ORGANIC CHEMISTRY –II

1. ALKYL HALIDES (R–X)

Synopsis :

- Alkyl halides are esters of alcohols and hydracids.
  $R - OH + Hx \rightarrow R - X + H_2O$

Naming of alkyl halides	IUPAC	Common
$CH_3 - Cl$	Chloromethane	Methyl chloride
$C_2H_5 - Cl$	Chloroethane	Ethyl chloride
$CH_3 - CH_2 - CH_2 - Cl$	1 – Chloro propane	n – propyl chloride
$CH_3 - \underset{\displaystyle CH_3}{\overset{\displaystyle \vert}{CH}} - Cl$	2 – Chloro propane	Isopropyl chloride
$CH_3 - CH_2 - CH_2 - CH_2 - Cl$	1- Chloro butane	n-butyl chloride
$CH_3 - \underset{\displaystyle CH_3}{\overset{\displaystyle \vert}{CH}} - CH_2 - Cl$	1 – chloro – 2- methyl propane	Isobutyl chloride
$CH_3 - CH_2 - \underset{\displaystyle Cl}{\overset{\displaystyle \vert}{CH}} - CH_3$	2 Chloro butane	Sec-butyl chloride
$CH_3 - \underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{\displaystyle \vert}{\overset{\displaystyle \vert}{C}}}} - CH_2 - Cl$	1 – Chloro 2, 2– dimethyl propane	neo pentyl chloride

- Based on the carbon to which halogen is attached, alkyl halides are classified into primary, secondary and tertiary halides.

  Primary alkyl halides : $R - CH_2 - X$ **Secondary alkyl halides :** $R - \underset{\displaystyle R}{\overset{\displaystyle \vert}{CH}} - X$

  $CH_3 - CH_2 - Cl$

  $CH_3 - \underset{\displaystyle Cl}{\overset{\displaystyle \vert}{CH}} - CH_3$

  $CH_3 - \underset{\displaystyle CH_3}{\overset{\displaystyle \vert}{CH}} - CH_2 - Cl$

  Tertiary alkyl halides : $R - \underset{\displaystyle R}{\overset{\displaystyle R}{\overset{\displaystyle \vert}{\overset{\displaystyle \vert}{C}}}} - X \rightarrow$ Eg : $CH_3 - \underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{\displaystyle \vert}{\overset{\displaystyle \vert}{C}}}} - Cl$

- Based on the number of halogens, alkyl halides are of the following types :

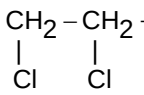
  1. Alkyl mono halides : General molecular formula $\rightarrow C_n H_{2n+1} X$

  $CH_3 - Cl$

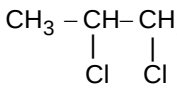
  $C_2H_5 - Cl$

  2. Alkyl dihalides: General molecular formula $\rightarrow C_nH_{2n}X_2$

Eg: $CH_3–CHCl_2$ → gem dihalide (ethylene chloride)


→ vicinal dihalide

$CH_3 – CH_2 – CHCl_2$ → propyledene chloride (geminal dihalide)


→propylene chloride (vicinal)

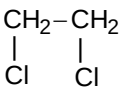
3. Alkyl trihalides : General molecular formula → $C_nH_{2n-1}X_3$

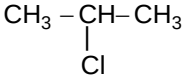
Eg: $CHCl_3$, $CHBr_3$, CHI_3

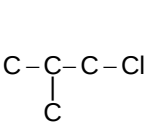
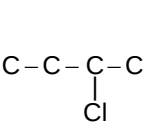
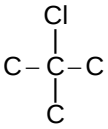
- **Alkyl tetrahalides :** General molecular formula → $C_nH_{2n-2}X_4$

  Eg: CCl_4, CBr_4

- **Isomerism in alkyl halides :** Alkyl halides will exhibit chain and position isomerism .

$C_2H_4Cl_2$ → $CH_3 – CHCl_2$  position isomer

C_3H_7Cl → $CH_3 – CH_2 – CH_2 – Cl$ 

C_4H_9Cl → a) $C – C – C – C – Cl$ b)  c)  d) 

a, b → chain isomerism

a, c → positional isomerism

a, d → both chain and position isomerism

b, c → both chain and position isomerism

b, d → only position isomerism

c, d → chain isomerism

- **Ethyl chloride :**

Methods of preparation :

1) From ethane (C_2H_6): Ethane on controlled chlorination in the presence of sunlight gives ethyl chloride at 400°C.

$$C_2H_6 + Cl_2 \xrightarrow[400°C]{h\upsilon} C_2H_5 - Cl + HCl$$

We cannot prepare ethyl chloride by this method as we get other mixture of halides.

2) From ethylene : Ethylene in the presence of anhydrous Aluminium chloride reacts with HCl to give ethyl chloride.

$$CH_2 = CH_2 + HCl \xrightarrow[\text{anhydrous}]{AlCl_3} CH_3 - CH_2 - Cl$$

3) From ethyl alcohol :

a) Grove's process : Ethyl alcohol on reaction with HCl in the presence of Lewis acid gives ethyl chloride.

$$C_2H_5OH + HCl \xrightarrow{an.ZnCl_2} C_2H_5Cl + H_2O$$

$ZnCl_2$ acts as lewis acid as it forms co-ordinate covalent bond with oxygen. $ZnCl_2$ prevents backward reaction. Other reagents used are dimethylamine, pyridine and conc. sulphuric acid

b) Ethyl alcohol on reaction with PCl_3, PCl_5 and $SOCl_2$ (thionyl chloride) gives ethyl chloride.

$$3C_2H_5OH + PCl_3 \rightarrow 3C_2H_5Cl + H_3PO_3$$

$$C_2H_5OH + PCl_5 \rightarrow C_2H_5Cl + POCl_3 + HCl$$

$$C_2H_5OH + SOCl_2 \xrightarrow[(C_5H_5N)]{\text{pyridine}} C_2H_5Cl + SO_2 \uparrow + HCl$$

Pyridine being basic it absorbs HCl. The SO_2 goes away. Hence, back ward reaction is prevented

- Among PCl_3, PCl_5 and $SOCl_2$. The thionylchloride is effective chlorinating agent as it prevents backward reaction because the gaseous product escapes out and pyridine absorbs HCl.

Physical properties :

- It is a colourless gas with sweet smell.
- It is insoluble in water and readily soluble in organic solvents.
- Ethyl chloride will not give white ppt with $AgNO_3$ solution because it is a covalent compound.
- **Chemical properties :** Alkyl halides will undergo nucleophilic substitution reactions because the –vely charged halide ion can be replaced by a strong base or a strong nucleophile such as OH^-, CN^-, NC^-, NO_2^- , ONO^-, $OC_2H_5^-$, NH_3 etc.
- **Reactivity :** Due to highly polar nature of $\overset{\delta+}{C}-\overset{\delta-}{Cl}$ bond ethyl chloride is highly reactive. Therefore alkyl halides are considered as synthetic tools in the hands of organic chemistry.
- Due to low bond dissociation energy, alkyl halides are more reactive.
- The order of reactivity of alkyl halides is as follows :

  R - Cl < R – Br < R – I

$$\underset{\text{primary}}{CH_3-CH_2-CH_2-CH_2-Cl} < \underset{\text{sec ondary}}{CH_3-\underset{Cl}{\underset{|}{CH}}-CH_2CH_3} < \underset{\text{tertiary}}{CH_3-\underset{CH_3}{\underset{|}{C}}-Cl}$$

- In addition to nucleophilic substitution ethyl chloride also undergoes reduction, elimination, hydrolysis etc.

  It will not undergo oxidation and addition.
- **Reduction :** Ethyl chloride is reduced to ethane with the reducing agents like Zn + HCl or H_2 / Ni or Pd.

$$C_2H_5-Cl + 2H \xrightarrow[pd/H_2]{Zn/HCl,\ LiAlH_4} C_2H_6 + HCl$$

- **Elimination :** In the presence of alcoholic potash , ethyl chloride undergoes elimination to give ethylene.

$$C_2H_5-Cl + \underset{(alc)}{KOH} \rightarrow C_2H_4 + KCl + H_2O$$

- **Hydrolysis :** With aqueous KOH or NaOH ethyl chloride gives ethyl alcohol.

$$C_2H_5-Cl + \underset{(aq)}{KOH} \rightarrow C_2H_5OH + KCl$$

- **With Potassium cyanide (KCN):** Ethyl chloride on reaction with aqueous alcoholic potassium cyanide gives ethyl cyanide.

$$C_2H_5Cl + KCN \rightarrow C_2H_5-CN + KCl$$

(little amount of ethylisocyanide (C_2H_5NC) will be produced)

- **With Silver cyanide (AgCN):** Ethyl chloride on reaction with aqueous alcoholic silver cyanide gives ethyl isocyanide.

$$C_2H_5-Cl + AgCN \rightarrow C_2H_5NC + AgCl$$

(Small amount of ethyl cyanide will form)

KCN is ionic whereas AgCN is covalent.

- **With Potassium nitrite (KNO_2) :** Ethyl chloride on reaction with potassium or sodium nitrite

gives nitroethane as the major product. Dimethyl formamide (DMF) is used as solvent.

$$C_2H_5Cl + KNO_2 \xrightarrow{DMF} C_2H_5NO_2 + KCl$$

(Small amount of ethyl nitrite (C_2H_5ONO (30%)) will also form)

- **With Silver nitrite ($AgNO_2$) :** with hot aqueous alcoholic silver nitrite ethyl chloride gives ethyl nitrite as the major product.

$$C_2H_5Cl + AgONO \rightarrow C_2H_5 - O - N = O + AgCl$$

(Small amount of nitroethane ($C_2H_5NO_2$) will also form).

KNO_2 is ionic, $AgNO_2$ is covalent.

- KCN is ionic, AgCN is covalent
- KNO_2 is ionic , $AgNO_2$ is covalent
- **With moist silver oxide (Ag_2O) :** Ethyl chloride gives ethyl alcohol on reaction with moist silver oxide.

$$C_2H_5 - Cl + AgOH \rightarrow C_2H_5OH + AgCl$$

- **With dry silver oxide (Ag_2O) :** with dry Ag_2O ethyl chloride gives diethyl ether

$$2C_2H_5 - Cl + Ag_2O \rightarrow C_2H_5 - O - C_2H_5 + 2AgCl$$

- **With sodium Ethoxide (Williamson's synthesis):** Ethyl chloride on reaction with sodium ethoxide gives diethyl ether.

$$C_2H_5Cl + NaOC_2H_5 \rightarrow C_2H_5 - O - C_2H_5 + NaCl$$

- **With Ammonia (NH_3) :** Ethyl alcohol on reaction with ammonia finally gives quaternary ammonium chloride.

$$C_2H_5 - Cl + HNH_2 \xrightarrow[-HCl]{} C_2H_5 - NH_2 \xrightarrow[-HCl]{C_2H_5Cl}$$

$$(C_2H_5)_2NH \xrightarrow[-HCl]{C_2H_5Cl} (C_2H_5)_3N \xrightarrow{C_2H_5Cl} (C_2H_5)_4N^+Cl^-$$

(quaternary ammonium chloride)

- **With silver acetate :** with silver acetate ethyl chloride gives ethyl acetate

$$C_2H_5Cl + AgOOCCH_3 \rightarrow CH_3 - COOC_2H_5 + AgCl$$

- **With sodium acetylide :** with sodium acetylide ethyl chloride gives 1–butyne.

$$C_2H_5 - Cl + NaC \equiv CH \rightarrow C_2H_5 - C \equiv CH + NaCl$$

- **With Benzene :** In the presence of Lewis acid ethyl chloride reacts with benzene to give ethyl benzene.

$$C_2H_5 - Cl + C_6H_6 \xrightarrow[AlCl_3]{anhydrous} C_2H_5 - C_6H_5 + HCl$$

- **Reaction with magnesium :** Ethyl chloride on reaction with magnesium in dry ether gives ethyl magnesium chloride (Grignard's reagent)

$$C_2H_5Cl + Mg \xrightarrow{dry\ ether} C_2H_5MgCl$$

(Grignard's reagent)

- **With Na (Wurtz reaction) :** In the presence of dry ether two moles of ethyl chloride reacts with sodium to give butane.

$$2C_2H_5Cl + 2Na \xrightarrow{dry\ ether} C_2H_5 - C_2H_5 + 2NaCl$$

- **Uses of Ethylchloride :**

1) used in refrigeration 2) as local Anaesthatic 3) As ethylating agent

4) In the preparation of sulphonyl chloride ($R - SO_2Cl$).

5) In the preparation of Anti – knocking agents like TEL (Tetra ethyl lead)

CHLOROFORM [$CHCl_3$] :

It is discovered by liebeg and named by Dumas because it gives formic acid on hydrolysis.

Methods of preparation :

- **From methane (CH_4)** : Methane on controlled chlorination in the presence of sunlight gives chloroform.

$$CH_4 + 3Cl_2 \xrightarrow{h\upsilon} CHCl_3 + 3HCl$$

From Carbontetrachloride (CCl_4): Carbontetrachloride on reduction with iron filings and water gives chloroform.

$$CCl_4 + 2[H] \xrightarrow{Fe,H_2O} CHCl_3 + HCl$$

On large scale chloroform is prepared by this method.

- **From chloral hydrate :** By the distillation of chloral hydrate with NaOH, pure chloroform can be obtained.

$$\underset{\text{(Chlorol hydrate)}}{CCl_3CH(OH)_2} + NaOH \rightarrow CHCl_3 + H_2O + HCOONa$$

Even though there are two hydroxyl groups on the same carbon, chloral hydrate is stable due to intra-intermolecular hydrogen bonding.

From ethyl alcohol :

- By the distillation of ethyl alcohol and bleaching powder
- This is suitable as laboratory and industrial method.
- About 40% of yield is obtained.
- In this method the following process will occur.

  1) Hydrolysis 2) Oxidation 3) Chlorination
- Cl_2 liberated from bleaching powder acts as an oxidising agent and chlorinating agent.

  i) Hydrolysis of bleaching powder :

$$CaOCl_2 + H_2O \rightarrow Ca(OH)_2 + Cl_2$$

  ii) Oxidation of ethyl alcohol :

$$CH_3 - CH_2 - OH + Cl_2 \rightarrow CH_3 - CHO + 2HCl$$

  iii) Chlorination of acetaldehyde :

$$CH_3 - CHO + 3Cl_2 \rightarrow \underset{\text{(chloral)}}{CCl_3 - CHO} + 3HCl$$

  iv) Hydrolysis of chloral :

$$2CCl_3 - CHO + Ca(OH)_2 \rightarrow 2CHCl_3 + (HCOO)_2Ca$$

- **From acetone :**
- By the distillation of acetone and bleaching powder chloroform is obtained.

  i) Hydrolysis of bleaching powder:

$$CaOCl_2 + H_2O \rightarrow Ca(OH)_2 + Cl_2$$

  ii) Chlorination of acetone :

$$CH_3 - \underset{\underset{O}{\|}}{C} - CH_3 + 3Cl_2 \rightarrow CCl_3 - \underset{\underset{O}{\|}}{C} - CH_3 + 3HCl$$

  iii) Hydrolysis of trichloro acetone :

$$2CCl_3 - \underset{\underset{O}{\|}}{C} - CH_3 + Ca(OH)_2 \rightarrow 2CHCl_3 + (CH_3COO)_2Ca$$

- **Physical properties :**
  1) It is a colourless liquid with sweet odour.
  2) It is slightly soluble in H_2O but readily soluble in organic solvents.
  3) It self is good solvent for fats, oils, resins, waxes, etc.
  4) It is denser than water.
  5) It is not inflammable but its vapours burn with green flame.
  6) It's vapours cause unconsciousness.
  7) It will not give precipitate with silver nitrate solution because it is covalent in nature.
- **Chemical reactions;**
- **Oxidation :** In the presence of air and light chloroform is oxidised to a poisonous gas carbonyl chloride (phosgene)

$$CHCl_3 + \frac{1}{2}O_2 \xrightarrow{h\upsilon} COCl_2 + HCl$$

Hence, chloroform is kept in dark-brown or blue bottles to which 1% ethyl alcohol is added. Ethyl alcohol converts phosgene to ethyl carbonate .

$$2C_2H_5OH + COCl_2 \rightarrow (C_2H_5)_2CO_3 \downarrow + 2HCl$$

By adding small amount of $AgNO_3$, HCl is precipitated to AgCl.

$$AgNO_3 + HCl \rightarrow AgCl \downarrow + HNO_3$$

- **Reduction :**

a) Chloroform on reduction with Zn + HCl gives methylene dichloride

$$CHCl_3 + 2[H] \xrightarrow{Zn/HCl} CH_2Cl_2 + HCl$$

b) with zinc and water, chloroform is reduced to methane.

$$CHCl_3 + 6[H] \xrightarrow{Zn/H_2O} CH_4 + 3HCl$$

- **Chlorination :** Chloroform on reaction with chlorine in the presence of sunlight gives carbontetrachloride.

$$CHCl_3 + Cl_2 \xrightarrow{h\upsilon} CCl_4 + HCl$$

- **Hydrolysis :** Chloroform on hydrolysis with aqueous KOH finally gives potassium formate.

$$HCCl_3 + 3KOH_{(aq)} \xrightarrow{-3KCl} HC(OH)_3 \xrightarrow{-H_2O} HCOOH \xrightarrow[-H_2O]{KOH} HCOOK$$

- **Nitration :** with nitric acid vapour chloroform gives chloropicrin (trichloronitromethane) which is used as tear gas and insecticide. $Cl_3CH + HO - NO_2 \rightarrow Cl_3C - NO_2 + H_2O$.

(chloropicrin is also called as tear gas)

- **With Silver :** Chloroform with silver powder gives acetylene.

$$2CHCl_3 + 6Ag \rightarrow C_2H_2 + 6AgCl$$

- **With acetone :** In the presence of KOH chloroform reacts with acetone to give chloretone which is a hypnotic drug.

$$CH_3 - \underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}} = O + CHCl_3 \rightarrow CH_3 - \underset{\displaystyle CH_3}{\overset{\displaystyle CCl_3 \\ |}{\overset{|}{C}}} - OH$$

Chloretone $\rightarrow$ hypnoticdrug

- **Riemer - Tiemann reaction :**

Phenol reacts with chloroform in presence of NaOH to give salicylaldehyde

$$C_6H_5OH + CHCl_3 + 3NaOH \rightarrow C_6H_5(OH)CHO + 3NaCl + 2H_2O$$

- **Carbyl amine reaction : (isocyanide test)**
  Chloroform reacts with primary amine in the presence of KOH to give bad smelling isocyanide.
- Both aliphatic and aromatic primary amines will give this test.
- This reaction is useful for testing primary amines and chloroform.

$$R - NH_2 + CHCl_3 + 3KOH \rightarrow R - NC + 3KCl + 3H_2O$$

$$C_6H_5NH_2 + CHCl_3 + 3KOH \rightarrow C_6H_5NC + 3KCl + 3H_2O$$

Uses of chloroform :

- It can be used in anesthesia but it is not used nowadays.
- Used as solvent for fats, oils, resins, waxes etc.
- For testing primary amines, bromides and iodides.
- In the preservation of Biological specimens
- In the preparation of hypnotic drug i.e. chloretone.
- In the preparation of insecticide such as chloropicrin.

Tests for chloroform :

- Isocyanide test.
- It gives silver mirror with tollens reagent.
- It does not give any ppt with $AgNO_3$.

MECHANISM OF NUCLEOPHILIC SUBSTITUTION REACTIONS OF HALOALKANES

- Carbon compounds in which sp^3 carbon is bonded to more electronegative atom or group undergo two types of reactions
  a) S_N1 Substitution reactions
  b) S_N2 Elimination reactions
- **<u>SUBSTITUTION REACTION:</u>** The replacement of electronegative atom or group by another atom or group is called nucleophilic substitution. It is of two types
  a) $S_N1$reaction b) S_N2 reaction
- Nucleophillic substitution depends on the following
  i) The structure of alkyl halide
  ii) The reactivity and structure of nucleophile
  iii) The concentration of the nucleophile and
  iv) The solvent in which the reaction is carried out.

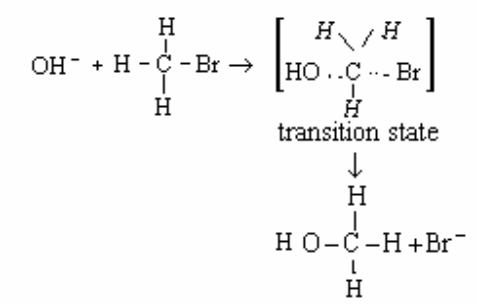
MECHANISM OF S_N2 REACTIONS:

- A nucleophillic substitution in which rate depends on concentrations of both alkyl halide and nucleophile is called S_N2 reaction

  Eg : $CH_3Br + OH^- \rightarrow CH_3OH + Br^-$

- It is second order reaction
- Rate $\alpha[CH_3Br][OH^-]$
- Rate = . $K\left[CH_3Br\right]\left[OH^-\right]$
- So with increase of concentration of CH_3Br or OH^-, rate of S_N2 reaction increases.

- The mechanism occurs in a single step.
- The mechanism involves the formation of transition state.



FACTORS AFFECTING S_N2 REACTIONS

a) <u>Structure of alkyl halide:</u>

- When the hydrogens of are replaced by CH_3Br methyl groups the rate of S_N2 reaction with a given nucleophile decreases

$$CH_3Br > CH_3CH_2Br > CH_3 - CH_2CH_2Br > (CH_3)_2CHBr > (CH_3)_3CBr$$

- So the order of relative reactivity of alkyl halides towards S_N2 reaction is

  Methyl halide > 1^o > 2^o > 3^o Alkyl halide

b) <u>Influence of the leaving group for S_N2 :</u>

- Reactivity order of S_N2 reaction according to relatively leaving ability is RI > RBr > RCl > RF.
- As iodine is a better leaving group due to large size, it is released at a faster rate in the presence of incoming nucleophile.
- Relative nucleophilicity towards CH_3I in methanol is

$$RS^- > I^- > CN^- > CH_3O^- > Br^- > NH_3 > Cl^- > F^-$$

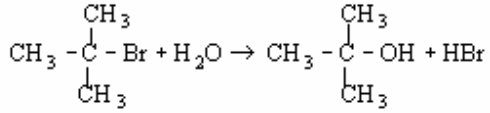
c) <u>Solvent effect in S_N2 reaction :</u> The rates of many S_N2 reactions are affected by the solvent. Polar aprotic solvents increase the rates of S_N2 reactions.

Eg : The order of the affect of solvent is $CH_3OH < H_2O <$ dimethylsulphoxide $< CH_3CN$ < dimethyl formide (DMF) .

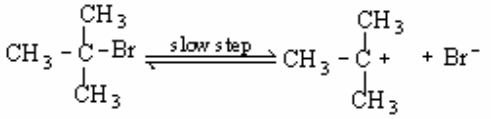
MECHANISM OF S_N1 REACTIONS:

- A nucleophilic substitution in which rate depends on only concentration of alkyl halide is called reaction
- It is first order reaction

  Eg :

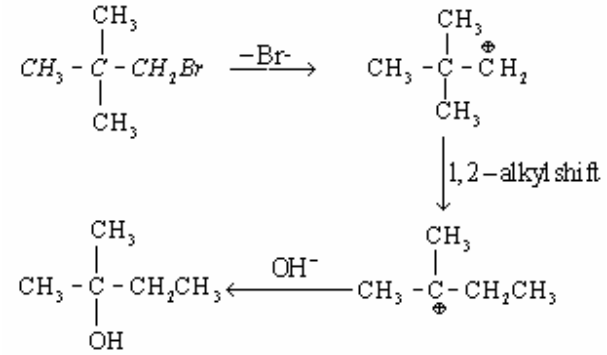


- In these reactions, Rate [alkylhalide]
- The mechanism of S_N1 reaction involves two steps.
- First step involves the formation of carbocation. It is the slow step or rate determining step.

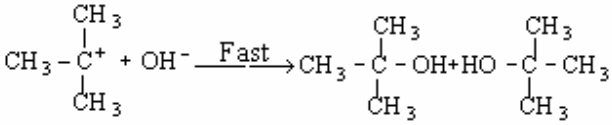


- The carbocation is planar as the central positively charged carbon atom is sp^2 hybridized.

  When the intermediate carbocation is capable or undergoing rearrangement, lesser stable carbocation ($1^o < 2^o < 3^o$) rearranges to the more stable carbocation and hence under such conditions unexpected product is formed.



n Second step involves the attack of the nucleophile on the carbocation. It is the fast step. Nucleophile can attack from either side of the carbocation resulting in the formation of products.



FACTORS AFFECTING S_N1 REACTION

a) **<u>Structure of alkyl halides:</u>** The relative order of reactivity of various halo alkanes towards **S_N1** reaction is

Benzyl halide > Allyl halide > Tertiary alkyl halide > Secondary Alkyl halide > Primary alkyl halide.

- It is due to the greater stability of tertiary carbocation than that of a secondary carbocation and the secondary carbocation is more stable than a primary one. For the same reason allylic and benzylic halides show high reactivity towards the S_N1 reaction.

b) **<u>Influence of leaving group:</u>**

- Leaving group reactivity for S_N1 reaction may be given as $H_2O < Cl^- < Br^- < I^-$

c) **<u>Solvent effect in reaction:</u>**

- S_N1 reaction takes place much more readily in polar solvents than in nonpolar solvents.
- Order of solvent effect in S_N1 reactions is $CH_3COOH < C_2H_5OH < CH_3OH < HCOOH < H_2O$
- **<u>Effect of the attacking nucleophile:</u>** Since the nucleophile comes only after the rate determining step, it has no influence on the rate of $S_N1$reaction.

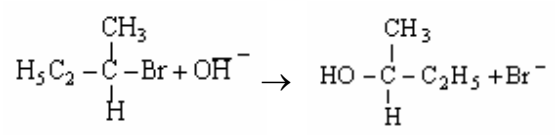
STEREOCHEMICAL OBSERVATION IN NUCLEOPHILIC SUBSTITUTION REACTIONS OF ALKYL HALIDES :

a) In mechanism, the intermediate carbonium ion can be attacked by nuelcophile from either side. So if the compound is optically active, then we get two compounds i.e compound with same

configuration and compound with inverted configuration. If equimolar mixture is obatined then it is Racemic mixture.

b) In S_N2 mechanism nucleophile attacks the compound from opposite side of leaving group hence the product obtained will have inverted configuration. If the alkyl halide taken is optically active i.e if the reactant is d-isomer then the product is . vice-versa. This inversion of configuration is called Walden inversion

Eg:

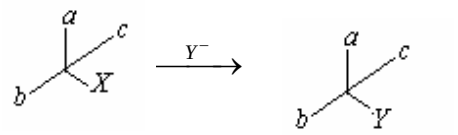


In the above example inversion of configuration is observed.

EXPLANATION OF TERMS INVOLVED

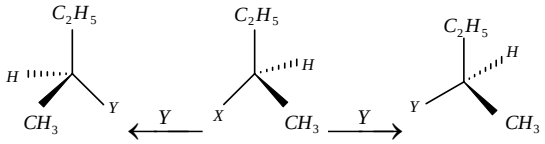
Retention : Retention of confiugration is the preservation of integrity of the spatial arrangement of bonds to an asymmetric centre during a chemical reaction or transformation.

Ex :



The above example XCabc is converted into the YCabc having the same relative configuration.

Inversion, retention and racemisation : There are three outcomes for a reaction at an asymmetric carbon atom. Consider the replacement of a group X by Y in the following reaction :



A + B

If (A) is the only compound obtained, the process is called retention of configuration.

If (B) is the only compound obtained, the process is called inversion of configuration.

If a 50 : 50 mixture of the above two is obtained then the process is called racemisation and the product is optically inactive.

$$CH_3 - CH_2Cl + KOH \xrightarrow[\Delta]{alcohol} CH_2 = CH_2 + H_2O + KCl$$

.

a) **Zaistev (Saytzeff's) rule :** According to this rule, during elimination reactions, an alkene which has more number of alkyl groups attached to the double bonded carbon atoms is formed predominantly.

Eg : 2-bromopentane on heating with alcoholic KOH predominantly produce 2-pentene (81%)

$$CH_3-CH_2-CH=CH-CH_3 \quad (2-penetene \quad 81\%)$$

$$\xleftarrow{OH^-} CH_3CH_2-CH_2-CHBr-CH_3 \xrightarrow{OH^-}$$

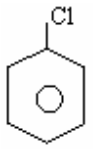
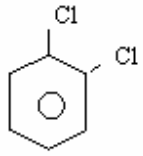
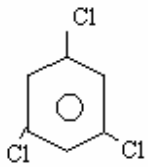
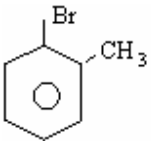
$$CH_3-CH_2-CH_2-CH=CH_2 \quad (1-pentene \quad 19\%)$$

- Whether the reaction is going to be substitution or elimination depends on several factors like nature of akyl halide strength and size of nucleophile, the reaction conditions etc.
- A bulky nucelophile prefers elimination reaction.
  A primary alkyl halide prefers S_N2 reaction.
  A tertiary alkyl halide prefers S_N1 or elimination depending on the stability of carbocation or alkenes.
  A secondary alkyl halide prefers for S_N1 or elimination depending on nucleophile.

HALO ARENES

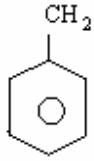
Halo arenes are obtained by replacement of hydrogen atom of aromatic hydrocarbon by halogen

I. Naming of Haloarenes

Haloarene	Common name	IUPAC name
	*chloro benzene*	*chloro benzene*
	*O – dichloro benzene*	*1,2 dichloro benzene*
	*sym trichloro benzene*	*1,3,5 – trichloro benzene*
	*O – bromo toulene*	*1 – bromo –2 – methyl benzene*

ARYL ALKYL HALIDE OR ARALKYL HALIDE:

Halogen atom is attached to carbon of the side chain of aromatic ring



benzylbromide(commonname)
bromophenylmethane(IUPACname)

NATURE OF C - X BOND : Haloarenes are less reactive than that of haloalkanes because

i) In haloarenes, halogen atom is attached to sp^2 hybridized carbon of arene but in haloalkanes, halogen is attached to sp^3 carbon. sp^2 orbital has more 's' character than sp^3 orbital. Hence C-X bond in haloarenes has shorter distance (169 pm) than in halo alkanes (177 pm). So in halo arenes C-X is stronger bond. Therefore, it is less reactive towards nucelophilic substitution reactions.

ii) Due to resonance effect, C-X bond in halo arenes acquires a partial double bond character and the cleavage of C-X bond becomes more difficult than in halo alkanes.

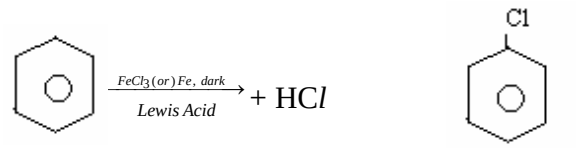
iii) Phenyl cation is unstable as it can not be stabilized through resonance.

iv) Benzene has more electron density. Therefore a stronger nucleophile can not approach it easily.

CHLORO BENZENE

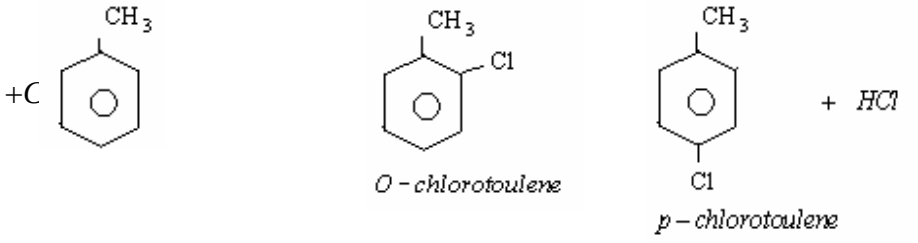
I) Preparation :

A) F**r**om Benzene By Electrophilic Substitution :

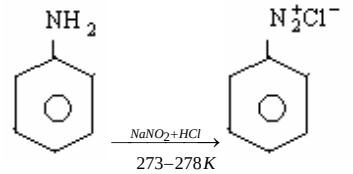


Iodo benzene cannot be prepared by this method because reaction with I_2 is reversible. Hence HI formed should be immediately oxidized by using oxidizing agents like HNO_3, HIO_4 etc.Fluorine being reactive, fluoro benzene cannot be prepared by this method.

Similarly toulene reacts with Cl_2 in presence of Fe/dark to give mixture of o- and p-chloro toulene



B) SANDMEYER'S REACTION (LAB METHOD) :

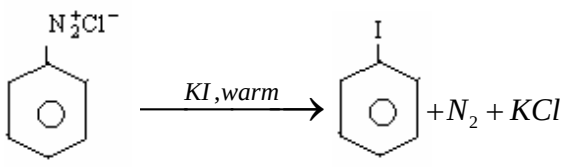


$$C_6H_5N_2^+Cl^- \xrightarrow{Cu_2Cl_2} C_6H_5Cl + N_2$$

$C_6H_5N_2^+Cl^- \xrightarrow{Cu_2Br_2} C_6H_5Br + N_2$

In Sandmeyer's reaction Cu_2Cl_2 or Cu_2Br_2 will be used

C) PREPARATION OF IODO BENZENE



II)_Chemical properties of chloro benzene

A) Nucleophilic substitution reactions of

CHLOROBENZENE : Chlorobenzene is less reactive towards nucleophilic substitution reactions than haloalkanes.

I) REPLACEMENT OF HALIDE BY HYDROXYL GROUP :

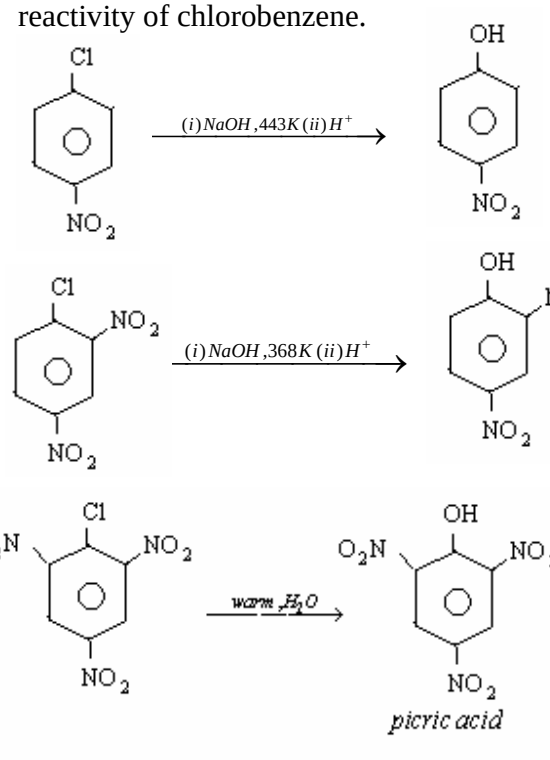
Chlorobenzene is converted to phenol by heating in aqueous NaOH solution at 300 atm. pressure and 623 K (Dow's process)

$C_6H_5Cl \xrightarrow[350^oC,300\ atm]{NaOH\,(aq)} C_6H_5O^-Na^+$

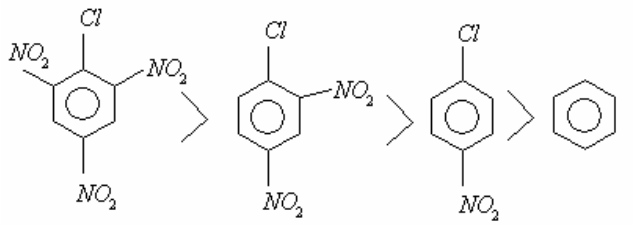
$C_6H_5O^-Na^+ \xrightarrow{H^+/H_2O} C_6H_5OH + NaOH$

.

The presence of electron with drawing groups like $-NO_2$ at ortho and para positions increases the reactivity of chlorobenzene.



REACTIVITY ORDER OF SUBSTITUTED CHLORO BENZENE



a) NO_2 group at ortho and para positions withdraw electron density from the ring facilitating the attack of nucleophile. The carbanion formed is resonance stabilized.

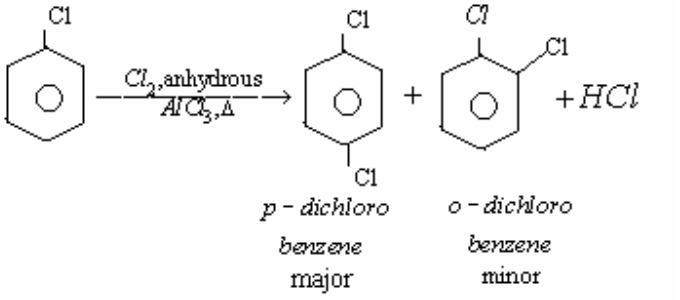
b) If electron withdrawing $-NO_2$ is at meta position , no electron density is found in any resonance structures on carbon to which $-NO_2$ is attached. Therefore, if electron with drawing group is in meta position, there will be no effect on the replacement of halo group by -OH group.

B) <u>ELECTROPHILIC SUBSTITUTION REACTIONS</u> :

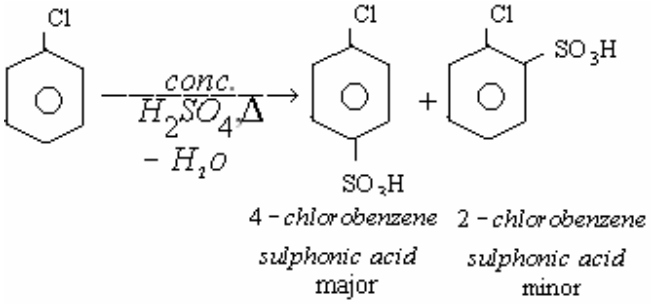
Halogen atom on benzene ring is deactivating but ortho and para directing. Halogen atom on benzene ring increases the electron density at ortho and para positions than at meta position due to +M effect. Again halogen atom has -I

effect and has tendency to withdraw electrons from the ring. So the ring gets slightly deactivated when compared to benzene.Therefore, electrophilic substitution reactions are slow in chloro benzene than in benzene.

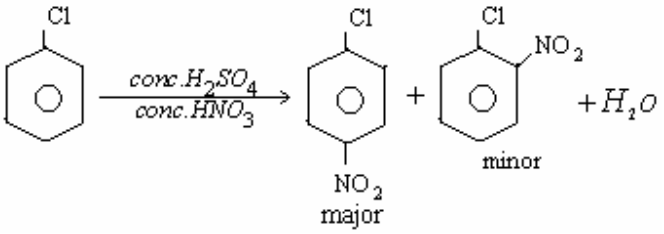
- **HALOGENATION :**



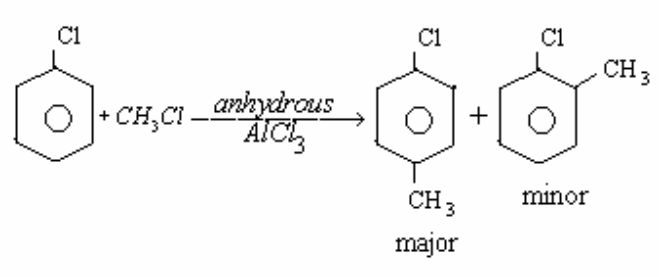
- **SULPHONATION :**



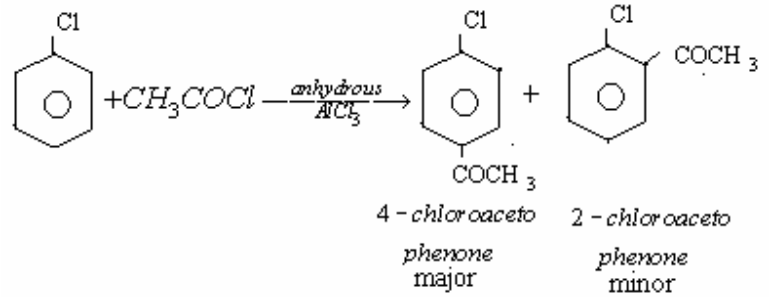
- **NITRATION :**



- **ALKYLATION :**



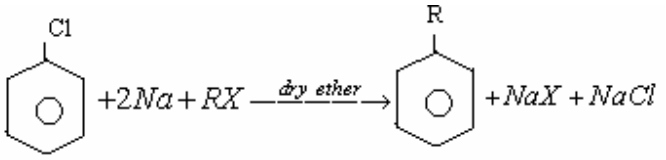
- **ACETYLATION :**



Note : In the electrophilic substitution reactions, inductive effect destabilizes the intermediate carbocation, but resonance effect stabilizes the intermediate carbocation.

- **REACTION WITH METALS :**

a) Wurtz - Fittig reaction



b) Fittig reaction :

