10. HALOALKANES AND HALOARENES

These are compounds containing halogen atoms attached to an alkyl or aryl group. The general representation of **haloalkanes** is **R-X** and that of **haloarenes** is **Ar-X** [where X = F, Cl, Br, I].

Preparation of Haloalkanes

1) From alcohols

a) By the action of concentrated halogen acids on alcohols in presence of anhydrous $ZnCl_2$ as catalyst.

$$R\text{-}OH + HX \xrightarrow{\text{an. } ZnCl_2} R\text{-}X + H_2O$$

b) Alkyl chlorides are obtained by the action of PCl_3, PCl_5 or $SOCl_2$ with alcohols.

$$3R\text{-}OH + PCl_3 \longrightarrow 3\,R\text{-}Cl + H_3PO_3$$

$$R\text{-}OH + PCl_5 \longrightarrow R\text{-}Cl + POCl_3 + HCl$$

$$R\text{-}OH + SOCl_2 \longrightarrow R\text{-}Cl + SO_2 + HCl$$

Among these methods, the reaction with thionyl chloride ($SOCl_2$) is preferred, since the biproducts are gases and are easily escaped from the reaction medium.

For the preparation of alkyl bromides and iodides, alcohols are treated with bromine or iodine in presence of red phosphorus, since PBr_3 and PI_3 are unstable.

$$R\text{-}OH \xrightarrow{X_2/\text{Red P}} R\text{-}X \qquad (\text{where } X_2 = Br_2 \text{ or } I_2)$$

2) Halogen Exchange Reactions

a) ***Finkelstein reaction***: Alkyl chlorides or bromides when treated with NaI in dry acetone, alkyl iodides are formed. This reaction is known as Finkelstein reaction.

$$R\text{-}X + NaI \longrightarrow R\text{-}I + NaX \qquad (\text{where } X = Cl, Br)$$

b) ***Swarts reaction***: Alkyl chloride or bromide is treated with a metallic fluoride like silver fluoride (AgF) or Mercurous fluoride (Hg_2F_2) or cobalt fluoride (CoF_2) or Antimony fluoride (SbF_3), alkyl fluoride is formed. This reaction is known as Swarts reaction.

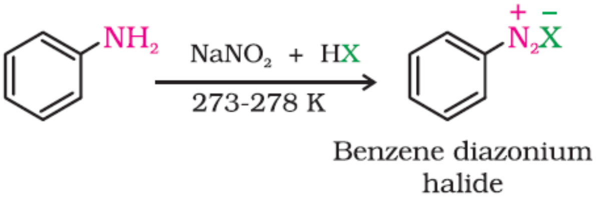
$$R\text{-}X + AgF \longrightarrow R\text{-}F + AgX \qquad (\text{where } X = Cl \text{ or } Br)$$

E.g.: $2\,CH_3\text{-}Br + CoF_2 \longrightarrow 2\,CH_3\text{-}F + CoBr_2$

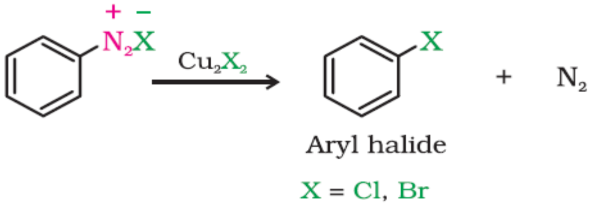
Preparation of Haloarenes

From amines by Sandmeyer's reaction:

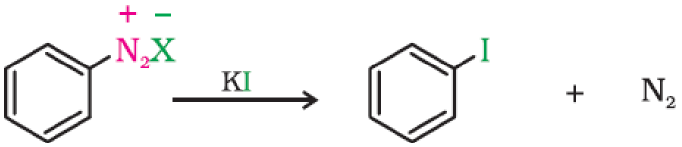
When an aromatic primary amine (like aniline) is treated with HCl and sodium nitrite ($NaNO_2$) at cold condition (0 – 5^0C), an aromatic diazonium salt is formed. This reaction is called *Diazotisation*.



When a diazonium salt is treated with HX in presence of cuprous halide (Cu_2X_2), we get a halobenzene. This reaction is called Sandmeyer's reaction.



For the preparation of iodobenzene, the diazonium salt is treated with potassium iodide (KI).



CHEMICAL REACTIONS OF HALOALKANES - Nucleophilic Substitution Reactions

These are reactions in which a weak nucleophile is replaced by a strong nucleophile [Nucleophiles are electron rich species attacks at electron deficient centre].

The important Nucleophilic substitution reactions of haloalkanes are:

1. ***Reaction with aqueous alkali***: Haloalkanes react with aq. NaOH or KOH to form *alcohols*.

   $R\text{-}X + KOH(aq) \longrightarrow R\text{-}OH + KX$

   E.g.: $CH_3\text{-}CH_2\text{-}Br + KOH(aq) \longrightarrow CH_3\text{-}CH_2\text{-}OH + KBr$
2. ***Reaction with water:*** Haloalkanes react with water to form *alcohols*.

   $R\text{-}X + H_2O \longrightarrow R\text{-}OH + HX$
3. ***Reaction with Sodium alkoxide (R-ONa) [Williamson's ether synthesis]:*** Haloalkanes react with sodium alkoxide to give *ethers* (R-O-R).

   $R\text{-}X + R\text{-}ONa \longrightarrow R\text{-}O\text{-}R + KX$

   e.g.: $CH_3\text{-}Br + CH_3\text{-}CH_2\text{-}ONa \longrightarrow CH_3\text{-}O\text{-}CH_2\text{-}CH_3 + NaBr$
4. ***Reaction with Sodium iodide (NaI):*** Alkyl halides (Chlorides or Bromides) react with sodium alkoxide to form *alkyl iodides*.

   $R\text{-}X + NaI \longrightarrow R\text{-}I + NaX$ [X = Cl or Br]
5. ***Reaction with ammonia:*** Alkyl halides react with alcoholic ammonia to give a mixture of *1^0, 2^0 and 3^0 amines and quaternary ammonium salt*.

   $R\text{-}X + NH_3 \longrightarrow R\text{-}NH_2 + R_2NH + R_3N + R_4N^+X^-$

   If ammonia is in excess, only primary amine is formed.
6. ***Reaction with KCN:*** Alkyl halides react with alcoholic KCN to give *alkane nitriles or alkyl cyanides* (R-CN).

   $R\text{-}X + KCN \longrightarrow R\text{-}CN + KX$
7. ***Reaction with Silver cyanide (AgCN):*** Alkyl halides react with AgCN to give *alkyl isocyanides or carbyl amines* (R-NC).

   $R\text{-}X + AgCN \longrightarrow R\text{-}NC + AgX$
8. ***Reaction with Potassium nitrite (KNO_2):*** Alkyl halides react with KNO_2 to give *alkane nitrite* (R-ONO).

   $R\text{-}X + KNO_2 \longrightarrow R\text{-}ONO + KX$
9. ***Reaction with Silver nitrite ($AgNO_2$)*** : Alkyl halides react with $AgNO_2$ to give *nitroalkane* ($R\text{-}NO_2$)

   $R\text{-}X + AgNO_2 \longrightarrow R\text{-}NO_2 + AgX$
10. ***Reaction with Silver salts of carboxylic acid***: Alkyl halides react with silver salts of carboxylic acid (R-COOAg) to give *esters* (R-COOR).

    $R\text{-}X + R\text{-}COOAg \longrightarrow R\text{-}COOR + AgX$
11. ***Reduction:*** Alkyl halides when reduced with lithium aluminium hydride ($LiAlH_4$) to give *alkane*.

    $R\text{-}X + [H] \xrightarrow{LiAlH_4} R\text{-}H + HX$

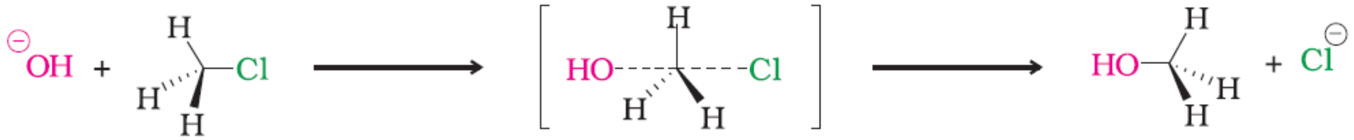
Mechanism of Nucleophilic Substitution Reactions

There are two types of mechanisms: *Substitution Nucleophilic bimolecular (S_N2) and Substitution Nucleophilic unimolecular (S_N1)*

1. ***Substitution Nucleophilic Bimolecular (S_N2) Mechanism***:

Here the incoming nucleophile interacts with alkyl halide causing the carbon-halogen bond to break while forming a new carbon-OH bond. These two processes take place simultaneously in a single step and no intermediate is formed. In the case of optically active alkyl halides, this mechanism proceeds through ***inversion of configuration***.

An example is the reaction between CH_3Cl and hydroxide ion to yield methanol and chloride ion. This reaction follows a second order kinetics, i.e., the rate depends upon the concentration of both the reactants. Mechanism of this reaction is:



The order of reactivity of alkyl halides towards S_N2 reaction is: Primary halide > Secondary halide > Tertiary halide.

2. ***Substitution nucleophilic unimolecular (S_N1)***:

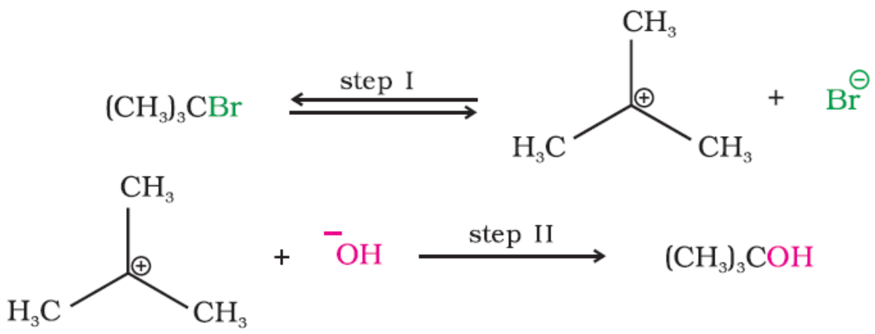
S_N1 reaction occurs in two steps. In the first step, the C—X bond undergoes slow cleavage to produce a carbocation and a halide ion. In the second step, the carbocation is attacked by the nucleophile to form the product. Here first step is the slowest and reversible. So it is the rate determining step. Since this step contains only one reactant, it follows first order kinetics.

E.g.: The reaction between tert-butyl bromide and hydroxide ion to give tert-butyl alcohol.

$$(CH_3)_3CBr + {}^{-}OH \longrightarrow (CH_3)_3COH + Br^{-}$$

2-Bromo-2-methylpropane 2-Methylpropan-2-ol

This reaction occurs in two steps. In step I, the polarised C—Br bond undergoes slow cleavage to produce a carbocation and a bromide ion. The carbocation thus formed is then attacked by nucleophile in step II to form the product.



Thus in S_N1 reaction, there is an intermediate called carbocation. The greater the stability of the carbocation, the greater will be the rate of the reaction.

The order of reactivity of alkyl halides towards S_N1 reaction is: $3^0 > 2^0 > 1^0$.

In the case of optically active compounds, the S_N1 reaction proceeds through retention of configuration.

<u>Differences between S_N1 and S_N2 reactions</u>

S_N1 Reaction	**S_N2 Reaction**
Proceeds in 2 steps	Proceeds in a single step
An intermediate (carbocation) is formed	No intermediate is formed
Order of the reaction is 1	Order is 2
For optically active compounds, the reaction proceeds through retention of configuration.	For optically active compounds, the reaction proceeds through inversion of configuration.
The order of reactivity of alkyl halide is $3^0 > 2^0 > 1^0$	The order of reactivity of alkyl halide is $1^0 > 2^0 > 3^0$

Stereochemical Aspects of nucleophilic substitution Reactions

Plane Polarised light

It is a light beam in which the particles vibrate in only one direction. It is produced by passing ordinary light beam through a Nicol prism. When such a light beam is passed through solutions of certain compounds, they rotate the plane of polarisation. Such compounds are called ***optically active compounds***. The angle by which the plane polarised light is rotated is called *optical rotation*, which is measured by an instrument called polarimeter. If a compound rotates the plane polarised light towards *right* (i.e. clock-wise direction), it is called *dextro rotatory or d-form or + form* and if it rotates the plane polarised light towards *left* (i.e. anticlock-wise direction), it is called laevo *rotatory or l-form or – form*. The d and l form of a compound are called ***optical isomers*** and the phenomenon is called ***optical isomerism***.

Molecular asymmetry and Optical isomerism

Optical isomerism is due to molecular asymmetry. If all the 4 valencies of a carbon atom are satisfied by 4 different groups, it is called **asymmetric carbon or chiral carbon or stereo centre**. The resulting molecule is called *asymmetric molecule*. Such molecules are non-super imposable to their mirror images and are called ***chiral molecules*** and this property is known as ***chirality***. The molecules which are super imposable to their mirror images are called achiral molecules.

A chiral carbon is denoted by an asteric (*) mark.

e.g.: 2-Chlorobutane [$CH_3 - \overset{*}{C}HCl - CH_2 - CH_3$]

Here the 2nd C is chiral, since all the four valencies of this C are satisfied by 4 different groups.

Other examples: 2-butanol [$CH_3 - \overset{*}{C}HOH - CH_2 - CH_3$]

2-bromopropanoic acid [$CH_3 - \overset{*}{C}HBr - COOH$]

Lactic acid [$CH_3 - \overset{*}{C}HOH - COOH$]

Enantiomers

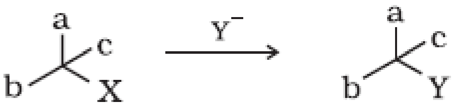
The stereo isomers related to each other as non-super imposable mirror images are called ***enantiomers***. They have identical physical properties. They differ only in the direction of rotation of the plane polarised light. If one of the enantiomers is dextro rotatory, the other will be laevo rotatory.

Racemic mixture

A mixture containing d and l form of a compound in equal proportion has zero optical rotation and such a mixture is called ***racemic mixture or racemic modification***. It is denoted by dl or (±). Here the rotation due to one isomer is cancelled by the rotation due to the other isomer. The process of conversion of an enantiomer in to a racemic mixture is called **racemisation**.

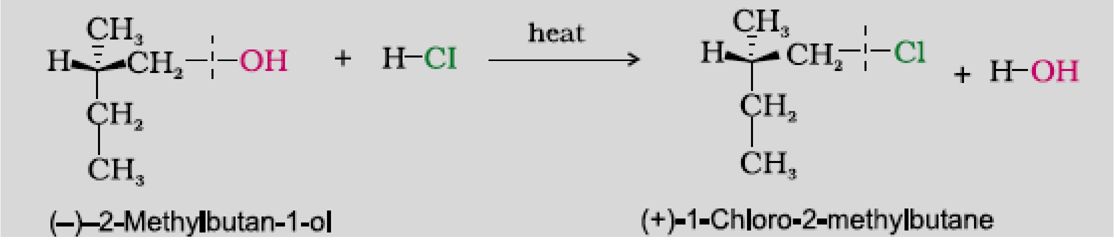
Retention and Inversion of configuration

If during a chemical reaction, there is no change in the spatial arrangement of bonds to an asymmetric centre, we can say that the reaction proceeds through *retention* of configuration. (Or, preservation of the integrity of configuration of a compound is termed as retention).

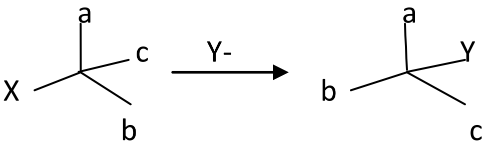


In general, if during a chemical reaction, no bond to the stereo centre is broken, the product will have the same configuration as that of the reactant. Such reactions always proceed through retention of configuration.

E.g. Reaction of 2-Methyl-1-butanol with HCl.

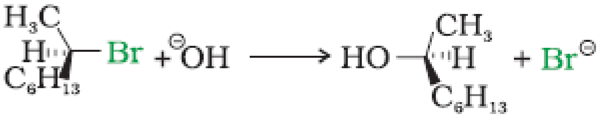


If during a chemical reaction, the incoming group is attached to a position opposite to that of the leaving group, the configuration of the resulting product is inverted and we can say that the reaction proceeds through *inversion of configuration*.



<u>Nucleophilic Substitution and Optical Activity</u>

In the case of optically active alkyl halides, the product formed as a result of S_N2 mechanism has the inverted configuration. This is because here the nucleophile attacks on the side opposite to that of the halogen atom.

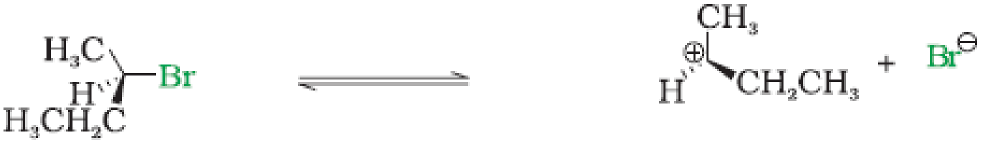


(-) 2-Bromooctane (+) octan-2-ol

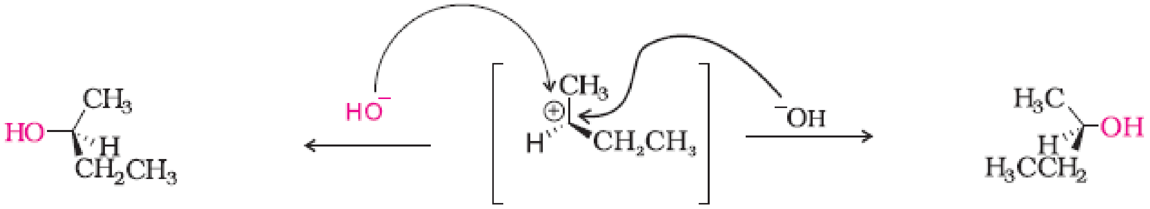
In the case of optically active alkyl halides, S_N1 reactions follow through *racemisation*. Here the intermediate carbocation formed is sp^2 hybridised and hence it is planar. So the attack of nucleophile can take place from either side resulting in a mixture of products with opposite configuration.
e.g. Hydrolysis of optically active 2-bromobutane results in the formation of ($\pm$) 2-butanol, a racemic mixture.

$$CH_3 - CHBr - CH_2 - CH_3 \xrightarrow{OH^-} CH_3 - CHOH - CH_2 - CH_3 + Br^-$$

Step – I



Step – II

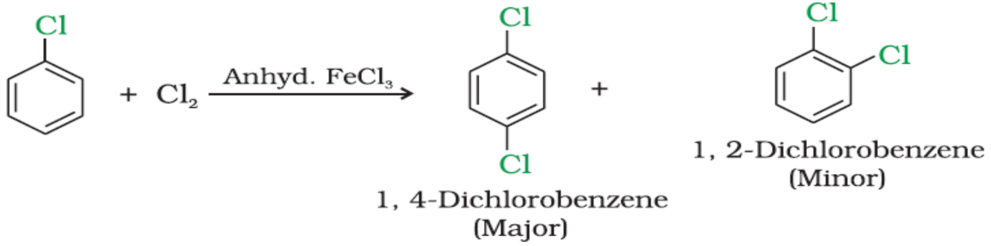


(-) 2-Butanol Planar carbocation (+) 2-butanol

Reactions of Haloarenes - Electrophilic substitution reactions

Halo group is an ortho-para directing group. So the incoming electrophile enters at these positions.

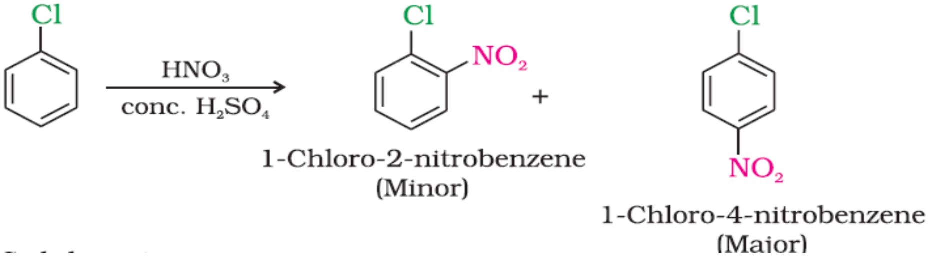
i) ***Halogenation***: Haloalkanes react with chlorine in presence of anhydrous ferric chloride to form o-dichlorobenzene and p-dichlorobenzene.



1, 4-Dichlorobenzene (Major)

1, 2-Dichlorobenzene (Minor)

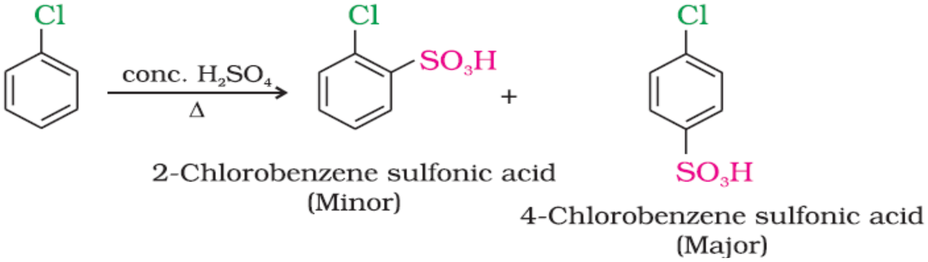
ii) ***Nitration***: On nitration using Conc. HNO_3 and Conc. H_2SO_4 (Nitrating mixture), chlorobenzene gives p-nitrochlorobenzene as the major product.



1-Chloro-2-nitrobenzene (Minor)

1-Chloro-4-nitrobenzene (Major)

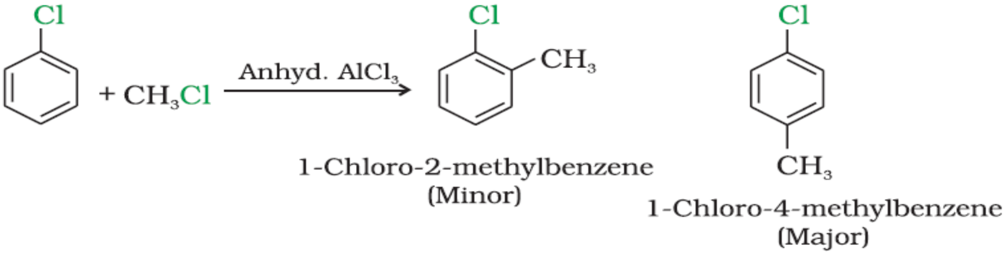
iii) ***Sulphonation***: On sulphonation using Conc. H_2SO_4, chlorobenzene gives para-chlorobenzenesulphonic acid as the major product.



2-Chlorobenzene sulfonic acid (Minor)

4-Chlorobenzene sulfonic acid (Major)

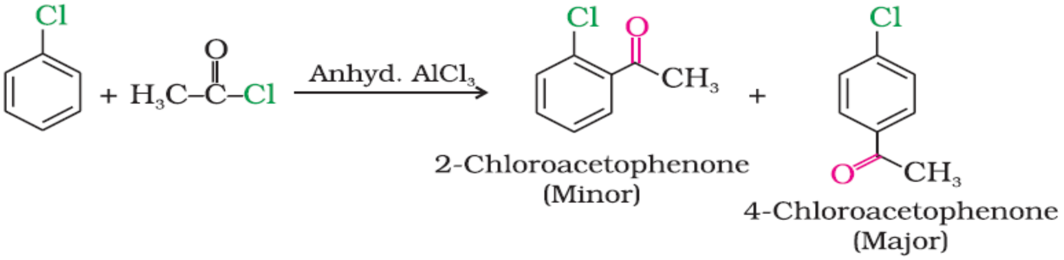
iv) ***Friedel – Crafts Alkylation***: Chlorobenzene when treated with methyl chloride (CH_3-Cl) in presence of anhydrous $AlCl_3$, we get p-chlorotoluene as the major product.



1-Chloro-2-methylbenzene (Minor)

1-Chloro-4-methylbenzene (Major)

v) ***Friedel – Crafts Acylation***: Chlorobenzene when treated with acetyl chloride (CH_3-CO-Cl) in presence of anhydrous $AlCl_3$, we get p-chloroacetophenone as the major product.



2-Chloroacetophenone (Minor)

4-Chloroacetophenone (Major)