SECTION I
HALOAKANES

Compounds derived from alkanes by the replacement of one or more Hydrogen atoms by corresponding number of halogen atoms (fluorine, chlorine, bromine or iodine) are termed as haloalkanes.

Alkyl halides are represented by general formula $C_nH_{2n+1}X$, here $X$ is halogen atom.

**ORBITAL STRUCTURE**

In alkyl halides, carbon-halogen $\sigma$ bond is formed by overlap of $sp^3$ hybrid orbital of carbon and half filled valence $p$-orbital of halogen atom:

Haloalkanes may be classified on the basis of number of halogen atoms

1) Monohalogen derivatives
   - One halogen atom is attached to carbon atom. Its general formula is $C_nH_{2n+1}X$
   - Example $CH_3Cl$ (methyl chloride).

2) Dihalogen derivatives
   - These are derived by replacement of two hydrogen atoms by two halogen atoms
   - Dihalides derivatives are of three types

   a) Gem-dihalides
      - Halogen atoms are attached to same carbon atom. These are called alkylidene halides.
HALOALKANES AND HALOARENES

(b) Vic-dihalides
Halogen atoms are attached to adjacent (vicinal) carbon atoms. These are termed as alkylene halides.

\[ \text{CH}_3 - \text{CH} - \text{CH}_2 \]
\[ \text{Cl} \quad \text{Cl} \]

Propylene chloride (1,2-Dichloropropane)

(c) \(\alpha–\omega\) halides (terminal halides)
Halogen atoms are attached to terminal carbon atoms. These are also called polymethyl halides.

\[ \text{Br} - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{Br} \]

Trimethyl di bromide (1,3-dibromopropane)

(3) Trihalogen derivatives
Trihalogen derivatives are derived by replacing three hydrogen atoms by three halogen atoms. General formula is \(C_nH_{2n-1}X\)

\[ \text{CH}_3 - \text{CH}_2 - \text{C} - \text{Cl} \]
\[ \text{Cl} \]

1,1,1-trichloropropane
CLASSIFICATION OF MONOHALOGEN COMPOUNDS

(1) Alkyl halides are classified as primary $1^\circ$, secondary $2^\circ$, tertiary $3^\circ$ depending upon nature of carbon to which halogen is attached.

(2) Compounds containing $sp^3$, $C – X$ bond
   (a) Alkyl halides
       $CH_3 – CH_2 – CH_2 – Cl$ (1-chloropropane)
   (b) Allylic carbon
       Halogen atom attached to allylic carbon, i.e. carbon atom next to $C = C$.
       Example

(3) Compound containing $sp^2$, $C – X$ bond
   Vinylic halides
   In these halides, halogen atom is attached to vinylic carbon, i.e. one of the carbon atoms of $C = C$
   $CH_2 = CH – Cl$ (Chloroethene or vinyl chloride)
HALOALKANES AND HALOARENES

1-bromocyclohex-1-ene

(4) Compounds containing sp, C – X bond Haloalkynes
In these halides, the halogen atom is attached to one of the carbon atoms of
C ≡ C – Br (Bromoethyne)

ISOMERISM OF MONOHALOGEN COMPOUNDS
(1) Chain isomerism: This is due to different arrangement of carbon in alkyl group
CH₃ – CH₂ – CH₂ – CH₂ – Cl (1-chlorobutane)
CH₃ - CH - CH₂ -Cl
   \[CH₃\]
1-chloro-2-methylpropane

(2) Position isomerism: This is due to different position of halogen atom in the
molecules
CH₃ – CH₂ - CH₂ - CH₂ – Cl
CH₃ - CH₂ - CH - CH₂
   \[Cl\]
2- chlorobutane

(3) Optical isomerism: This is due to presence of an asymmetric carbon atom
(asymmetric carbon atom : all four substituent atoms or molecules attached to
carbon are different)
H
H₃C - C* - C₂H₅
   \[Cl\]
* asymmetric carbon atom

(4) Conformations: Haloalkanes can also form conformers due to free rotation of C-C
bond.
GENERAL METHODS OF PREPARATION

(1) From alcohol

(a) Action of hydrogen halides

1° alcohols follow S_N2 whereas 2° and 3° alcohol follow S_N1 mechanism. In these S_N mechanisms, the nucleophile (X-) attacks the protonated alcohol molecule with elimination of water.

\[
R - O\!H + H^+ \rightarrow R - O\!H_2
\]

\[
X + R - O\!H_2 \rightarrow R-X + H_2O
\]

Since nucleophilicity (i.e., tendency to donate electron pair to the carbon) of halide ion decreases in the order I^- > Br^- > Cl^-, the order of reactivity of halogen acid decreases in the same order HI > HBr > HCl

Order of reactivity of different alcohol is

Allyl > 3° alcohol > 2° alcohol > 1° alcohol

\[
R - OH \xrightarrow{HCl(\text{conc})\text{Anhyd ZnCl}_2} R - Cl + H_2O
\]

HCl do not require anhyd. ZnCl_2 for 3° alcohol because 3° are very reactive.

The mixture (1:1) of con. HCl and anhyd ZnCl_2 is called LUCAS reagent. It is used to distinguish 3°, 2°, 1° alcohols because their reactivity towards this reagent is 3° alcohol > 2° alcohol > 1° alcohol

\[
R - OH \xrightarrow{HBr/H_2SO_4\text{reflux}} R - Br + H_2O
\]

\[
R - OH \xrightarrow{KBr/H_2SO_4\text{reflux}} R - Br + H_2O
\]

The mixture of KBr and H_2SO_4 is not used in case of secondary and tertiary alcohol as they can cause dehydration.

Rearranged product may also be obtained due to hydrate or methyl shift in carbocation intermediate.
HALOALKANES AND HALOARENES

(b) Action of phosphorous halide

\[
R - OH \xrightarrow{\text{reflux}(57\%)} R - I + H_2O
\]

PBr\textsubscript{3} and PI\textsubscript{3} are obtained in situ by action of red phosphorus and bromine or iodine respectively.

4\textsuperscript{th} method gives good yield of 1\textsuperscript{o} haloalkanes but poor yields 2\textsuperscript{o} and 3\textsuperscript{o} haloalkanes because secondary and tertiary alcohol on heating forms alkene.

(c) Action of thionyl chloride

Darzen’s method

\[
R - OH + SOCl_2 \xrightarrow{\text{pyridine}} R - Cl + SO_2(g) + HCl(g)
\]

This method is preferred because other two byproducts are escapable gases.
SOBr₂ is less stable and SOI₂ does not exist. Thus R-Br and RI can’t be prepared by Darzen’s method.

d) Hunsdiecker reaction

\[
RCOOAg + Br₂ \xrightarrow{cCl₄(Reflux)} R - Br + CO₂(g) + AgBr
\]

\[
CH₃CH₂COOAg + Br₂ \xrightarrow{cCl₄(Reflux)} CH₃CH₂ - Br + CO₂(g) + AgBr
\]

The reaction gives product with one carbon atom less than fatty acid and yield of halide is 1° > 2° > 3°

(2) Halide exchange method

(a) Finkelstein reaction

\[
R - X + NaI \xrightarrow{acetone} R - I + NaX; X = Cl, Br
\]

NaCl or NaBr is precipitated in dry acetone. It facilitates forward reaction

(b) Swarts reaction

\[
CH₃ - Br + AgF \rightarrow CH₃ - F + AgBr
\]

Other than AgF, Hg₂F₂, CoF₂ or SbF₃ can also be used.

(3) Halogenation of alkanes

\[
R - H + X₂ \xrightarrow{hv} R - H + HX
\]

\[
CH₃CH₂CH₂CH₃ \xrightarrow{hv} CH₃CH₂CH₂CH₂Cl + CH₃CH₂CHClCH₃
\]

Iodination being reversible process requires the presence of oxidizing agent such as HIO₃, conc. HNO₃

a) Abstraction of hydrogen for a particular halogen follows order

Allylic > 3° > 2° > 1° > CH₄

b) Abstraction of halogen go the above reaction follows order

F₂ > Cl₂ > Br₂ > I₂

c) Direct halogeination proceed through free radical mechanism

\[
CH₄ + Cl₂ \xrightarrow{hv} CH₃Cl \xrightarrow{hv} CH₂Cl₂ \xrightarrow{hv} CHCl₃ \xrightarrow{hv} CCl₄
\]

(4) Addition of hydrogen halide to alkene

\[
-C = C^- + HX \rightarrow -C - C^- \rightarrow H X
\]

Reaction follows electrophilic addition mechanism

CH₃-CH = CH₂ + HBr \rightarrow CH₃CHBrCH₃ [ absence of peroxide, Markonikoff’s addition]

CH₃-CH = CH₂ + HBr \rightarrow CH₃CH₂CH₂Br [ presence of peroxide, Anti-Markonikoff ]
Haloalkanes and haloarenes

HCl and HI do not show peroxide effect.

Product may be obtained due to 1,2-hydride or 1,2-methyl shift.

Addition of bromine in CCl₄ to an alkene results in discharge of reddish brown colour of bromine constitutes an important method for detection of double bond in a molecule.

```
H H
\( \text{H} \text{C} = \text{C} \text{- H} + \text{Br}_2 \xrightarrow{\text{Br} - \text{CH}_2 - \text{CH}_2 - \text{Br}} \)
```

Physical Properties of Alkyl Halides

(1) Physical state and smell:

Haloalkanes, the lower members are colourless gas at room temperature. The other alkyl halides up to C₁₈ are colourless sweet smelling liquids while higher members are colourless solids.

(2) Boiling point:

(i) The boiling point increases from \( \text{R - F} \) to \( \text{R - I} \)

\( \text{R-F} < \text{R-Cl} < \text{R-Br} < \text{R-I} \)

Iodine has a larger surface area and outer electrons are loosely bounded. This makes iodine a highly polarizable atom. A polarizable atom increases London forces of attraction which causes an increase in boiling point.

(ii) Boiling point increases with increase in size of alkyl group

\( \text{CH}_3\text{X} < \text{C}_2\text{H}_6 < \text{C}_3\text{H}_7\text{X} \text{ etc} \)

For isomeric alkyl halides, boiling point decreases with branching.

(3) Solubility

Halo-alkanes are polar in nature. Yet they are insoluble in water but soluble in organic solvents. It is not soluble in water because they are not able to form hydrogen bond with water molecule.

(4) Bond strength

In haloalkanes, bond strength of carbon-halogen bond decreases with increase in the bond length as one move from fluorine to iodine

\( \text{C - F} > \text{C - Cl} > \text{C - Br} > \text{C - I} \)
(5) Density
The densities of haloalkanes increase with atomic mass of halogen and decreases with increase in size of alkyl group.
(i) For same alkyl group, density follows the order
\( R-I > R-Br > R-Cl > R-F \)
(ii) Same halogen density follows
\( \text{CH}_3\text{X} > \text{C}_2\text{H}_5\text{X} > \text{C}_3\text{H}_7\text{Cl} \)
(iii) Fluoro and chloroalkanes are lighter than water whereas bromides and iodides are heavier than water.

(6) Dipole moment
(i) Haloalkanes are polar compounds and their polarity depends on electronegativity of halogen. Dipole moment of halomethanes are
\( \text{CH}_3\text{Cl} > \text{CH}_3\text{F} > \text{CH}_3\text{Br} > \text{CH}_3\text{I} \)
1.86 D  1.84D  1.83D  1.63D
(ii) Dipole moment of fluoromethane is less than chloromethane is due to very small size of fluorine.

CHEMICAL PROPERTIES, REACTIVITY OF HALOALKANES

1) Nucleophilic substitution reaction
(a) \( S_{N1} \) mechanism (Unimolecular nucleophilic substitution)
(i) In this type, the rate of reaction depends only on the concentration of the substrate i.e. haloalkane and the reaction is of the first order change i.e.
\[ \text{Rate} \propto [\text{substrate}] \text{ or Rate} = [R-X] \]
(ii) This type of reaction proceeds in TWO steps as
STEP I: The haloalkanes undergoes heterolytic fission forming an intermediate, carbocation. This step is slow and hence is the rate determining step of the reaction.
\[ R - X \xrightarrow{\text{slow step}} R^+ + X^- \]
STEP II: The carbocation ion being a reactive species, immediately reacts with the nucleophile [ :Nu⁻ ] to give the substitution product
\[ R^+ + :\text{Nu}^- \rightarrow \text{R-Nu} \]
(iii) If the haloalkane is optically active then the product is racemic mixture.
(iv) The order of reactivity depends upon the stability of carbocation in the first step:
\( \text{R}_3\text{C} - X > \text{R}_2\text{CH} - X > \text{R} - \text{CH}_2\text{-}X > \text{CH}_3 - X \)
Tertiary  Secondary  Primary  Methyl
(v) \( S_{N1} \) order
Benzyl > allyl > \( 3^\circ > 2^\circ > 1^\circ > \) methyl halide
(b) \(S_N2\) mechanism (Bimolecular nucleophilic substitution)

(i) In this type, the rate of reaction depends on the concentration of both substrate and nucleophile and the reaction second order change.
Rate \(\propto [\text{Substrate}][\text{nucleophile}]\)
Rate = \(k [R-X][\text{Nu}^-]\)

(ii) Hydrolysis of methyl chloride is an example of \(S_N2\) reaction and high concentration of nucleophile (OH\(^-\)) favours \(S_N2\) reaction. The chlorine atom present in methyl chloride is most electronegative than carbon atom. Therefore C-Cl bond is partially polarised \(\ce{H3C^δ+ - Cl^δ-}\).

(iii) When the methyl chloride is attacked by OH\(^-\) strong nucleophile form the opposite side of chlorine atom, a transition state results in which both OH and Cl are partially attached to carbon atom

![Transition state diagram]

(iv) In transition state chlorine starts taking hold of electron pair through which it is bonded to carbon and OH\(^-\) ion offers a pair of electrons for the formation of bond with carbon. Finally chlorine leaves the molecule as a chloride ion (Cl\(^-\)). \(S_N2\) reaction of optically active halides are concentrated reactions and configuration of carbon is changed. This process is called inversion of configuration also known as Walden inversion

(v) \(S_N2\) reaction is favoured by small groups on the carbon, atom attached to halogens, so
\[
\text{CH}_3 - X > \text{RCH}_2 - X > \text{R}_2\text{CH} - X > \text{R}_3\text{C} - X
\]

(vi) \(S_N2\) order
Methyl > 1° > 2° > 3° > allyl > benzyl

NUCLEOPHILIC SUBSTITUTION REACTION OF ALKYL HALIDES

**SUMMARY**

\[
R - X + KOH(aq) \rightarrow R - OH + KX
\]

\[
R - X + AgOH \text{ (or } Ag_2O \text{)} \rightarrow R - OH + AgX
\]

\[
R - X + Ag_2O \text{(dry)} \rightarrow R - O - R + 2AgX
\]

\[
R - X + KSH \rightarrow R - SH + KX
\]
HALOALKANES AND HALOARENES

\[
R - X + \quad R'ONa \quad \rightarrow \quad R - S - R' + NaX
\]

Sodium alkoxide

\[
R - X + R'C \equiv C^-Na^+ \rightarrow R - OH + KX
\]

Sodium alkynide

\[
R - X + R'COOAg \rightarrow R - COOR' + AgX
\]

\[
R - X + KNO_2 \rightarrow R - O - N = O + KX
\]

\[
R - X + AgNO_2 \rightarrow R - NO_2 + KX
\]

\[
R - X + NH_3 \text{ (alcoholic)} \xrightarrow{RX} \quad RNH_2
\]

\[
R - X + AgCN \rightarrow R - \text{N} \equiv \text{C} - AgX
\]

\[
R - \text{NH} - \text{CH}_3 \quad \xrightarrow{\text{Na/C}_2\text{H}_5\text{OH} \text{ reduction}}
\]

**Some important points**

(i) Groups which possess two nucleophilic centre are called ambident nucleophiles. Example cyanides and nitrites.

(ii) KCN is predominantly ionic and provides cyanide ions in solution. Although both carbon and nitrogen atoms are in position to donate electron pairs, the attack takes place mainly through carbon atom and not nitrogen atom since C-C bond is more stable than C-N bond. Therefore when haloalkanes reacts with KC≡N alkyl cyanides is obtained.

\[
K^+ \text{C} \equiv N + R^\delta+ - X^\delta- \rightarrow R - C \equiv N + K-X
\]

(iii) AgCN is mainly covalent and nitrogen is free to donate electron pair forming isocyanide as main product.

\[
\text{Ag} \xrightarrow{\text{C} \equiv N^+ \searrow \text{C}} \quad R - X \xrightarrow{\text{alkylisocyanide}} \quad R - \text{NC} + AgX
\]
2) Elimination reaction-dehydro-halogenation

(a) Alkyl halides undergoes β – elimination reaction in presence of potassium hydroxide in ethanol to yield alkene

\[
\text{H} \quad \text{H} \\
R-\overset{\beta}{\text{C}} \overset{\alpha}{\text{C}} \overset{\text{H}}{\text{H}} + \overset{\text{+}}{\text{KOH}} \text{(alco.)} \\
\rightarrow \overset{\text{R-}}{\text{C}} = \overset{\text{C-H}}{\text{C-H}} + \overset{\text{KX}}{\text{KX}} + \overset{\text{H}_2\text{O}}{\text{H}_2\text{O}}
\]

(b) Reactivity of haloalkanes towards elimination reaction is

Tertiary > Secondary > primary

This is due to +I effect of the alkyl group which increases polarity of C-X bond

(c) In dehydrohalogenation of secondary and tertiary haloalkanes there is a possibility of formation of two isomers, then it is governed by Saytzeff’s rule which can be summarized as

“In dehydrohalogenation reactions, the preferred product is that alkene which has greater number of alkyl group attached to doubly bonded carbon atoms.”

3) Reaction with metals

(a) With magnesium (Grignard reagent)

\[
\text{R} - \text{X} + \overset{\text{dry ether}}{\text{Mg}} \text{ (Dry powder) Grignard reagent } \rightarrow \text{R - Mg - I}
\]

Carbon –magnesium is highly polar covalent where as magnesium halogen bond is ionic

(b) Reaction with sodium (Wurtz reaction)

\[
\text{R} - \text{X} + 2\text{Na} + \overset{\text{dry ether}}{\text{X}} \rightarrow \text{R - R + 2NaX}
\]

(c) Reaction with lithium

\[
\text{CH}_3 - \text{CH - CH}_3 + 2\text{Li} \rightarrow \text{CH}_3 - \text{CH - CH}_3 + \text{LiBr}
\]

\[
\text{CH}_3 - \text{CH - CH}_3 + 2\text{Li} \rightarrow \text{CH}_3 - \text{CH - CH}_3 + \text{LiBr}
\]
HALOALKANES AND HALOARENES

(d) Reaction with zinc (Frankland reagent)

\[ 2C_2H_5Br + 2Zn \xrightarrow{\text{ether, } \Delta} (C_2H_5)_2Zn + ZnBr_2 \]

(e) Wurtz – Fitting reaction

\[ R - X + 2Na + \text{dry ether} \rightarrow R + 2NaX \]

(f) Corey-house reaction

\[ RX \xrightarrow{\text{Li/Et}_3O} RLi \xrightarrow{\text{CuI}} R_2CuLi \]

\[ R' - X + R_2CuLi \rightarrow R' - R + RCU + LiX \]

SECTION II
HALOARENES

Compound in which the halogen atom is linked directly to the carbon atom of benzene are called arylhalides or haloarenes.

CLASSIFICATION OF HALOARENES

1. Compounds containing \( sp^3 \) \( C - X \) bond

   Benzylic halides
   In these halides, the halogen atom is attached to a benzylic carbon i.e. the carbon atom of the side chain carrying the aryl group.

2. Compound containing \( sp^2 \) \( C - X \) bond

   Aryl halides: These are the compounds in which the halogen atom is bonded to \( sp^2 \) – hybridized carbon atom of an aromatic ring.

3. On the basis of number of halogen atoms
GENERAL METHODS OF PREPARATION OF HALOARENES

1) Direct halogenations of aromatic hydrocarbon

Direct iodination is not possible since, the reaction is reversible with iodine. Thus the reaction is carried in the presence of oxidizing agent. Such as HIO₃, HNO₃.

5HI + HIO₃ → 3I₂ + 3H₂O
MECHANISM OF HALOGENATION

STEP I
Generation of electrophile i.e. halonium in by action of Lewis acid on the halogen

\[
\text{Cl} - \text{Cl} + \text{FeCl}_3 \rightarrow \text{Cl}^+ + \text{FeCl}_4^-
\]

STEP II
The electrophile attacks the benzene ring to form an intermediate known as \(\sigma\)-complex or a carbocation (arenium ion) which is stabilized by resonance.

The formation of intermediate arenium ion is slow and hence is the rate determining step of the reaction.

STEP III
The carbocation, loses a proton (\(\text{H}^+\) to the base \(\text{FeCl}_4^-\) to give chloro-benzene)
2) Side chain halogenations
   Halogenation in the presence of heat or sunlight and in absence of halogen carrier takes place at the side chain
   \[
   \begin{align*}
   \text{CH}_3 \text{Cl}, h^\nu & \rightarrow \text{CH}_2\text{Cl} \\
   \text{CH}_3 \text{Cl}, h^\nu & \rightarrow \text{CHCl}_2 \\
   \text{CH}_3 \text{Cl}, h^\nu & \rightarrow \text{CCl}_3 \\
   \end{align*}
   \]
   Side chain halogenations takes place by free radical mechanism.

3) From diazonium salt
   i) Sandmeyer’s reaction
   \[
   \begin{align*}
   \text{CuCl/HCl} & \rightarrow \text{Cl} \\
   \text{CuBr/HBr} & \rightarrow \text{Br} \\
   \text{KI} & \rightarrow \text{I} + \text{N}_2
   \end{align*}
   \]
   Replacement of the diazonium group by iodine is done simply by shaking the diazonium salt with potassium iodide.
HALOALKANES AND HALOARENES

ii) Balz-Schiemann reaction

$$\begin{align*}
\text{+} & \\
\text{N}_2\text{Cl}^- & \quad \quad \text{+} \\
\text{HBF}_4^- & \quad \quad \Delta \\
\text{Cl} & \quad \quad \text{+} \\
\text{N}_2 + \text{BF}_3
\end{align*}$$

4) Rasching process

$$\begin{align*}
2\text{Cl} + 2\text{HCl} + \text{O}_2 & \quad \quad \text{Cu}_2\text{Cl}_2, 200^\circ C \\
\rightarrow & \quad \quad \text{Cl} \\
2\text{Cl} + 2\text{H}_2\text{O}
\end{align*}$$

5) Hunsdiecker reaction

$$\begin{align*}
\text{CO}_2\text{Ag} & \\
+ \text{Br}_2 & \quad \quad \text{distillation} \\
\rightarrow & \\
\text{Br} & \\
+ \text{CO}_2 + \text{AgBr}
\end{align*}$$

PHYSICAL PROPERTIES OF HALOARENES

1) Physical state and smell
Haloarenes are generally colourless liquids with pleasant odour or are crystalline solids with characteristic smell.

2) Boiling point
i) The boiling point of monohalogen derivatives of benzene are in order: Iodo > Bromo > Chloro > Fluoro.
ii) Boiling and melting points increases as the size of the aryl group increases.
iii) Melting point of the para isomers are always higher than that of ortho or meta isomers. This is due to the reason that para isomer is more symmetrical and hence its molecules pack closely in the crystal lattice. As a result intermolecular and therefore, greater energy lattice and it melts at higher temperature.

3) Solubility
Aryl halides are insoluble in water but readily miscible with organic solvents.

4) Density
Aryl halides are heavier than water. Their density follows the order: Aryl iodide > aryl bromide > aryl chloride.

5) Dipole moment
The dipole moment of haloarenes lies as follows: Flurobenzene < Chlorobenzene < Bromobenzene ≈ Iodobenzene
CHEMICAL PROPERTIES OF HALOARENES

1) Nucleophilic substitution

Aryl halides are extremely less reactive towards nucleophilic substitution reactions due to following reasons

(i) Resonance effect: In haloarenes, the electron pairs of halogen atom are in conjugation with π-electrons of the ring and the following resonating structures are possible

\[
\begin{align*}
\text{C-Cl bond acquires a partial double bond character due to resonance. As a result, the bond cleavage in haloarene is difficult than haloalkane and therefore, they are less reactive towards nucleophilic substitution reaction.}
\end{align*}
\]

(ii) Difference in hybridisation of carbon atom in C-X bond

In haloalkane, the carbon atom attached to halogen is sp\(^3\) hybridized, whereas in case of haloarenes, the carbon atom attached to halogen is sp\(^2\) hybridized

\[
\begin{align*}
\text{The sp}^2 \text{ hybridised carbon with a greater s-character is more electronegative and can hold the electron pair of C-X bond more tightly than sp}^3 \text{-hybridised carbon in haloalkanes with less s-character. Thus C-Cl bond length in haloalkane is 177pm. While in haloarenes is 169pm. Since it is difficult to break a shorter bond than a longer bond, Therefore haloarenes are less reactive than haloalkanes towards nucleophilic substitution reaction.}
\end{align*}
\]

(iii) Instability of phenyl cation

In case of haloarenes, the phenyl cation formed as a result of self ionization, will not be stabilized by resonance and therefore S\(_{N1}\) mechanism is ruled out

(iv) Because of the possible repulsion it is less likely for the electron rich nucleophile to approach electron rich arenes
2) Replacement by hydroxyl group

The presence of electron withdrawing group (-NO$_2$) at ortho and para positions increases the reactivity of haloarenes.

3) Electrophilic substitution

- Due to resonance, the electron density increases more at ortho and para-positions than at meta- positions and hence the electrophile is more likely to attack on these position resulting in formation of o- and p- substituted product.
- Halogen atom because of its −I effect has some tendency to withdraw electron from benzene ring. As a result, the ring gets somewhat deactivated and hence the electrophilic substitution reactions in haloarenes occur slowly.
HALOALKANES AND HALOARENES

(i) Halogenation

\[
\text{Anhyd. FeCl}_3 \quad \begin{align*}
\text{C}_6\text{H}_5 & + \text{Cl}_2 \\
\Rightarrow & \quad \text{Cl} \\
\Rightarrow & \quad \text{Cl} \\
\Rightarrow & \quad 1, 4\text{-dichloro benzene (major)} \\
\Rightarrow & \quad 1, 2\text{-dichloro benzene (minor)}
\end{align*}
\]

(ii) Nitration

\[
\text{HNO}_3 \quad \text{(conc. H}_2\text{SO}_4) \quad \begin{align*}
\text{C}_6\text{H}_5 & + \text{Cl}_2 \\
\Rightarrow & \quad \text{Cl} \quad \text{NO}_2 \\
\Rightarrow & \quad \text{Cl} \quad \text{NO}_2 \\
\Rightarrow & \quad 1\text{-chloro-2-nitro benzene (minor)} \\
\Rightarrow & \quad 1\text{-chloro-4-nitro benzene (major)}
\end{align*}
\]

(iii) Sulphonation

\[
\text{(conc. H}_2\text{SO}_4) \quad \begin{align*}
\text{C}_6\text{H}_5 & + \text{Cl}_2 \\
\Rightarrow & \quad \text{Cl} \quad \text{SO}_3\text{H} \\
\Rightarrow & \quad \text{Cl} \quad \text{SO}_3\text{H} \\
\Rightarrow & \quad 2\text{-chlorobenzene sulphonic acid (minor)} \\
\Rightarrow & \quad 4\text{-chlorobenzene sulphonic acid (major)}
\end{align*}
\]

(iv) Friedel-Craft reaction

(a) Alkylation

\[
\text{Cl} \quad + \text{CH}_3\text{Cl} \quad \text{anhdy. AlCl}_3 \quad \begin{align*}
\Rightarrow & \quad \text{Cl} \quad \text{CH}_3 \\
\Rightarrow & \quad \text{Cl} \quad \text{CH}_3 \\
\Rightarrow & \quad 1\text{-chloro-2-methyl benzene (minor)} \\
\Rightarrow & \quad 1\text{-chloro-4-methyl benzene (major)}
\end{align*}
\]
(b) Acylation

\[
\begin{align*}
\text{Cl} &+ \text{H}_3\text{C}-\text{C} - \text{Cl} \xrightarrow{\text{anhyd. AlCl}_3} \text{Cl} \text{-CH}_3 \\
\text{Cl} &+ \text{Cl} \text{-CH}_3
\end{align*}
\]

2-chloroacetophenone (minor) +

4-chloroacetophenone (major)

4) Fitting reaction

\[
\begin{align*}
2\text{C} & + 2\text{Na} \xrightarrow{\text{ether}} \text{Diphenyl} + 2\text{NaX}
\end{align*}
\]

POLYHALOGEN COMPOUNDS

1. Dichloromethane (CH\textsubscript{2}Cl\textsubscript{2})

(A) Uses: It is used as

(i) A solvent in drug industry
(ii) Paint remover and propellant in aerosols
(iii) A cleaning agent for metals

(B) Environmental impact

(i) Its direct contact to our skin develops redness and burning sensation
(ii) It is harmful to our central nervous system
(iii) Its high level in air causes nausea, numbness in figure and toes

2. Trichloromethane CH\textsubscript{3}Cl\textsubscript{3} (Chloroform)

- Chloroform is a sweet smelling liquid boiling point 334K, non-inflammable but its vapour causes unconsciousness.
• When exposed to sunlight and air it slowly decomposes into phosgene (CoCl₂), a poisonous gas. It is therefore stored in closed dark coloured bottle completely filled so that air is kept out
\[2\text{CHC}_3 + \text{O}_2 \rightarrow 2\text{COCl}_2 + 2\text{HCl}\]
(A) Uses: It is used
(i) As a solvent for fats, oils, varnishes, waxes, resins and rubber etc.
(ii) For the preparation of chloretone (a drug) and chloropicrin (insecticide)
(iii) As an anesthetic after being mixed with ether
(iv) In the manufacture of Freon (refrigerant)

(B) Environmental impact
(i) On inhalation, it depresses the central nervous system and causes headache and dizziness.
(ii) Chronic exposure damages liver and kidneys.
(iii) On exposure to sunlight and air it slowly decomposes into phosgene.
(iv) Ethanol (1%) is added to retard the oxidation of phosgene into harmless ethyl carbonate.

(C) Tests of chloroform: It gives isocyanide test (Pungent smell). Pure CHCl₃ does not give white precipitate with AgNO₃, but with Tollen’s reagent, it gives grey precipitate of silver. On heating with Fehling’s solution, it gives brown precipitate.

3. Tri-iodomethane CHI₃ (Iodoform)
• It is a yellow crystalline solid pungent characteristic odour. Melting point is 392K and is steam volatile. It is used as an antiseptic for dressing wound

(A) Uses: It is used as
(i) As an antiseptic for dressing of wound.
(ii) In the manufacture of certain pharmaceuticals.

(B) Environmental impact
(i) When it comes in contact with skin, iodine is liberated which is responsible for antiseptic properties.
(ii) It has an objectionable smell.

4. Tetra chloromethane CCl₄ (carbon tetra chloride)
• It is a liquid, boiling point 350K, non-flammable, hence used as a solvent for fats, oils, waxes and resins etc. It is used as a fire extinguishers under the same name pyrene.

(A) Uses: It is used
(i) As a fire extinguishers
(ii) As a solvent and also dry-cleaning
(iii) In medicine as helmenthicide for elimination of hook worm

(B) Environmental impact
(i) Its vapours when breathed causes nausea, dizziness, vomiting and may cause damage nerve cells permanently
(ii) On exposure it causes cancer, irregular heart beat and a person may go to coma.
(iii) Its vapour depletes ozone layer. Ozone hole permits the ultraviolet radiation to reach on earth and may cause skin cancer, eye disease and disorder, it may adversely affect our immune system

5. Freons (CFC’s)

* Freons are small organic molecules containing C, Cl and F. The most common freons are CF\textsubscript{2}Cl (Freon-12) and CF\textsubscript{3}Cl (Freon-11)

(A) Uses
   (i) In air conditioning and domestic refrigerators for cooling purpose
   (ii) As propellents in aerosol and foams to spray out deodorants, cleaners and Insecticides. Halothane (CF\textsubscript{3}CHBrCl) is used as inhalation anaesthetic.

(B) Environmental impact
   Most Freon eventually makes its way into the atmosphere where it diffuses unchanged into the stratosphere. In stratosphere, Freon is able to initiate radical chain reaction that can upset the natural ozone layer surrounding earth.

6. \(p,p’\) – Dichlorodiphenyl trichloro ethane (DDT)

- It is prepared by heating chlorobenzene with chloral in presence of conc H\textsubscript{2}SO\textsubscript{4}

![Chemical Reaction]

(A) Uses:
   (i) As an effective insecticide for mosquitoes, flies and crop pests.
   (ii) As an antimalarial.

(B) Environmental impact
   It is non-biodegradable and its residue accumulates in environment, a cause of danger. It is not metabolized by the system and get deposited on the tissue, thus raises alarming danger. It is highly toxic to fish.