Unit - 11

ALCOHOLS, PHENOLS AND ETHERS

1. Write IUPAC names of the following compounds :

$$\begin{array}{ccc} & & \text{CH}_2\text{OH} \\ | & & | \\ \text{(i)} & \text{CH}_3\text{--}\text{CH}_2\text{--}\text{CH}\text{--}\text{CH}\text{--}\text{CH}\text{--}\text{CH}_3 \\ | & & | \\ & & \text{CH}_2\text{CI} & \text{CH}_3 \\ \end{array}$$

- (ix) $C_6H_5OC_3H_7$
- (x) CH₃CH₂OCH₂CH₂CH₂CI
- 2. Write the structures of the compounds whose names are given below :
 - (i) 3, 5-dimethoxyhexane-1, 3, 5-triol
 - (ii) cyclohexylmethanol
 - (iii) 2-ethoxy-3-methylpentane
 - (iv) 3-chloromethylpentan-2-ol
 - (v) p-nitroanisole
- 3. Describe the following reactions with example :
 - (i) Hydroboration oxidation of alkenes
 - (ii) Acid catalysed dehydration of alcohols at 443K.
 - (iii) Williamson synthesis
 - (iv) Reimer-Tiemann reaction.
 - (v) Kolbe's reaction
 - (vi) Friedel-Crafts acylation of Anisole.
- 4. Complete the following reactions:

(i)
$$CH_3CH_2CH_2CHO \xrightarrow{Pd/H_2}$$

(ii)
$$CH_3CHO \xrightarrow{(i) CH_3MgBr}$$
 \longrightarrow $(ii) H^+/H_2O$

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(iii)
$$CH_3CH_2OH \xrightarrow{Cu/573K}$$

(iv)
$$C_6H_5OH + Br_2 \xrightarrow{H_2O}$$

$$(ix) \quad (CH_3)_3C - O - C_2H_5 + HI \longrightarrow$$

$$(x) \qquad \frac{\text{conc. HNO}_3}{\text{conc. H}_2\text{SO}_4}$$

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- 5. What happens when:
 - (i) aluminium reacts with tert-butyl alcohol
 - (ii) phenol is oxidised with chromic acid
 - (iii) cumene is oxidised in the presence of air and the product formed is treated with dilute acid.
 - (iv) phenol is treated with conc. HNO₃.
 - (v) phenol is treated with chloroform in presence of dilute NaOH.
- 6. How will you convert
 - (i) propene to propan-l-ol.
 - (ii) anisole to phenol
 - (iii) butan-2-one to butan-2-ol
 - (iv) ethanal to ethanol
 - (v) phenol to ethoxybenzene
 - (vi) 1-phenylethene to 1-phenylethanol
 - (vii) formaldehyde to cyclohexylmethanol
 - (viii) butyl bromide to pentan-1-ol.
 - (ix) toluene to benzyl alcohol
 - (x) 1-propoxypropane to propyl iodide
 - (xi) ethyl bromide to 1-ethoxyethane
 - (xii) methyl bromide to 2-methoxy-2-methylpropane
 - (xiii) ethyl bromide to ethoxybenzene
 - (xiv) ethanol to benzyl ethyl ether.

7. Identify the missing reactant or product A to D in the following equations:

(i)
$$(A) + HNO_3 + H_2SO_4$$
 O_2N NO_2

(ii)
$$CH_3 + dil. H_2SO_4 \longrightarrow (B)$$

(iii) (C) +
$$H_2O \xrightarrow{H^+} CH_3(CH_2)_2 C(CH_3)$$
 (OH) (CH₂)₂CH₃

(vi)
$$CH_3OC_6H_5 + HI \longrightarrow (D)$$

8. Identify X, Y and Z in the following sequence of reactions:

(i) Phenol
$$\xrightarrow{Zn \text{ dust}} X \xrightarrow{CH_3Cl} Y \xrightarrow{KMnO_4} Z$$

(ii) Ethanol
$$\xrightarrow{PBr_3} X \xrightarrow{\text{alc. KOH}} Y \xrightarrow{\text{dil.H}_2SO_4} Z$$

(iii)
$$CH_3$$
 HI $X + CH_3I$

$$X + conc. HNO_3 \longrightarrow Y$$
 (a dinitro compound)

$$X + Br_2(aq) \longrightarrow Z$$
 (a tribromo product)

10. Write the mechanism for following reactions :

(i)
$$\searrow$$
C=C \swarrow + H₂O $\stackrel{\text{H}^+}{\longleftarrow}$ \searrow C-C $\stackrel{\text{C}}{\longleftarrow}$

(acid catalysed hydration of alkenes)

- (ii) $CH_3 CH_2 OH \xrightarrow{H^+} CH_2 = CH_2$ (acid catalysed dehydration of alcohols)
- (iii) $2CH_3CH_2OH \xrightarrow{H^+} CH_3CH_2OCH_2CH_3$ (acid catalysed nucleophilic substitution reaction)
- (iv) $CH_3OCH_3 + HI \longrightarrow CH_3OH + CH_3I$
- (v) $(CH_3)_3C O CH_3 + HI \longrightarrow CH_3OH + (CH_3)_3 CI$
- 11. Give reason for the following:
 - (i) The C-O-C bond angle in dimethyl ether is (111.7°)
 - (ii) Alcohols have higher boiling points than ethers of comparable molecular masses.
 - (iii) Phenols are more acidic than alcohols.
 - (iv) Nitrophenol is more acidic than o-methoxyphenol.
 - (v) Phenol is more reactive towards electrophilic substitution reaction than benzene.
 - (vii) The following is not an appropriate method for the preparation of t-butyl ethyl ether:

- (a) What would be the major product of this reaction?
- (b) Write suitable reaction for the preparation of t-butyl ethyl ether.
- (viii) The following is not an appropriate method for the preparation of 1-methoxy-4-nitrobenzene;

- (x) Write the suitable reaction for the preparation of 1-methoxy-4-nitrobenzene
- (ix) o-nitrophenol is steam volatile but p-nitrophenol is not.
- (x) phenol is less polar than ethanol.
- (xi) The phenyl methyl ether reacts with HI fo form phenol and iodomethane and not iodobenzene and methanol.

- (xii) methanol is less acidic than water.
- (xiii) alcohols can act as weak base as well as weak acids.
- (xiv) phenols do not give protonation reaction readily.
- (xvi) absolute ethanol can not be obtained by factional distillation of ethanol and water mixture.
- 12. Arrange the following in the increasing order of property shown:
 - (i) methanol, ethanol, diethylether, ethyleneglycol. (Boiling points)
 - (ii) phenol, o-nitrophenol, m-nitrophenol, p-nitrophenol. (Acid strength)
 - (iii) dimethylether, ethanol, phenol. (Solubility in water)
 - (iv) n-butanol, 2-methylpropan-1-ol, 2-methylpropan-2-ol. (Acid strength)
- 13. Give a chemical test to distinguish between the following pair of compounds.
 - (i) n-propyl alcohol and isopropylalcohol
 - (ii) methanol and ethanol
 - (iii) cyclohexanol and phenol.
 - (iv) propan-2-ol and 2-methylpropan-2-ol.
 - (v) phenol and anisole
 - (vi) ethanol and diethyl ether
- *14. Which of the following compounds gives fastest reaction with HBr and why?
 - (i) $(CH_3)_3COH$
 - (ii) CH₃CH₂CH₂OH

- *15. What is the function of $ZnCl_2$ (anhyd) in Lucas test for distinction between 1°, 2° and 3° alcohols.
- 16. An alcohol A ($C_4H_{10}O$) on oxidation with acidified potassium dichromate gives carboxylic acid B ($C_4H_8O_2$). Compound A when dehydrated with conc. H_2SO_4 at 443 K gives compound C. Treatment of C with aqueous H_2SO_4 gives compound D ($C_4H_{10}O$) which is an isomer of A. Compound D is resistant to oxidation but compound A can be easily oxidised. Identify A, B, C and D and write their structures.

 $[\textbf{Ans.:} \qquad [\textbf{A}]: (\textbf{CH}_3)_2 \textbf{CHCH}_2 \textbf{OH} \qquad [\textbf{B}]: \textbf{CH}_3 \textbf{CH} (\textbf{CH}_3) \textbf{COOH}$

[C] : $(CH_3)_2C = CH_2$ [D] : $(CH_3)_3C - OH$

*17. An organic compound A having molecular formula C₆H₆O gives a characteristic colour with aqueous FeCl₃. When A is treated with NaOH and CO₂ at 400 K under pressure, compound B is obtained. Compound B on acidification gives compound C which reacts with acetyl chloride to form D which is a popular pain killer. Deduce the structure of A, B, C and D. What is the common name of Drug D?

[Ans.:

19. An ether A (C₅H₁₂O) when heated with excess of hot concentrated HI produced two alkyl halides which on hydrolysis from compounds B and C. Oxidation of B gives an acid D whereas oxidation of C gave a ketone E. Deduce the structures of A, B, C, D and E.

- (B) CH₃CH₂OH
- (C) CH₃CHOHCH₃
- (D) CH₃COOH
- (E) CH₃COCH₃
- 20. Phenol, C₆H₅OH when it first reacts with concentrated sulphuric acid, forms Y.Y is reacted with concentrated nitric acid to form Z. Identify Y and Z and explain why phenol is not converted commercially to Z by reacting it with conc. HNO₃.

[Ans. :

Phenol is not reacted directly with conc. \mbox{HNO}_3 because the yield of picric acid is very poor]

21. Synthesise the following alcohols from suitable alkenes.

(a)
$$CH_3$$
 (b) OH

- 22. How are the following ethers prepared by williumson synthesis?
 - (a) Ethoxybenzene
- (b) 2-methoxy-2-methylpropane