Chapter 10: Haloalkanes and Haloarenes

1. **General Formula:** R – X (Alkyl halide or Haloalkane)   Ar –X (Alkyl halide or Haloarene)

Where, R = Alkyl group like $-CH_3$ X = F, Cl, Br, I   Ar = Phenyl group

2. Classification: On the basis of number of halogen atoms it can be classified as mono, di and poly (tri, tetra etc) Haloalkanes (Haloarenes), for example

C_2H_5X

Monohaloalkane

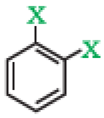
CH_2X-CH_2X

Dihaloalkane

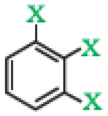
$CH_2X-CHX-CH_2X$

Trihaloalkane

Monohaloarene

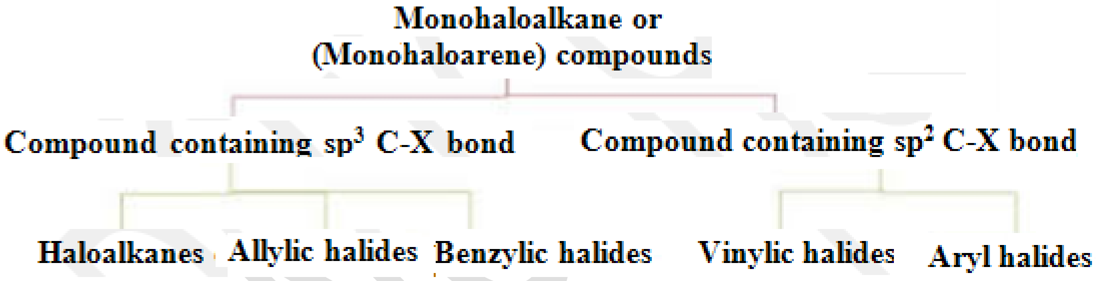


Dihaloarene



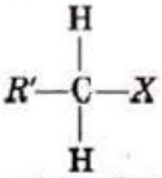
Trihaloarene

1) Classification of Monohaloalkane or Monohaloarene compounds: It further categorized according to hybridization of carbon atom like as



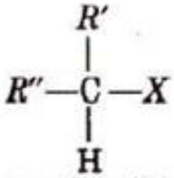
i) Compound containing sp^3 C-X bond: Halogen is bonded with sp^3 hybridized carbon. This class includes-

a) Haloalkanes or alkyl halide:



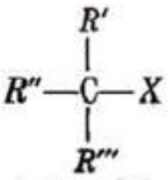
$R'-C(H)(H)-X$

primary (1°)



$R''-C(R')(H)-X$

secondary (2°)



$R''-C(R')(R''')-X$

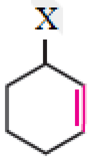
tertiary (3°)

b) Allylic halides:

$CH_2 = CH- CH_2 - X$

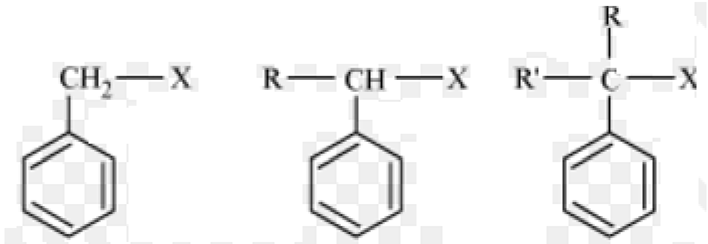
Allyl halide

(3- halo-1- propene)



3-Halocyclohex-1-ene

c) Benzylic halides:

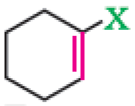


primary (1°) (Benzyl halide) secondary (2°) tertiary (3°)

ii) Compound containing sp^2 C-X bond: Halogen is bonded with sp^2 hybridized carbon. This class includes-

a) Vinylic halides:

CH2 = CH – X
Vinyl Halide

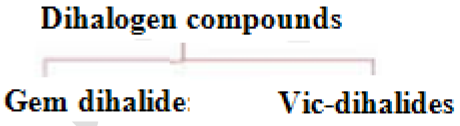


1-Halocyclohex-1-ene

b) Aryl halides:

Halobenzene

2) Classification of dihalogen compounds:

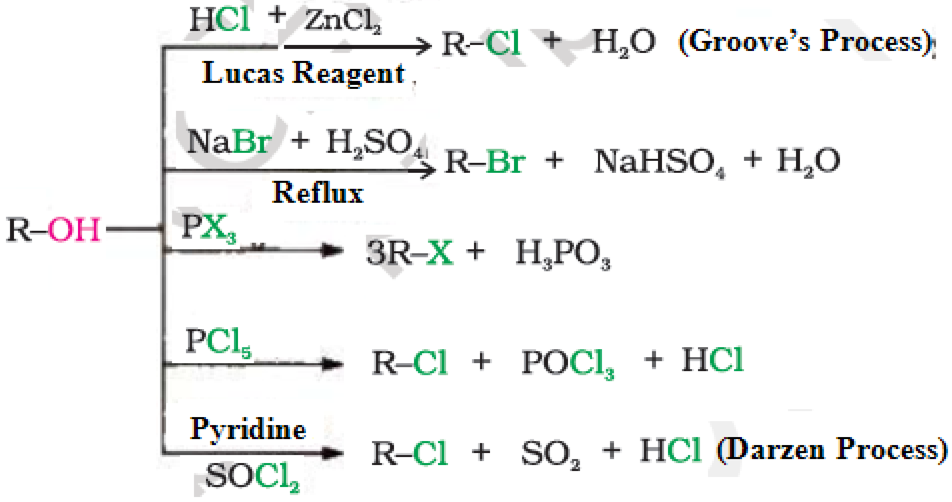


a) Gem dihalide: CH_3- $CHCl_2$

b) Vic-dihalides: Cl – CH_2- CH_2 – Cl

3. Preparation of Haloalkanes:

1) From alcohols: Haloalkanes are best prepared from alcohols, which are easily accessible.



- In Groove's method, $ZnC1_2$ is used to weaken the C-OH bond. In case of 3° alcohols, $ZnC1_2$ is not required.
- The reactivity order of halogen acids is $HI > HBr > HCl$.
- Darzen procedure is the best method for preparing alkyl halides from alcohols since both the by products (SO_2 and HCl) are gaseous and escape easily.

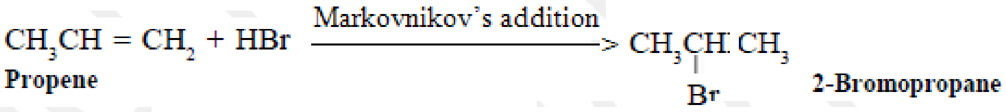
2) From Alkanes (Free Radical Halogenation of Alkanes):

$$CH_3CH_2CH_2CH_3 \xrightarrow[\text{or heat}]{Cl_2/\text{UV light}} CH_3CH_2CH_2CH_2Cl + CH_3CH_2CHClCH_3$$

3) From Alkenes:

i) Addition of Hydrogen Halides on Alkenes:

$$\underset{\text{Ethene}}{CH_2 = CH_2} + HBr \longrightarrow \underset{\text{Bromoethane}}{CH_3 - CH_2 - Br}$$



$$\underset{\text{Propene}}{CH_3CH = CH_2} + HBr \xrightarrow{\text{Markovnikov's addition}} CH_3\underset{Br}{\underset{|}{C}H}CH_3 \quad \text{2-Bromopropane}$$

$$\underset{\text{Propene}}{CH_3CH = CH_2} + HBr \xrightarrow[\text{benzoyl peroxide}]{\text{Anti Markovnikov's addition}} \underset{\text{1 – Bromopropane}}{CH_3CH_2 - CH_2 - Br}$$

ii) Addition of Halogens:

4) Hunsdiecker's Reaction: This method applied for decrease the number of carbon atoms.

$$R\text{-}COOAg + Br_2 \xrightarrow[\text{Reflux}]{CCl_4} R\text{-}Br + AgBr + CO_2$$

5) Halide exchange:

i) By Finkelstein Reaction:

$$R–X + NaI \xrightarrow{\text{dry acetone}} R–I + NaX \qquad X=Cl, Br$$

ii) By Swarts Reaction: It's carried out in the presence of metallic fluoride like AgF, Hg_2F_2, COF_2 or SbF_3.

$$H_3C–Br + AgF \longrightarrow H_3C–F + AgBr$$

4. Physical Properties of Haloalkanes

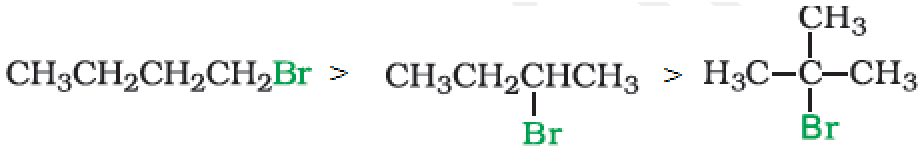
1) Boiling point:

i) Haloalkanes have higher boiling points as compared to those of corresponding alkanes.

ii) Increase in size and mass of the halogen atom the magnitude of van der Waals forces of attraction increases so the order of B.P. is in the following order-

$$R – I > R – Br > R – CI > R – F$$

iii) The boiling points of isomeric Haloalkanes decreases with increase in branching-



$$CH_3CH_2CH_2CH_2Br > CH_3CH_2\underset{Br}{\underset{|}{C}}HCH_3 > H_3C-\overset{CH_3}{\overset{|}{\underset{Br}{\underset{|}{C}}}}-CH_3$$

iv) $CH_3CH_2CH_2X > CH_3CH_2X > CH_3X$

2) Bond strength: Bond strength of Haloalkanes decreases as the size of the halogen atom increases. Thus, the order of bond strength is

$$CH_3F > CH_3Cl > CH_3Br > CH_3I$$

3) Dipole moment: It decreases as the electronegativity of the halogen decreases.

4) Solubility: Haloalkanes though polar but are insoluble in water as they do not form hydrogen bonding with water. They are soluble in organic solvent.

5) Density: Density order is

RI > RBr > RCl > RF (For the same alkyl group)

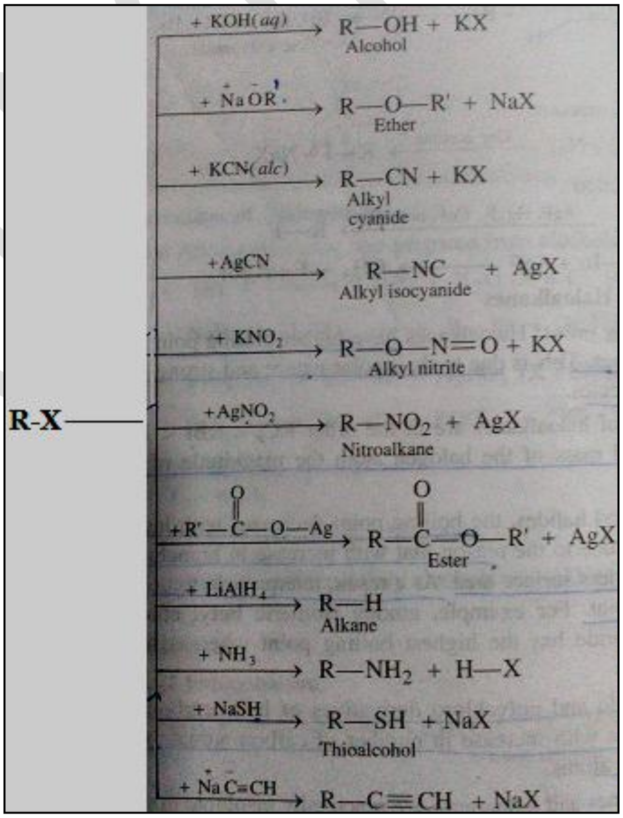
$CH_3I > C_2H_5I > C_3H_7I$

Density increase with increase number of halogen atoms $CCl_4 > CHCl_3 > CH_2Cl_2$

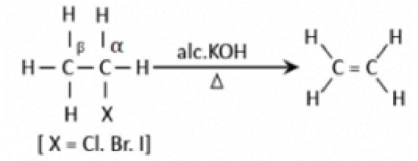
5. Chemical Properties of Haloalkanes:

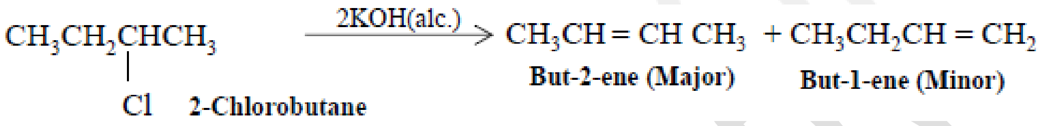
1) Nucleophilic Substitution Reactions:

$$\overset{-}{Nu} + -\overset{|}{\underset{|}{C}}\overset{\delta+\ \delta-}{-X} \longrightarrow -\overset{|}{\underset{|}{C}}-Nu + X^-$$



2) Elimination Reaction (dehydrohalogenation): When alkyl halides, reacted with alcoholic solution of potassium hydroxide, it eliminate one molecule of halogen acid (HX) to form alkenes. This is also example of beta elimination reaction because hydrogen atom is removed from beta carbon.





$$CH_3CH_2\underset{\displaystyle Cl}{\underset{|}{C}}HCH_3 \xrightarrow{2KOH(alc.)} CH_3CH=CH\,CH_3 + CH_3CH_2CH=CH_2$$

2-Chlorobutane **But-2-ene (Major)** **But-1-ene (Minor)**

In above reaction, the major product is formed according to the **Saytzeff's Rule.** Ease of dehydrohalogenation among halides: 3° > 2° > 1°

3) Reaction with metals:

i) Reaction with Magnesium: $CH_3CH_2Br + Mg \xrightarrow{\text{dry ether}} CH_3CH_2MgBr$ Grignard reagent

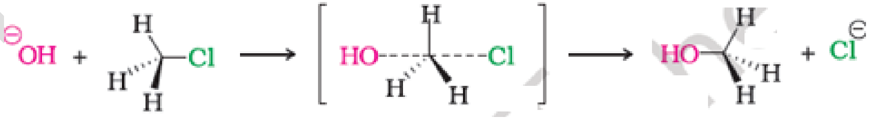
ii) Reaction with Sodium (Wurtz Reaction): $2RX + 2Na \xrightarrow{\text{dry ether}} RR + 2NaX$

Grignard reagent is never isolated in the solid state as it explodes in dry state. So it is used as ethereal solution.

6. Mechanism of Nucleophilic Substitution in Alkyl Halides: Nucleophilic substitution reactions are of two types-

1) S_N2 type (Bimolecular nucleophilic reactions):

- It proceeds in one steps and the reaction is of second order.
- Bimolecular (or 2nd order) means that the rate of an S_N2 reaction is directly proportional to the molar concⁿ of two reacting molecules, the alkyl halide 'substrate' and the Nucleophiles: Rate = k [RX] [Nu^-] (This is a rate equation and k is a constant).
- In this process the Nucleophile must hit the back side of the a-carbon. The bond form b/w Nucleophile with partially positive carbon and the leaving group, X^- , departs simultaneously.



Transition State

- The rate of an S_N2 reaction depends upon 4 factors:
  - a) The nature of the substrate (the alkyl halide)
  - b) The power of the nucleophile
  - c) The ability of the leaving group to leave
  - d) The nature of the solvent

- Methyl halide reacts quickly in S_N2 reactions but 3° does not react because the back side of a α-carbon in a 3° alkyl halide is completely blocked. So the reactivity order of alkyl halide towards S_N2 mechanism is-

$$\begin{matrix} 3^\circ & < & 2^\circ & < & 1^\circ & < & Me^\circ \\ R_3C\text{-}Br & & R_2HC\text{-}Br & & RH_2C\text{-}Br & & H_3C\text{-}Br \end{matrix}$$

- The α-carbon in vinyl and aryl halides is completely hindered due to the overlapping of p-orbitals that form the π bonds so these alkyl halides do not undergo S_N2 reactions.
- Rate of reaction in S_N2 mechanism depends on the strength of the attacking nucleophile. Strength of some common nucleophiles is

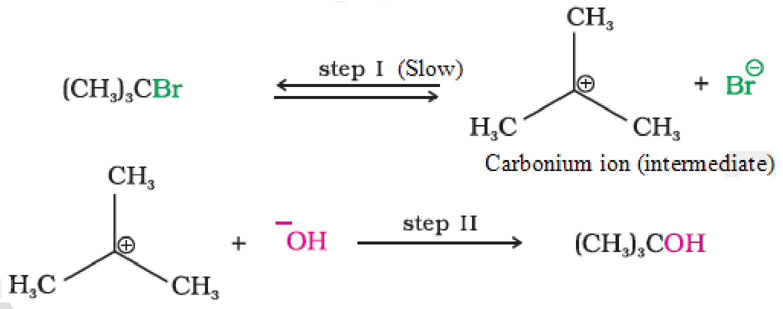
$$CN^- > I^- > OR^- > OH^- > CH_3COO^- > H_2O > F^-$$

- Non-polar solvents (hydrocarbons), strong nucleophiles and high concentration of nucleophiles favor S_N2 mechanism.

2) S_N1 type (Unimolecular nucleophilic reactions):

- It proceeds in two steps and the reaction is of first order.
- Unimolecular (or 1st order) means that the rate of an S_N1 reaction is directly proportional to the molar concentration of only one reactant i.e. the alkyl halide but not depend on the Nucleophiles:

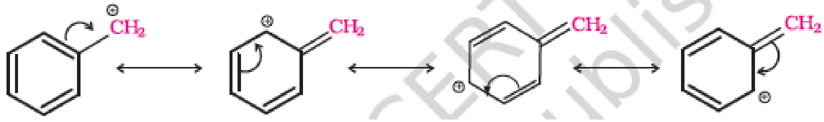
  Rate = k [RX] (This is a rate equation and k is a constant).
- In the 1st step, alkyl halide undergoes slow heterolysis to produce carbonium ion (an intermediate) and a halide ion. In the second step, Nucleophiles rapidly combines with the carbonium ion to complete the substitution reaction.



- Highly substituted alkyl halides form a more stable carbonium ion so the order of reactivity of substrates for S_N1 reactions is the reverse of S_N2 reactions.

$$\begin{matrix} 3^\circ & > & 2^\circ & > & 1^\circ & > & Me^\circ \\ R_3C\text{-}Br & & R_2HC\text{-}Br & & RH_2C\text{-}Br & & H_3C\text{-}Br \end{matrix}$$

- For the same reason, Allylic and Benzylic (phenylic) hailide show reactivity towards the S_N1 reaction because the carbocation thus formed gets stabilized through resonance as show



- So the overall order of reactivity of substrates for S_N1 reactions is the reverse of S_N2 reactions.

3°	>	2°	>	1°	>	vinyl	>	phenyl	>	Me°
R_3C-Br		R_2HC-Br		RH_2C-Br		$CH_2=CH$-Br		ϕ-Br		H_3C-Br

- Relative reactivity of alkyl halides for same alkyl group is: RI > RBr > RCI > RF
- Polar solvents (-OH or $-NH_2$ group), low concentration of nucleophiles and weak nucleophiles favor S_N1 mechanism.
- Thus the primary alkyl halides almost always react predominantly by S_N2 mechanism and tertiary alkyl halides react predominantly by S_N1 mechanism. Secondary alkyl halides may react by both the mechanism without much preference.

SN1 Reaction Vs SN2 Reaction

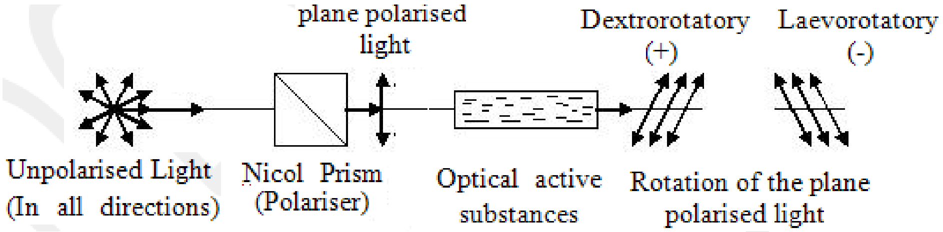
Sr.No.	S_N1 (Unimolecular)	S_N2 (Bimolecular)
1	Substract affects the reaction rate	Substract and nucleophile affects the reaction rate
2	Rate = k [RX]	Rate = k [RX] [Nu-]
3	Has only one step	Has two steps
4	A stable carbocation form during the reaction	Carbocation not form during the reaction
5	Carbocation stability	Steric hindrance
6	Order of reactivit of alkyl halide 3° > 2° > 1°	Order of reactivit of alkyl halide 1° > 2° > 3°
7	No effect on reaction rate (Weak or neutral nucleophile favored the reaction rate)	Strong nucleophile cause fast reaction rate
8	Product can be racemic mixture since retention or inversion of stereochemistry can happen	Inversion of stereochemistry happen all the time
9	Favored by polar (polar protic) solvent (e.g. alcohols)	Favored by non polar (aprotic) solvent (e.g. acetone)

7. Stereochemical aspects of nucleophilic substitution reactions: In case of optical active halide, S_N2 reactions proceeds with complete Stereochemical inversion while S_N1 reaction proceeds with racemisation.

For understand this concept, require learning following basic principals or terms of stereochemistry

1) Stereoisomerism: Molecules that have the same molecular formula and sequence of bonded atoms (constitution), but differ in the three-dimensional orientations of their atoms in space is called Stereoisomerism.

2) Plane polarised light: Polarised light is light that vibrates in a single direction due to its passage through a polariser. It is obtained by passing a monochromatic light through a Nicol prism.

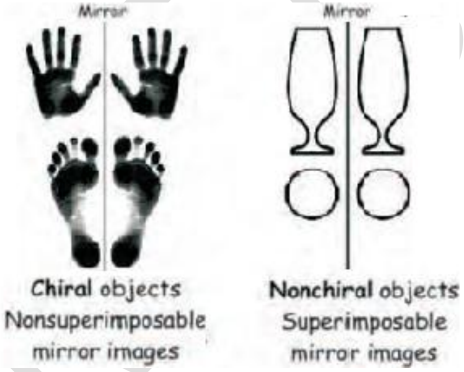


3) Optical active substances: Those substances which rotate the plane of polarisation, when it is passed through their solution are called optical active substances and this phenomenon is called optical activity.

4) Optical rotation: The property of rotating the plane of polarisation either towards left (laevorotatory) or towards right (dextrorotatory) is called optical rotation.

5) Asymmetric molecule (Asymmetric carbon): The carbon atom which attached with four different groups of substituents is called asymmetric molecules or carbon.

6) Chiral: An object which is non-superimposable on its mirror image is said to be chiral. The property of being chiral is known as chirality.



7) Enantiomers: The stereoisomers which are non-superimposable mirror images are called Enantiomers. Enantiomers (substrate) rotate the plane of polarised light to the same extent but in opposite direction.

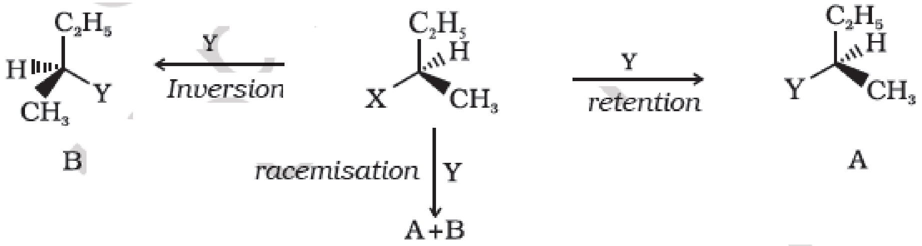
8) Retention: If the relative configuration of atoms (groups) around a stereo centre remains the same before and after the reaction, the reaction is said to proceed with retention of configuration.

9) Inversion: If the relative configuration of atoms (groups) around a stereo centre in the product is opposite to that in reactant, the reaction is said to proceed with inversion of configuration.

10) Racemic mixture: A mixture containing two enantiomers in equal proportions will have zero optical rotation, as the rotation due to one isomer will be cancelled by the rotation of other isomer. Such a mixture is known as racemic mixture (racemic modification). It represent by prefixing dl or (±) before the name. For example (±) butan-2-ol.

11) Racemisation: The process of conversion of enantiomers into a racemic mixture is known as racemisation.

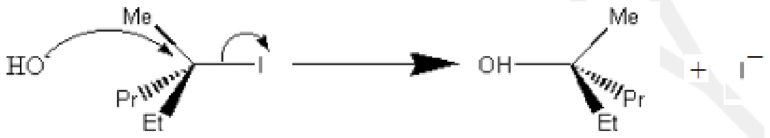
12) Inversion, retention and racemisation: There are three outcomes for a reaction at an asymmetric carbon atom as following



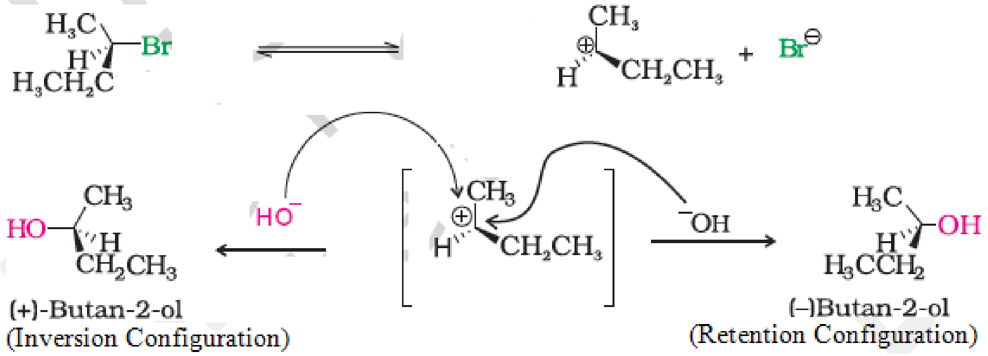
If only compound A is obtained, the process is called retention of configuration.
If only compound B is obtained, the process is called inversion of configuration.
If a 50:50 mixture of compound A and B is obtained, then the process is called racemisation and the product is optically inactive, as one isomer will rotate light in the direction opposite to another.

13) S_N2 and S_N1 mechanism by Stereochemical theory: In case of optical active halide, S_N2 reactions proceeds with complete Stereochemical inversion while S_N1 reaction proceeds with racemisation.

The product formed during S_N2 reactions has the inverted configuration as compared to the reactant because the nucleophile attaches on the opposite side of the halogen atom. It can be explain by following examples



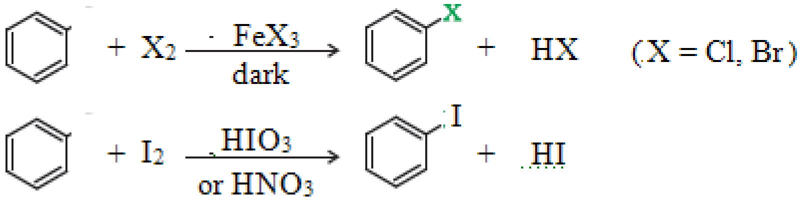
In case of optical active halide, S_N1 reaction proceeds with racemisation because the carbocation formed in the first step being sp^2 hybridised is planar ((achiral) so the possibility of attack the nucleophile may be able from both side resulting in a mixture of products, one having the same configuration (nucleophile attaching on the same position as halide ion) and another having opposite configuration (nucleophile attaching on the opposite side to halide ion). It can be explained by hydrolysis of optically active 2-bromobutane, which results in the formation of (±)-butane-2-ol.



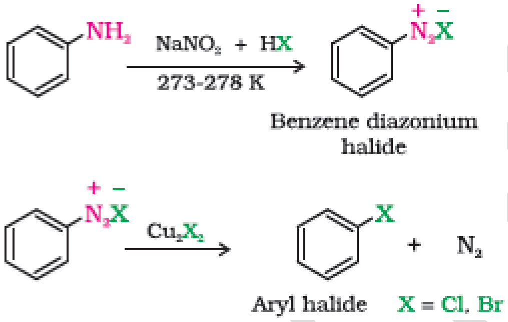
Aryl Halide

1. General Methods of Preparation of Aryl Halides:

1) By direct Halogenation of Benzene: It is an electrophilic substitution reaction.



2) Sandmeyer's Reaction (From Benzene Diazonium Salt):



2. Physical Properties of Aryl Halides:

1) Aryl halides are colorless liquids or colorless solids with characteristic odour.

2) Boiling point generally increases with increase in the size of aryl group or halogen atom.

Boiling point order is: Ar – I > Ar – Br > Ar – Cl > Ar – F

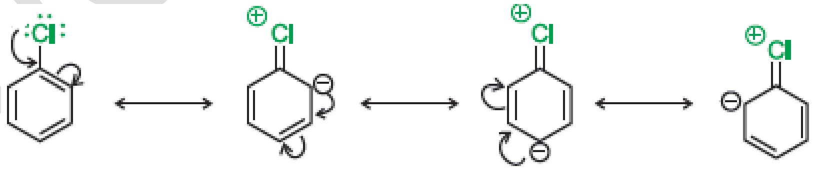
3) The melting point of p -isomer is more than ortho and meta isomer. This is because of more symmetrical nature of p-isomer.

4) Due to resonance in chlorobenzene, C-CI bond is shorter and hence, its dipole moment is less than that of cyclo hexyl chloride.

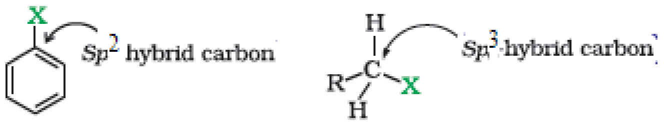
3. Chemical Properties of Aryl Halides:

1) Nucleophilic Substitution Reaction: Aryl halides are less reactive towards nucleophilic substitution reaction. Their low reactivity is attributed due to the following reasons:

i) Due to resonance: C-X bond has partial double bond character. As a result, the bond cleavage in Haloarene is difficult than Haloalkane so they are less reactive toward nucleophile substitution reaction.



ii) Difference in hybridisation in C-X bond:

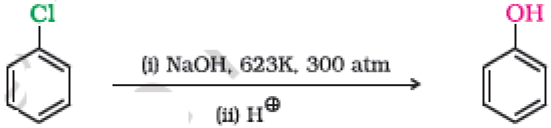


iii) It is less likely approach to Nucleophile with electron rich arenes due to the possible repulsion.

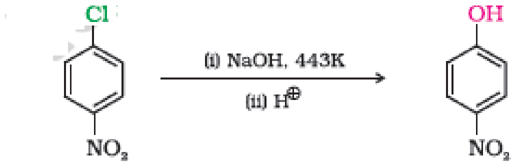
iv) Instability of phenyl carbocation: The phenyl carbocation formed due to self ionisation will not be stabilized by resonance and hence, S_N1 mechanism is ruled out.

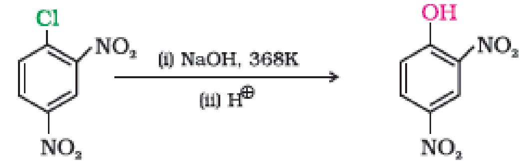
But at high temperature and pressure several nucleophilic substitution reaction are carried out like as

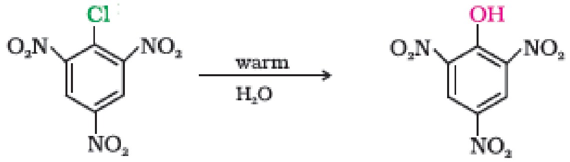
Dow's Methods:



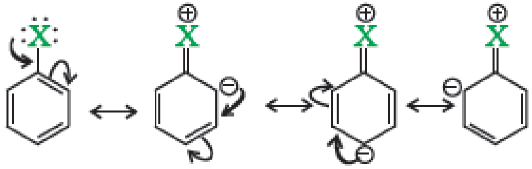
If aryl halides having electron withdrawing groups (like – NO_2, $-SO_3H$, etc.) at ortho and para positions, those increase the reactivity of Haloarenes and undergoes nucleophilic substitution reaction easily.





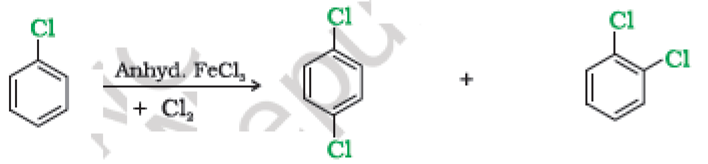


2) Electrophilic Substitution Reactions: In Haloarenes, halogens are slightly deactivating group as compared to benzene due to it's –I effect but ortho, para directing, hence electrophilic substitution reactions in Haloarenes occur slowly as compare to benzene.



Followings are main electrophile substitution reactions of aryl halides-

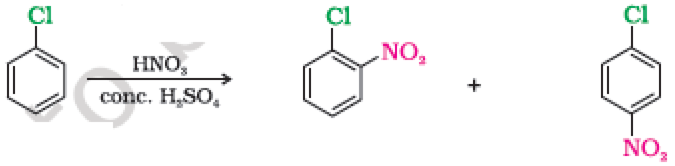
(i) Halogenation



1, 4-Dichlorobenzene (Major)

1, 2-Dichlorobenzene (Minor)

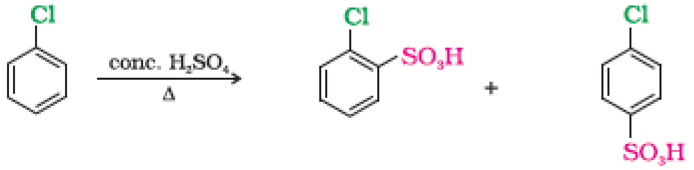
(ii) Nitration



1-Chloro-2-nitrobenzene (Minor)

1-Chloro-4-nitrobenzene (Major)

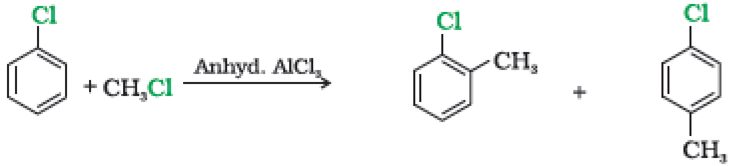
(iii) Sulphonation



2-Chlorobenzenesulfonic acid (Minor)

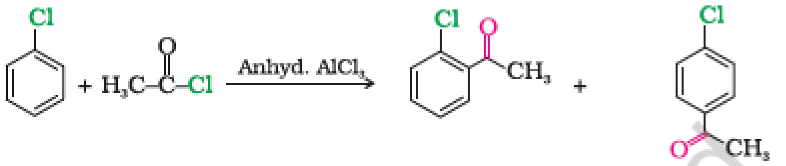
4-Chlorobenzenesulfonic acid (Major)

(iv) Friedel-Crafts reaction



1-Chloro-2-methylbenzene (Minor)

1-Chloro-4-methylbenzene (Major)



2-Chloroacetophenone (Minor)

4-Chloroacetophenone (Major)

3) Reaction with Metals:

(i) Wurtz-Fittig reaction:

(ii) Fittig reaction:

Diphenyl

Polyhalogen Compounds

1. Dichloromethane (Methylene chloride, CH_2Cl_2): It is widely used as a solvent, as a propellant in aerosols. Direct contact of dichloromethane in humans causes intense burning and milk redness of the skin. It is prepared by halogenations of methane.

$$CH_4 + 2Cl_2 \xrightarrow{h\upsilon} CH_2Cl_2 + 2HCl$$

2. Trichloromethane (Chloroform, $CHCl_3$): It is prepared as

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

Properties:

- Oxidation of $CHCl_3$ gives poisonous gas phosgene (carbonyl chloride).

$$CHCl_3 + O_2 \rightarrow 2COCl_2 + 2HCl$$

- To avoid this oxidation $CHCl_3$ store in dark brown bottles and filled up to the top. 1% ethanol is added to chloroform which converts harmful phosgene gas into diethyl carbonate.

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

- $CHCl_3$ is widely used in the production of freon refrigerant R-22.
- On nitration, it gives tear producing insecticide substance chloropicrin.

3. Tri-iodo methane (Iodoform, CHI_3): Iodoform when comes in contact with organic matter, decomposes easily to free iodine. Earlier it used as antiseptic, due to its objectionable smell, it has been replaced by other formulations containing iodine. It prepared by iodoform method-

$$CH_3COCH_3 + 3I_2 + 4NaOH \rightarrow CHI_3 + CH_3COONa + 3NaI + 3H_2O$$

4. Tetrachloro methane (Carbon Tetrachloride, CCl_4): CCl_4 is a colorless, non-inflammable, poisonous liquid, soluble in alcohol and ether.

Uses: Carbon tetrachloride is used as a solvent for oils, fats and resins. It also used for dry cleaning and as fire extinguisher under the name 'pyrene'. It is prepared as

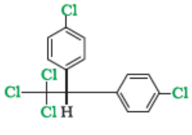
$$CH_4 + 4Cl_2 \xrightarrow{h\upsilon} CCl_4 + 4HCl$$

5. Freons: The chlorofluorocarbon compounds of methane and ethane are collectively known as freons. Dichlorodifluoromethane (Freon-12) is one of the most common freons in industrial use. It is manufactured from CCl_4 by Swarts reaction.

$$CCl_4 + 2SbF_3 \xrightarrow[SbCl_5]{Heat} 2SbCl_3 + 3CCl_2F_2 \quad (\text{Freon-12})$$

They are extremely stable, unreactive, non toxic, non corrosive and easily liquefiable gases. Uses: These are usually produced for aerosol propellants, refrigeration and air conditioning purposes. Use of freons is being reduced and banned because they are responsible for ozone layer depletion.

6. DDT (p, p'-Dichlorodiphenyltrichloroethane): DDT is the first chlorinated organic insecticide. Its stability and fat solubility is a great problem. It is prepared from chloral and chlorobenzene in the presence of conc. H_2SO_4·



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