Unit - 10

HALOALKANES AND HALOARENES

1. Write the IUPAC names of the following compounds.

(i) \[
\begin{array}{c}
\text{Br} \\
\text{CH}_3\text{C} \equiv \text{CH}_2\text{CH}_3 \\
\text{CH}_2\text{CH}_2\text{CH}_3
\end{array}
\]

(ii) \[
\begin{array}{c}
\text{CH}_3\text{C} \equiv \text{CH}_2\text{Br} \\
\text{CH}_3
\end{array}
\]

(iii) \[
\begin{array}{c}
\text{CH}_2\text{Cl} \\
\text{Cyclic structure}
\end{array}
\]

(iv) \[
\begin{array}{c}
\text{CH}_2\text{Br} \\
\text{CH}_3\text{(CH}_2)_2\text{C} \equiv \text{C(CH}_3)_2\text{CHCH}_2\text{CH}_3
\end{array}
\]

(v) \[
\begin{array}{c}
\text{H}_3\text{C} \\
\text{Cyclic structure}
\end{array}
\]

(vi) \[
\begin{array}{c}
\text{OH} \\
\text{CH}_3\text{CH} = \text{CH}\text{CH} = \text{CH}_3
\end{array}
\]

(vii) \[
\begin{array}{c}
\text{HC} \\
\text{H}_3\text{C}
\end{array}
\]

(ix) \[
\begin{array}{c}
\text{(CCl}_3)_3\text{CCI}
\end{array}
\]
2. Write the structure of following halogen compounds
   (i) 2-chloro-3-methylpentane
   (ii) 2-(2-chlorophenyl)-1-iodooctane
   (iii) 1-bromo-4-sec-butyl-2-methylebenzene.
   (iv) p-bromotoluene.
   (v) chlorophenylmethane

3. Arrange the following in the increasing order of properly indicated :
   (i) bromomethane, chloromethane, dichloromethane. (Increasing order of boiling points).
   (ii) 1-chloropropane, isopropyl chloride, 1-chlorobutane (Increasing order of boiling point)
   (iii) dichloromethane, chloroform, carbon terachloride. (Increasing order of dipole moment.
   (iv) CH₃F, CH₃Cl, CH₃Br, CH₃I (Increasing reactivity towards nucleophilic substitution and increasing order of dipole moment)
   (v) o,m,p-dichlorobenzenes (Increasing order of melting points).

4. Complete the following reactions :
   (i) \( \text{CH}_2=\text{CH} + \text{HBr} \rightarrow \)
   (ii) \( \text{CH}_3 - \text{CH}_2 - \text{Cl} + \text{Ag NO}_2 \rightarrow \)
   (iii) \( \text{CH}_2\text{CH}=\text{CH}_2 + \text{HBr} \rightarrow \text{peroxide} \)
   (iv) \( \text{NaOH (aq)} \rightarrow \)
(v) \[ \text{CH}_2\text{CH}_3 \xrightarrow{\text{Br}_2/\text{heat} \atop \text{uv light}} \]

(vi) \[ \text{CH}_3 + \text{HI} \]

(vii) \[ \text{HO} + \text{SOCl}_2 \]

(viii) \[ \text{CH}_3\text{CH}_2\text{Br} + \text{NaI} \xrightarrow{\text{acetone}} \]

(ix) \[ \text{C}_6\text{H}_5 + \text{Br}_2 \xrightarrow{\text{uv light}} \]

(x) \[ (\text{CH}_3)_3\text{CBr} + \text{KOH} \xrightarrow{\text{ethanol} \atop \text{heat}} \]

(xi) \[ \text{CH}_3\text{CH}_2\text{Br} + \text{KCN} \xrightarrow{\text{aq. EtOH}} \]

(xii) \[ \text{Br} + \text{Mg} \xrightarrow{\text{dry \ EtHER}} \]

(xiii) \[ \text{C}_6\text{H}_5\text{ONa} + \text{C}_2\text{H}_5\text{Cl} \]

(xiv) \[ \text{CH}_3\text{CHCH}_2\text{CH}_3 + \text{Na} \xrightarrow{\text{dry \ ether}} \]

(xv) \[ \text{CH}_3\text{CHCH}_2\text{CH}_3 + \text{NaOH (aq)} \]

(xvi) \[ \text{C}_6\text{H}_5 \text{N}_2\text{Cl}^- + \text{KI} \]
5. How will you bring about the following conversions?
   (i) benzene to 3-bromonitrobenzene
   (ii) ethanol to but-1-yne
   (iii) 1-bromopropane to 2-bromopropane
   (iv) benzene to 4-bromo-1-nitrobenzene
   (v) aniline to chlorobenzene
   (vi) 2-methyl-1-propene to 2-chloro-2-methylpropane
   (vii) ethyl chloride to propanoic acid
   (viii) but-1-ene to n-butyl iodide
   (ix) benzene to phenylchloromethane.
   (x) tert-butyl bromide to isobutyl bromide.

6. Identify the products formed in the following sequence:

(i) \[
\begin{align*}
  \text{Cl} & \quad \text{NaCN} \quad \text{A} \quad \text{H}^+ / \text{H}_2\text{O} \quad \text{B}
\end{align*}
\]

(ii) \[
\begin{align*}
  \text{Br} & \quad \text{Br} \quad \text{alc. KOH} \quad \text{A} \quad \text{NaNH}_2 \quad \text{B}
\end{align*}
\]

(iii) \[
\begin{align*}
  \text{C}_9\text{H}_6\text{CH}_2\text{CHBrCH}_3 & \quad \text{alc. KOH} \quad \text{A} \quad \text{HBr} \quad \text{B}
\end{align*}
\]

(iv) \[
\begin{align*}
  \text{CH}_3\text{CH} = \text{CH} \quad \text{Br} & \quad \text{alc. KOH} \quad \text{X} \quad \text{HBr} \quad \text{H}_2\text{O}_2 \quad \text{Y}
\end{align*}
\]

(v) \[
\begin{align*}
  \text{CH}_3\text{CH}_2\text{CH} = \text{CH} \quad \text{+ Br}_2 & \quad \text{CCl}_4 \quad \text{A}
\end{align*}
\]

(vi) \[
\begin{align*}
  \text{CH}_3\text{CH}_2\text{CH} = \text{CH}_2 & \quad \text{+ Br}_2 \quad \text{heat} \quad \text{UV light} \quad \text{B}
\end{align*}
\]

(vii) \[
\begin{align*}
  \text{Br} & \quad \text{A} \quad \text{B}
\end{align*}
\]
7. Explain the following reactions with suitable example:
   (i) Finkelstein reaction.
   (ii) Swarts reaction.
   (iii) Wurtz reaction.
   (iv) Wurtz-Fitting reaction
   (v) Friedel-Craft’s alkylation reaction.
   (vi) Friedel-Craft’s acylation reaction
   (vii) Sandmeyer reaction.

8. Write the major products and name the rule responsible for the formation of the product.
   (i) \[ \text{CH}_3\text{CH}_2\text{CH}_3 + \text{KOH} \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{OH} \]
   (ii) \[ \text{CH}_3\text{CH}_2\text{CH} = \text{CH} + \text{HBr} \rightarrow \text{CH}_3\text{CH} = \text{CH}_2 + \text{HBr} \]

9. Write the difference between
   (i) enantiomers and diastereomers
   (ii) retention and inversion of configuration.
   (iii) electrophilic and nucleophilic substitution reactions.

10. Give a chemical test to distinguish between the following pairs of compounds:
    (i) chlorobenzene and cyclohexylchloride.
    (ii) vinyl chloride and ethyl chloride.
    (iii) n-propyl bromide and isopropyl bromide.

11. Give mechanism of the following reactions:
    (i) \[ (\text{CH}_3)_3\text{C} - \text{Cl} + \text{OH}^- \rightarrow (\text{CH}_3)_3\text{C} - \text{OH} \]
    (ii) \[ \text{CH}_3 - \text{Cl} + \text{OH}^- \rightarrow \text{CH}_3 - \text{OH} \]
12. Which compound in each of the following pairs will react faster in S_N2 reaction with OH^- and why?
   (i) CH_3Br or CH_3I
   (ii) (CH_3)_3 CCl or CH_3Cl

13. In the following pairs which halogen compound undergoes faster SN1 reaction?
   (i) \[
   \begin{array}{c}
   \text{Cl} \\
   \text{and}
   \end{array}
   \begin{array}{c}
   \text{Cl} \\
   \text{Cl}
   \end{array}
   \]
   (ii) \[
   \begin{array}{c}
   \text{Cl} \\
   \text{and}
   \end{array}
   \begin{array}{c}
   \text{Cl} \\
   \text{Cl}
   \end{array}
   \]
   (iii) (CH_3)_3 C – Cl and C_6H_5CH_2Cl
   (iv) C_6H_5CH_2Cl and C_6H_5C(Cl)C_6H_5
   (v) CH_2 = CH – Cl and CH_2 = CH – CH_2Cl

14. Give reasons for the following:
   (i) The bond length of C–Cl bond is larger in haloalkanes than that in haloarenes.
   (ii) Although alkyl halides are polar in nature but are not soluble in water.
(iii) tert-butyl bromide has lower boiling point than n-Butyl bromide.
(iv) haloalkanes react with KCN to form alkyl cyanide as main product while with AgCN alkyl isocyanide is the main product.
(v) sulphuric acid is not used in the reaction of alcohol with KI.
(vi) thionyl chloride is the preferred reagent for converting ethanol to chloroethane.
(vii) haloalkanes undergo nucleophilic substitution reaction easily but haloarenes do not undergo nucleophilic substitution under ordinary conditions.
(viii) chlorobenzene on reaction with fuming sulphuric acid gives ortho and para chlorosulphonic acids.
(ix) 2, 4-dinitro chlorobenzene is much more reactive than chlorobenzene towards hydrolysis reaction with NaOH.
(x) Grignard reagent should be prepared under anhydrous conditions.
(xi) the dipole moment of chlorobenzene is lower than that of cyclohexyl chloride.
(xii) neopentyl bromide undergoes nucleophilic substitution reactions very slowly
(xiii) vinyl chloride is unreactive in nucleophilic substitution reaction.
(xiv) An optically inactive product is obtained after the hydrolysis of optically active 2- bromobutane.

[Hint : The hydrolysis reaction occurs by S_N 1 pathway. The carbocation is formed first which gives a mixture of (±) butan-2-ol in the second step].

(xv) methyl iodide is hydrolysed at faster rate than methyl chloride.
15. Write the different products and their number formed by the monochlorination of following compounds:
   (i) \( \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3 \)
   (ii) \( (\text{CH}_3)_2\text{CHCH}_2\text{CH}_3 \)
   (iii) \( (\text{CH}_3)_2\text{CHCH(\text{CH}_3)_2} \)
   [Hint: (i) Two, (ii) four, (iii) three]

16. (a) When 3-methylbutan-2-ol is treated with HBr, the following reaction takes place:

\[
\begin{align*}
\text{CH}_3\text{CH} \cdots \text{CH} \cdots \text{CH}_3 & \quad \text{HBr} \quad \text{CH}_3\text{C} - \text{CH} \cdots \text{CH}_3 \\
\text{CH}_3 & \quad \text{Br}
\end{align*}
\]

Give the mechanism for this reaction.

(b) In the following reaction:
\[
\begin{align*}
\text{CH}_3 & \quad \text{H}_2\text{C} \cdots \text{C} \cdots \text{CH} \quad \text{= CH}_3 \quad \text{H}_2\text{O/} \text{H}^+ \quad \text{CH}_3 \\
\text{OH} & \quad \text{CH}_3
\end{align*}
\]

major and minor products are:

(i) \( \text{CH}_2 \cdots \text{C} \cdots \text{CH} \cdots \text{CH}_2 \quad \text{OH} \quad \text{CH}_3 \)
(ii) \( \text{CH}_2 \cdots \text{C} \cdots \text{CH}_2 \cdots \text{CH}_3 \quad \text{OH} \quad \text{CH}_3 \)
(iii) \( \text{Cl}_3 \cdots \text{C} \cdots \text{Cl} \cdots \text{Cl}_3 \quad \text{OH} \quad \text{CH}_3 \)
(iv) \( \text{I}_3 \cdots \text{C} \cdots \text{Cl}_2 \cdots \text{Ol} \quad \text{OH} \quad \text{CH}_3 \)

Ans. Major (iii) minor (i)

17. Give one use of each of following:
   (i) Freon-12
   (ii) DDT
   (iii) Carbon tetrachloride
   (iv) Iodoform
18. An optically active compound having molecular formula C₇H₁₅Br reacts with aqueous KOH to give C₇H₁₅OH, which is optically inactive. Give mechanism for the reaction.

\[ \text{C}_7\text{H}_7\text{Br} + \text{KOH} \rightarrow \text{C}_7\text{H}_7\text{OH} \]

[Ans. : (i) \( \text{C}_2\text{H}_5\text{C}^-\text{Br} \rightarrow \text{C}^+ \text{H}_5\text{C}_2\text{C}_3\text{H}_7 \) (Slow)]

(ii) \( \text{C}_2\text{H}_7\text{OH} \rightarrow \text{C}_2\text{H}_7\text{O}^- \)

A racemic mixture is obtained which is optically inactive.

19. An organic compound C₈H₉Br has three isomers A, B and C. A is optically active. Both A and B gave the white precipitate when warmed with alcoholic AgNO₃ solution in alkaline medium. Benzoic acid, terephthalic and p-bromobenzoic acid were obtained on oxidation of A, B and C respectively. Identify A, B and C.

[Ans. : (A) \( \text{H}_2\text{C}^-\text{CHBr} \) (B) \( \text{CH}_2\text{Br} \) (C) \( \text{CH}_2\text{CH}_2\text{Br} \)]

*20. An alkyl halide X having molecular formula C₆H₁₃Cl on treatment with potassium tert-butoxide gives two isomeric alkenes Y and Z but alkene y is symmetrical. Both alkenes on hydrogenation give 2, 3-dimethylbutane. Identify X, Y and Z.

[Ans.]

\( \text{X} \) \( \text{CH}_3\text{CH} \text{Cl} \), \( \text{Y} \) \( \text{CH}_3\text{CH} = \text{CH} \text{CH}_3 \), \( \text{Z} \) \( \text{CH}_3\text{CH} = \text{CH} = \text{CH}_2 \)

111  \hspace{1cm} \text{XII – Chemistry}
21. An organic compound (A) having molecular formula C₃H₇Cl on reaction with alcoholic solution of KCN gives compound B. The compound B on hydrolysis with dilute HCl gives compound C. C on reduction with H₂/Ni gives 1-aminobutane. Identify A, B and C.

[Ans.: (A) CH₃CH₂CH₂Cl, (B) CH₃CH₂CH₂CN, (C) CH₃CH₂CH₂CONH₂]

22. Identify A, B, C, D, E, R and R’ in the following sequence of reactions:

\[ \text{Br} - \text{CH₂} - \text{CH} = \text{CH}_2 \rightarrow \text{1-bromoprop-2-ene} \]

\[ \text{CH₃} - \text{CH} - \text{CH} - \text{CH₃} \rightarrow \text{4-bromo-2,4-dimethylhexane} \]

\[ \text{CH₃} - \text{CH} - \text{CH} = \text{CH}_2 \rightarrow \text{2-methyl-3-phenylpentane} \]

\[ \text{CH₂} - \text{C} - \text{CH₂} - \text{CH₃} \text{COON} \rightarrow \text{5-oxohexanoic acid} \]