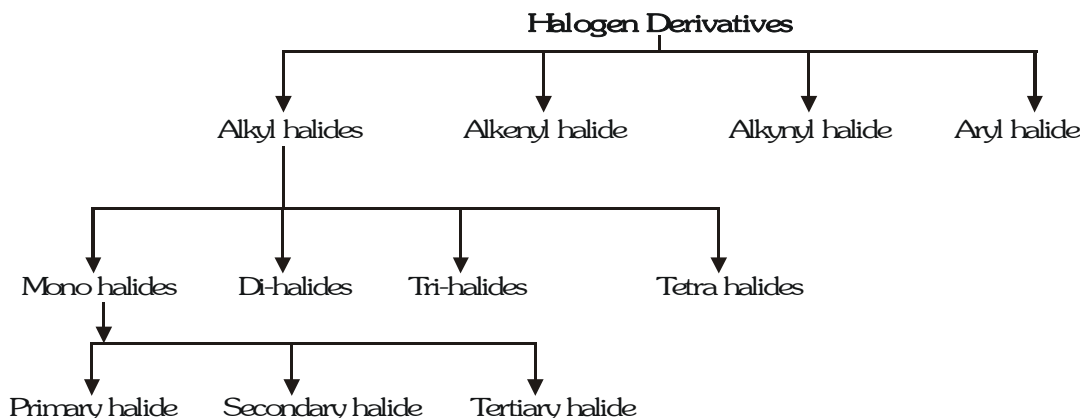


ALKYL HALIDE AND ARYL HALIDE

Compounds derived from hydrocarbons by replacement of one or more H-atoms by corresponding no. of halogen atoms are known as halogen derivatives.

Classification :

On the basis of nature of hydrocarbon from which they are obtained, hydrocarbon derivatives can be classified as :



(a) Alkyl halides : Halogen derivative of alkanes.

(b) Alkenyl halides : Halogen derivative of alkenes.

(c) Alkynyl halides : Halogen derivative of alkynes

(d) Aryl halides : Halogen derivative of arenes (aromatic)

◆ **Alkyl halides** : They are further classified on the basis of halogen atoms introduced in the molecule. e.g.

(i) **Mono halides**: These involves replacement of one H-atom by halogen atom.

General formula $C_nH_{2n+1}X$

Example : CH_3Cl Methyl chloride (Chloro methane)

CH_3CH_2Br Ethyl bromide (Bromo ethane)

(ii) **Dihalides** : Replacement of two H-atom by halogen atoms.

General formula $C_nH_{2n}X_2$

Example : CH_2X_2 Methylene dihalide

$\begin{array}{c} CH_2X \\ | \\ CH_2X \end{array}$ Ethylene dihalide or Vicinal dihalide

$\begin{array}{c} CH_3 \\ | \\ CHX_2 \end{array}$ Ethylidene dihalide or geminal dihalide

(iii) **Trihalides** : Replacement of three H-atoms by halogen atoms. General formula - $C_nH_{2n-1}X_3$.

Example : CHX_3 Trihalo methane or haloform

(iv) **Tetra halide and Perhalo compounds** : Replacement of 4 H-atoms by halogen atoms

(in $CH_4 \longrightarrow CCl_4$) \longrightarrow Tetrahalides.

When all the H-atoms from an alkane are replaced by halogen atoms, then the compounds are called as perhalo compound - General formula $C_nH_{2n-2}X_4$ (tetra halide).

$CH_4 \longrightarrow CX_4$ (Per halo methane)

$C_2H_6 \longrightarrow C_2X_6$ (Per halo ethane)

❑ **MONO HALIDES** : These are classified on the basis of nature of C-atom carrying the halogen atom .

(A) **Primary halide or 1⁰ alkyl halides** : Halogen atom attached with a primary or 1⁰ C-atom.

Example : CH_3-X Halo methane or methylhalide
 $\text{CH}_3-\text{CH}_2-\text{X}$ Halo ethane or ethyl halide
 $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{X}$ 1-Halo propane or n-propyl halide

(B) **Secondary or 2⁰ alkyl halides** : Halogen atom linked with 2⁰ C-atom.

Example : $\begin{array}{c} \text{CH}_3-\text{CH}-\text{CH}_3 \\ | \\ \text{X} \end{array}$ 2-halo propane
or
Iso propyl halide

$\begin{array}{c} \text{CH}_3-\text{CH}-\text{CH}_2-\text{CH}_3 \\ | \\ \text{X} \end{array}$ 2-halo butane
or
Sec. butyl halide

(C) **Tertiary halide or 3⁰ alkyl halide** : halogen atom linked with 3⁰ C-atom.

Example : $\begin{array}{c} \text{R} \\ | \\ \text{R}-\text{C}-\text{X} \\ | \\ \text{R} \end{array}$ (tert.alkyl halide)

❑ **Isomerism** : Alkyl halides show position and chain isomerism -

Example : $\text{C}_3\text{H}_7\text{Cl} \longrightarrow \begin{array}{c} \text{CH}_3\text{CH}_2\text{CH}_2\text{Cl} \\ \text{CH}_3\text{CHCH}_3 \\ | \\ \text{Cl} \end{array} \left. \vphantom{\begin{array}{c} \text{CH}_3\text{CH}_2\text{CH}_2\text{Cl} \\ \text{CH}_3\text{CHCH}_3 \\ | \\ \text{Cl} \end{array}} \right\} \text{Position isomers}$

Example : $\text{C}_4\text{H}_9\text{Cl}$ (a) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$ 1 - chloro butane

(b) $\begin{array}{c} \text{CH}_3 \\ \diagup \\ \text{CH}-\text{CH}_2\text{Cl} \\ \diagdown \\ \text{CH}_3 \end{array}$ 1-chloro-2-methyl propane

(c) $\begin{array}{c} \text{CH}_3-\text{CH}_2-\text{CH}-\text{CH}_3 \\ | \\ \text{Cl} \end{array}$ 2 - chloro butane

(d) $\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_3-\text{C}-\text{Cl} \\ | \\ \text{CH}_3 \end{array}$ 2-chloro-2-methyl propane

a, b \longrightarrow Chain isomers

a, c \longrightarrow Position isomers

a, d \longrightarrow Chain and position isomers

b, c \longrightarrow Chain and position isomers

b, d \longrightarrow Position isomers

c, d \longrightarrow Chain isomers

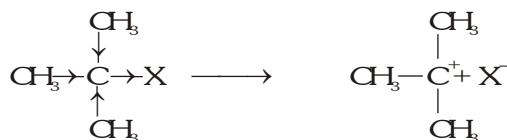
Reactivity order : The order of reactivity of alkyl halides is - $\text{RI} > \text{RBr} > \text{RCI} > \text{RF}$

Bond energy values : C-I (57. 4), C-Br (65.9), C-Cl (78.5) and C-F (105.4) K.cal/mole

C-I bond is most reactive because lower energy is required to break the bond. On the basis of nature of alkyl

group the reactivity order of alkyl halide is - tert > Sec. > Primary

Since alkyl groups, are electron repelling or electron releasing, larger no. of alkyl groups on C-atom of C-X greater is the electron density on C-atom hence ease in release of X atom as X^- ion (+ I effect of alkyl group)



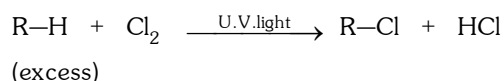
Alkyl halides are generally more reactive than the corresponding alkanes due to the presence of polar covalent

($\overset{\delta+}{\text{C}}-\overset{\delta-}{\text{X}}$) bond. So alkyl halides (R-X) undergo nucleophilic substitution reaction.

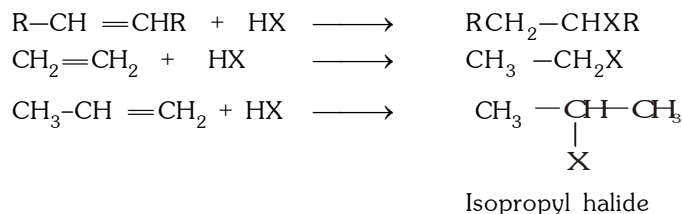
The centre for attacking Nu[⊖] is $\overset{+}{\text{C}}$ atom

□ **General Method of Preparation of Monohalides :**

1. **By direct halogenation of alkanes :**

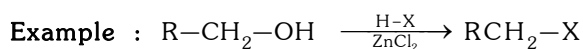


2. **By the addition of H-X on alkenes :**

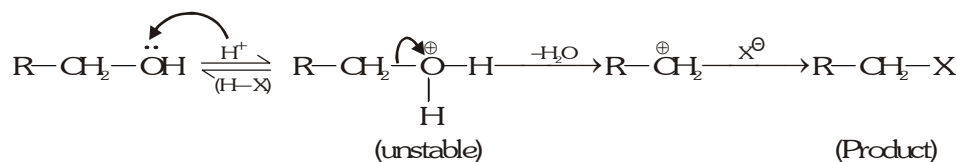


3. **By Alcohols :**

(a) **By the action of hydrogen halides :**

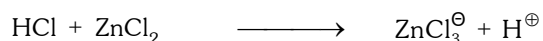


Mechanism :



In this reaction intermediate carbocation is formed so rearrangement (H⁺ shifting or CH₃⁺ shifting) can take place.

ZnCl₂ act as dehydrating agent and absorbs H₂O from the reaction so good yield of halide is obtained. Also it generates H⁺ from HCl.

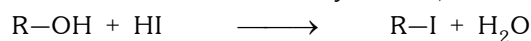


Reactivity order for alcohol :

Reactivity \propto stability of intermediate carbocation, so reactivity order : **Tert. alc. > Sec. alc. > Pri. alc.**

Reactivity order of H-X is : **HI > HBr > HCl**

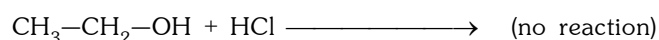
HI is maximum reactive so it reacts readily with 1, 2 and 3 alcohols.



HCl and also 1 alcohol are less reactive so ZnCl₂ or some amount of H₂SO₄ is needed to increase the reactivity.



At normal condition :

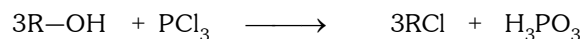


Note : HCl + ZnCl₂ is called as **lucas reagent**, alcohol gives turbidity with lucas reagent.

Reactivity towards lucas reagent (difference in 1, 2 and 3 alcohol).

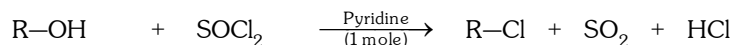
	1 alcohol	2 alcohol	3 alcohol
Time to give turbidity	in 30 min.	in 5 min.	in 1 min.

(b) By the action of phosphorus halides (S_N1 mechanism) :



PBr_3 and PI_3 are less stable, thus for bromides and Iodides, (P + Br_2) Or (P + I_2) mixture is used.

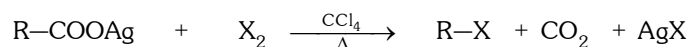
(c) By reaction with thionyl chloride - (Darzen's procedure) (S_Ni and S_N2 mechanism) :



One mole One mole

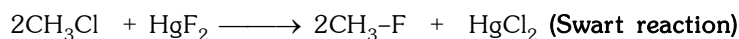
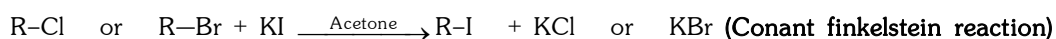
Because of less stability of $SOBr_2$ and SOI_2 , $R-Br$ and RI does not obtained by this method.

4. Borodine - Hunsdicker's reaction :



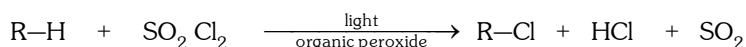
Silver salt of (Cl₂ or Br₂)
a fatty acid

5. By halide exchange :



$R-I$ and $R-F$ can be prepared by this method only.

6. By reaction of alkanes with sulphuryl chloride (SO_2Cl_2) :



□ Physical Properties :

(a) The lower members CH_3F , CH_3Cl , CH_3Br , C_2H_5Cl and C_2H_5F are gases at room temp.
 CH_3I and members upto C_{18} are colourless sweet smelling liquids.

(b) Higher B.P. than parent alkanes.

Decreasing order of B.P. is : $R-I > R-Br > R-Cl > R-F$

among isomeric $R-X$ decreasing order of B.P. is : **Primary** > **Secondary** > **tertiary**

(c) $R-F$ and $R-Cl \longrightarrow$ lighter than water

$R-Br$ and $R-I \longrightarrow$ heavier than water

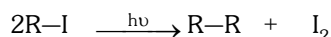
Decreasing order of density is : $R-I > R-Br > R-Cl > R-F$

(d) $R-X$ are polar co-valent compounds but insoluble in water because they can not form H-bonds. They dissolve in organic solvents.

(e) $R-X$ burns with a green flame due to interaction of X with Cu wire. (Beilstein test)

(f) The stability order is : $R-F > R-Cl > R-Br > R-I$

$R-I$ is least stable and darken in light due to photodecomposition.



□ Chemical Properties :

A. Nucleophilic substitution reaction (S_N) : Due to electronegativity difference the $\begin{array}{c} | \\ -C- \\ | \end{array} X$ bond is highly

polarised bond. $\left(\begin{array}{c} | \\ -C^{\delta+}-X^{\delta-} \\ | \end{array} \right)$

Thus the C-atom of the $\overset{\delta+}{C}-\overset{\delta-}{X}$ bond becomes centre to attack by a nucleophile (Nu^\ominus).

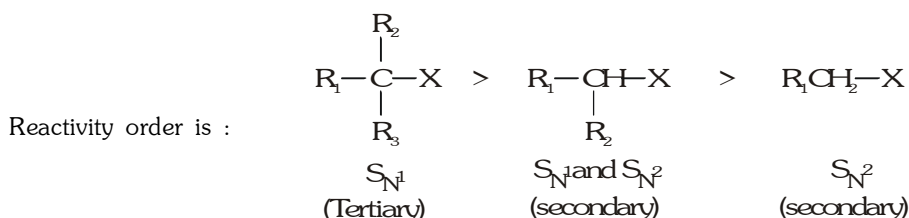
X^\ominus ion from R-X molecule is substituted by a Nu^\ominus . i.e. S_N reaction are the most common reactions in R-X.

$$R-X + Nu^\ominus \longrightarrow R-Nu + X^\ominus$$

These may be takes place by two ways -

(a) S_{N1} mechanism

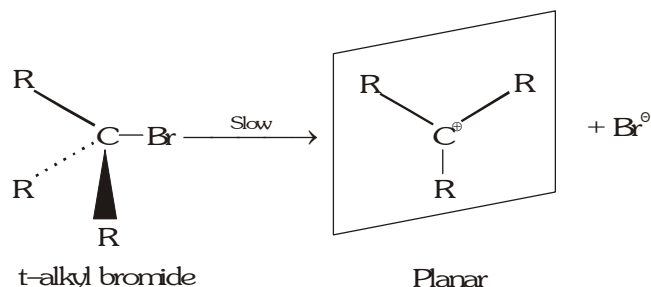
(b) S_{N2} mechanism



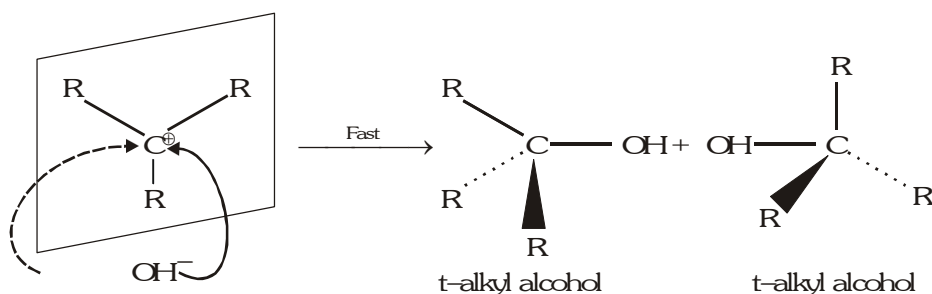
□ Mechanism of S_{N1} and S_{N2} :

◆ **S_{N1} Mechanism** : S_{N1} stands for uni molecular nucleophilic substitution. The mechanism involves two steps. Consider the hydrolysis of tert. butyl bromide with aqueous NaOH.

Step 1: The alkyl halide ionises to give a planar carbonium ion. The carbonium ion is planar because the central positively charged carbon is sp^2 hybridized.



Step-2 : The nucleophile can attack the planar carbonium ion from either side to give the product.



(i) Ionisation is the rate determining step because it is the slow step. In other words, the rate at which alcohol is formed should depend upon the concentration of tertiary alkyl halide alone.

$$\therefore \text{Rate} = K[R_3C-Br]$$

It is obvious that the reaction follows first order kinetics, therefore reaction is called S_{N1} .

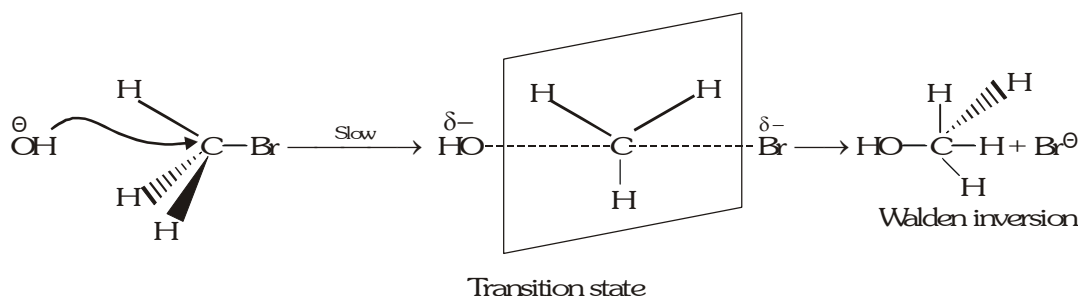
(ii) The reactivity order for S_{N1} reaction \propto stability of carbocations formed by halides.

\therefore reactivity order of halides (S_{N1}) varies as follows :

Benzyl halide > Allylhalide > 3 halide > 2 halide > 1 halide > methyl halide.

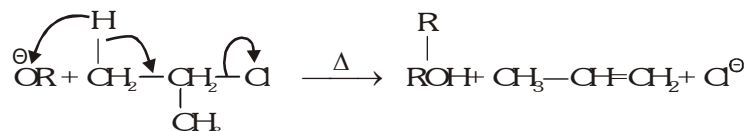
(iii) Remember that in case alkyl halide is optically active, S_{N1} reactions lead to racemisation.

- ◆ **S_N2 mechanism** : S_N2 stands for bimolecular nucleophilic substitution. In this type of nucleophilic substitution reaction, there occurs bond making and bond breaking simultaneously.



- Reactivities of alkyl halides in S_N2 substitution is governed by steric factors. The bulkier the group, that less reactive it will be.
- Reactivity order of alkyl halide varies as follows : $\text{CH}_3\text{X} > 1 \text{ halide} > 2 \text{ halide} > 3 \text{ halide}$
- The order of reactivity among 1 alkyl halides is : $\text{CH}_3\text{X} > \text{C}_2\text{H}_5\text{X} > \text{C}_3\text{H}_7\text{X}$ etc.
Remember that in case alkyl halide is optically active, S_N2 reactions lead to Walden inversion.
- Thus in short 3 alkyl halides react by S_N1 , 1 by S_N2 and 2 by either or both of them S_N1 and S_N2 depend upon the nature of the alkyl halide and the reagent.
- For a given alkyl group the order of reactivity is - (for S_N1 and S_N2 both) : $\text{RI} > \text{RBr} > \text{RCl} > \text{RF}$
- In addition to substitution reaction alkyl halide also undergo elimination reactions to form alkene with the removal of a molecule of hydrogen halide (dehydrohalogenation). In dehydrohalogenation, hydrogen and halogen atoms are eliminated from two adjacent carbon atoms, the reaction also known as β -elimination may proceed by E_1 & E_2 mechanism (analogous to S_N1 and S_N2 mechanism).
The order of elimination reaction is : $3 \text{ halides} > 2 \text{ halides} > 1 \text{ halides}$
- In general 3 halides tend to react by elimination; 1 halides by substitution and 2 halides by either or both of the reactions.

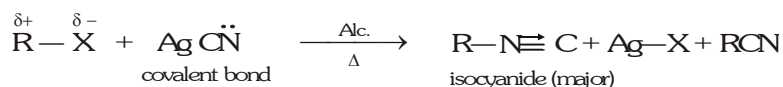
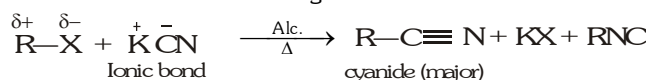
B. Elimination Reactions (ER) : Alkyl halides also undergo ER in the presence of base as Nu^\ominus (Loss of H-X and formation of $=$ bond)



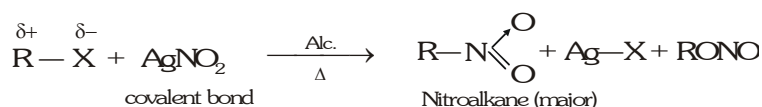
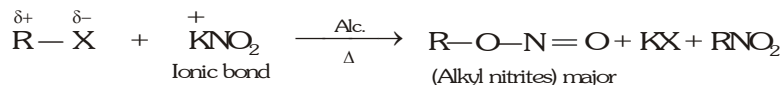
1. Nucleophilic substitution reaction (S_N) :

	Replacement of	Product
$\text{R-X} \rightarrow$	(a) $\xrightarrow[\text{X by -OH}]{\text{HOH (Boil)}}$	$\text{R-OH (alcohol)} + \text{HX}$
	(b) $\xrightarrow[\text{X by -OH}]{\text{KOH aq. } \Delta}$	$\text{R-OH (alcohol)} + \text{KX}$
	(c) $\xrightarrow[\text{X by -OH}]{\text{moist Ag}_2\text{O}}$	$\text{R-OH (alcohol)} + \text{AgX}$
	(d) $\xrightarrow[\text{X by -SH (Mercapto Gp.)}]{\text{KSH alc. } \Delta}$	$\text{R-SH} + \text{KX}$ Alkane thiol (Mercaptane)
	(e) $\xrightarrow[\text{X by SR}]{\text{NaSR}}$	$\text{RSR}' + \text{NaX}$ Thioether
	(f) $\xrightarrow[\text{X by (RCOO)}]{\text{R' COOAg } \Delta}$	$\text{R' COOR} + \text{AgX}$ (Alkyl alkanoate) ester

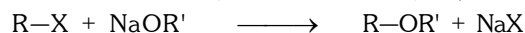
(g) Reaction with KCN and AgCN :



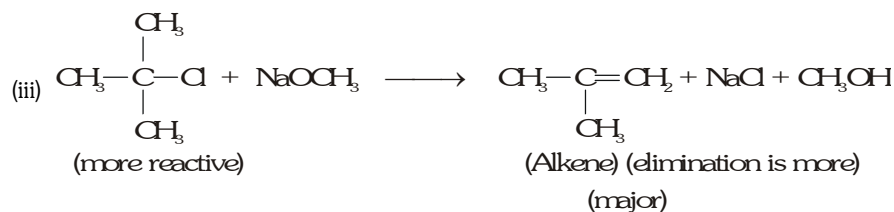
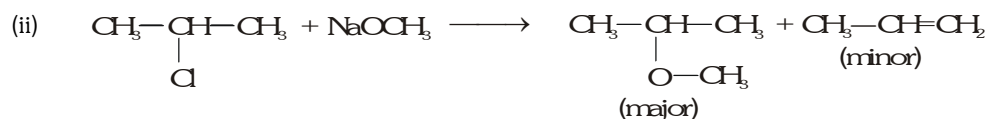
(h) Reaction with KNO₂ and AgNO₂



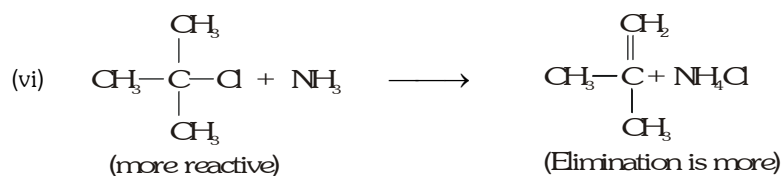
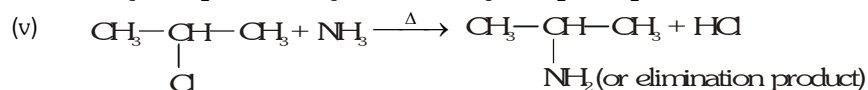
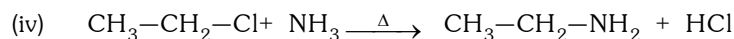
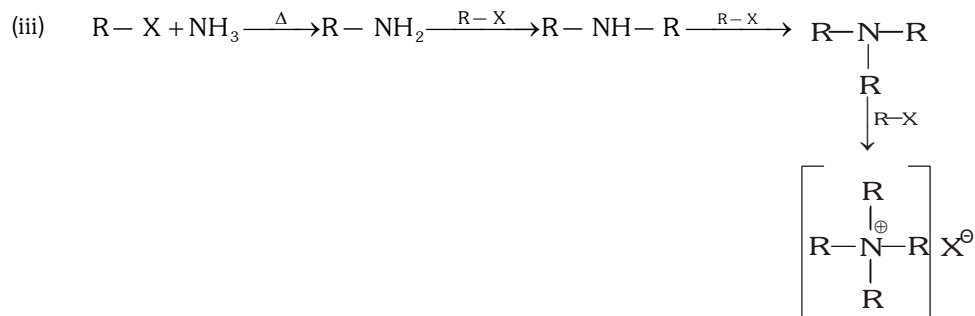
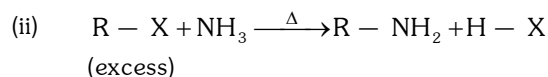
(i) Reaction with NaOR' (Sodium alkoxide) : **(williamson synthesis reaction)**



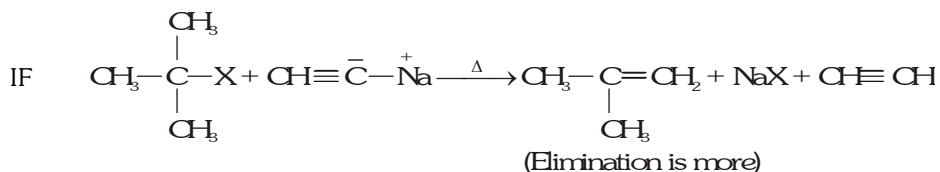
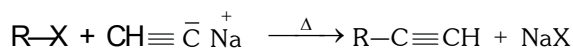
Example : (i) $\text{CH}_3-\text{CH}_2-\text{Cl} + \text{NaOCH}_3 \longrightarrow \text{CH}_3-\text{CH}_2-\text{O}-\text{CH}_3$ (major)



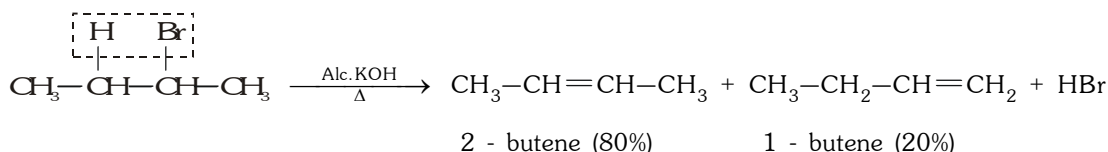
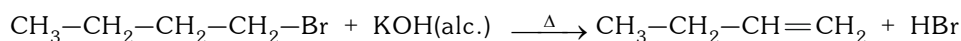
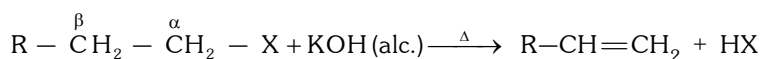
(j) Reaction with NH₃ :



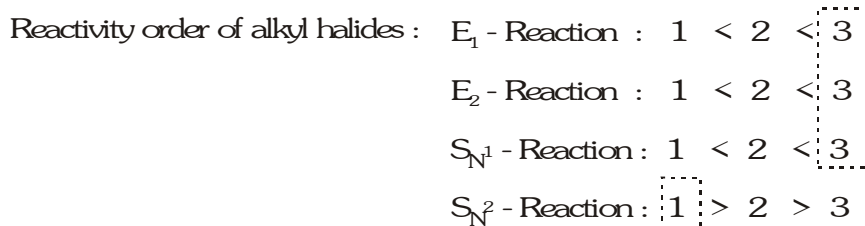
(k) Reaction with $\text{CH}\equiv\text{C}^-\text{Na}^+$:



2. **Elimination Reaction :** (Dehydrohalogenation) Alkyl halides undergo β - elimination on treatment with KOH (alc.)



◆ **Competition between substitution and elimination reactions :**



Alkyl halides	$\text{S}_{\text{N}}2/\text{E}_2$	$\text{S}_{\text{N}}1/\text{E}_1$
1 Alkyl halides	Mainly give substitution unless sterically hindered alkyl halide or sterically hindered base in which case elimination is favoured	Can not undergo $\text{S}_{\text{N}}1/\text{E}_1$
2 Alkyl halides	Both substitution and elimination, stronger base/ bulkier base or high temp. greater percentage of elimination.	Both substitution and elimination high temp. greater of percentage of elimination
3 Alkyl halides	Mainly elimination	Both substitution and elimination, high temp greater percentage of elimination.

(i) $\text{S}_{\text{N}}2/\text{E}_2$ is favoured by high conc. of good nucleophile or strong base. (CH_3O^- , HO^-)

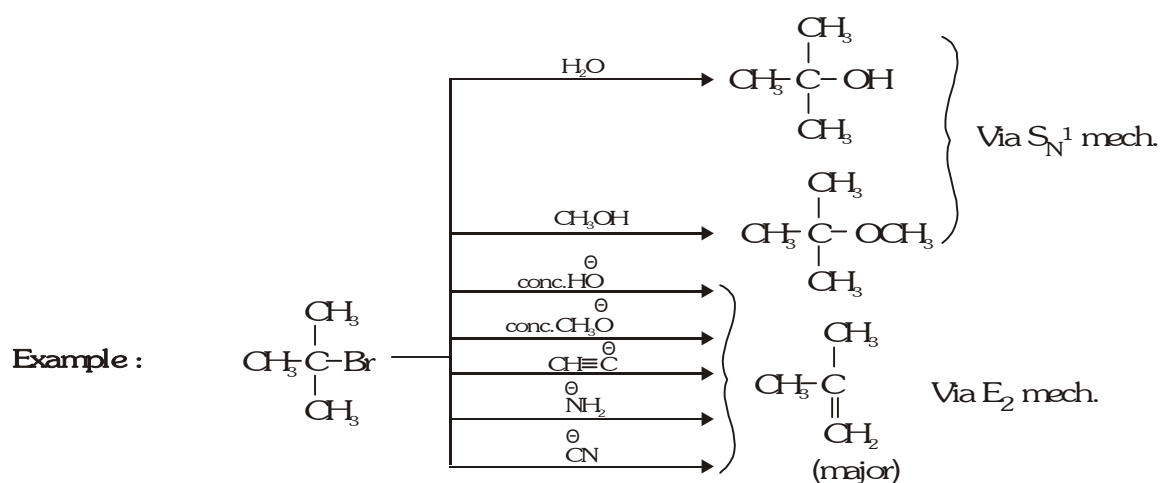
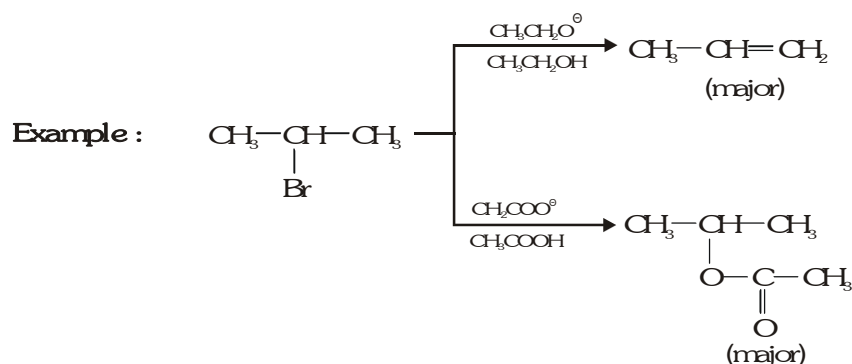
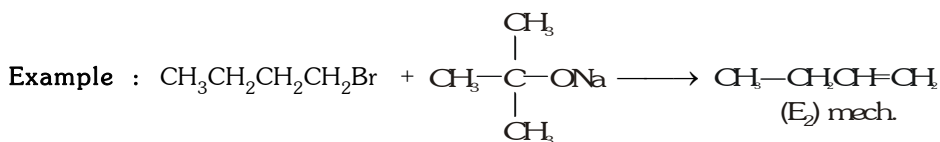
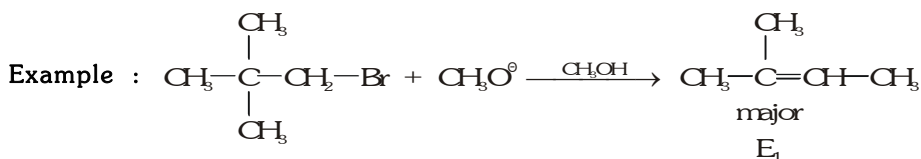
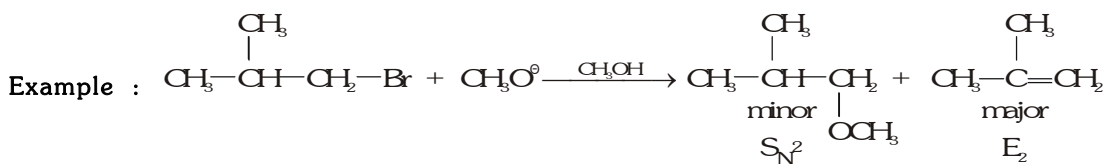
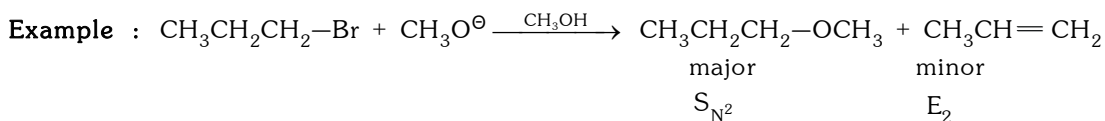
Rate of Reaction \propto (Substrate) (Reagent)

(ii) $\text{S}_{\text{N}}1/\text{E}_1$ is favoured by low conc. of poor nucleophile or weak base (CH_3OH , H_2O)

(iii) If an alkyl halide, undergoes $\text{S}_{\text{N}}2/\text{S}_{\text{N}}1$ - Reaction then $\text{S}_{\text{N}}2$ will be favoured by high conc. of good nucleophile (negatively charged) in presence of polar aprotic solvent . where as $\text{S}_{\text{N}}1$ - reaction is favoured by low conc. of poor nucleophile (neutral) in presence of polar protic solvent.

Polar protic solvent : H_2O , CH_3OH , HCOOH .

Polar aprotic solvent : DMSO , CH_3CN , $\text{C}_2\text{H}_5\text{-O-C}_2\text{H}_5$



Saytzeff rule : According to this rule "The dehydrohalogenation of an alkyl halide results preferentially in the production of more alkylated alkene i.e. more stable alkene.

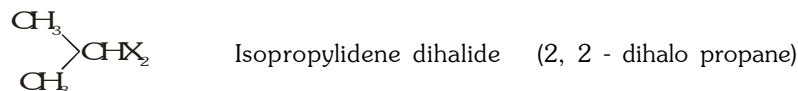
General formula $C_nH_{2n}X_2$. Two H - atom of alkanes, replaced by two halogen atoms to form dihalides.

Dihalides are classified as :

(a) **Gem dihalide** : The term Gem is derived from geminal means - same position.

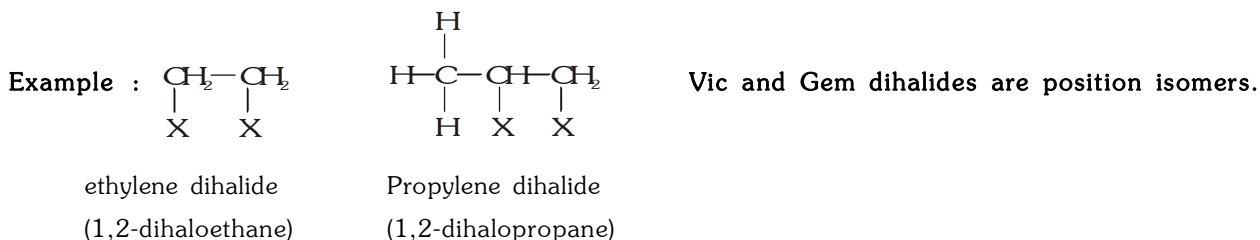
Two similar halogen atoms are attached to same C - atom

Example : CH_3CHX_2 ethylidene dihalide (1, 1 - dihalo ethane)

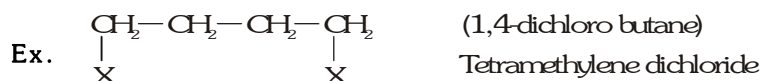


(b) **Vic dihalides** : Vic term from - Vicinal means adjacent C - atoms

Two halogen atoms are attached on adjacent carbon atom.



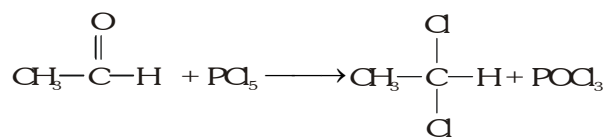
(c) **α , ω dihalides** : Halogen atoms are attached with terminal C - atom. They are separated by 3 or more C - atom . They are also known as polymethylene halides.



General Method of Preparation :

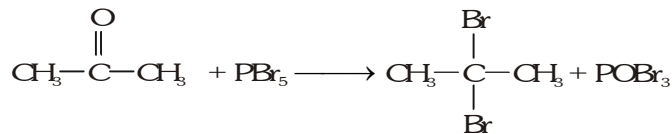
(a) **Gem dihalides** :

(i) By the reaction of PCl_5 on carbonyl compound.



Acetaldehyde

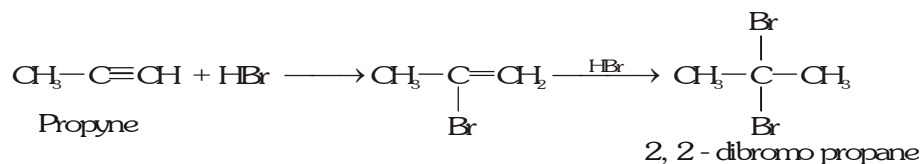
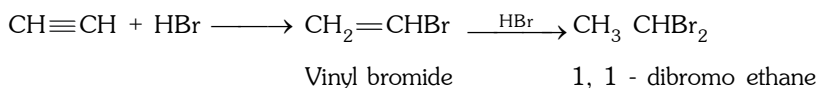
Ethylidene chloride



Acetone

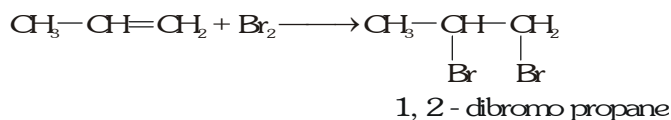
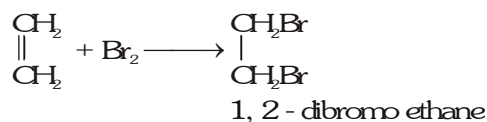
2, 2 - dibromo propane

(ii) By addition of halogen acids on alkynes :

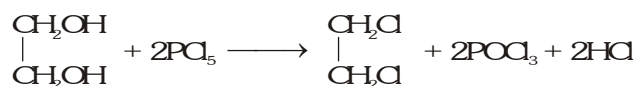


(b) Vic-dihalides :

(i) By the addition of halogens to alkenes :

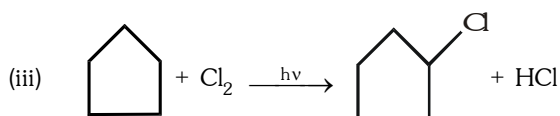
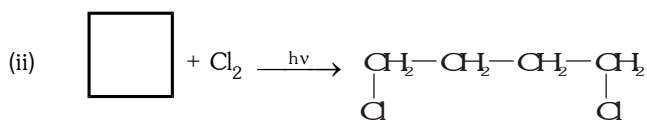
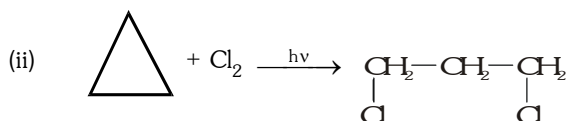


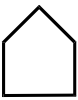
(ii) By the action of PCl_5 on glycols :



(c) $\alpha - \omega$ dihalides :

(i) $\text{CH}_2=\text{CH}-\text{CH}_2\text{Br} + \text{HBr} \longrightarrow \text{Br}-\text{CH}_2-\text{CH}_2-\text{CH}_2\text{Br}$
 1, 3 - dibromo propane



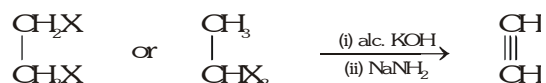
Note : Here  has less tendency to open the ring.

Physical Properties :

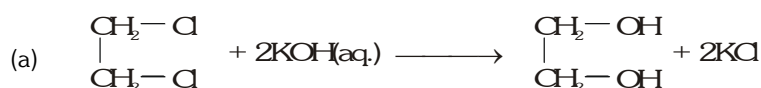
- (i) Lower members are colourless, oily liquids with sweet smell. Higher members are solid.
- (ii) The reactivity of gemdihalides is lesser than vicinal or mono halides. [Reason - in presence of one halogen atom (Strong attracting -I effect) the other halogen atom can not be so easily replaced.
- (iii) These are heavier than water.

Chemical Properties :

(i) **Action of $\text{KOH}(\text{alc.})$:** (Dehydrohalogenation)



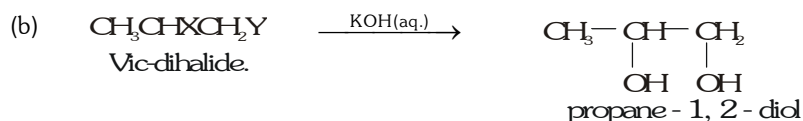
(ii) **Action of $\text{KOH}(\text{aq.})$:** (Hydrolysis) It is a distinction test for gem and vic dihalides.



Glycol

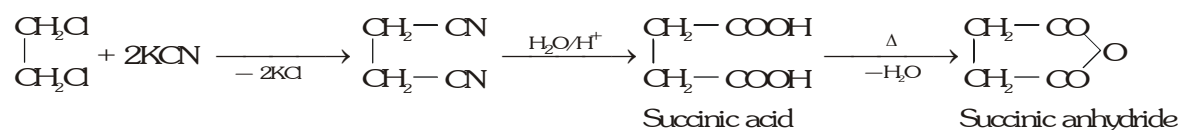
Vic - dihalide.

1, 2 - ethane diol.

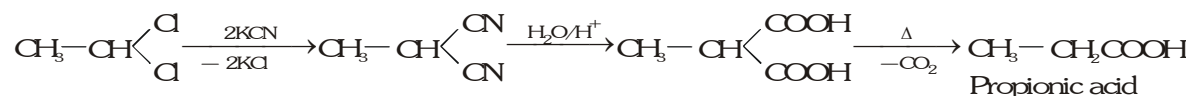


(iii) **Reaction with KCN** : Gem and Vic dihalide gives different products

Vic. :



Gem. :

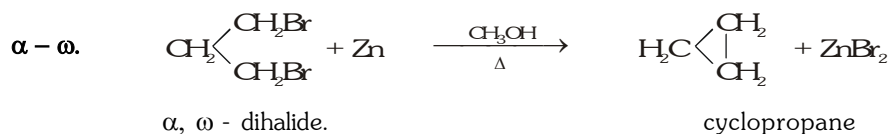
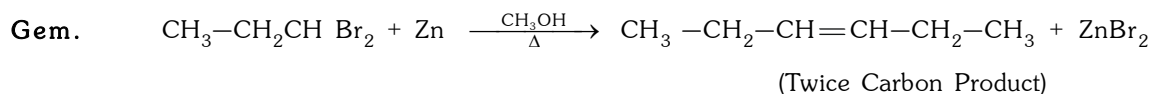
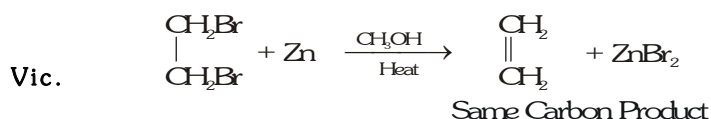


(i) - CN group on acid hydrolysis gives - COOH

(ii) Two - COOH group on one C - atom on heating always lose CO₂ to form monocarboxylic acid.

(iii) Two - COOH group on vic. C - atom on heating lose H₂O to form anhydride.

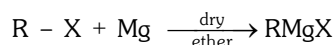
(iv) **Dehalogenation** :



GRIGNARD REAGENT

□ General Method of Preparation :

Grignard reagents are prepared in the laboratory by the action of alkyl halides on magnesium metal in the presence of dry ether.




(Grignard reagent)

(Alkyl magnesium halide)

The ease of formation of Grignard reagent is in the order $\text{RI} > \text{RBr} > \text{RCI}$

Ether is used to dissolved the Grignard reagent by coordination.

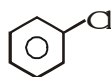
❑ Chemical Reactions :

RMgX	(i) O_2 (ii) H_3O^+	$\text{R}-\text{OH}$	1 Alcohol
	$\text{H}_2\text{CO}/\text{H}_3\text{O}^+$	RCH_2-OH	1 Alcohol
	 $/\text{H}_3\text{O}^+$	$\text{R}-\text{CH}_2-\text{CH}_2-\text{OH}$	1 Alcohol
	$\text{RCHO}/\text{H}_3\text{O}^+$	R_2CHOH	1 Alcohol
	$\text{HCOOEt}/\text{H}_3\text{O}^+$	R_2CHOH	2 Alcohol
	$\text{RCOR}/\text{H}_2\text{O}$	$\text{R}_3\text{C}-\text{OH}$	3 Alcohol
	$\text{RCOOEt}/\text{H}_2\text{O}$	$\text{R}_3\text{C}-\text{OH}$	3 Alcohol
	HCOOEt	RCHO	aldehyde
	$\text{RCN}/\text{H}_2\text{O}$	RCOR	Ketone
	RCOOEt	RCOR	Ketone
	$\text{CO}_2 + \text{H}_2\text{O}$	RCOOH	Acids
	HOH or ROH or NH_3 or $\text{Ph}-\text{OH}$ or $\text{R}-\text{NH}_2$ or $\text{RNH}-\text{R}$ or $\text{CH}\equiv\text{CH}$ or $\text{Ph}-\text{NH}_2$	$\text{R}-\text{H}$	Alkane
	$\text{R}-\text{X}$	$\text{R}-\text{R}$	Alkane
	R_3N	No reaction	
	$\text{ClCH}_2-\text{CH}=\text{CH}_2$	$\text{R}-\text{CH}_2-\text{CH}=\text{CH}_2$	Alkene
	$\text{Cl}-\text{NH}_2$	$\text{R}-\text{NH}_2$	1 Amine
	$\text{Cl}-\text{CN}$	$\text{R}-\text{CN}$	Cyanides
	X_2	$\text{R}-\text{X}$	Alkyl halide
	ClCOOEt	RCOOEt	Ester

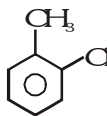
ARYL HALIDE

If halogen atom is directly attached to the benzene ring, then compound is called as Haloarene.

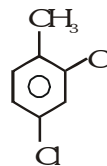
Example :



(Chlorobenzene)



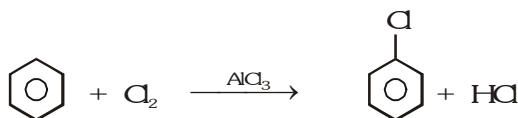
(2-Chlorotoluene)



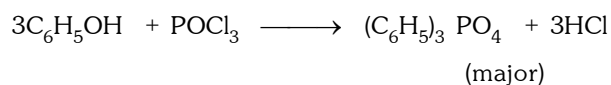
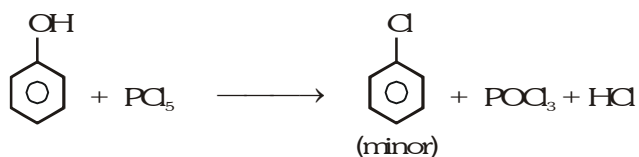
(2,4-Dichlorotoluene)

❑ General Methods of Preparation :

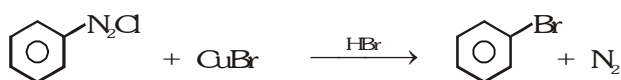
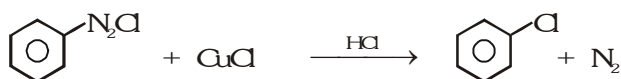
◆ Halogenation of Benzene :



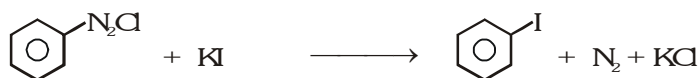
◆ From Phenol :



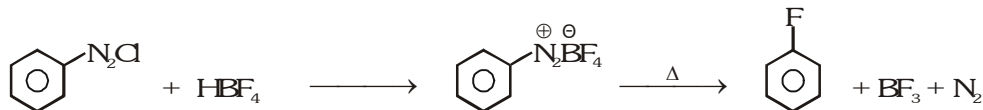
◆ Sandmeyer's reaction :



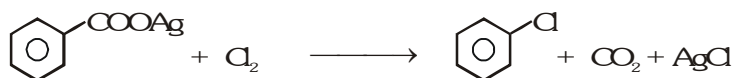
◆ Reaction with KI :



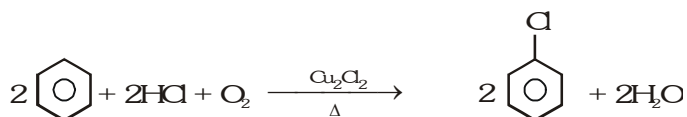
◆ Balz-schiemann's reaction :



◆ Hunsdicker reaction :



◆ Raschig Process :

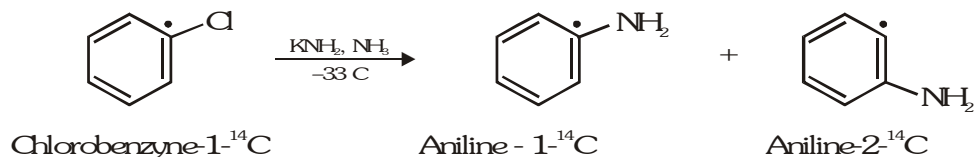


□ Chemical Properties :

- (i) Chlorobenzene is essentially inert to aqueous sodium hydroxide at room temperature.
- (ii) Aryl halide are very less reactive than alkyl halides in nucleophilic substitution reactions.
- (iii) The carbon-halogen bonds of aryl halides are too strong & aryl cations are too high in energy to permit aryl halides to ionize readily $\text{S}_{\text{N}}1$ -type process.
- (iv) The optimal transition state geometry required for $\text{S}_{\text{N}}2$ process cannot be achieved.
- (v) Nucleophilic attack from the side opposite the carbon-halogen bond is blocked by the aromatic ring.

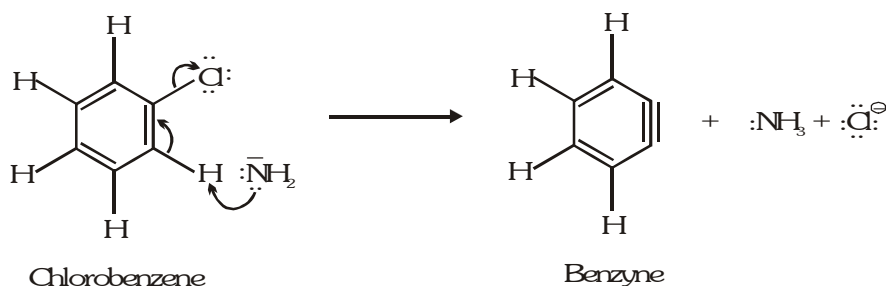
The Elimination-Addition Mechanism of Nucleophilic Aromatic Substitution (Benzyne) :

(i) Very strong base such as sodium or potassium amide react with aryl halide, even those without electron withdrawing substituents to give products corresponding to nucleophilic substitution of halide by the base.

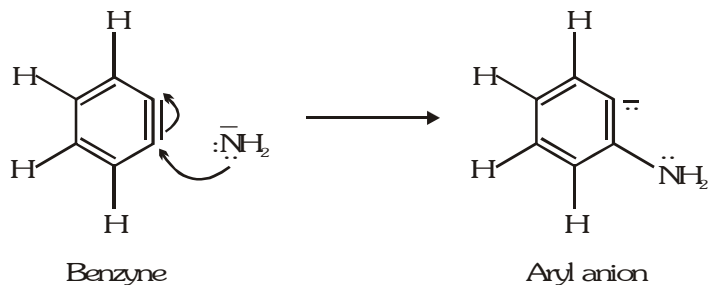


Mechanism

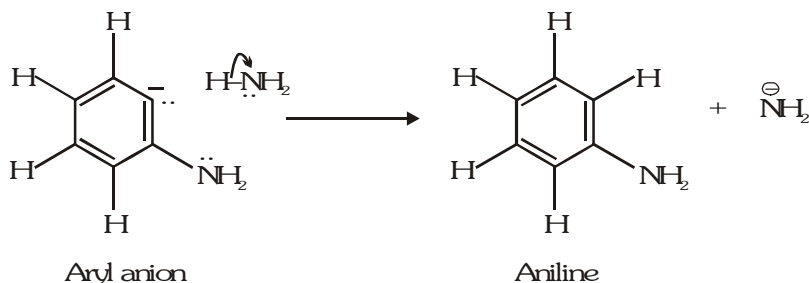
Step-1 : Elimination stage ; Amide ion is a very strong base and brings about the dehydrohalogenation of chlorobenzene by abstracting a proton from the carbon adjacent to the one that bears the leaving group. The product of this step is an unstable intermediate called benzyne.



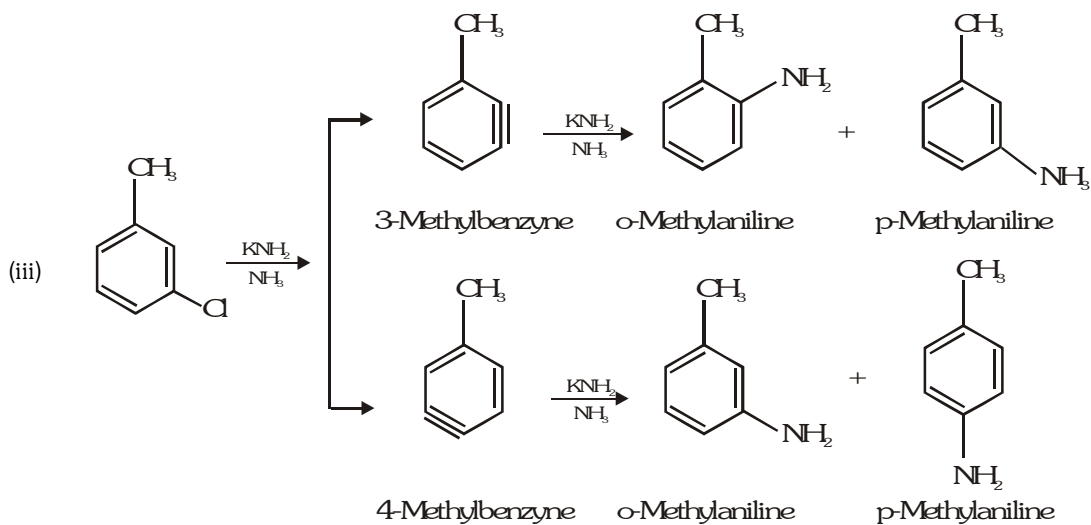
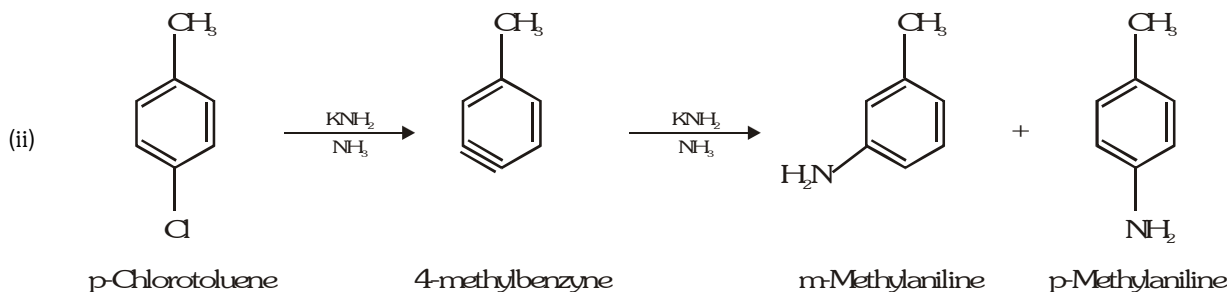
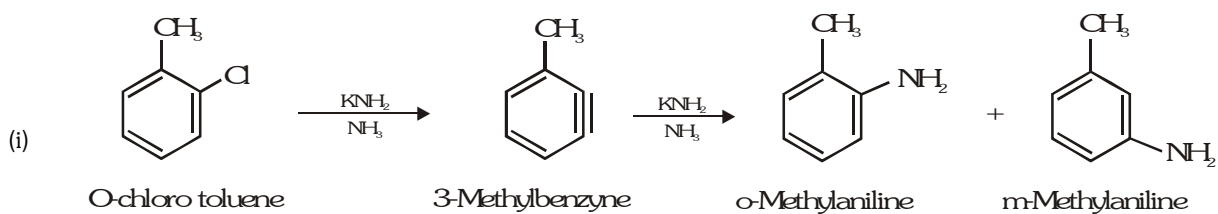
Step-2 : Beginning of addition phase ; Amide ion acts as a nucleophile and adds to one of the carbons of the triple bond. The product of this step is a carbanion.



Step-3 : Completion of addition phase ; The aryl anion abstracts a proton from the ammonia used as the solvent in the reaction.

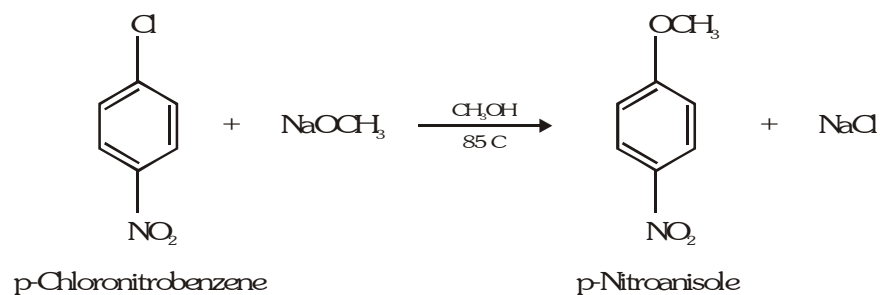


NOTE : The sp^2 orbital in the plane of the ring in benzyne are not properly aligned for good overlap thus π bonding is weaker than alkyne.

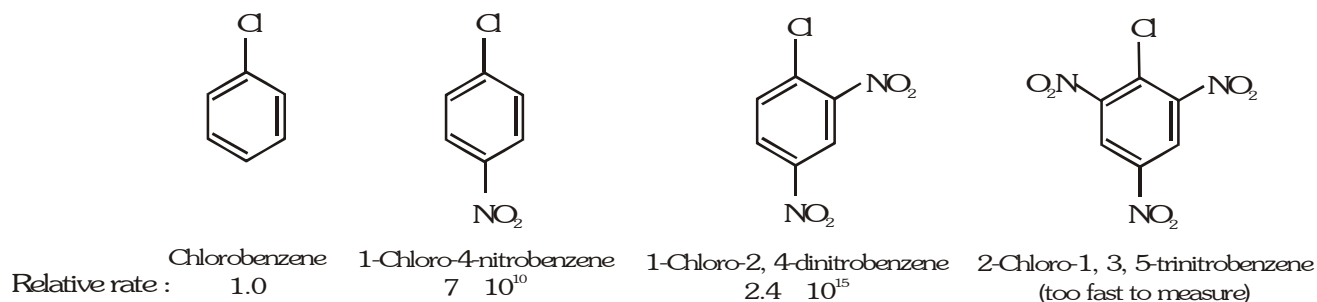


Nucleophilic Aromatic Substitution by the addition Elimination Mechanism :

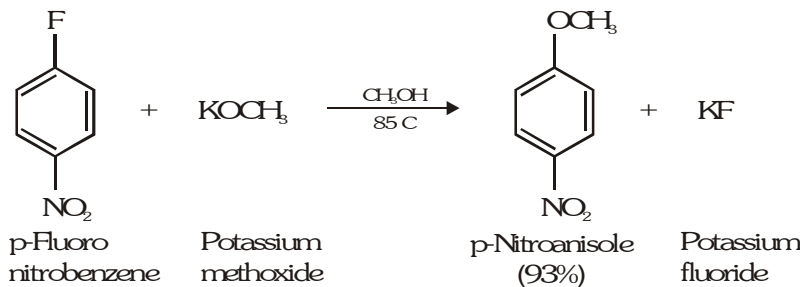
(i) The generally accepted mechanism for nucleophilic aromatic substitution in nitro-substituted aryl halides.



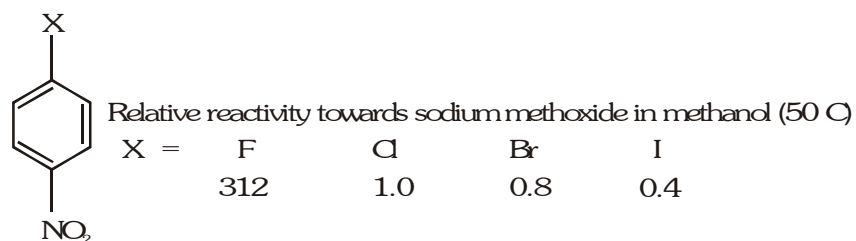
- (ii) An ortho - nitro group exert a comparable rate-enhancing effect, m-chloronitrobenzene while much more reactive than chlorobenzene itself, is thousand of times less reactive than either o-or p-chloronitrobenzene.
- (iii) The effect of o- & p-nitro substituents is cumulative, as the rate data for substitution with methoxide ion in a series of nitro-substituted chlorobenzene derivative demonstrate increasing rate of reaction as :



- (iv) In contrast to nucleophilic substitution in alkyl halides, where alkyl fluorides are exceedingly unreactive, aryl fluorides undergo nucleophilic substitution readily when the ring bears an o-or a p-nitro group.



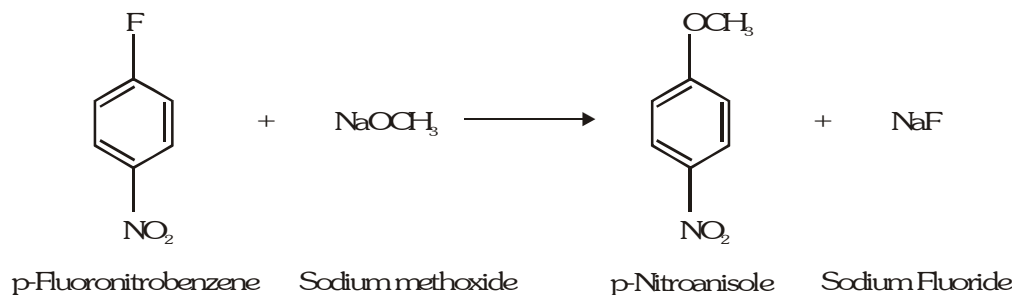
- (v) Indeed, the order of leaving group reactivity in nucleophilic aromatic substitution is the opposite of that seen in aliphatic substitution.
- (vi) Fluoride is the best reactive leaving group in nucleophilic aromatic substitution, iodide the least reactive.



- (vii) Kinetic studies of many of the reactions described in this section have demonstrated that they follow a second-order rate law.

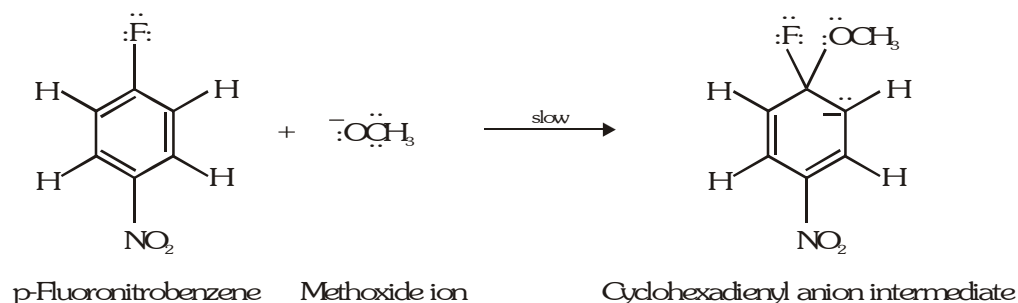
$$\text{Rate} = k[\text{aryl halide}][\text{nucleophile}]$$

- (viii) Second order kinetics is usually interpreted in terms of a bimolecular rate determining step.

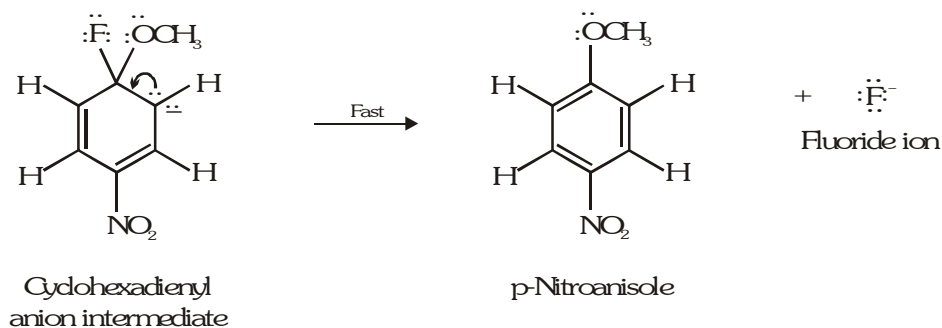


Mechanism :

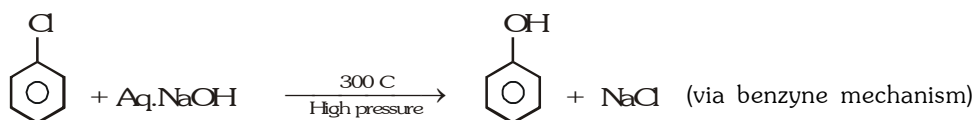
Step -1 - Addition stage. The nucleophile, in this case methoxide ion, adds to the carbon atom that bears the leaving group to give a cyclohexadienyl anion intermediate.



Step -2 - Elimination stage. Loss of halide from the cyclohexadienyl intermediate restores the aromaticity of the ring and gives the product of nucleophilic aromatic substitution.

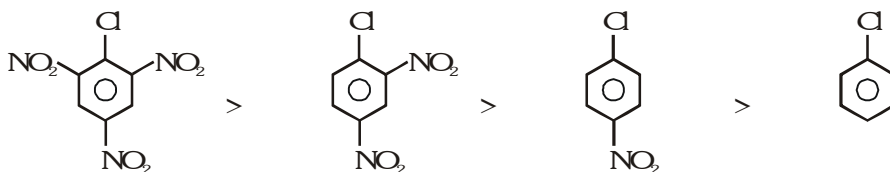


(a) Dow process :

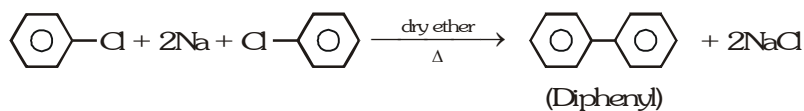


Presence of deactivating group in ortho and para position makes the nucleophilic substitution easier.

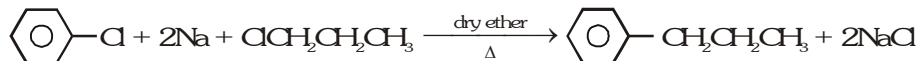
Reactivity Order : (Towards nucleophilic substitution)



◆ Fitting reaction :



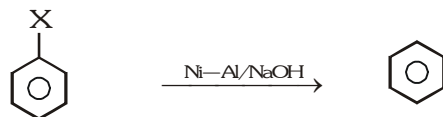
◆ Wurtz fitting reaction :



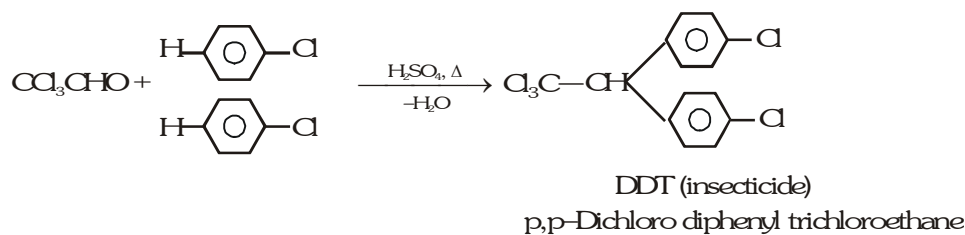
◆ Formation of aryl magnesium halide :



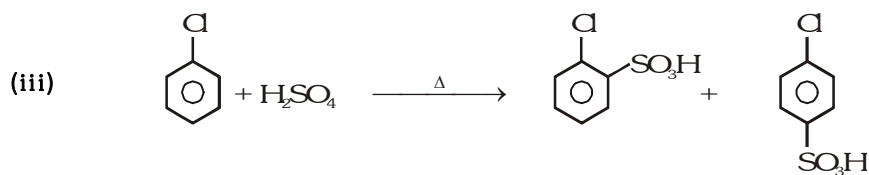
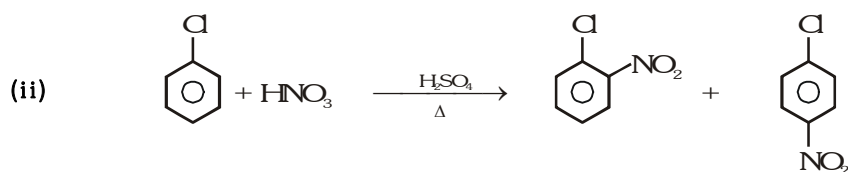
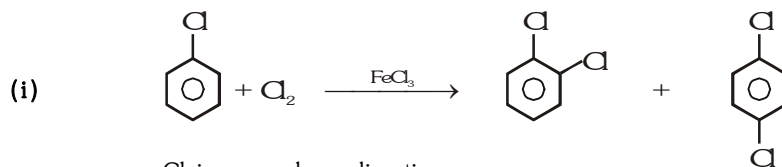
◆ Reduction :



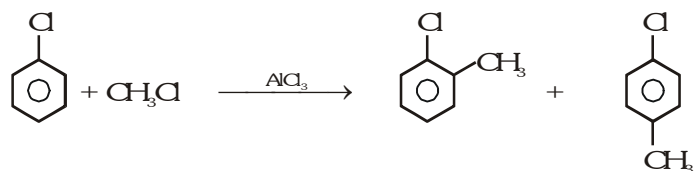
◆ With Chloral :



◆ Electrophilic Substitution Reaction :

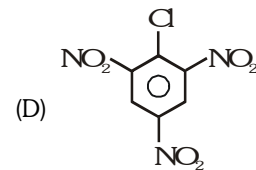
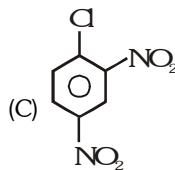
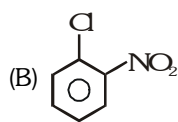
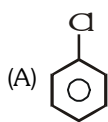


(iv) Friedal Craft Reaction :



SOLVED EXAMPLES

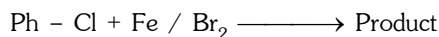
Ex.1 Which of the following undergoes Hydrolysis most easily :



Ans. (D)

Sol. If there is more m-directing group then there will be more nucleophilic substitution reaction.

Ex.2 The product in the following reaction is :



(A) o- bromo-chloro benzene

(B) p- bromo-chloro benzene

(C) (A) and (B) both

(D) 2, 4, 6-tribromo chloro benzene

Ans. (C)

Sol. Since - Cl group is deactivating and o/p directing group so only o- and p- products are formed.

Ex.3 The most reactive towards SN^1 is :

(A) PhCH_2Cl

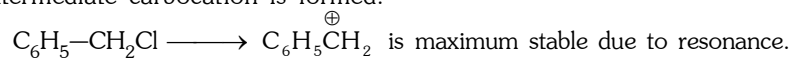
(B) Ph-Cl

(C) $\text{CH}_3\text{CHCl}(\text{CH}_3)$

(D) $\text{p-NO}_2\text{-Ph-CH}_2\text{-Cl}$

Ans. (A)

Sol. $\text{S}_{\text{N}}1$ the intermediate carbocation is formed.



Ex.4 Which of the following is used as insecticide :

(1) D.D.T.

(2) Chloritone

(3) Chloropicrin

(4) (A) and (C) both **Ans. (D)**