

11.11. Write the mechanism of hydration of ethene to yield ethanol. Ans: Direct addition of H_2O to ethene in presence of an acid does not occur. Indirectly, ethene is first passed through concentrated H_2SO_4 , when ethyl hydrogen sulphate is formed.

$$\begin{aligned} & \text{H}_2\text{SO}_4 \longrightarrow \text{H}^+ + \text{-OSO}_2\text{OH} \\ & \text{CH}_2 = \text{CH}_2 + \text{H}^+ \longrightarrow \text{CH}_3 - \text{CH}_2^+ \xrightarrow{\prime} \xrightarrow{-\text{OSO}_2\text{OH}} \text{CH}_3\text{CH}_2\text{OSO}_2\text{OH} \\ & \text{Ethyl carbonation} \end{aligned}$$

Ethylhydrogen sulphate is then boiled with water undergoes hydrolysis to form ethanol.

$$H_2\ddot{O} + CH_3 - CH_2 - OSO_2OH \longrightarrow CH_3 - CH_2 - O + H_3\ddot{O} + CH_3 - CH_2 - OH + H_3\ddot{O}$$
Ethylhydrogen Ethanol

11.12. You are given benzene, cone. $\rm H_2SO_4$ and NaOH. Write the equations for the preparation of phenol using these reagents. Ans:

11.13. Show how will you synthesise

- (i) 1-phenylethanol from a suitable alkene.
- (ii) cyclohexylmethanol using an alkyl halide by an SN₂ reaction.
- (iii) Pentan-I-ol using a suitable alkyl halide?
- (i) Addition of H₂O to ethenylbenzene is presence of dil H₂SO₄.

(ii) Hydrolysis of cyclohexylmethyl bromide by aqueous NaOH gives cyclohexylmethanol.

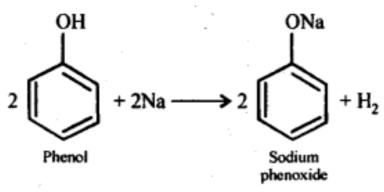
(iii) Hydrolysis of 1-bromopentane by aqueous NaOH gives pentan-1-ol.

$$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Br} + \text{NaOH} \xrightarrow{\hspace*{1cm} \frac{\Delta}{S_N^2, \text{Hydrolysis}}} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2 - \text{OH} + \text{NaBr}_2\text{CH}_2\text{CH}_2 + \text{OH} + \text{NaBr}_2\text{CH}_2\text{CH}_2 + \text{OH} + \text{NaBr}_2\text{CH}_2 + \text{OH} + \text{NaBr}_2\text{CH}_2 + \text{OH} + \text{NaBr}_2\text{CH}_2 + \text{OH} + \text{NaBr}_2\text{CH}_2 + \text{OH} + \text{NaBr}_2 + \text{OH} + \text{NaBr}_2 + \text{OH} + \text{OH}$$

11.14. Give two reactions that show the acidic nature of phenol. Compare its acidity with that of ethanol.

Ans: The reactions showing acidic nature of phenol are:

(a) Reaction with sodium: Phenol reacts with active metals like sodium to liberate H, gas.



(b) Reaction with NaOH: Phenol dissolves in NaOH to form sodium phenoxide and water.

$$2 \longrightarrow + \text{NaOH} \longrightarrow + \text{H}_2\text{O}$$

Phenol is more acidic than ethanol. This is due to the reason that phenoxide ion left after the loss of a proton from phenol is stabilized by resonance, while ethoxide ion left after less of a proton from ethanol, is not.

11.15. Explain why is ortho-nitrophenol more acidic than orthomethoxyphenol?

Ans: Due to strong -R and - I-effect of the -NO $_2$ group, electron density of the O - H bond decreases and hence the loss of a proton becomes easy.

Further, after the loss of a proton, the o-nitrophenoxide ion left behind is stabilized by resonance and electron withdrawing -NO₂ group which withdraws electrons and disperses the negative charge.

$$\bigcup_{i=1}^{O_{\overline{i}}} \bigvee_{i=1}^{N} \bigcap_{i=1}^{O_{\overline{i}}} \longleftrightarrow etc.$$

In contrast, due to +R effect of the -OCH, group, it increases the electron density of the O-H bond thereby making the loss of proton difficult.

$$\bigcap_{O-H} \bigcirc_{OCH_3} \longleftrightarrow \bigcap_{O-H} \bigcirc_{CCH_3}$$

Further more, the o-methoxyphenoxide ion left after the loss of a proton is destabilized by resonance. The two negative charges repel each other thereby destabilizing the o-methoxy phenoxide ion.

Further the presence of electron donating -OCH₃ group intensifies the negative charge thereby destabilising the phenoxide ion. Thus, o-nitrophenol is more acidic than o-methoxyphenol.

11.16. Explain how does the - OH group attached to a carbon of benzene ring activate it towards electrophilic substitution?

Ans: Phenol may be regarded as a resonance hybrid of structures I-V, shown below.

$$\stackrel{\ddot{O}H}{\longleftrightarrow} \longleftrightarrow \stackrel{\ddot{O}H}{\longleftrightarrow} \stackrel{+\ddot{O}H}{\longleftrightarrow} \stackrel{+$$

As a result of +R effect of the -OH group, the electron density in the benzene ring increases thereby facilitating the attack of an electrophile. In other words, presence of -OH group, activates the benzene ring towards electrophilic substitution reactions. Further, since the electron density is relatively higher at the two o-and one p-position, therefore electrophilic substitution occurs mainly at o-and p-positions.

11.17. Give equations of the following reactions:

- (i) Oxidation of propan-I-ol with alkaline KMnO_4 solution.
- (ii) Bromine in CS₂ with phenol.
- (iii) Dilute HNO3 acid with phehoL

(iv) Treating phenol with chloroform in presence of aqueous NaOH. Ans:

11.18 Explain the following with an example

- (i) Kolbe's reaction
- (ii) Reimer Tiemann reaction -
- (iii) Williamson ether synthesis
- (iv) Unsymmetrical ether

Ans:

(i) Kolbe's reaction: Sodium phenoxide when heated with $\rm CO_2$ at 400K under a pressure of 4-7 atmospheres followed by acidification gives 2-hydroxybenzoic acid (salicylic acid) as the major product along with a small amount of 4-hydroxybenzoic acid. This reaction is called Kolbe's reaction.

(ii) Reimer-Tiemann reaction: Treatment of phenol with $CHCl_3$ in presence of aqueous sodium or potassium hydroxide at 340 K followed by hydrolysis of the resulting product gives 2-hydroxybenzaldehyde (salicyialdehyde) as the major product. This reaction is called Reimer-Tiemann reaction.

(iii) Williamson's ether synthesis: It involves the treatment of an alkyl halide with a suitable sodium alkoxide to obtain ethers. The sodium alkoxide needed for the purpose is prepared by the action of sodium on a suitable alcohol. In this reaction alkyl halide should primary. Secondary and tertiary halides will predominantly give an alkene.

$$\begin{array}{c} \text{CH}_3\text{CH}_2 - \overline{\text{O}} - \text{Na}^+ + \text{Br} - \text{CH}_2\text{ CH}_3 \\ \text{Sodium ethoxide} \end{array} \xrightarrow{\text{Ethylbromide}} \\ \begin{array}{c} \underline{\text{330 K}} \\ \text{Ethylbromide} \end{array} \xrightarrow{\text{CH}_3\text{CH}_2} - \text{O} - \text{CH}_2\text{CH}_3 + \text{Na}^+\text{Br}^-$$

(iv) Unsymmetrical ether: If the alkyl or aryl groups attached to the oxygen atom are different, ethers are called unsymmetrical ethers. For example, ethylmethylether, methylphenylether, 4-chlorophenyl-4-nitrophenyl ether, etc.

11.19. Write the mechanism of acid dehydration of ethanol to yield ethene.

Ans: The mechanism of dehydration of alcohols to form alkenes occur by the following three steps:

(a) Formation of protonated alcohol:

$$CH_3CH_2 - \overset{\bullet}{O} - H + \overset{\bullet}{H} \stackrel{\leftarrow}{\longleftarrow} CH_3CH_2 - \overset{+}{O} \stackrel{+}{\longleftarrow} \overset{H}{H}$$
(Oxonium Salt)

(b) Formation of carbocation:

$$CH_3CH_2$$
 \xrightarrow{f} \xrightarrow{H} \xrightarrow{Slow} CH_3CH_2 \xrightarrow{h} $\xrightarrow{h$

(c) Elimination of a proton to form ethene:

11.20. How are the following conversions carried out?

- (i) Propene → Propan -2-ol
- (ii) Benzyl chloride \rightarrow Benzyl alcohol
- (iii) Ethyl magnesium chloride \rightarrow Propan-I-ol
- (iv) Methyl magnesium bromide \rightarrow 2-Methylpropan-2-ol Ans:

(i)
$$CH_3$$
— $CH = CH_2 + Conc. H_2SO_4$ \longrightarrow CH_3 — $CH - CH_3$
 $\xrightarrow{H_2O, \Delta}$
 CH_3 — CH - CH_3
 OSO_3H
 CH_3 — CH - CH_3
 OH
 OH
 OH

********* END *******