

ALCOHOLS, PHENOLS AND ETHERS

1.1. Classify the following as primary, secondary and tertiary alcohols.

- (ii) $H_2C = CH CH_2OH$
- (iii) CH₃CH₂CH₂OH
- (iv) H,C CH OH

(vi)
$$CH = CH - C - OH$$
 CH_3
 CH_3

Ans: Primary alcohols: (i), (ii), (iii)

Secondary alcohols: (iv), (v)

Tertiary alcohols: (vi)

11.2. Identify aliylic alcohols in the above examples.

Ans: (ii) and (iv) i.e. H₂C=CH – CH₂OH and

11.3. Name the following compounds according to IUPAC system.

(iv)
$$H_2C = CH - CH - CH_2 - CH_2 - CH_3$$

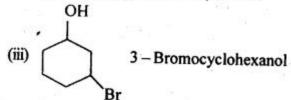
OH

(v)
$$CH_3 - C = C - CH_2OH$$

 $CH_3 Br$

Ans:

2, 5-Dimethylhexane - 1, 3 - diol



(iv)
$$H_2C = CH - CH - CH_2 - CH_2 - CH_3$$

OH

(v)
$$CH_3 - C = C - CH_2OH$$

 $H_3C - Br$

2-Bromo-3-methyl but-2-en-1-ol

11.4. Show how are the following alcohols prepared by the reaction of a suitable Grignard reagent on methanal ?

Ans:

(i)
$$CH_3$$
— CH — CH_2OH

$$CH_3$$

$$H$$

$$C = O + R - MgBr \xrightarrow{Dry} H$$

$$\downarrow H$$

$$\downarrow H' / H_1O$$

$$\Leftrightarrow H$$

$$Given: CH_3 - CH - CH_2OH$$

$$CH_3$$

$$\therefore R \text{ is } CH_3 - CH - CH_2OH$$

$$CH_3$$

11.5. Write structures of the products of the following reactions:

(ii)
$$CH_3 - CH = CH_2 \xrightarrow{H_2O/H^+}$$
 $CH_3 - C - OCH_3 \xrightarrow{NaBH_4}$

(iii) $CH_3 - CH_2 - CH - CHO \xrightarrow{NaBH_4}$
 CH_3

11.6. Give structures of the products you would expect when each of the following alcohol reacts with (a)HCI-ZnCl₂ (b)HBrand (c) SOCl₂

(i)Butan-1-ol

(ii)2-Methylbutan-2-ol

Ans:

(a) with
$$HCl - ZnCl_2$$
 $CH_3CH_2CH_2CH_2OH + HCl \xrightarrow{anhy}$
butan -1-ol (1°)

No reaction at room temperature

 CH_3
 $CH_3 - C - CH_2CH_3 + HCl \xrightarrow{anhy}$
 $CH_3 - C - CH_2CH_3 + HCl \xrightarrow{anhy}$
 $CH_3 - C - CH_2CH_3 + COH_3$
 $CH_3 - C - CH_2CH_3$
 $CH_3 - C - CH_2CH_3$

(b) with HBr

$$CH_{3}CH_{2}CH_{2}CH_{2}OH + HBr \xrightarrow{\Delta}$$

$$CH_{3}CH_{2}CH_{2}CH_{2}Br + H_{2}O$$

$$1-Bromobutane$$

$$CH_{3}$$

$$CH_{3}-C-CH_{2}CH_{3} + HBr \xrightarrow{\Delta}$$

$$OH$$

$$CH_{3}$$

$$\begin{array}{c} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH} + \text{SOCl}_2 \xrightarrow{\Delta} \\ \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CI} + \text{SO}_2 + \text{HCI} \\ \text{I-Cholorobutane} \\ \text{CH}_3 & \\ \text{CH}_3 - \text{C-CH}_2\text{CH}_3 + \text{SOCl}_2 \xrightarrow{\Delta} \\ \text{OH} & \\ \text{CH}_3 & \\ \text{CH}_3 - \text{C-CH}_2\text{CH}_3 + \text{SO}_2 + \text{HCI} \\ \\ \text{CI} \\ \text{2-Chloro-2-methyl-butane} \end{array}$$

11.7. Predict the major product of acid catalysed dehydration of

- (i) 1-nicthylcyclohcxanoland
- (ii) butan-1-ol

Ans:

11.8. Ortho and para nitrophenols are more acidic than phenol. Draw the resonance structures of the corresponding phenoxide ions.

Ans:

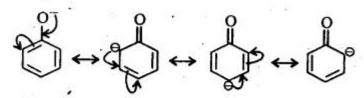
The resonance structures of o-and p- nitrophenoxide ions and phenoxide ion are given

below:

o-nitrophenoxide ion:

p-nitrophenoxide ion :

phenoxide ion:



Due to -R effect of $-NO_2$ group, o- and p-nitrophenoxide are more stable than phenoxide ion. As a result, o- and p-nitrophenols are more acidic than phenol.

11.9; Write the equations involved in the following reactions:

- (i) Reimer-Tiemann reaction
- (ii) Kolbe's reaction

Ans: (i) Reimer-Tiemann reaction

(ii) Kolbe's reaction

11.10. Write the reactions of Williamson synthesis of 2-ethoxy-3-methylpentane starting from ethanol and 3-methylpentan-2-ol.

Ans: In Williamsons's synthesis, the alkyl halide should be primary. Thus, the alkyl halide should be derived from ethanol and the alkoxide ion from 3-methylpentan-2-ol. The synthesis is as follows

$$\begin{array}{c} \text{CH}_3\text{CH}_2\text{OH} + \text{HBr} & \underline{\hspace{1cm}} \Delta \\ \text{CH}_3\text{CH}_2\text{CH} - \text{CH} - \text{OH} + \text{Na} & \underline{\hspace{1cm}} \Delta \\ | & | & | \\ \text{CH}_3 & \text{CH}_3 \\ & & \text{CH}_3\text{CH}_2 - \text{CH} - \text{CH} - \text{O}^- \text{Na}^+ + \text{H}_2 \\ & | & | & | \\ \text{CH}_3 & \text{CH}_3 \\ & & \text{CH}_3 & \text{CH}_3 \end{array}$$

11.11. Which of the following is an appropriate set of reactants for the preparation of I-methoxy-4- nitrobenzene and why?

Ans:

Chemically, both sets are equally probable.

11.12. Predict the products of the following reactions:

(i)
$$CH_3 - CH_2 - CH_2 - O - CH_3 - HBr \rightarrow$$

(iii)
$$OC_2H_5 + HBr \longrightarrow$$

Ans:

$$OC_2H_5 \longrightarrow OH + CH_3CH_2B_1$$
Phenol Bromoethane

(iii)

$$(iv)(CH_3)_3C-OC_2H_5+HI \longrightarrow$$