HALOALKANES AND HALOARENES

UNIT 10
After studying this Unit, you will be able to

- Name haloalkanes and haloarenes according to the IUPAC system of nomenclature from their given structures;
- Describe the reactions involved in the preparation of haloalkanes and haloarenes and understand various reactions that they undergo;
- Correlate the structures of haloalkanes and haloarenes with various types of reactions;
- Use stereochemistry as a tool for understanding the reaction mechanism;
- Appreciate the applications of organo-metallic compounds;
- Highlight the environmental effects of polyhalogen compounds
Classification of Halogen Derivatives

On the basis of number of halogen atoms present, halogen derivatives are classified as mono, di, tri, tetra, etc., halogen derivatives, e.g.,
On the basis of the nature of the carbon to which halogen atom is attached, halogen derivatives are classified as $1^\circ$, $2^\circ$, $3^\circ$, allylic, benzylic, vinylic and aryl derivatives, e.g.,
DIFFERENTIATION

LA
Write the structure of 1-bromo-4chlorobut-2-ene.

MA
Write the structure of 3-bromo-2-methylprop-1-ene.

HA
Write the structure of an isomer of compound $\text{C}_4\text{H}_9\text{Br}$, which is most reactive towards $\text{S}_\text{N}1$ reaction.
ASSIGNMENT

Draw the structures of all the eight structural isomers that have the molecular formula C5H11Br. Name each isomer according to IUPAC system and classify them as primary, secondary or tertiary bromide.
General Methods of Preparation of Haloalkanes

1. From Alcohols

In Groove’s method, ZnCl$_2$ is used to weaken the C-OH bond. In case of 3° alcohols, ZnCl$_2$ is not required.

The reactivity order of halogen acids is HI > HBr > HCl.
2. Free Radical Halogenation of Alkanes

\[
\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3 + \text{Cl}_2 \xrightarrow{\text{UV light or Heat}} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl} + \text{CH}_3\text{CH}_2\text{CHCH}_3 \quad \text{Cl}
\]
Addition of Hydrogen Halides on Alkenes

C=C=C + HBr → C=C=C

2-bromopropane

C=C=C + HBr → C=C=C

Organic peroxide
1. Finkelstein Reaction

\[ R - X + NaI \xrightarrow{Acetone} R - I + NaX \]
\( (X = \text{Cl, Br}) \)

2. Swarts Reaction

\[ \text{H}_3\text{C} - \text{Br} + \text{AgF} \rightarrow \text{H}_3\text{C} - \text{F} + \text{AgBr} \]

Hg2F2, COF2 and SbF3 can also be used as a reagent for Swarts reaction.

3. Hunsdiecker Reaction

\[ \text{CH}_3\text{COOAg} + \text{Br}_2 \xrightarrow{\text{CCl}_4} \text{CH}_3\text{Br} + \text{AgBr} + \text{CO}_2 \]
Physical Properties of Haloalkanes

1. Boiling point orders

R – I > R – Br > R – Cl > R – F
CH3 – (CH2)2 – CH2Br > (CH3)2 CHCH2Br > (CH3)3CBr
CH3CH2CH2 > CH3CH2X > CH3X

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

CH3F > CR3Cl > CR3Br > CH3I

3. Dipole moment decreases as the electronegativity of the halogen decreases.
4. Haloalkanes though polar but are insoluble in water as they do not form hydrogen bonding with water.

5. Density order is

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

CH3I > C2H5I > C3H7I
DIFFERENTIATION

LA
Write the structure of an isomer of compound C₄H₉Br, which is most reactive towards S_N1 reaction.

MA
Write the IUPAC name of (CH₃)₂CH•CH(Cl)CH₃.

HA
What happens when CH₃—Br is treated with KCN?
ASSIGNMENT

Arrange each set of compounds in order of increasing boiling points. (i) Bromomethane, Bromoform, Chloromethane, Dibromomethane. (ii) 1-Chloropropane, Isopropyl chloride, 1-Chlorobutane.
Chemical Reactions of Haloalkanes

1. Nucleophilic Substitution Reactions (SN reactions)

\[
\text{Nu} + \text{C}^\delta+ \text{X} \rightarrow \text{C}^\delta- \text{Nu} + \text{X}^-
\]

- \( \text{KOH} (\text{aq}) \rightarrow \text{C}_2\text{H}_5\text{OH} + \text{KBr} \)
- \( \text{NH}_3 \rightarrow \text{C}_2\text{H}_5\text{NH}_2, (\text{C}_2\text{H}_5)_2\text{NH}, (\text{C}_2\text{H}_5)_3\text{N} \)
- \( \text{KCN} \rightarrow \text{C}_2\text{H}_5\text{CN} + \text{KBr} \)
- \( \text{AgCN} \rightarrow \text{C}_2\text{H}_5\text{NC} + \text{AgBr} \)
- \( \text{KNO}_2 \rightarrow \text{C}_2\text{H}_5\text{ONO} + \text{KBr} \)
- \( \text{AgNO}_2 \rightarrow \text{C}_2\text{H}_5\text{NO}_2 + \text{AgBr} \)
- \( \text{R}^\prime\text{ONa}, \Delta \rightarrow \text{C}_2\text{H}_5\text{O} - \text{R}^\prime + \text{NaBr} \)
- \( \text{Na} - \text{C} = \text{C} - \text{H}, \Delta \rightarrow \text{C}_2\text{H}_5\text{C} = \text{CH} + \text{NaBr} \)
- \( \text{R}^\prime\text{COOAg}, \Delta \rightarrow \text{C}_2\text{H}_5\text{O} - \text{C} - \text{R}^\prime + \text{AgBr} \)
kCN is predominantly ionic and provides cyanide ions in solution, which is ambident nucleophile and bind with carbon side to form as the major product, while AgCN is covalent and form isocyanide as the major product.

Like KCN, KNO2 form R-ONO while AgNO2 produces R-NO2 as product. Vinyl chloride is less reactive towards nucleophilic substitution reactions due to resonance.
Methodology/Approach used for class room delivery. Nucleophilic substitution reactions are of two types

(a) SN1 type (Unimolecular nucleophilic reactions proceed in two steps):

\[
\begin{align*}
\text{alkyl halide} & \quad \xrightarrow{\text{Step 1}} \quad \text{planar carbocation} \\
\text{CH}_3\text{C-X} & \quad \xrightarrow{-X^- \text{ (Slow)}} \quad \text{CH}_3\text{C}^+\text{CH}_3 \\
\text{CH}_3\text{C}^+\text{CH}_3 & \quad \xrightarrow{\text{Step 2}} \quad \text{CH}_3\text{C-Nu} \\
& \quad \text{CH}_3\text{CH}_3
\end{align*}
\]
Methodology/Approach used for class room delivery. Rate, \( r = k [RX] \). It is a first order reaction.

Reactivity order of alkyl halide towards SN1 mechanism

\[ 3^\circ > 2^\circ > 1^\circ \]

Polar solvents, low concentration of nucleophiles and weak nucleophiles favour SN1 mechanism.

In SN1 reactions, partial racemisation occurs due to the possibility of frontal as well as backside attack on planar carbocation.
(b) SN2 type (Bimolecular nucleophilic substitution)

These reactions proceed in one step and is a second order reaction with \( r = k[RX][Nu] \).

During SN2 reaction, inversion of configuration occurs (Walden inversion) i.e., starting with dextrorotatory halide a laevo product is obtained and vice-versa, e.g.,

Reactivity of halides towards SN2 mechanism is

\[ 1^\circ > 2^\circ > 3^\circ \]
Rate of reaction in SN2 mechanism depends on the strength of the attacking nucleophile. Strength of some common nucleophiles is


Non-polar solvents, strong nucleophiles and high concentration of nucleophiles favour SN2 mechanism.

Relative rates of some alkyl halides in SN1 and SN2 reactions are in the order

$S_{N1} : (CH_3)_3CX > C_6H_5–CH_2–X > CH_2=CH–CH_2X$

$\quad > (CH_3)_2CHX > CH_3CH_2X > CH_3X$

$S_{N2} : C_6H_5CH_2X > CH_2=CH–CH_2X > CH_3X$

resonance stabilised

$\quad > CH_3CH_2X > (CH_3)_2CHX > (CH_3)_3CX$
Resonating structure of benzyl carbocations are
DIFFERENTIATION

LA
Predict the order of reactivity of the following compounds in SN 1 and SN2 reactions: (i) The four isomeric bromobutanes (ii) C6H5CH2Br, C6H5CH(C6H5 )Br, C6H5CH(CH3 )Br, C6H5C(CH3)(C6H5 )Br

MA
1. Which would undergo $S_N2$ reaction faster in the following pair and why?
$CH_3—CH_2—Br$ and $CH_3—CH_3 | C— | Br CH_3$

HA
Which would undergo $S_N1$ reaction faster in the following pair?
$CH_3—CH_2—CH_2—Br$ and $CH_3—CH— | Br CH_3$
ASSIGNMENT

Name the following halides according to IUPAC system and classify them as alkyl, allyl, benzyl (primary, secondary, tertiary), vinyl or aryl halides: (i) (CH3 ) 2CHCH(Cl)CH3  
(ii) CH3CH2CH(CH3 )CH(C2H5 )Cl  
(iii) CH3CH2C(CH3 ) 2CH2 I  
(iv) (CH3 ) 3CCH2CH(Br)C6H5  
(v) CH3CH(CH3 )CH(Br)CH3  
(vi) CH3C(C2H5 ) 2CH2Br  
(vii) CH3C(Cl)(C2H5 )CH2CH3  
(viii) CH3CH=C(Cl)CH2CH(CH3 ) 2  
(ix) CH3CH=CHC(Br)(CH3 ) 2  
(x) p-ClC6H4CH2CH(CH3 )
2. Elimination Reactions

Dehydrohalogenation is a β – elimination reaction in which halogen is from α-carbon atom and the hydrogen from the α-carbon according to Saytzeff rule, e.g.

![Reaction Equation]

Ease of dehydrohalogenation among halides 3° > 2° > 1°

i.e., 

\[
(CH_3)_3CCl > (CH_3)_2CHCl > CH_3CH_2Cl
\]
3. Reduction

\[
\text{C}_2\text{H}_5\text{Br} + \text{H}_2 \xrightleftharpoons[\text{Ni, 575 K}]{\text{Ni, 575 K}} \text{C}_2\text{H}_6 + \text{HBr}
\]

\[
\text{C}_2\text{H}_5\text{I} + \text{HI} \xrightarrow[\text{Red P, 420 K}]{\text{Red P, 420 K}} \text{C}_2\text{H}_6 + \text{I}_2
\]

4. Reaction with Metals

(i) Wurtz reaction

\[
\text{RX} + 2\text{Na} + \text{XR} \xrightarrow{\text{Dry ether}} \text{R} - \text{R (alkane)} + 2\text{NaX}
\]

(ii) Wurtz-Fittig reaction

\[
\text{C}_6\text{H}_5\text{Cl} + 2\text{Na} + \text{ClCH}_3 \xrightarrow{\text{Dry ether}} \text{C}_6\text{H}_5\text{CH}_3 + 2\text{NaCl}
\]

(iii) Reaction with Mg

\[
\text{C}_2\text{H}_5\text{Br} + \text{Mg} \xrightarrow{\text{Dry ether}} \text{C}_2\text{H}_5\text{Mg} - \text{Br}
\]

(Grignard's reagent)
5. Isomerisation

\[ \text{CH}_3\text{CH}_2\text{CH}_2\text{Cl} \xrightarrow{573 \text{ K}} \text{CH}_3\text{CH}:=\text{CH}_3 \]

1-chloropropane

or anhy. AlCl₃
DIFFERENTIATION

LA
Which one of the following has the highest dipole moment? (i) CH2Cl 2 (ii) CHCl 3 (iii) CCl4

MA
A hydrocarbon C5H10 does not react with chlorine in dark but gives a single monochloro compound C5H9Cl in bright sunlight. Identify the hydrocarbon.

HA
Write the isomers of the compound having formula C4H9Br.
ASSIGNMENT

How will you bring about the following conversions? (i) Ethanol to but-1-yne
(ii) Ethane to bromoethene
(iii) Propene to 1-nitropropane
(iv) Toluene to benzyl alcohol
(v) Propene to propyne
(vi) Ethanol to ethyl fluoride
(vii) Bromomethane to propanone
(viii) But-1-ene to but-2-ene
(ix) 1-Chlorobutane to n-octane
(x) Benzene to biphenyl.
General Methods of Preparation of Aryl Halides

1. By Halogenation of Aromatic Hydrocarbons

It is an electrophilic substitution reaction.

2. By Side Chain Halogenation
3. From Benzene Diazonium Salt

4. From Phenol
Physical Properties of Aryl Halides

• Aryl halides are colourless liquids or colourless solids with characteristic odour.

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

  \[ \text{Ar – I > Ar – Br > Ar – Cl > Ar – F} \]

• The melting point of p-isomer is more than 0- and m-isomer.

• This is because of more symmetrical nature of p-isomer.

Due to resonance in chlorobenzene, C-Cl bond is shorter and hence, its dipole moment is less than that of cyclohexylchloride.
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:

Due to resonance, C-X bond has partial double bond character. Stabilisation of the molecule by delocalisation of electrons. (Instability of phenyl carbocation.

However, aryl halides having electron withdrawing groups (like – NO2, -SO3H, etc.) at ortho and para positions undergo nucleophilic substitution reaction easily.
(i) NaOH, 623 K, 300 atm
(ii) H^+

(i) NaOH, 443 K
(ii) H^+
2. Electrophilic Substitution Reactions

Halogens are deactivating but O, p-directing. Thus, chlorination, nitration, sulphonation and Friedel Craft’s reaction give a mixture of o- and p- chloro substituted derivatives.

(i) Halogenation

![Chemical reaction image]

(ii) Nitration

![Chemical reaction image]
(iii) Sulphonation

(iv) Friedel-Crafts reaction
3. Reaction with Metals

(i) Wurtz Fittig reaction

(ii) Fitting reaction
(iii) Ullmann reaction

Dihalogen Derivatives

Dichloromethane (CH$_2$Cl$_2$) 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.
Trihalogen Derivatives

1. Chloroform [Trichloromethane, CHCl₃]

(i) \[ \text{Sunlight} \]
\[ \text{CH}_4 + 3\text{Cl}_2 \rightarrow \text{CHCl}_3 + 3\text{HCl} \]
 Controlled chlorination

(ii) Haloform reaction
\[ \text{C}_2\text{H}_5\text{OH} + \text{Cl}_2 \rightarrow \text{CH}_3\text{CHO} + 2\text{HCl} \text{[Oxidation]} \]
\[ \text{CH}_3\text{CHO} + 3\text{Cl}_2 \rightarrow \text{CCl}_3 \cdot \text{CHO} + 3\text{HCl} \text{[Chlorination]} \]
\[ 2\text{CCl}_3 \cdot \text{CHO} + \text{Ca(OH)}_2 \rightarrow 2\text{CHCl}_3 + (\text{HCOO})_2\text{Ca} \]
[Hydrolysis]
Properties

1. Oxidation of CHCl₃ gives poisonous gas phosgene (carbonyl chloride).

\[
2\text{CHCl}_3 + \text{O}_2 \xrightarrow{\text{Light}} 2\text{COCl}_2 + 2\text{HCl} \text{ phosgene}
\]

To avoid this oxidation CHCl₃ is stored in dark brown bottles and filled to the brim. 1% ethanol is added to chloroform which converts harmful phosgene gas into diethyl carbonate.

2. CHCl₃ is widely used in the production of freon refrigerant R-22.

3. On nitration, it gives tear producing insecticide substance chloropicrin
\[
\text{CHCl}_3 + \text{HONO}_2 \text{(conc.)} \rightarrow \text{NO}_2 \cdot \text{CCl}_3 + \text{H}_2\text{O} \\
\text{chloropicrin}
\]

4. On dehalogenation, it gives \( \text{C}_2\text{H}_2 \) (acetylene).

\[
\text{CHCl}_3 + 6\text{Ag} + \text{CHCl}_3 \xrightarrow{\Delta} \text{CH} \equiv \text{CH} + 6\text{AgCl}
\]

5. When subjected to hydrolysis, it gives formate.

\[
\text{CHCl}_3 + 3\text{NaOH} \rightarrow \text{CH} - \text{OH} - \text{OH} - \xrightarrow{-\text{H}_2\text{O}} \text{HCOONa}
\]
2. Iodoform (tri-iodornethane, CHl3)

Iodoform is prepared by iodoform reaction.

\[
\text{CH}_3\text{COCH}_3 + 3\text{I}_2 + 4\text{NaOH} \rightarrow \text{CH}_3\text{I} + 3\text{NaI} + \text{CH}_3\text{COONa} + 3\text{H}_2\text{O}
\]

Compounds containing either CH3CO- or CH3CH(OH) group form yellow colour iodoform with I2 and NaOH.

Iodoform when comes in contact with organic matter, decomposes easily to free iodine, an antiseptic. Due to its objectionable smell, it has been replaced by other formulations containing iodine.
DIFFERENTIATION

Arrange the compounds of each set in order of reactivity towards $S\ N_2$ displacement:

**LA**
(i) 2-Bromo-2-methylbutane, 1-Bromopentane, 2-Bromopentane

**MA**
(ii) 1-Bromo-3-methylbutane, 2-Bromo-2-methylbutane, 2-Bromo-3-methylbutane

**HA**
(iii) 1-Bromobutane, 1-Bromo-2,2-dimethylpropane, 1-Bromo-2-methylbutane, 1-Bromo-3-methylbutane.
ASSIGNMENT

How the following conversions can be carried out?
(i) Propene to propan-1-ol
(ii) Ethanol to but-1-yne
(iii) 1-Bromopropane to 2-bromopropane
(iv) Toluene to benzyl alcohol
(v) Benzene to 4-bromonitrobenzene
(vi) Benzyl alcohol to 2-phenylethanoic acid
(vii) Ethanol to propanenitrile
(viii) Aniline to chlorobenzene
(ix) 2-Chlorobutane to 3, 4-dimethylhexane
(x) 2-Methyl-1-propene to 2-chloro-2-methylpropane
Polyhalogen Derivatives

1. Tetrachloromethane (Carbon Tetrachloride, CCl₄)

**Preparation**

(i) \[ \text{CH}_4 + 4\text{Cl}_2 \xrightarrow{\text{Sunlight}} \text{CCl}_4 + 4\text{HCl} \]

(ii) \[ \text{CHCl}_3 + \text{Cl}_2 \xrightarrow{\text{hv}} \text{CCl}_4 + 2\text{HCl} \]

CCI₄ is a colourless, non-inflammable, poisonous liquid, soluble in alcohol and ether.

**Uses**

Carbon tetrachloride is used as a solvent for oils, fats, resins in dry cleaning as fire extinguisher under the name ‘pyrene’.
2. Freons

The chlorofluorocarbon compounds of methane and ethane are collectively known as freons. These are usually produced for aerosol propellants, refrigeration and air conditioning purposes. Carbon tetra chloride when reacts with antimony trifluoride in the presence of SbCl5 as catalyst, dichlorofluromethane (freon) is obtained.

3. 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. H2SO4·
DIFFERENTIATION

Give the uses of

LA
Freon 12, DDT
MA
Carbon tetrachloride
HA
Iodoform.
ASSIGNMENT

Draw the structure of

- Freon 12
- DDT
- Carbon tetrachloride
PRACTICE QUESTIONS/ASSESSMENT

- Write the equations for the preparation of 1-iodobutane from (i) 1-butanol (ii) 1-chlorobutane (iii) but-1-ene.
- What are ambident nucleophiles? Explain with an example.
- Which compound in each of the following pairs will react faster in SN 2 reaction with –OH? (i) CH₃Br or CH₃ I (ii) (CH₃ ) ₃CCl or CH₃Cl
- Predict all the alkenes that would be formed by dehydrohalogenation of the following halides with sodium ethoxide in ethanol and identify the major alkene: (i) 1-Bromo-1-methylcyclohexane (ii) 2-Chloro-2-methylbutane (iii) 2,2,3-Trimethyl-3-bromopentane.
• How will you bring about the following conversions? (i) Ethanol to but-1-yne (ii) Ethane to bromoethene (iii) Propene to 1-nitropropane (iv) Toluene to benzyl alcohol (v) Propene to propyne (vi) Ethanol to ethyl fluoride (vii) Bromomethane to propanone (viii) But-1-ene to but-2-ene (ix) 1-Chlorobutane to n-octane (x) Benzene to biphenyl.

• Explain why (i) the dipole moment of chlorobenzene is lower than that of cyclohexyl chloride? (ii) alkyl halides, though polar, are immiscible with water? (iii) Grignard reagents should be prepared under anhydrous conditions?

• Give the uses of freon 12, DDT, carbon tetrachloride and iodoform