwise direction (left side) is considered to be negative ( $\alpha = -ve$ ).
- 6) **Dextro rotatory compounds:-** The compound or molecules which can rotate plane of plane polarized light in the clockwise direction are called dextro rotatory compounds. They are denoted as d-compounds or (+ve compounds).  
Ex. 1) d glucose, (+ve) glucose. 2) d lactic acid (+) lactic acid.
- 7) **Laevo rotatory compounds:-** The compounds or molecule which can rotate plane of plane polarized light in the anticlockwise direction are called laevo rotatory compounds. They are denoted as l-compounds or (-) compounds.  
Ex. 1) l-glucose, (-ve) glucose, 2) l-lactic acid, (-) lactic acid.
- 8) **Racemic mixture or Racemates:-** It is equimolar or equal quantity mixture of dextro and the laevo isomers of the same compounds. The racemate is optically inactive i.e. does not rotate plane of the plane polarized light. Because, dextro and laevo isomers cancel the rotation of each other. This is called **external compensation**. The mixture can be resolved into its constituents. The racemic mixture is denoted as dl compound or (l) compound.  
Ex. 1) (dl) glucose, ( $\pm$ ) glucose, 2) (dl) lactic acid, ( $\pm$ ) lactic acid.
- 9) **Enantiomers:-** Stereo isomers which are having same molecular and structural formula but have different configurations and related as non-superimposable mirror images are called enantiomers or enantiomorphs. They rotate the plane of plane polarized light through the same angle but in opposite direction. Enantiomers have same physical properties such as melting point, boiling point, refractive index, etc. They only differ in the sign of angle of rotation.

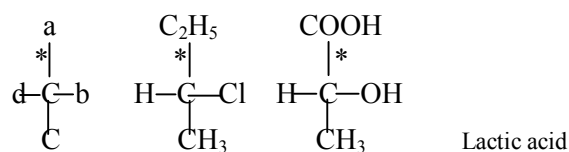
### Conditions for optically activity

Following three conditions are essential for optical activity.

- 1) A Molecule must be asymmetric in nature i.e. it has no line of symmetry which will divide it into two equal halves.



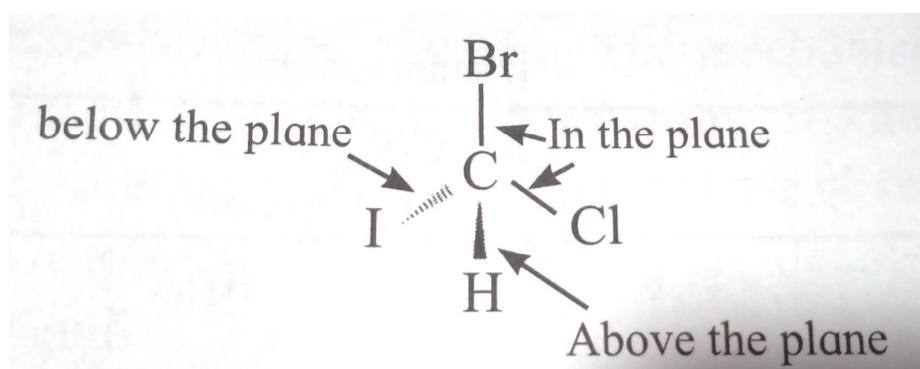
- 2) Such an asymmetric molecule should have two configurations which are related as non-superimposable mirror images.
- 3) Van't Hoff and le-Bel concept of asymmetric carbon atom or chiral carbon atom.  
According to this theory, "When a tetrahedral carbon is attached to four different groups or atoms, It is called chiral carbon atom or asymmetrical carbon atom." The compounds containing chiral carbon atom are optically active because such a compound automatically satisfies two conditions of optical activity.



A molecule having chiral carbon atom has no line of symmetry. Such a molecule definitely has two configurations which are related as non-superimposable mirror images one of the configurations is dextro rotatory while the other is laevo rotatory.

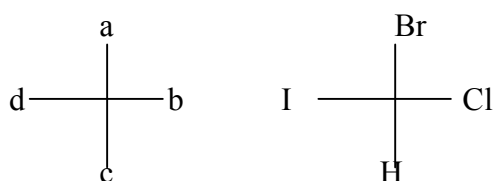
### Diagrammatic representation of chiral carbon.

Asymmetric carbon has four bonds with four different groups or atoms. Out of them, two bonds are in the plane of the paper. They are denoted by ordinary lines. The third bond is above this plane i.e. in front of carbon. It is denoted by thick line. The fourth bond is below the plane of paper i.e. behind the carbon and is denoted by dotted lines. This becomes representation of chiral carbon on a plane paper.



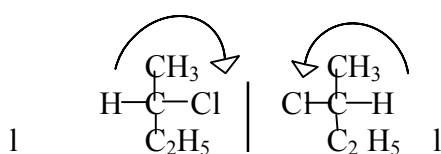
### Fischer's Projection formula

Chiral carbon is shown by a cross mark and four substituent's are indicated.



### Q. Explain optical activity of 2-chlorobutane i.e. sec. butyl chloride.

- 2-chlorobutane contains asymmetric carbon atom which is attached to four different groups or atoms such as  $CH_3$ ,  $Cl$ ,  $C_2H_5$ ,  $H$ . Therefore, according to Van't Hoff Le-Bel theory, this compound is optically active.
- The molecules of secondary butyl chloride has no line of symmetry. i.e. it is asymmetric molecule. Also, it has two configurations which are related to each other as non superimposable object & mirror image.



- 3) Out of two configurations, one is dextro rotatory. It is denoted as *d*-2chlorobutane. It rotates plane of plane polarised light in clockwise direction. Other configuration is laevo rotatory denoted as *l*-2chlorobutane. It rotates plane of plane polarized light in anti clockwise direction.
- 4) Equal quantity or equimolar mixture of dextro & laevo isomers of sec. butyl chloride is called **racemic mixture**. It is denoted as (*dl*) 2-chlorobutane. It is optically inactive i.e. it can't rotate plane of plane polarized light. This is due to external compensation. However racemic mixture may be resolved.
- 5) The dextro & laevo isomers are called enantiomers/ enantiomorphs. They have same physical properties except optical activity or angle of rotation.

## GOC

### (General Organic Chemistry)

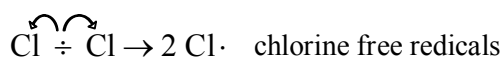
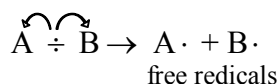
#### Cleavages in bonds (Bond Fission):

##### 1. Homolysis or Homolytic fission.

Breaking of a covalent bond in which the shared electron pair is symmetrically distributed between the bonded atoms producing free radicals is called **homolysis or homolytic fission**.

After homolysis each atom retains single electron. Such chargeless atoms having an **odd electron** are called **free radicals**. They are extremely reactive. The reactions in which homolysis occur are called **Free radical reactions**.

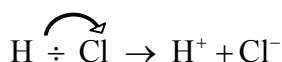
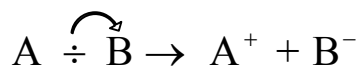
Free radicals are paramagnetic in nature as they always contain odd (unpaired) electrons.



##### 2. Heterolytic Fission or Heterolysis

Breaking of covalent bond in which the shared pair of electrons is **unsymmetrically distributed** between the bonded atoms producing ions is called heterolysis or heterolytic fission. During Heterolysis **generally** more electronegative atom retains shared electron pair & is converted into anion. The other less electronegative atom gets converted into cation.

The reactions in which heterolysis occur are called **"ionic reactions"**.

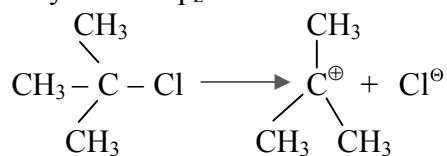


##### 3. Carbonium ion or Carbocation

Organic species in which central carbon carries unit positive charge & has six electron in the valence orbit is called **carbonium ion**. During the formation of carbonium ion, the shared electron pair is shifted away from carbon. After heterolysis, carbon gets unit +ve charge. & becomes carbocation. In carbonium ion, carbon carrying unit +ve charge is in  $sp^2$  hybridized state. A carbonium ion has planer **trigonal geometry** (bond angle of  $120^\circ$  each)

Carbon atom in carbocation forms three  $sp^2$  hybrid orbitals. These three  $sp^2$  hybrid orbitals forms three sigma bonds with hydrogen or with other alkyl group.

The unhybridized  $p_z$  orbital of carbon remains vacant.



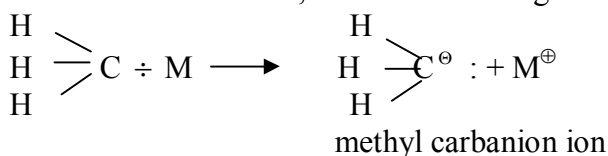
Carbocation

#### 4. Carbanion ion or carbanion

Organic species in which central carbon carries unit negative charge & has eight electrons in the valence orbit is called **carbanion ion**. During the formation of carbanion ion, the shared electron pair is shifted towards carbon. When heterolysis occurs, carbanion is formed.

In carbanion ion negatively charged carbon is in  $sp^3$  hybridized state & it has tetrahedral unsymmetrical pyramidal geometry & bond angle is of  $107^\circ$ . This carbon forms four  $sp^3$  H.O. Out of which three  $sp^3$  H.O. form sigma bonds with three H-atoms & fourth  $sp^3$  H.O. contains pair of electrons.

So in the valence orbit, carbon contain eight electrons.



#### 5. Nucleophilic Reagents or Nucleophiles

The reagents having attraction for +ve centers or protonated centers are called **nucleophilic reagents or nucleophiles**. Nucleophiles are themselves negatively charged (anions) or they are the neutral molecules having lone pairs of electrons.

All nucleophilic reagents are themselves **Lewis bases**.

**Anionic Nucleophile :-**  $\text{OH}^-$ ,  $\text{CN}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{C}^-$

**Neutral Nucleophile:-**  $\text{NH}_3$ ,  $\text{R-NH}_2$ ,  $\text{C}_5\text{H}_5\text{N}$ ,  $\text{H}_2\text{O}$ ,  $\text{R-O-R}$

#### 6. Electrophilic reagents or electrophiles

The reagents having attraction for negative centre or electron rich centre are called electrophilic reagents or electrophile. The electrophiles are themselves positively charged (cations) or they are electron deficient neutral molecules. All electrophilic reagents are necessarily **Lewis Acids**.

cationic electrophile -  $\text{H}^+$ ,  $\text{H}_3\text{O}^+$ ,  $\text{Cu}^{++}$ , etc

Neutral electrophiles :-  $\text{AlCl}_3$ ,  $\text{BF}_3$ ,  $\text{SO}_3$ ,  $\text{CO}_2$ ,  $\text{AlBr}_3$  etc

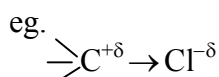
#### Q. Distinguish between carbonium ion & carbanion ion.

Carbonium	Carbanion ion
1. Organic species in which central carbon carries unit positive charge is carbonium ion.	1. Organic species in which central carbon has negative charge is carbanion
2. It has six electrons in valence orbit.	2. It has eight electrons in valence orbit.
3. It is in $sp^2$ hybridized state.	3. It is in $sp^3$ hybridized state.
4. Carbonium has planar trigonal geometry.	4. Carbanion has unsymmetrical pyramidal geometry.
5. It is electron deficient & acts as Lewis acid.	5. It is electron rich & acts as Lewis base.
6. It acts as electrophile.	6. It acts as nucleophile.
7. bond angle is of $120^\circ$	7. bond angle is of $107^\circ$

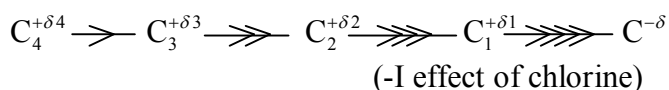
#### Mobilities of Electrons in the bond.

##### 1) Inductive effect or I-effect:

- i) The shifting of shared electron pairs of sigma covalent bond towards more electronegative atoms without leaving the octet, producing permanent fractional charges is called **inductive effects**. Such a bond is called polar covalent bond. Inductive effect is also called **transmission effect**.

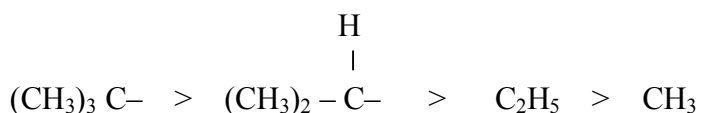


- ii) The inductive effect can be relayed along the carbon chain. Consider the example of n- butyl chloride.



Due to electronegativity difference, shared electron pair between  $C_1$  & Cl will be shifted away from  $C_1$  towards chlorine. This produces fractional negative charge on Cl & a fractional positive charge on  $C_1$ . Due to this positive charge, the paired electrons between  $C_1$  &  $C_2$  is shifted away from  $C_2$ , towards  $C_1$ . This will produce little positive charge on  $C_2$ . The effects continues along the carbon chain & the successive carbons also become polarized.

- iii) Inductive effect is a permanent effect. The fractional charges are present permanently on the carbon atoms. However Inductive effect rapidly decreases away from the site of its origin. So it is considered only upto fourth carbon i-e upto  $C_4$ .
- iv) This effect is of two types. Highly electro negative (more electronegative than hydrogen) or electron withdrawing functional groups produce the inductive effect, working away from the chain. This is called  $-I$  effect. For example, the functional group such as Cl, Br, I, O,  $>C=O$ ,  $COOH$ ,  $-NO_2$ ,  $-NH_2$  groups can produce  $-I$  effect.
- v) Atoms or group of atoms which have more tendency to withdraw electrons and show the  $-I$  effect are in the decreasing order of  
 $-NO_2 > -CN > -COOH > -COOR > -F > -Cl > -Br > -I > -OCH_3 > -C_6H_5 > -H$ .
- vi) Decreasing order of  $-I$  effect of halogen family is  
 $-F > -Cl > -Br > -I$
- vii) The electron releasing or electropositive (less electronegative than hydrogen) functional groups produce the inductive effect, working into the chain. This is called  $+I$  effects. For ex. alkyl radicals ( $-R$ ), the metals like Mg, Zn, K, etc can produce  $+I$  effect.
- $$C^{-\delta 4} \longleftarrow C^{-\delta 3} \longleftarrow C^{-\delta 2} \longleftarrow C^{-\delta 1} \longleftarrow M^{+\delta}$$
- viii) Atoms or groups of atom having electron releasing tendency show  $+I$  effect. Following is the decreasing order of  $-I$  effects

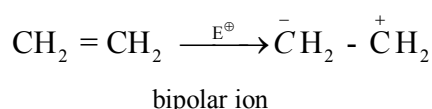


## 2. Electromeric Effect

**Definition:** Complete transfer of  $\pi$  electrons of a multiple bond towards one of the atom due to the attack of a reagent producing a dipolar ion is called **electromeric effects**. It is temporary effect.

Electromeric effect is observed only when there are multiple bonds (double / triple bonds) between two atoms. A multiple bond consist of  $\sigma$  bond &  $\pi$  bond. The  $\sigma$  bond is strong while  $\pi$  bond is weak.

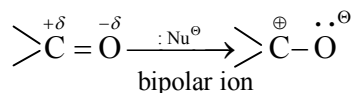
For ex: In alkenes double bond consists of one  $\sigma$  & one  $\pi$  ( $\sigma+\pi$ ). When an electrophilic reagent approaches to alkene, the electron pair of a  $\pi$  bond is completely transferred towards one of the carbon atom. This carbon gets unit -ve charge. While other carbon becomes positively charged. The electromeric effect results in formation of dipolar ion.



Electromeric effect may also be observed in carbonyl group. This group has a double bond between carbon and oxygen. When a nucleophilic reagent approaches the carbonyl group pi



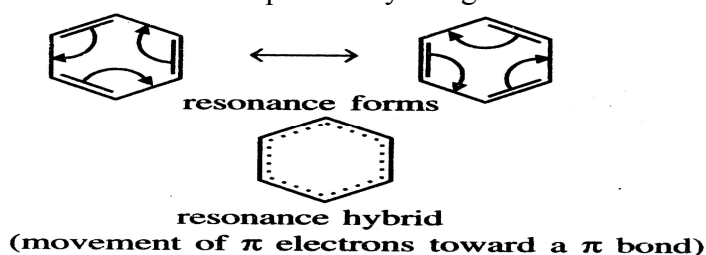
electrons are completely transferred to more electronegative oxygen which becomes -vely charged while carbon becomes +vely charged. Thus electromeric effect produces dipolar ions.



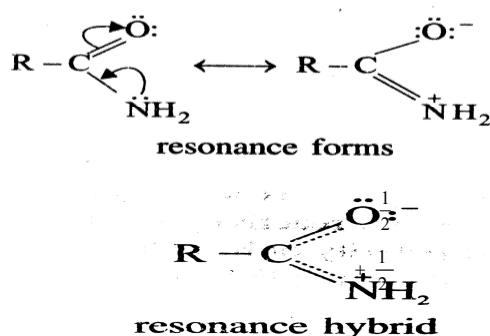
The electromeric effect is temporary. If the reagent is withdrawn the effect disappears & pi bond is re-established.

### 3) Resonance or Mesomeric Effect

It is a phenomenon in which a compound exists in more than one equivalent electronic structures. Such structure may explain few properties. But none can explain all the properties. The actual structure is in between these resonating structure & considered as **resonance hybrid**. The phenomenon of resonance can be explained by using benzene molecule.



Energy of the actual structure of molecule is less than any of the resonating structure. Due to less energy, the resonance hybrid is more stable than resonating structure. The difference in energy between the actual structure and one of the most stable resonating structure is called **Resonance stabilization energy or resonance energy**. Thus resonance increases stability of compound. The stability of molecule is directly proportional to resonance energy. (Stability  $\propto$  resonance energy.)



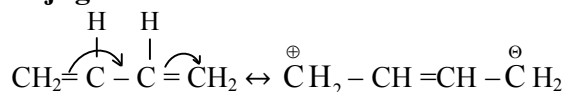
- \* Resonating structure should have same position of nuclear atom
- \* More the number of resonating structures, more is the stability.

### Conjugation:

A given atom or group is said to be in conjugation with an unsaturated system if it is directly linked to one of the atoms of the multiple bond through a single bond with pi bond, positive charge, negative charge, odd electron or lone pair electron.

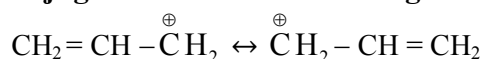
### Types of Conjugation:

#### i) Conjugation between C = C and C = C

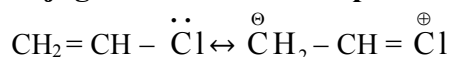




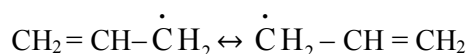
## ii) Conjugation between +ve charge and C = C



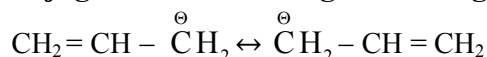
## iii) Conjugation between lone pair and C = C



## iv) Conjugation between odd electron and C = C



## v) Conjugation between negative charge and C = C

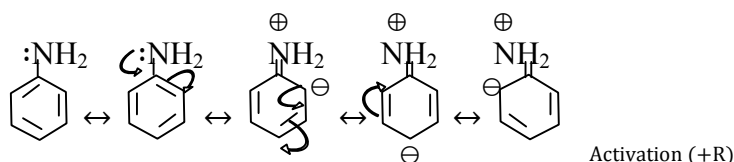


## Types of Resonance:

Depending upon the substituent in aromatic compounds there are two types of the resonance is possible.

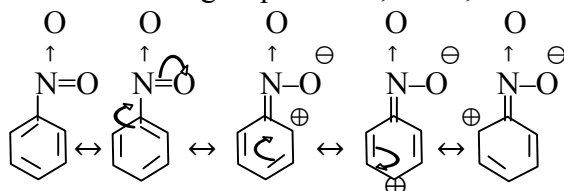
### (1) Positive Resonance: (+R)

An electron is transferred by functional group towards benzene ring. It is also called activation of benzene ring. Such type of effect in which benzene ring is activated is called positive resonance effect and it is denoted by +R. The groups – OH, – OR, – NH<sub>2</sub>, Br, I, Cl Shows +R effect.



### (2) Negative Resonance :

Substituent which have tendency to withdraw electrons from benzene ring is called deactivation of benzene ring and such substituent shows negative resonance effect and denoted by –R effect. The groups –CHO, –CN, –COOR, –NO<sub>2</sub>, etc. shows negative resonance effect.



Negative resonance in nitrobenzene (Deactivation OR – R)

### Q.1 Distinguish between Electrophile & Neucleophile.

Electrophile	Neucleophile
1. Electrophiles are positively charged species.	1. Neucleophites are negatively charged species.
2. They are attracted towards negative center.	2. They are attracted towards positive center.
3. They are Lewis acids.	3. They are Lewis bases.
4. Cations and electron deficient species are electrophiles.	4. Anions and electron rich species are neucleophiles.
5. H <sup>+</sup> , H <sub>2</sub> O <sup>+</sup> , NO <sub>2</sub> <sup>+</sup> , BF <sub>3</sub> , AlCl <sub>3</sub>	5. HO <sup>–</sup> , CN <sup>–</sup> , NN <sub>3</sub> , R – O – R, H <sub>2</sub> O

## Q.2 Distinguish between Inductive effect and electromeric effect.

Inductive effect	Electromeric effect
1. Inductive effect occurs in sigma bond or single bond.	1. Electromeric effect occurs in multiple bond or pi bond.
2. There is shifting of shared electron pair in inductive effect.	2. There is complete transfer of electron pair takes place.
3. Due to inductive effect, atoms get fractional charges.	3. Electromeric effect produces unit charges on atoms.
4. Charges are permanent	4. Charges are temporary.
5. Attack of reagent does not required in inductive effect.	5. Electromeric effect occurs due to attack of reagents.

### Types of Organic Reactions

Organic reactions are classified into following four reactions:-

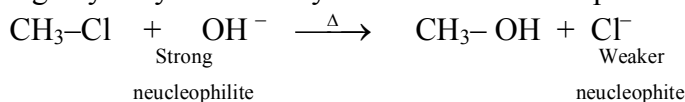
#### 1) Substitution Reaction:-

A reaction in which an atom or group of atoms is replaced by another atoms or group of atoms is called substitution reaction.

Depending upon attacking species or substituent's they are classified into three classes:-

##### A) Nucleophilic substitution reactions:-

In these reactions an atom or group of atoms in a molecule is replaced by nucleophile e.g. Hydrolysis of methyl chloride is an example of nucleophilic substitution reaction.



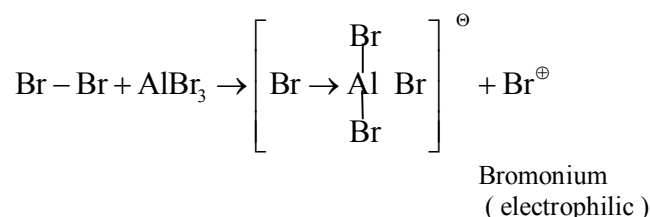
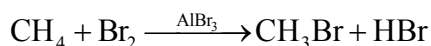
\*all substitution reactions of haloalkanes are nucleophilic substitutions.

##### B) Electrophilic Substitution reaction:-

Substitution takes place by electrophile is called electrophilic substitution reaction.

eg. Nitration of benzene is an example of electrophilic.

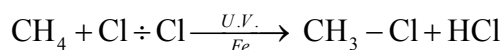
\*Bromination & iodination of haloalkanes are electrophilic substitution.



##### C) Free radical substitution reaction

In these reactions an atom or group of atoms is replaced by free radical.

eg. Chlorination of methane is an example of free radical substitution reaction.



#### 2) Addition reaction :-

The reaction in which two molecules react to form a single product are called addition reaction. Organic compounds containing double bonds or triple bonds give addition reaction.

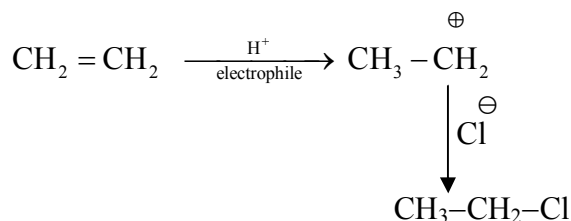
eg. Alkenes, Alkynes, aromatic compounds such as benzene etc. shows the addition reactions.

**Addition reactions are of three types:-**

**A) Electrophilic addition reaction:-**

In compounds having multiple bonds, due to electromeric effect, pi bonds electrons are shifted to one of the atom producing site for attack of electrophile. Such a reaction is called electrophilic addition reaction.

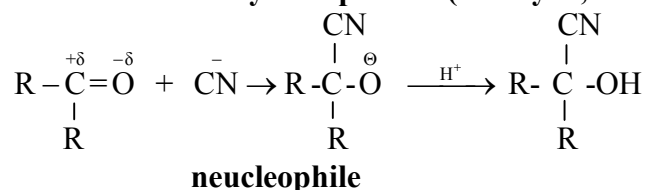
**\* Addition of alkenes & alkynes are always electrophilic.**



**B) Nucleophilic addition reaction:-**

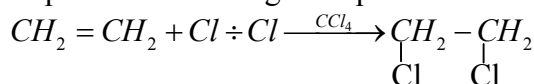
Compounds like carbonyl group (  $\text{>C=O}$  ) get polarized due to electromeric effect and carbon get positive charge and oxygen get negative charge. The nucleophile attack on the positive centre. e.g.

**\* all additions of carbonyl compounds (aldehyde, ketone) are nucleophilic.**



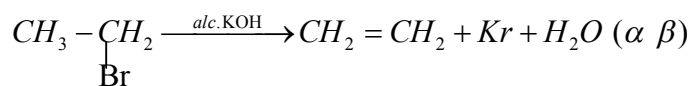
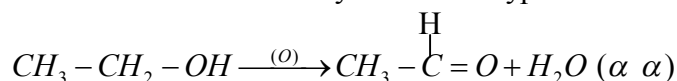
**C) Free radical reaction:-**

Compounds containing multiple bonds can undergo free radical addition reaction.



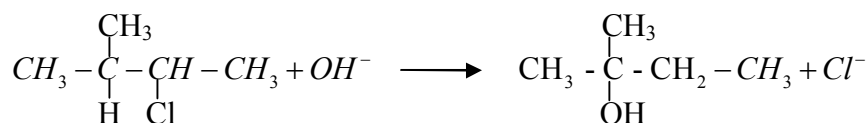
**3) Elimination Reaction:-**

Reactions in which products are formed by a loss of small molecules such as  $\text{H}_2\text{O}$ ,  $\text{HX}$  etc are called elimination reaction. Elimination reaction are reverse of addition reaction. Elimination results in the  $\pi$  bond. They are of two types such as a)  $\alpha\alpha$  elimination b)  $\alpha\beta$  elimination.



**4) Rearrangement Reactions:-**

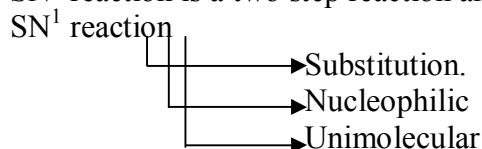
Reactions in which products get converted from reactants by the rearrangement of atom in the reacting molecules are called rearrangement reactions.



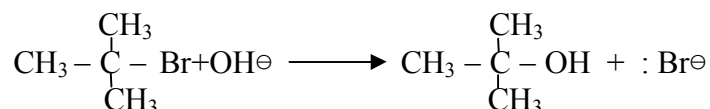
## Mechanism of Hydrolysis of Alkyl Halides

**Q.1) Explain  $S_N^1$  mechanism OR Explain mechanism of alkaline hydrolysis of 2-bromo-2-methyl propane (tertiary butyl bromide). or Explain mechanism having 50% inversion of configuration.**

$S_N^1$  reaction is a two step reaction and given by only tertiary alkyl halide.



- 1) When t-butyl bromide is boiled with aqueous potash, it undergoes alkaline hydrolysis giving t-butyl alcohol.

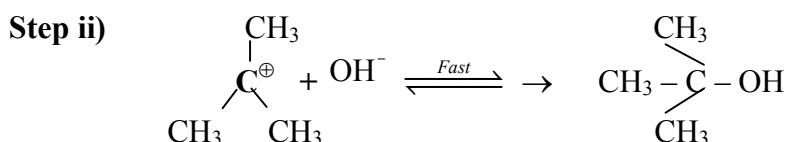
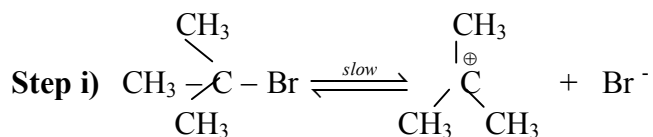


### 2) Mechanism:

Above hydrolysis is completed in two steps. The first step is slow. In this slow step, only t-butyl bromide undergoes ionization. This ionization is possible due to the presence of electron releasing 3 alkyl radicals. A transition state  $TS_1$  is formed which is converted into t-butyl carbonium ion. This carbocation acts as intermediate.

Second step is fast. In this fast step, nucleophile approaches tertiary carbon forming a transition state  $TS_2$ . It is converted into product.

In the fast step, carbonium ion is attacked by nucleophile either from the front side or from the back side. Accordingly the configuration may be retained or inverted respectively. Thus there is only 50% inversion of configuration during  $S_N^1$  reaction.



### 3) Kinetics of reaction:-

In the rate determining slow step only t-butyl bromide takes part. Therefore it is a unimolecular reaction. As the rate depends upon concentration of one reactant, it is also a first order reaction.

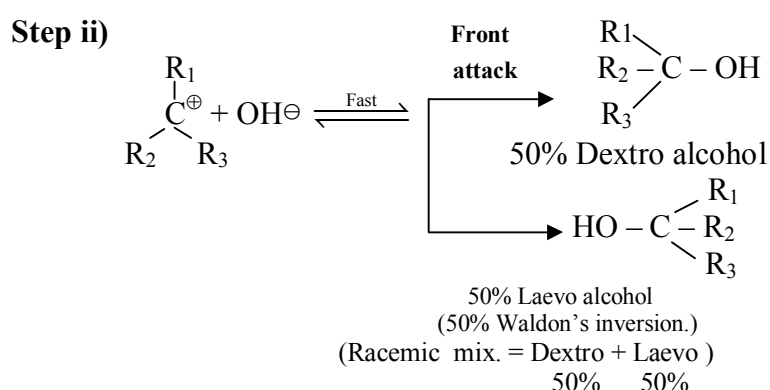
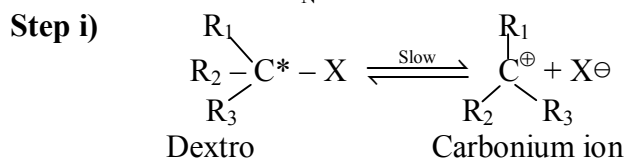
$$\text{Rate} \propto [(\text{CH}_3)_3\text{C}-\text{Br}]$$

The hydrolysis of t-butyl bromide is a nucleophilic substitution unimolecular reaction so represented as  $S_N^1$  reaction.

### Q.2) Explain stereo chemistry of $S_N^1$ reaction.

Suppose a t-alkyl halide contains chiral carbon atom. It will be optically active. Suppose the dextro isomer of this compound undergoes alkaline hydrolysis.

In the rate determining slow step, an intermediate carbonium ion is formed. In the second and the fast step, this carbonium ion may be attacked either from the front side or from the back side. In the front side attack, configuration of product alcohol is retained giving 50% dextro isomer of the alcohol. In the back side attack, there is inversion of configuration. This produces 50% laevo isomer of alcohol. Thus the product is a racemic mixture and optically inactive. The  $S_N^1$  reaction results in racemisation, due to 50% Walden's inversion.

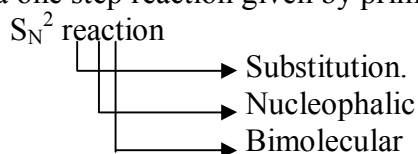


### Characteristics/ Salient features of $S_N^1$

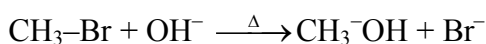
- Two step reaction
- Bond breaking of C – X bond & bond formation of C – OH bond occurs in different steps.
- Carbocation may be attacked by front or back side.
- Racemisation occurs

### Q.3) Explain mechanism of alkaline hydrolysis of bromomethane OR methyl bromide. or Explain mechanism of hydrolysis having 100% inversion.

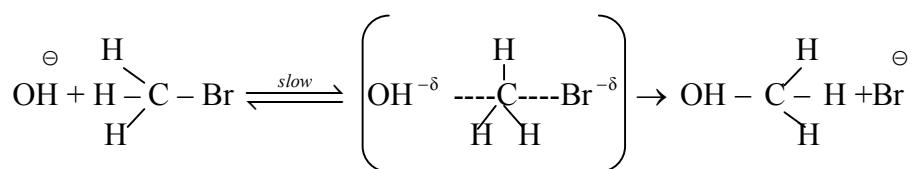
$S_N^2$  is a one step reaction given by primary alkyl halide.



- When bromomethane is boiled with aqueous potash it undergoes alkaline hydrolysis giving methanol.



- Mechanism:-** Above hydrolysis is completed in single step which is slow. In this slow step, nucleophile attacks primary carbon from opposite side of halogen. This is called **back side attack**. A transition state is formed in which both halogen and nucleophile are partially bonded to primary carbon. They are on the same axis. This transition state is then converted into products. Due to back side attack, there is 100% inversion of configuration in  $S_N^2$  reaction.



**T.S.**

- 3) **Kinetics of reaction:-** In the rate determining slow step, both reactants take part. Rate depends upon concentration of both. Therefore it is a bimolecular as well as second order reaction.  
 Rate  $\propto [\text{CH}_3\text{-Br}] [\text{OH}^-]$   $\therefore$  Rate =  $K[\text{CH}_3\text{-Br}] [\text{OH}^-]$

The hydrolysis of methyl bromide is a nucleophilic substitution bimolecular reaction. So represented as  $\text{S}_\text{N}^2$  reaction.

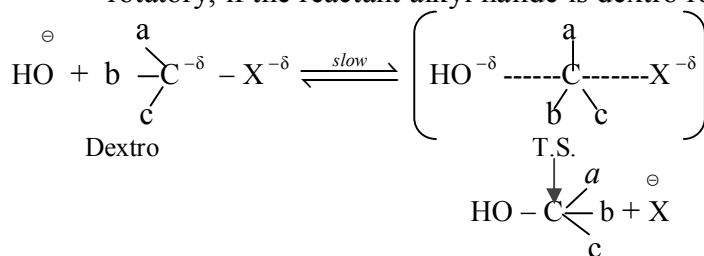
#### Characteristics of Salient features of $\text{S}_\text{N}^2$

1. One step reaction
2. Only back side attacked.
3. In the T.S. the leaving group (Br) and nucleophile are partially bonded to primary carbon and are on the same axis.
4. Negative charge is equally distributed
5. In the T.S. three covalent bond of carbon are in one plane and the axis is perpendicular to this plane.
6. There is Walden inversion

#### Q.4) Explain stereochemistry of $\text{S}_\text{N}^2$ reaction.

Consider a primary alkyl halide having chiral carbon atom, so that it will be optically active. Suppose the dextro isomer undergoes alkaline hydrolysis.

Due to the backside attack, there is 100% Walden inversion of configuration. Due to this the product alcohol will have opposite optical activity i.e. the product alcohol will be laevo rotatory, if the reactant alkyl halide is dextro rotatory.



(100% Walden's inversion)

#### Q.5) Why t-alkyl halide does not undergo $\text{S}_\text{N}^2$ mechanism?

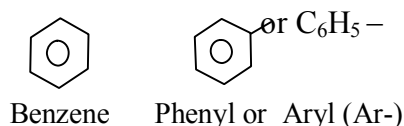
**Steric hindrance** - In tertiary alkyl halide, maximum space around tertiary carbon is occupied by bulky alkyl radicals. When the nucleophile tries to attack tertiary carbon from the back side, it is pushed back by these radicals. This is called **steric hindrance**. Thus, due to the steric hindrance  $\text{S}_\text{N}^2$  is not possible in t-alkyl halides.

**Q.6) Distinguish between  $S_N^1$  and  $S_N^2$ .**

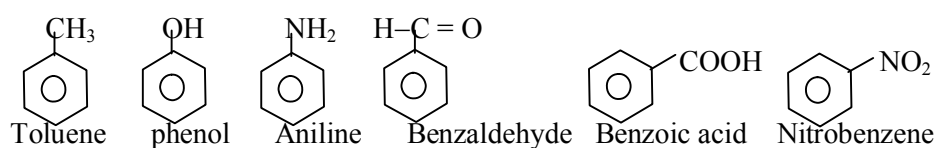
$S_N^1$	$S_N^2$
1. $S_N^1$ is unimolecular as well as first order reaction	1. $S_N^2$ is a bimolecular & second order reaction.
2. $S_N^1$ is completed in two steps and has two T.S.	2. $S_N^2$ is completed in a single step and has only one T.S.
3. Bond breaking and bond formation occurs in separate steps.	3. Bond breaking and bond formation occurs in same steps.
4. Nucleophile attacks either from front or from back side.	4. There is back side attack always.
5. Polar solvent such as water favours $S_N^1$ , as it is ionic reaction.	5. Non polar solvent favours $S_N^2$ .
6. Lower concentration of nucleophile prefer $S_N^1$ .	6. Higher concentration of nucleophile prefer $S_N^2$ .
7. No effect of nucleophiles.	7. Strong nucleophile like $OH^-$ , $CN^-$ prefer $S_N^2$ reaction.
8. Main substrate is t-alkyl halide.	8. Main substrate is primary alkyl halide.
9. There is 50% inversion of configuration, resulting in the racemisation.	9. There is 100% inversion.

**Haloarenes**

- \* Aromatic hydrocarbons are called as arenes. Ex. benzene, toluene, etc.
- \* When one hydrogen is removed from benzene, the radical is called phenyl radicals.



- \* Following are common names of some aromatic compounds.

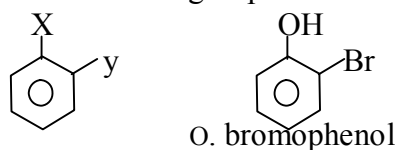


**Names of disubstituted benzene.**

When two functional groups are directly attached to the benzene ring, depending upon their position, different names are used.

**1) Ortho:-**

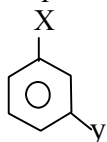
If the two functional groups are on adjacent carbon atoms (1,2) position, it is called ortho.





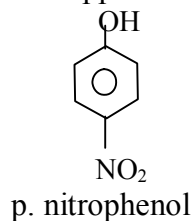
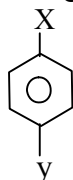
### 2) Meta:-

If the groups are on alternate carbon atoms (1,3) position it is called meta.

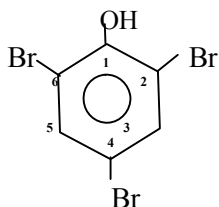


### 3) Para:-

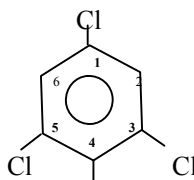
If functional groups are on opposite carbon atoms (1,4 position), it is called para.



However if more than two functional groups are attached to the benzene ring then above names cannot be used.



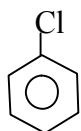
2,4,6 tribromophenol



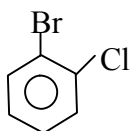
1,3,5 trichlorobenzene

### Definition of Haloarenes

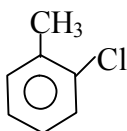
Haloarenes are defined as aromatic compounds in which hydrogen atoms of the benzene nucleus are replaced by halogen atoms. So in haloarenes, halogen atoms are directly attached to the benzene ring.



Chlorobenzene



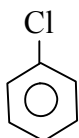
O. bromochlorobenzene



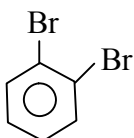
O. Chlorotoluene

### Classification:

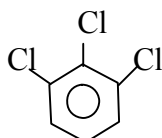
Haloarenes are classified on the basis of number of halogens directly attached to benzene nucleus.



monohalorene



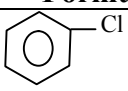
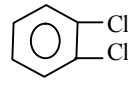
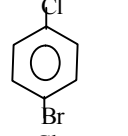
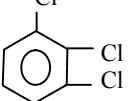
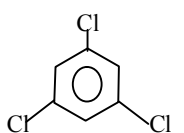
Dihaloarene



Trihaloarene

**Nomenclature:**

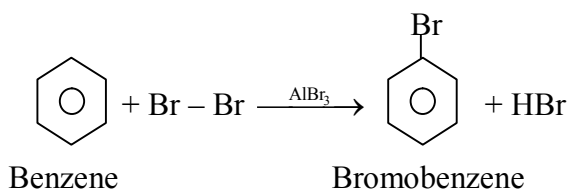
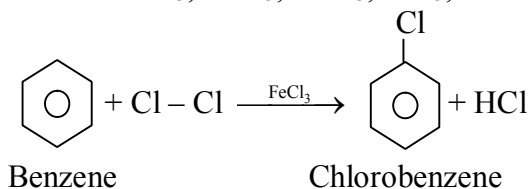
In IUPAC system these compounds are named as halobenzenes. Positions of halogens are indicated by suitable numbers.

Formula	Common Name	IUPAC Name
	Phenyl chloride aryl chloride	Chlorobenzene
	O dichlorobenzene	1,2 dichlorobenzene
	P bromochlorobenzene	1, bromo 4 chlorobenzene
	----	1,2,3 trichlorobenzene
	Symmetrical trichlorobenzene	1,3,5 trichlorobenzene

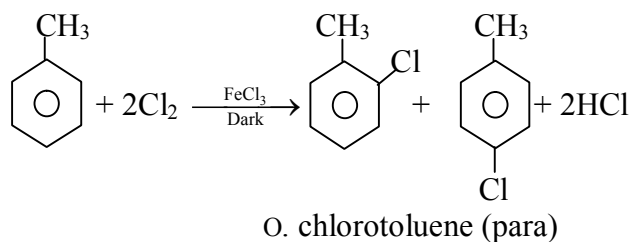
**Methods of Preparation of Haloarenes**

**1) Electrophilic halogenations of arenes.**

Aromatic hydrocarbons or arenes such as benzene or toluene undergo electrophilic halogenations on treatment with halogens. Reaction takes place in the presence of Lewis acid such as  $\text{FeCl}_3$ ,  $\text{AlCl}_3$ ,  $\text{AlBr}_3$ ,  $\text{BCl}_3$ , etc.

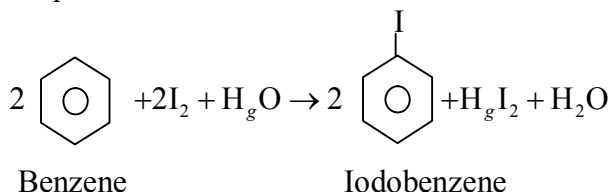


Toluene undergoes chlorination in dark. (In the presence of sunlight chlorination may occur in the side chain.) Toluene on chlorination gives mixture of ortho chlorotoluene and para chlorotoluene.



### Iodination:

Arene reacts with iodine giving aryl iodide - But the reaction is reversible, therefore in the reaction vessel, one of the oxidizing agent such as  $\text{HgO}$ , or  $\text{HIO}_3$  or  $\text{HNO}_3$  is added. It oxidizes  $\text{H-I}$  and prevents backward reaction.



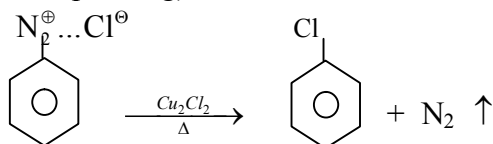
### 2) Sandmayer's Reaction

#### Decomposition of benzene diazonium chloride (salt)

In the sandmayer's reaction, diazonium salt is decomposed in the presence of **cuprous salt**.

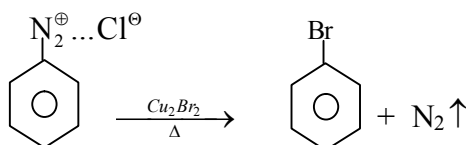
#### a) Preparation of chlorobenzene:-

When benzene diazonium chloride is heated with cuprous chloride (sandmayer's reaction), (corresponding) chlorobenzene is formed.



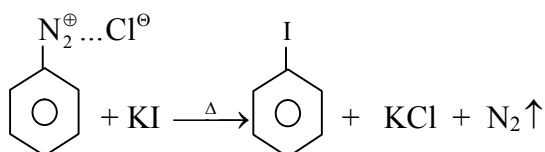
#### b) Preparation of bromobenzene:-

When benzene diazonium chloride is heated with cuprous bromide (sandmayer's) bromobenzene is formed.



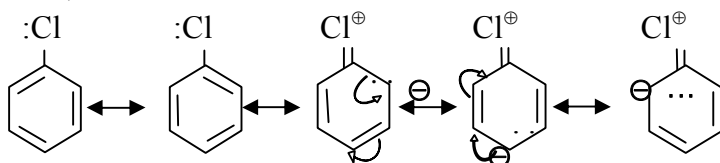
#### c) Preparation of iodobenzene:-

When benzene diazonium chloride is heated with  $\text{K-I}$  iodobenzene is formed.



### Resonance in Chlorobenzene

In haloarenes, lone pair of electrons of the halogen takes part in resonance. Thus,  $6\pi$  electrons of benzene and lone pair of halogen ( $6+2$ ) such 8 electrons take part in resonance. The electron ring is extended over seven atoms (6 carbon + 1 halogen also). In some resonating structures chloronium ion is formed, in which  $\text{C-Cl}$  bond has double bond character.



### Chemical properties of Haloarenes

Haloarenes undergo two types of reactions such as nucleophilic substitution and electrophilic substitution.

#### Nucleophilic Substitution:

These are the reaction in which halogen of halo-arenes are replaced by nucleophile such as  $\text{OH}^-$ ,  $\text{CN}^-$ , etc.

#### Q.) Why haloarenes are less reactive towards nucleophiles than alkyl halides?

Haloarenes under normal condition do not undergo nucleophilic substitution due to following reasons:-

- In alkyl halides ( $\text{R-X}$ ) carbon is in  $\text{sp}^3$  hybridized state and forms only sigma bonds with halogens. Therefore the  $\text{C-Cl}$  bond length in alkyl chloride is longer i.e. 177 pm. But in haloarenes, carbon atom is in  $\text{sp}^2$  hybridised state and  $\text{C-Cl}$  bond has double bond character due to resonance. Therefore bond length decreases and becomes 169 pm. Due to this reason,  $\text{C-Cl}$  bond is shorter and stronger in aryl halides.
- Lone pair of electron of halogen takes part in the resonance. So halogen is reluctant to be replaced.
- If halogen is removed from haloarenes, then resulting carbonium ion i.e.  $\text{C}^+$  is not stabilized, so  $\text{S}_\text{N}^1$

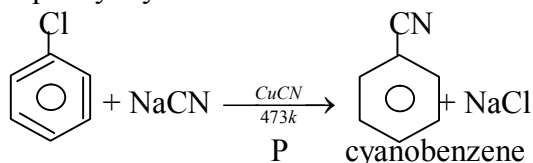


mechanism fails.

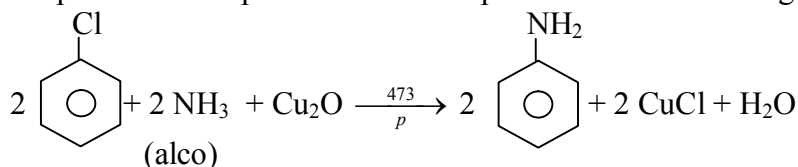
- The benzene ring and electron cloud around it causes steric hindrance to the nucleophile. Therefore  $\text{S}_\text{N}^2$  mechanism fails.

Due to above reasons, haloarenes become less reactive than alkyl halides. These haloarenes do not undergo nucleophilic substitution easily. However, under drastic conditions, following nucleophilic reactions occur in haloarenes:-

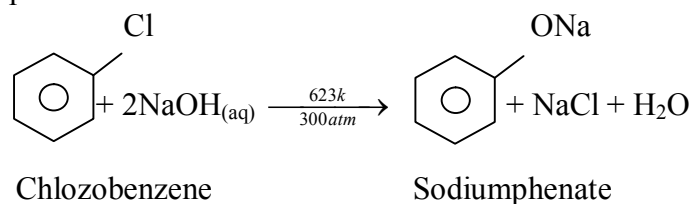
- Reaction with sodium cyanide:-** Chlorobenzene is heated with sodium cyanide at 473K, under pressure. Reaction occurs in the presence of cuprous cyanide as a catalyst giving cyanobenzene or phenyl cyanide.



- Reaction with alcoholic ammonia (Ammonolysis):-** Chlorobenzene undergoes ammonolysis in the presence of cuprous oxide under pressure at 473K. This gives aniline.



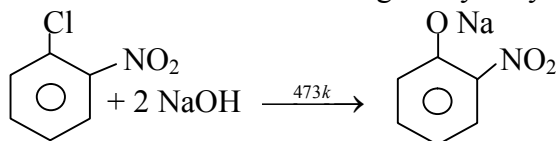
- Hydrolysis of chlorobenzene by aqueous caustic soda:** Chlorobenzene is hydrolysed in the presence of aqueous caustic soda at 623K under 300 atm pressure. The final product is sodium phenoxide.



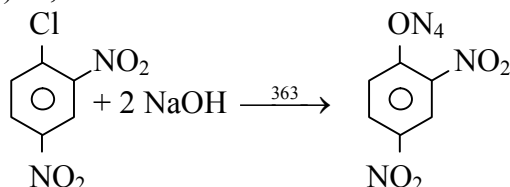
#### 4) Hydrolysis of chlorobenzene by aqueous caustic soda in the presence of electron withdrawing group:-

If electron withdrawing groups such as  $\text{NO}_2$  is present at ortho or para position, then nucleophilic substitution occurs easily. Because the nitro group is involved in the resonance, instead of Cl. Therefore, halogen can be easily substituted.

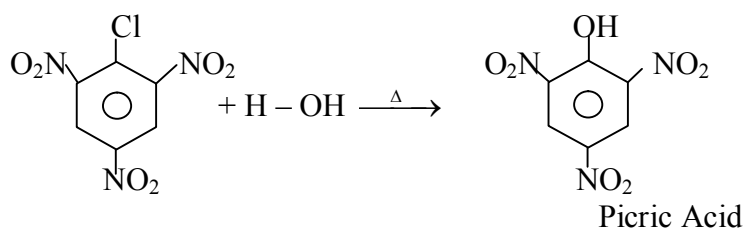
a) O-nitrochlorobenzene undergoes hydrolysis by caustic soda at only 473K.



b) 2,4 dinitrochlorobenzene is further easily hydrolysed at 363K.



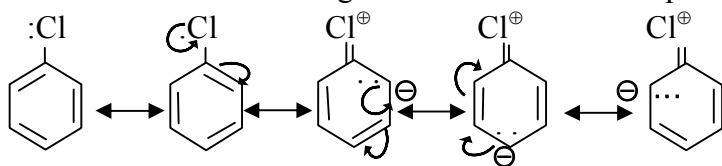
c) In 2,4,6 trinitrochlorobenzene, there are three electron withdrawing nitro groups. Hydrolysis becomes so easy that it is carried out by warm water.



\* If the electron withdrawing nitro group is at meta position, it does not help in the resonance so hydrolysis requires drastic condition. (Chlorine involves its lone pair in the resonance)

#### Electrophilic Substitution

In chlorobenzene due to +R effect, the chlorine atom is ortho or para directing. It means the new incoming electrophilic substituent joins at either ortho or at para position. This is because chlorine atom activates the benzene ring due to which ortho and para positions become negatively charged.

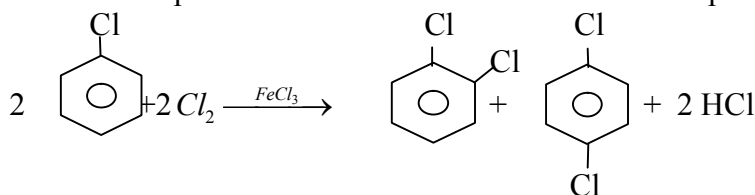


Following are electrophilic substitution reactions of chlorobenzene.

##### 1) Halogenation (Chlorination):-

It is defined as electrophilic substitution in which hydrogen atoms of the benzene nucleus are replaced by halogen atoms.

Chlorobenzene reacts with chlorine in the presence of anhydrous  $\text{FeCl}_3$  giving a mixture of ortho and para isomers of dichlorobenzene. But the para product is a major product.

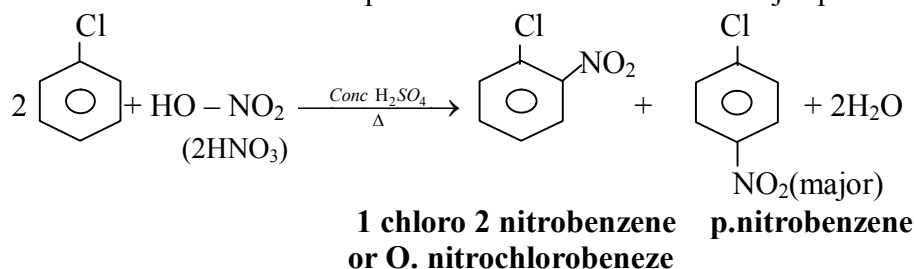


O.dichlorobenzene    P. dichlorobenzene

## 2) Nitration of chlorobenzene by nitrating mixture. (conc. $\text{HNO}_3$ + conc. $\text{H}_2\text{SO}_4$ ).

It is an electrophilic substitution in which hydrogen atoms of the benzene nucleus are replaced by nitro group ( $-\text{NO}_2$ ).

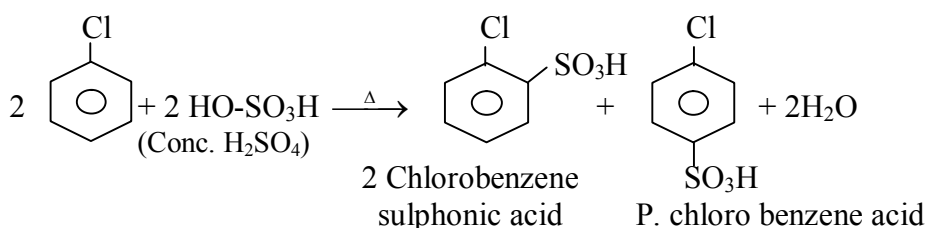
Chlorobenzene when heated with nitrating mixture i.e. concentrated  $\text{HNO}_3$  + concentrated  $\text{H}_2\text{SO}_4$ , undergoes nitration. The nitration occurs either at ortho or at para position giving mixture of these two isomers. But para nitrochlorobenzene is a major product.



## 3) Sulphonation of chlorobenzene by concentrated $\text{H}_2\text{SO}_4$ :-

It is an Electrophilic substitution in which hydrogen atoms of the benzene nucleus are replaced by sulphonic group ( $-\text{SO}_3\text{H}$ ), the reaction is called sulphonation.

Chlorobenzene undergoes sulphonation when it is heated with concentration  $\text{H}_2\text{SO}_4$ . The reaction occurs at para position or ortho position. However, para product is a major product.



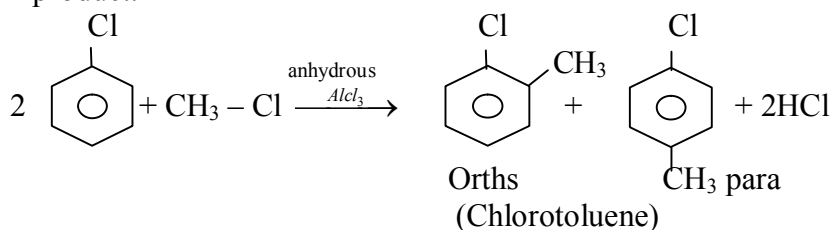
\* The electrophile is called sulphonium ion i.e  $\text{SO}_3\text{H}^+$

## 4) Friedel–craft's Reaction:-

It is defined as electrophilic substitution in which hydrogen atoms of the benzene nucleus in haloarenes are replaced by either alkyl radical ( $\text{R}\cdot$ ) or by acyl group ( $\text{R}-\overset{\text{O}}{\parallel}\text{C}-$ ).

### a) Fridal Craft's alkylation:-

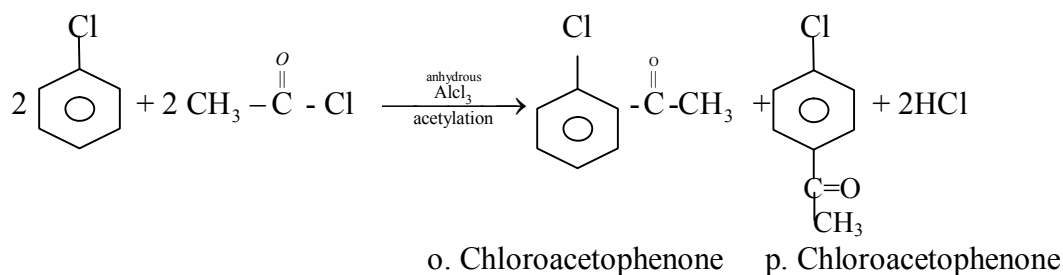
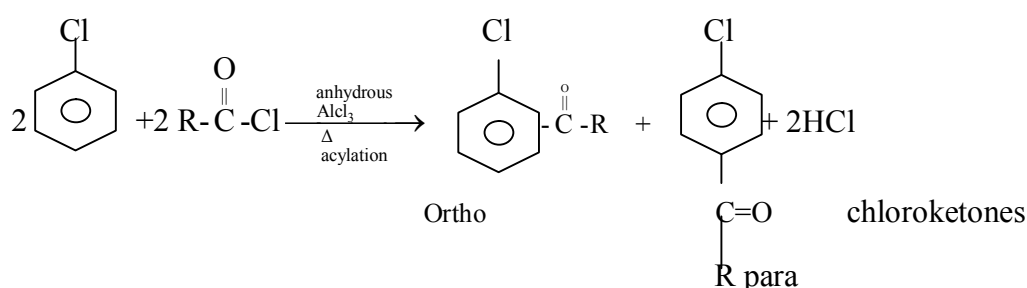
When chlorobenzene reacts with alkyl chloride in the presence of anhydrous  $\text{AlCl}_3$ , alkylation takes place either at ortho position or at para position. But the para product is a major product.



**b) Fridel craft's acylation:-**

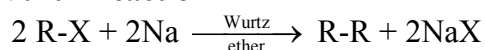
Chlorobenzene reacts with acyl chloride ( $R-CO-Cl$ ) in the presence of anhydrous  $AlCl_3$ , acylation takes place either at ortho position or at para position. It results in the formation of aromatic chloroketones. The para product is a major product.

Formula	Name of group	Process
$R - \overset{\overset{O}{\parallel}}{C} -$	acyl	acylation
$H - \overset{\overset{O}{\parallel}}{C} -$	formyl	formylation
$CH_3 - \overset{\overset{O}{\parallel}}{C} -$	acetyl	acetylation

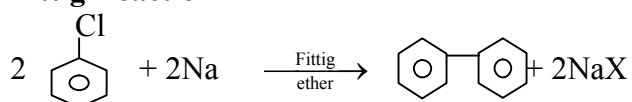


**5) Wurtz-Fittig Reaction (Reaction with sodium metal)**

**Wurtz-Reaction**



**Fittig Reaction**

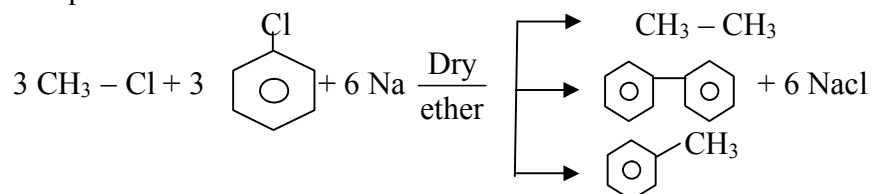


**Wurtz-Fitting Reaction**

Aryl halide ( $Ar-X$ ) is mixed with alkyl halide ( $R-X$ ). This mixture is treated with sodium metal in the presence of dry ether as the medium. This gives three types of hydrocarbons. Such a coupling reaction is called Wurtz-Fittig reaction.



For example, chlorobenzene and methyl chloride react with sodium metal in dry ether medium giving a mixture of toluene, ethane & diphenyl as shown in the following three equations.



### Uses and Environmental effects of some alkyl and aryl halides

#### A) Dichloromethane or Methylene Chloride. ( $\text{CH}_2\text{Cl}_2$ )

- 1) It is able to dissolve a wide range of organic compounds hence it is mainly used as an ideal solvent for many chemical reactions.
- 2) It is used as a degreaser i.e. remover of grease and paint.
- 3) It is used to decaffeinate or separate the substance named caffeine from tea and coffee.
- 4) It is used as aerosol spray propellant or the agent in the air fresheners or sprays that push the scent due to its volatile nature.

#### Hazards (environment effects):-

When present in excess amount in air being highly volatile causes nausea, numbness in finger & toes, dizziness and if in rare amount (traces) causes less vision and hearing. Also when comes in contact of eyes, it damages cornea.

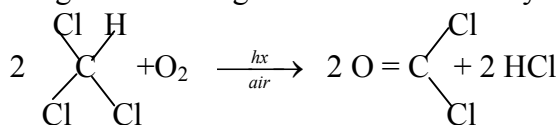
#### B) Trichloromethane or Chloroform ( $\text{CHCl}_3$ )

##### Uses:

- 1) Used in preparation of chlorofluoromethane or Freon refrigerant. (R-22 Industrial name).
- 2) Used as solvent in pharmaceutical (medical) industry and for producing pesticides and dyes.
- 3) It is a source of dichlorocarbene ( $\text{CCl}_2$ ) group.

#### Hazards:-

Previously chloroform was used as anaesthetic but nowadays it is replaced by ether due to its highly poisonous nature (toxicity) when chloroform is exposed to air and sunlight it reacts to form a poisonous compound called as phosgene. Hence it is preserved in dark, brown (amber) coloured well stoppered bottles. This phosgene is so hazardous that when mixed in air, causes headache and fatigue and damage to central nervous system. It may cause death.



#### C) Tetrachloromethane or Carbon tetrachloride ( $\text{CCl}_4$ )

##### Uses:

- 1) Used as dry cleaning agent and as a pesticide to kill pests.
- 2) Used as a solvent in production of refrigerants.
- 3)  $\text{CCl}_4$  is also called pyrene, when it is used as fire extinguisher.

#### Hazards:-

It has several adverse health effects such as eye irritation, damages nerve cells, vomiting sensation, dizziness, unconsciousness or death. Also when mixed with air, it causes ozone depletion which leads to human skin cancer.

### D) Iodoform or tri – iodomethane ( $\text{CHI}_3$ )

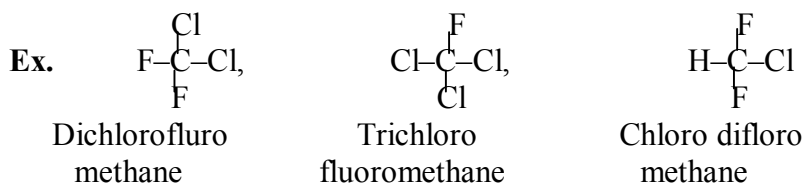
#### Uses:-

- 1) Used in medicine as heating agent & antiseptic, treating wounds and sores. It has this property due to liberation of free iodine.
- 2) As a disinfectant.

#### Hazards:-

It has strong smell. It causes difficulty in breathing, dizziness, nausea, depression of C.N.S.

### E) Freons:-



#### Uses:

- 1) They are used as propellants in aerosol food products, cosmetics & medical industry.
- 2) Freons containing bromine are used as fire extinguishers.
- 3) Also they are used as insecticides, solvent for cleaning clothes and metallic surfaces, as foaming agents for preparing foamed plastic and production of certain fluoro carbons.
- 4) Used as refrigerants and air conditioning being non-corrosive.

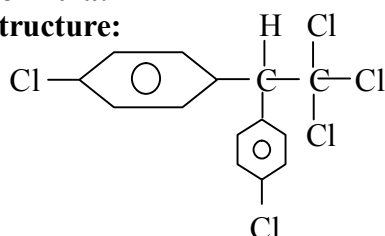
#### Hazards:

They cause ozone depletion and have low toxicity and low biological activity.

### F) D.D.T. or p.p.- Dichloro diphenyl trichloro ethane.

#### Formula:

#### Structure:



#### Uses:

- 1) As insecticides against mosquito causing malaria and typhoid.
- 2) Used to kill various insects such as housefly, body lice.

#### Hazards:-

It is non-biodegradable i.e. not destroyed by environmental destructive forces. It gets deposited and stored in fatty tissues. It produces highly dangerous ecological effects by remaining in soil, plants for long time. So it is being replaced by better and safer insecticides.