# 6. 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].

## Classification

I) On the basis of number of halogen atoms:

Based on this, haloalkanes and haloarenes are classified as mono, di or polyhalogen compounds. Monohalogen compounds contain only one halogen atom, dihalocompounds contain 2 halogen atoms and polyhalogen compounds contain more than 2 halogen atoms. II)Compounds containing $sp^3$ C-X bond: They include:

a) Alkyl halides or haloalkanes (R-X): Here the halogen atom is directly bonded to an $sp^3$ hybridized C atom of an alkyl group. They are further classified as primary, secondary or tertiary according to the nature of carbon to which halogen atom is attached. Their general formula may be:
Primary haloalkane: R-CH2-X
Secondary haloalkane: R2CH-X
Tertiary haloalkane: R3C-X

b) Allylic halides: Here the halogen atom is bonded to an $sp^3$ hybridized carbon atom next to a C = C bond. E.g.: CH2=CH-CH2X

c) Benzylic halides: These are compounds in which the halogen atom is bonded to an $sp^3$ hybridized carbon atom next to an aromatic ring. E.g.: C6H5-CH2-X III)Compounds having $sp^2$ C-X bond: They include

a) Vinylic halides: Here the halogen atom is directly bonded to an $sp^2$ hybridized carbon atom of a C=C bond. E.g.: CHFCH-X

b) Aryl halides: Here the halogen atom is directly bonded to an $sp^2$ hybridized carbon atom of an aromatic ring. E.g. : C6H5-X

## Nomenclature

Common name of alkyl halides is obtained by adding —yl halide to the word root (i.e. word root + yl halide) and the IUPAC name is obtained by adding the prefix 'halo' to the name of the parent alkane (i.e. halo + alkane). Some examples are:

| Compound | Common Name | IUPAC Name |
|---|---|---|
| cH3-a | Methyl chloride | Chloromethane |
| CH3-CH2-Br | Ethyl bromide | Bromoethane |
| CH3-CH2-CH2-Cl | n-Propyl chloride | I-Chloropropane |
| CH3-CHCl-CH3 | Isopropyl chloride | 2-Chloropropane |
| CH3-CH2-CH2-CH2-Br | N-Butyl bromide | I-Bromopropane |
| (CH3)3C-Cl | tert-butyl chloride | 2-Chloro-2-methyl propane |

| | | |
|---|---|---|
| (CH3)2CH-CH2-Br | Isobutyl bromide | I-Bromo-2-methylpropane |
| (CH3)3C-CH2-Cl | Neopentyl chloride | I-Chloro-2,2-dimethylpentne |
| C6H5-Cl | Chlorobenzene | Chlorobenzene |
| C6H5-CH2-1 | Benzyl iodide | Iodophenylmethane |

Methods of preparation

I From alcohols:

a) By the action of concentrated halogen acids on alcohols in presence of anhydrous ZnC12 as catalyst.

$$R\_OH + HX \xrightarrow{\text{Anhydrous ZnC12}} R\text{-}X + \}\text{-}.120$$

Reactions of primary and secondary alcohols with HI require the presence of anhydrous ZnCb, while tertiary alcohols do not require the catalyst.

b) Alkyl chlorides are obtained by the action of PC13, PC15 or SOC12 with alcohols.

3R-OH + PC13 →———————→3R_Cl + H3P03

R_OH + PC15→——————→R_CI + POC13 + HCI

R-OH + SOC12→———————→R_CI + S02 + HCI

Among these methods, the reaction with thionyl chloride (SOC12) is preferred, since the byproducts 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 PBr3 and P13 are unstable.

$X_2$ /Rep P

R-OH + — + R-X (where Br20r b) II)From Hydrocarbons

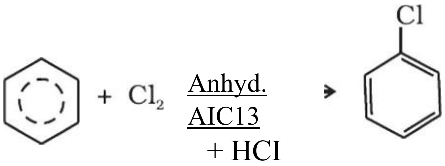
a) Free radical halogenation:

Alkanes react with chlorine or bromine in presence of sunlight; we get a mixture of mono, di and polyhaloalkanes. For e.g. when methane is chlorinated in presence of sunlight (uv light), we get a mixture of 4 products namely monochloromethane (methyl chloride, CH3-Cl), dichloromethane (methylene chloride, CH2C12), trichloromethane (chloroform, CHC13) and tetrachloromethane (carbon tetrachloride, cc14).

$$CH4 + C12\ 9 \xrightarrow{\text{uv light or heat}} CH3Cl + CH2C12 + CHC13 + CC14$$

b) Electrophilic substitution:

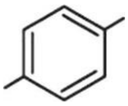
Benzene or its derivatives when heated with C12 or Br2 in presence of iron or Lewis acids like anhydrous FeC13 (ferric chloride) or AIC13, we get aryl chlorides or bromides.



Chlorobenzene

CH3 $\xrightarrow{Fe}$ CH3CH3

dark x x o -



Halotoluene P-Halotoluene

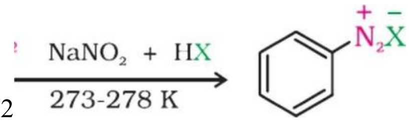
The ortho and meta isomers can be easily separated due to their large difference in melting point.

For the preparation of aryl iodides, arenes are treated with 12 in presence of an oxidising agent like HN03 or H104 (periodic acid) to oxidise the HI formed during the reaction.

c) Sandmeyer's reaction:

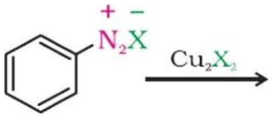
Aromatic primary amines when treated with mineral acids like HCI and sodium nitrite (NaN02) at cold condition (O — $5^0$C), an aromatic diazonium salt is formed. This reaction is called Diazotisation.

NH2



Benzene diazonium
halide

When a diazonium salt is treated with HX in presence of cuprous halide (Cu2X2), we get a halobenzene. This reaction is called Sandmeyer's reaction.



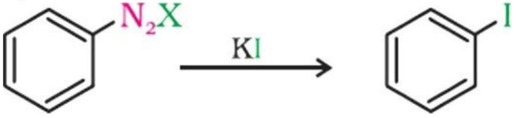
X

Aryl halide

X = Cl, Br

Note: If the cuprous halide is replaced by copper powder, the reaction is called Gattermann's reaction.

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



d) From alkene:

i) Addition of hydrogen halide (HX): Alkenes add HX (HCI, HBr or HI) to form alkyl halides. In the case of unsymmetrical alkenes, the addition takes place according to Markownikoff's rule. [The rule states that "when an unsymmetrical reagent is added to an unsymmetrical alkene, the negative part of the addendum (adding molecule) gets attached to the carbon containing lesser number of hydrogen atoms"] •

e.g. $CH_3$-CH=$CH_2$ + HBr→——————→ $CH_3$-$CH_2$-$CH_2$Br + CH3-CHBr-CH3 (minor) (major) ii) Addition of halogen: Alkenes add halogen to form vicinal dihalides (2 halogen atoms on adjacent C atoms). For e.g. addition of bromine in CC14 to an alkene results in the formation of vicinal dibromides and also in the discharge of the reddish brown colour of Br2 in CC14. So this is used as a test for unsaturation.

e.g. CHFCH2 + Br2 $\xrightarrow{cc14}$ * CH2Br- CH2Br

(1,2-dibromoethane)

Ill) Halogen Exchange Reactions

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

R-X + Na1 *-—— ----→ R-I + Nax (where X = Cl, Br)

CH3_CH2-Br + Nal →———————→ $CH_3$-$CH_2$-I + Nax

b) Swarts reaction: This method is used for the preparation of alkyl fluorides. Here alkyl chloride or bromide is treated with a metallic fluoride like AgF, Hg2F2, CoF2 or SbF3, to get alkyl fluoride.

AgF →–— —9 R-F + (where X = Cl or Br)

2 CH3-CH2-Br + CoF2 $^9$ -----+ 2 CH3-CH2-F + CoBr2

Physical Properties

Melting and boiling points:

In haloalkanes, the C-X bond is polar due to the greater electronegativity of halogen atom. Due to greater polarity and higher molar mass, the inter molecular forces of attraction (dipole-dipole and van der Waals forces) are strong and so they have higher melting and boiling points than hydrocarbons of comparable molar mass.

For the same alkyl group, the boiling points of alkyl halides decrease in the order: Rl> RBr> RCI> RF. This is because with the increase in size and mass of halogen atom, the magnitude of van der Waal forces increases.

The boiling points of isomeric haloalkanes decrease with increase in branching. This is because as branching increases, the surface area of the molecule decreases. So the van der forces decreases and hence the b.p.

Among isomeric dihalobenzenes, the para-isomers are high melting as compared to their ortho and meta-isomers. It is due to symmetry of para-isomers that fits in crystal lattice better as compared to ortho- and meta-isomers.

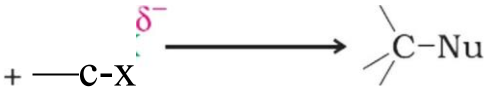
Solubility

The haloalkanes are only very slightly soluble in water. This is because they cannot form hydrogen bonds with water (except alkyl fluorides).

CHEMICAL REACTIONS OF HALOALKANES

i) 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]. In general these reactions can be represented by:



The important Nucleophilic substitution reactions of haloalkanes are:

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

R-X + KOH(aq) →———————→ R-OH + KX

e.g.: CH3-CH2-Br+ KOH(aq) →———————→ $CH_3$-$CH_2$-OH $_{+\ 1<Br}$

2. Reaction with water: Haloalkanes react with water to form alcohols.

R-X + 1-420 →———————→ R-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-X + R-0Na →------→ R-O-R + KX

   CH3_Br + $CH_3\text{-}CH_2\text{-}ONa$ →------→ $CH_3\text{-}O\text{-}CH_2\text{-}CH_3$+ NaBr

4. Reaction with Sodium iodide (Nal) [Finkelstein Reaction]: Alkyl halides (Chlorides or Bromides) react with sodium alkoxide to form alkyl iodides.

   R-x + Nal →------→ R-I + NaX [X = Cl or Br]

5. Reaction with ammonia [Hoffmann's reaction]: Alkyl halides react with alcoholic ammonia to give a mixture of $1^0$, $2^0$ and $3^0$ amines and quaternary ammonium salt.

   R-X + NH 3 →------→ R-NH2 + R2NH + R3N +$R_4N^+X^-$

   If ammonia is in excess, only primary amine is formed.

6. Reaction with KCN: Alkyl halides react with alcoholic KCN to give alkane nitriles (R-CN).

   R-X+ KCN →------→ R-CN+ KX

7. Reaction with Silver cyanide (AgCN): Alkyl halides react with AgCN to give alkyl isocyanides or carbyl amines (R-NC).

   R-X + AgCN — R-NC +AgX

   CN- is an ambident nucleophile. i.e. here both C and N contain lone pair of electrons and can bind to the carbon atom of the alkyl group either through C or through N. Another e.g. is N02.

   Reaction with KCN gives alkyl cyanides. This is because KCN is mainly ionic and gives CN- ions in solution. So both C and N are free to donate electron pairs. But C — C bond is stronger than C — N bond. So cyanides are formed as the major product. But AgCN is mainly covalent and only N is free to donate an electron pair. So isocyanides are the main product.

8. Reaction with Potassium nitrite (KN02): Alkyl halides react with KN02 to give alkane nitrite (R-ONO). R-X + $KNO_2$ →------→ R_ONO + KX

9. Reaction with Silver nitrite (AgN02) : Alkyl halides react with AgN02 to give nitroalkane (R-N02)

   R-X+ AgN02 →------→ R_N02 +AgX

10. Reaction with Silver salt of carboxylic acid (Hunsdiecker reaction) : Alkyl halides react with Silver salt of carboxylic acid (R-COOAg) to give esters (R-COOR).

    R-X + R-COOAg 9-----* R-COOR + Agx

11. Reduction: Alkyl halides when reduced with lithium aluminium hydride (LiAlH4) to give alkane.

    R-X + [H] $\xrightarrow{\text{LiAIH4}}$ R-H + HX

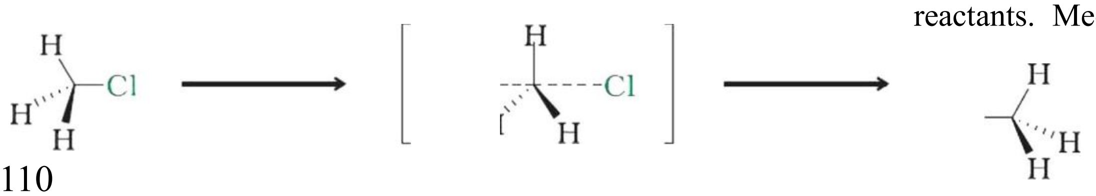
## Mechanism of Nucleophilic Substitution Reactions

There are two types of mechanisms: Substitution Nucleophilic bimolecular (SN2) and Substitution Nucleophilic unimolecular (SNI)

1. Substitution Nucleophilic Bimolecular (SN2) 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. As the reaction proceeds, the bond between the nucleophile and the carbon atom starts forming and the bond between carbon atom and leaving group (the halogen atom) weakens. In the case of optically active alkyl halides, during this process, the configuration of carbon atom inverts and hence this process is called as inversion of configuration. In the transition state, the carbon atom is simultaneously bonded to five atoms and therefore is unstable.

An example is the reaction between CH3Cl 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:



Oll

+HO -110

H

Since this mechanism requires the approach of the nucleophile to the carbon bearing the leaving group, the presence of bulky substituents on or near the carbon atom decreases the rate of this reaction. Thus the order of reactivity of alkyl halides towards SN2 reaction is: Primary halide > Secondary halide > Tertiary halide.

2. Substitution nucleophilic unimolecular (SNI):

SNI reactions are generally carried out in polar protic solvents (like water, alcohol, acetic acid, etc.). Here the 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.

(CH3)3CBr 011 ..-1____________________* (CH3)3COH+ $Br^-$

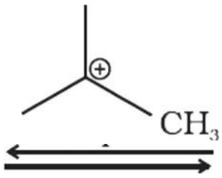
2-Bromo-2-methylpropane 2-Methylpropan-2-ol

This reaction occurs in two steps. In step l, 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 Il to form the product.

CH3

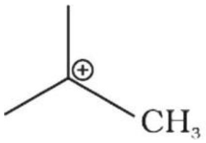
step I

(CH3)3CBr



wc

Cl1,



\+

OH

step I l

$(CH_3)_3COH$

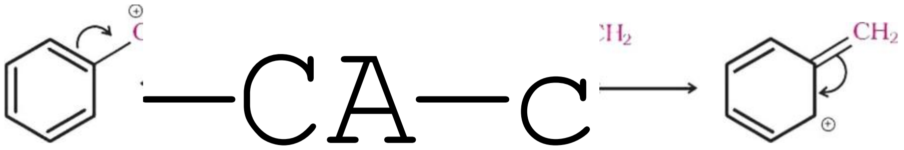
Hgc

Thus in SNI reaction, there is an intermediate called carbocation. The greater the stability of the carbocation, the greater will be the rate of the reaction. In case of alkyl halides, 3 $^0$ alkyl halides undergo SNI reaction very fast because of the high stability of 3 $^0$ carbocations. So the order of reactivity of alkyl halides towards SNI reaction is: 3 $^0 > 2^0 > 1^0$.

Allylic and benzylic halides show high reactivity towards the SNI reaction. This is because of the higher stability of the carbocation formed. The allyl and benzyl halides are stabilized through resonance as follows:

$$H_2C=\underset{H}{C}-\overset{\oplus}{C}H_2 \longleftrightarrow H_2\overset{\oplus}{C}-\underset{H}{C}=CH_2$$

Allyl carbocation



Benzyl Carbocation

For both the mechanisms, the reactivity of halides follows the order: R—I> R—Br>R—Cl>>R—F.

## Differences between SNI and SN2 reactions

| SNI Reaction | SN2 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 $1^0 > 2^0 >$ 30 |

## 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. anticlockwise direction), it is called laevo rotatory or I-form or —form. The d and I 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 [CH3 — CHCI — CH2 — CH3]

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

Other examples: 2-butanol [CH3 — CHOH —CH2 — CH3] 2-bromopropanoic acid [CH3 — CHBr — COOH]

Lactic acid [CH3 - CHOH - COOH]

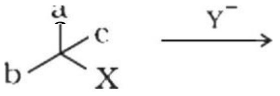
Enantiomers

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

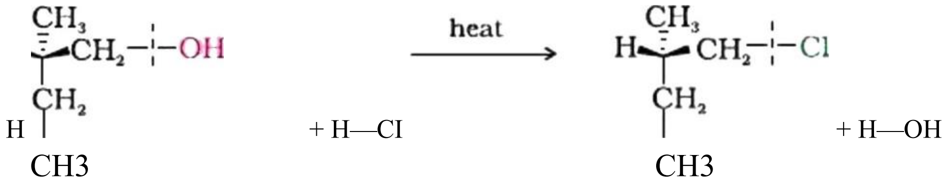
An equimolar mixture of d and I form of a compound has zero optical rotation and such a mixture is called racemic mixture or racemic modification. It is denoted by dl or (2). Here the rotation due to one isomer is cancelled by the rotation due to the other isomer. The process of conversion of an enantiomer 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).



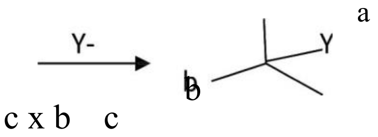
In general, if during a chemical reaction, no bond to the stereo centre is broken, the product will have the same configuration as that of the reactant. Such reactions always proceed through retention of configuration.

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



(—8-Methylbutan-1-01 (+)-1-Chloro-2-methylbutane

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.



Nucleophilic Substitution and Optical Activity

In the case of optically active alkyl halides, the product formed as a result of SN2 mechanism has the inverted configuration. This is because here the nucleophile attacks on the side opposite to that of the halogen atom.

H3C C113

HI • 13t- + -OH HO + Bt©coHiß
c€Ht3

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

In the case of optically active alkyl halides, SNI 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. Reaction of optically active 2-bromobutane with OH results in the formation of (+) 2-butanol, a racemic mixture.

OH_

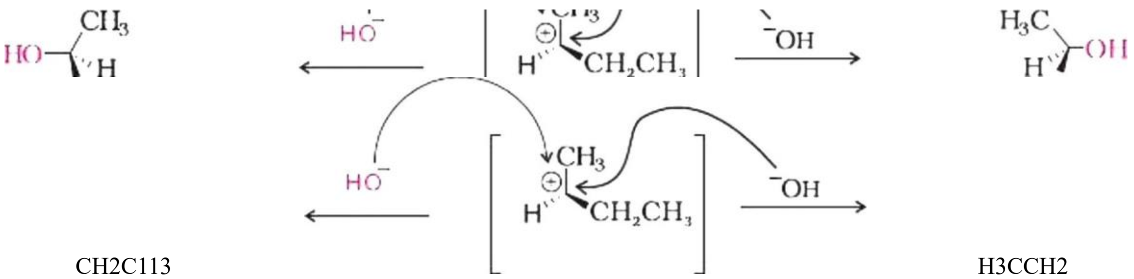
CH3- CHBr- CH3 →————→ CH3−CHOI-I - CHE CH3+ Br-

Step — I

li CH2CH3

H.,CH2C

Step – II



CH2C113 H3CCH2

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

**iiElimination Reactions**

Alkyl halides having ß-hydrogen atom when treated with alcoholic solution of KOH, they undergo elimination of one hydrogen halide molecule (dehydrohalogenation) to form alkenes. Since ß-hydrogen atom is eliminated, the reaction is also called ß-elimination.

e.g. : CH3CH2-Br + KOH (alc) -9-----* CH2 = a-b + KBr + H20

[Carbon on which halogen atom is directly attached is called a-carbon and the carbon atom adjacent to this carbon is called ß-carbon.]

If there is possibility of formation of more than one alkene during dehydrohalogenation reaction, the major product is selected by Zaitsev (Saytzeff) rule. The rule states that "in dehydrohalogenation reactions, if there is possibility of formation of more than one alkene the preferred product is that alkene which contains greater number of alkyl groups attached to the doubly bonded carbon atoms."

So if 2-bromobutane is treated with alcoholic KOH, 2-butene is formed as the major product.

CH3-CH2-CHBr-CH3 + KOH (alc) →——————→ CH3-CH2-CH=CH2 + CH3-CH=CH-CH3

2-Bromobutane I-butene (minor) 2-butene (major) iii) Reaction with metals

a) Alkyl halides react with Mg metal in ether medium to form alkyl magnesium halide (an organometallic compound) commonly called Grignard reagent.

ether
R-X + Mg →------——9 RMgX [Grignard reagent]
ether
CH3-CH2-Br + Mg 9------+ CH3-CH2MgBr

Grignard reagent is an example for organometallic compound. These are compounds in which carbon atom of an organic compound is directly bonded to metal atom. Other examples are tetraethyl lead, trimethyl aluminium etc.

In the Grignard reagent, the carbon-magnesium bond is covalent but highly polar and the magnesium halogen bond is ionic.

Grignard reagents are highly reactive and react with any source of proton (water, alcohols, amines etc) to give hydrocarbons (alkanes). It is therefore necessary to avoid even traces of moisture from a Grignard reagent.

R-MgX ı →-------→ R-H +MgX(OH) + 1-120
R-MgX + H →-------→ R-H +MgX(OR)
R-OH +R- →-------→ R-H +MgX($NH_2$)
MgX + NH3

b) Wurtz reaction: Alkyl halides react with sodium in dry ether to give alkanes with double the number of carbon atoms. This reaction is known as Wurtz reaction.

R-X +2 +X-R →-------→ R-R + 2NaX

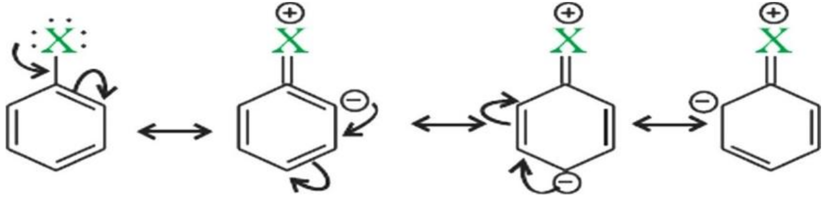
CH3-Br + Br-CH3 * — —- --→ $CH_3$-$CH_3$ + 2NaBr

Reactions of Haloarenes

1. Nucleophilic Substitution Reaction:

Aryl halides are less reactive towards Nucleophilic substitution reactions due to the following reasons:

i) Due to resonance effect: In haloarenes, the electron pairs on halogen atom are in conjugation with n-electrons of the ring and the following resonating structures are possible.



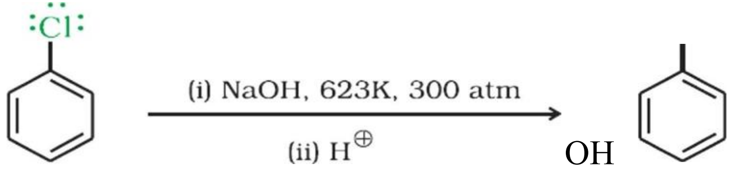
Due to resonance, the C—X bond acquires a partial double bond character. Since it is difficult to break a double bond, the replacement of halogen atom by other atoms is not easy. So haloarenes are less reactive towards nucleophilic substitution reactions.

ii) Due to the difference in hybridisation of carbon atom in C—X bond: In haloalkane, the halogen atom is attached to an sp $^{3}$ hybridised carbon while in haloarene, it is attached to an sp2 hybridised carbon. Due to the greater s-character of sp $^{2}$ hybridised carbon, it is more electronegative and can hold the electron pair of C—X bond more tightly than $sp^3$-hybridised carbon in haloalkane. So the C— X bond in haloarene is shorter than that in haloalkane. Since it is difficult to break a shorter bond than a longer bond, haloarenes are less reactive than haloalkanes towards Nucleophilic substitution reaction.

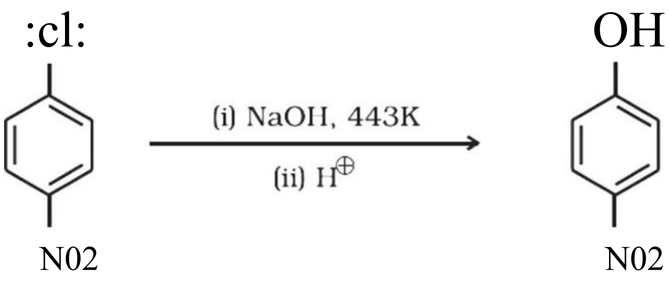
iii) Due to the instability of phenyl cation: In haloarenes, the phenyl cation formed as a result of self-ionisation will not be stabilized by resonance and therefore, SNI mechanism does not occur. iv) Due to the repulsion between nucleophile and electron rich benzene ring: Because of the possible repulsion, it is less likely for the electron rich nucleophile to approach electron rich arenes.

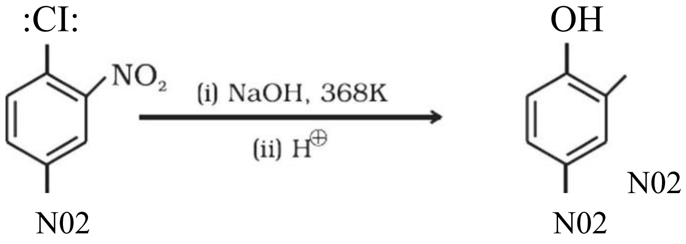
Replacement by hydroxyl group (Conversion to phenol)

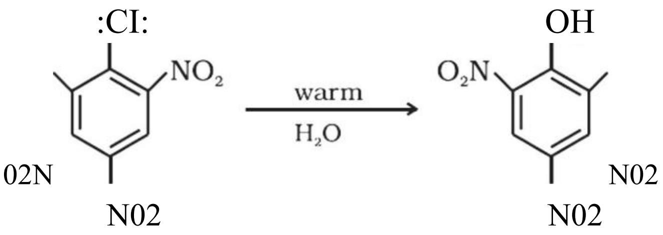
Chlorobenzene when heated with aqueous sodium hydroxide solution at a temperature of 623K and a pressure of 300 atmospheres followed by acidification, we get phenol.



The presence of an electron withdrawing group (-N02) at ortho- and para-positions increases the reactivity of haloarenes.



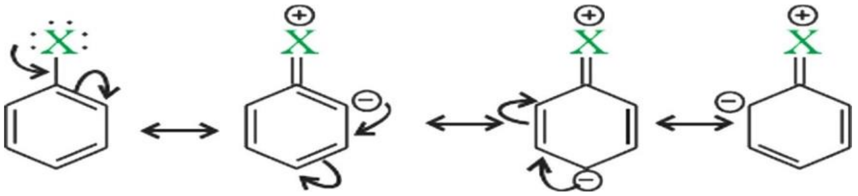




The effect is more when -N02 group is present at ortho and para- positions. However, no effect on reactivity is observed by the presence of electron withdrawing group at meta-position.

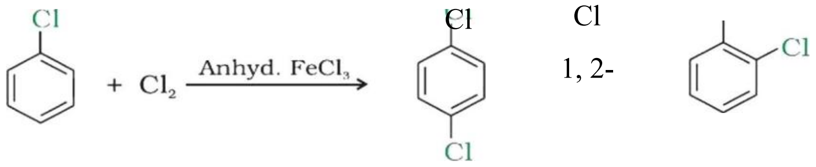
2. Electrophilic substitution reactions:

Haloalkanes are resonance stabilized as follows:



In the resonating structures, the electron density is greater on ortho-para positions. So the electrophile enters at these positions and hence halo group is an ortho-para directing group. Also, because of its electron withdrawing Inductive effect, the halogen atom has a tendency to withdraw electrons from the benzene ring. So it is a deactivating group. Hence the electrophilic substitution reactions in haloarenes occur slowly and require more vigorous conditions.

i) Halogenation: Haloalkanes react with halogen (Chlorine or bromine) in presence of anhydrous ferric chloride to form 0-dichlorobenzene and p-dichlorobenzene.



Cl

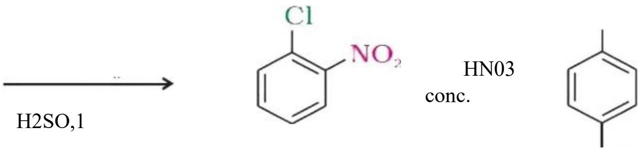
1, 2-

Dichlorobenzene (Minor)

1, 4-Dichlorobenzene

(Major) ii) Nitration: On nitration using Conc. HN03 and Conc. H2S04, chlorobenzene gives pnitrochlorobenzene as the major product.

ClCl



HN03

conc.

H2SO,1

I -Chloro-2-nitrobenzene

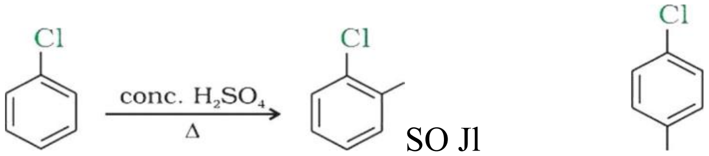
N02

(Minor)

1-Chloro-4-nitrobenzene

(Major)

iii)Sulphonation: On sulphonation using Conc. H2S04, chlorobenzene gives pchlorobenzenesulphonic acid as the major product



SO Jl

2-Chlorobcnzene sulfonic acid

sour

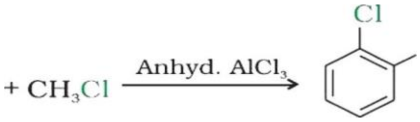
(Minor)

4-Chlorobenzene sulfonic acid

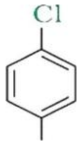
(Major)

iv)Friedel— Crafts Alkylation: Chlorobenzene when treated with methyl chloride (CH3-Cl) in presence of anhydrous AIC13, we get p-chlorotoluene as the major product.

Cl



CH3



1- Chloro-2-methylbenzene CH3

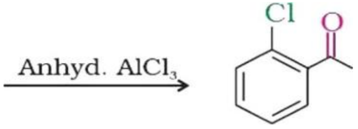
(Minor)

I -Chloro-4-mcthylbcnzcnc
(Maj or)

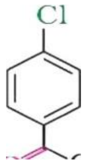
v) Friedel — Crafts Acylation: Chlorobenzene when treated with acetyl chloride (CH3-CO-Cl) in presence of anhydrous AIC13, we get p-chloroacetophenone as the major product.

Cl o

+ Hac -Cl



CH3



2-Chloroacetophcnone
(Minor)

O CH3

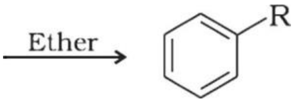
4-Chloroacetophenone
(Major)

3. Reaction with metals:

a) Wurtz-Fittig reaction: When a mixture of alkyl halide and aryl halide is treated with sodium in dry ether, an alkyl arene is formed and this reaction is called Wurtz-Fittig reaction.

X

+ Na + RX



For e.g. when Chlorobenzene is treated with methyl chloride in presence of metallic sodium in ether medium, we get toluene.

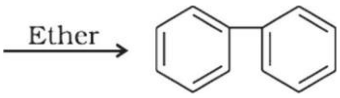
$$C_6H_5\text{-}Cl + 2Na + CH_3\_Cl \xrightarrow{\text{ether}} C_6H_5\text{-}CH_3 + 2NaCl$$

Chlorobenzene Toluene

b) Fittig reaction: Aryl halides when treated with sodium in dry ether, we get diaryls (diphenyls). This reaction is called Fittig reaction.

X

2 1



+ 2NaX

Diphenyl

## Polyhalogen compounds

Carbon compounds containing more than one halogen atom are usually referred to as polyhalogen compounds. Some polyhalogen compounds are:

1. Dichloromethane (Methylene chloride, CH2C12): It is widely used as a solvent, as a paint remover, as a propellant in aerosols, and as a process solvent in the manufacture of drugs. It is also used as a metal cleaning and finishing solvent.

2. Trichloromethane (Chloroform, CHC13): It is used as a solvent for fats, alkaloids, iodine and other substances. The major use of chloroform is in the production of the freon refrigerant R-22. Chloroform is slowly oxidised by air in the presence of light to an extremely poisonous gas, carbonyl chloride (COC12), also known as phosgene.

li qht
2CHC13 + 02 - c * 2COC12 + HCI

It is therefore stored in closed dark coloured bottles filled up to the neck in order to avoid air.

3. Tetrachloromethane (Carbon tetrachloride, CC14): It is used in the manufacture of refrigerants and propellants for aerosol cans. It is also used as feedstock in the synthesis of chlorofluorocarbons and other chemicals, pharmaceutical manufacturing, and general solvent use.
4. Freons: The chlorofluorocarbon compounds of methane and ethane are collectively known as freons. They are extremely stable, unreactive, non-toxic, non-corrosive and easily liquefiable gases. Freon 12 (CC12F2) is one of the most common freons in industrial use. It is manufactured from tetrachloromethane by Swarts reaction. These are usually produced for aerosol propellants, refrigeration and air conditioning purposes.
5. p,p'-DichlorodiphenyItrichloroethane(DDT): DDT was the first chlorinated organic insecticide. The effectiveness of DDT as an insecticide was first invented by Paul Muller. The structure of DDT is: