Chapter - 10

HALOALKANES AND HALOARENES

1. Write the IUPAC names of the following compounds.

(ii)
$$CH_3$$
 $C=C$ CH_2Br

$$\begin{array}{c} \operatorname{CH_2Br} \\ | \\ \operatorname{CH_3(CH_2)_2} - \operatorname{C(CH_3)_2} \\ \end{array} \text{CHCH_2CH_3}$$

(v)
$$CH_2Br - CH = CH - CH_2 - C \equiv CH$$

(ix)
$$(CCl_3)_3$$
 CCI

- 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, CH₃CI, 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)
$$CH = CH_2 + HBr$$

(ii)
$$CH_3 - CH_2 - CI + Ag NO_2 \longrightarrow$$

$$\begin{array}{c} CH_2CH_3 \\ \hline \\ (v) \end{array} \qquad \begin{array}{c} Br_2/heat \\ \hline \\ uv \ light \end{array}$$

(vii)
$$HO$$
 CH_2OH $+ SOCI_2$ \longrightarrow

(ix)
$$+$$
 Br₂ $\xrightarrow{UV \text{ light}}$

(x)
$$(CH_3)_3 CBr + KOH \xrightarrow{\text{ethanol}}$$

(xi)
$$CH_3CH_2Br + KCN \xrightarrow{aq. EtOH}$$

(xiii)
$$C_6H_5ONa + C_2H_5CI \longrightarrow$$

(xvi)
$$C_6 H_5 N_2^+ Cl^- + Kl \longrightarrow$$

- 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)
$$\stackrel{\text{NaCN}}{\longrightarrow}$$
 A $\stackrel{\text{H}^+/\text{H}_2\text{O}}{\longrightarrow}$ E

(ii) Br
$$\frac{\text{alc. KOH}}{\text{A}}$$
 A $\frac{\text{NaNH}_2}{\text{B}}$ B

(iii)
$$C_6H_5CH_2CHBrCH_3 \xrightarrow{alc. KOH} A \xrightarrow{HBr} B$$

(iv)
$$CH_3CH-CH_3 \xrightarrow{alc. KOH} X \xrightarrow{HBr} Y$$

Br

(v)
$$CH_3CH_2CH = CH_2 + Br_2 \xrightarrow{CCl_4} A$$

(vi)
$$CH_3CH_2CH = CH_2 + Br_2 \xrightarrow{heat} B$$

(viii) CH₃Br
$$\xrightarrow{\text{KCN}}$$
 A $\xrightarrow{\text{H}_3O^+}$ $\xrightarrow{\text{Li Al H}_4}$ $\xrightarrow{\text{ether}}$

- 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)
$$CH_3$$
— CH_2 — CH — CH_3 KOH
Br

(ii)
$$CH_3$$
— CH_2 — $CH = CH_2 + HBr \xrightarrow{\text{organic peroxide}}$

- 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)
$$(CH_3)_3C - CI + \bar{O}H \longrightarrow (CH_3)_3C - OH$$

(ii)
$$CH_3 - CI + OH^- \longrightarrow CH_3 - OH$$

(iii)
$$CH_3$$
— CH — CI + $OH^ \xrightarrow{\text{ethanol}}$ CH_3 — CH = CH_2
 CH_3

(iv)
$$+ Cl_2 \xrightarrow{FeCl_3}$$

- 12. Which compound in each of the following pairs will react faster in S_N^2 reaction with OH^- and why?
 - (i) CH₃Br or CH₃I
 - (ii) (CH₃)₃ CCl or CH₃Cl
- 13. In the following pairs which halogen compound undergoes faster SN1 reaction?

(i)
$$CI$$
 and CI

- (iii) $(CH_3)_3C CI$ and $C_6H_5CH_2CI$
- (iv) $C_6H_5CH_2CI$ and $C_6H_5C(CI)C_6H_5$
- (v) $CH_2 = CH CI$ and $CH_2 = CH CH_2CI$
- 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 Kl.
- (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_N1 pathway. The carbocation is formed first which gives a mixture of (\pm) butan-2-ol in the second step].

I.
$$HO-CH_3$$
 $OH^ CH_2CH_3$ H_3CH_2C $H_3CH_2CH_3$ H_3CH_2C $H_3CH_2CH_3$ H_3CH_2C $H_3CH_2CH_3$ H_3CH_2C

(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) CH₃CH₂CH₂CH₃
 - (ii) (CH₃)₂CHCH₂CH₃
 - (iii) (CH₃)₂CHCH(CH₃)₂

[Hint: (i) Two, (ii) four, (iii) three

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

Give the mechanism for this reaction.

(b) In the following reaction : CH_3 $H_3C - C - CH = CH_2 \xrightarrow{H_2O/H^+}$ CH_3

major and minor products are :

Ans. Major (iii) minor (i)

- 17. Give one use of each of following:
 - (i) Freon-12

- (ii) DDT
- (iii) Carbon tetrachloride
- (iv) lodoform

 An optically active compound having molecular formula C₇H₁₅Br reacts with aqueous KOH to give C₇H₁₅OH, which is optically inactive. Give mechanism for the reaction.

[Ans. : (i)
$$C_2H_5$$
— C —Br $\xrightarrow{-Br}$ C_3H_7 (Slow)

(ii)
$$HO - C - C_2H_7 \xrightarrow{OH^-} H_5C_2 \xrightarrow{C} C_3H_7 \xrightarrow{OH^-} H_5C_2 - C - OH$$
 product with inversion of configuration of configuration

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.

$$[\textbf{Ans.}: (A)] \begin{picture}(40,0)(0,0)(0,0) \put(0,0){(1,0)} \put$$

*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 symetrical. Both alkenes on hydrogenation give 2, 3-dimethylbutane. Identify X, Y and Z.

[Ans.

*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) CH₃CH₂CH₂CI, (B) CH₃CH₂CH₂CN, (C) CH₃CH₂CH₂CONH₂

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

(a)
$$\longrightarrow$$
 Br + Mg $\xrightarrow{\text{dry ether}}$ A $\xrightarrow{\text{H}_2\text{O}}$ B

(b) R-Br + Mg
$$\xrightarrow{\text{dry ether}}$$
 C $\xrightarrow{D_2O}$ CH₃-CH-CH₃

(c)
$$\longrightarrow$$
 $\stackrel{\text{Na/dry ether}}{\longleftarrow}$ R'X $\stackrel{\text{Mg}}{\longrightarrow}$ D $\stackrel{\text{H}_2O}{\longrightarrow}$ E

- 23. Which nomenclature is not occording to IUPAC system.
 - (i) Br CH_2 CH = CH_2 ; 1-bromoprop-2-ene

(ii)
$$CH_3 - CH_2 - CH_2 - CH_3 - CH_3 + CH_3 - CH_3 - CH_3 - CH_3 + CH_3 - CH$$

(iii)
$$CH_3 - CH - CH - CH_2 CH_3$$
, 2-methyl-3-phenylpentane CH_3

(iv)
$$CH_3 - C - CH_2 CH_2 - CH_2 COON$$
, 5-oxohexanoic acid O