

## **Unit - 11**

## **ALCOHOLS, PHENOLS AND ETHERS**

1. Write IUPAC names of the following compounds:



- (ix)  $C_6H_5OC_3H_7$
- (x) CH<sub>3</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CI
- 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) 
$$CH_3CHO \xrightarrow{(i) CH_3MgBr}$$



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

$$\text{(iv)} \quad \text{C}_6\text{H}_5\text{OH} + \text{Br}_2 \xrightarrow{\quad \text{H}_2\text{O} \quad} \\$$

(vii ) 
$$CH_3CH_2CH_2O - CH_3 + HBr \longrightarrow$$

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

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



(xiv) 
$$\frac{\text{SO}_{3}\text{H}}{\text{(ii) NaOH, }\Delta}$$

- 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. HNO<sub>3</sub>.
  - (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)  $(CH_2)_2CH_3$ 

(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) 
$$CH_3$$
  $HI \rightarrow X + CH_3I$ 

$$X + conc. HNO_3 \longrightarrow Y$$
 (a dinitro compound)  
 $X + Br_2(aq) \longrightarrow Z$  (a tribromo product)

10. Write the mechanism for following reactions :

(i) 
$$\searrow$$
C=C $\swarrow$  + H<sub>2</sub>O  $\stackrel{\text{H}^+}{\longleftarrow}$   $\searrow$ 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) 
$$2CH_3CH_2OH \xrightarrow{H^+} 413 \text{ K} \rightarrow CH_3CH_2OCH_2CH_3$$
 (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;

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- (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) CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>OH



- \*15. What is the function of ZnCl<sub>2</sub> (anhyd) in Lucas test for distinction between 1°, 2° and 3° alcohols.
- 16. An alcohol A (C<sub>4</sub>H<sub>10</sub>O) on oxidation with acidified potassium dichromate gives carboxylic acid B (C<sub>4</sub>H<sub>8</sub>O<sub>2</sub>). Compound A when dehydrated with conc. H<sub>2</sub>SO<sub>4</sub> at 443 K gives compound C. Treatment of C with aqueous H<sub>2</sub>SO<sub>4</sub> gives compound D (C<sub>4</sub>H<sub>10</sub>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.

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

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

\*17. An organic compound A having molecular formula C<sub>6</sub>H<sub>6</sub>O gives a characteristic colour with aqueous FeCl<sub>3</sub>. When A is treated with NaOH and CO<sub>2</sub> 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 (C<sub>5</sub>H<sub>12</sub>O) 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) CH<sub>3</sub>CH<sub>2</sub>OH
- (C) CH<sub>3</sub>CHOHCH<sub>3</sub>
- (D) CH<sub>3</sub>COOH
- (E) CH<sub>3</sub>COCH<sub>3</sub>
- 20. Phenol, C<sub>6</sub>H<sub>5</sub>OH 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. HNO<sub>3</sub>.

## [Ans. :

Phenol is not reacted directly with conc.  $\ensuremath{\mathsf{HNO}_3}$  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