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.

$$H_2SO_4 \longrightarrow H^+ + {}^-OSO_2OH$$

$$\underset{\text{Ethene}}{CH_2=CH_2} + H^+ \longrightarrow \underset{\text{Ethylcarbonation}}{CH_3-\overset{+}{C}H_2} \xrightarrow[\text{Fast}]{{}^-OSO_2OH} \underset{\text{Ethyl hydrogen sulphate}}{CH_3CH_2OSO_2OH}$$

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

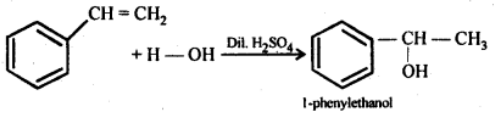
$$\underset{\text{Ethylhydrogen sulphate}}{H_2\ddot{O} + CH_3-CH_2-\ddot{O}SO_2OH} \longrightarrow CH_3-CH_2-\overset{+}{\ddot{O}}\overset{H}{\underset{H}{<}} \xleftarrow{H_2\ddot{O}} \underset{\text{Ethanol}}{CH_3-CH_2-OH} + H_3\overset{+}{O}$$

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

$$\underset{\text{Benzene}}{C_6H_6} \xrightarrow[\text{Sulphonation}]{\text{conc.}H_2SO_4,\Delta} \underset{\substack{\text{Benzene}\\\text{sulphonic acid}}}{C_6H_5SO_3H} \xrightarrow[573\,K]{NaOH,\text{fuse}} \underset{\substack{\text{Sodium}\\\text{phenoxide}}}{C_6H_5ONa} \xrightarrow[-NaCl]{\text{Dil HCl}} \underset{\text{Phenol}}{C_6H_5OH}$$

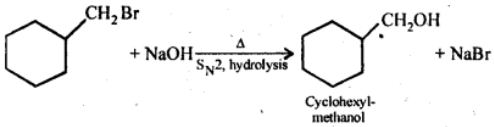
11.13. Show how will you synthesise
(i) 1-phenylethanol from a suitable alkene.
(ii) cyclohexylmethanol using an alkyl halide by an SN_2 reaction.
(iii) Pentan-l-ol using a suitable alkyl halide?
Ans:

(i) Addition of H_2O to ethenylbenzene is presence of dil H_2SO_4.



1-phenylethanol

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

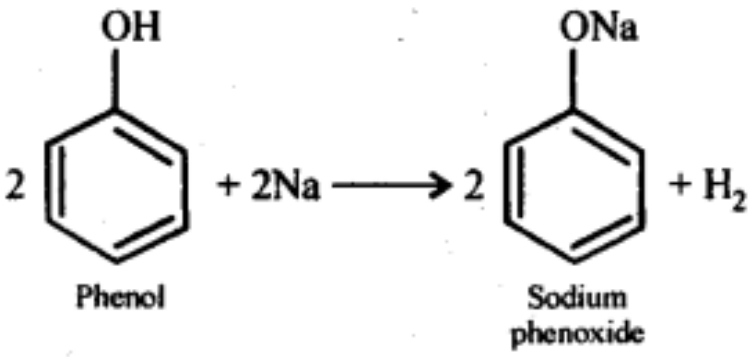


Cyclohexyl-methanol

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

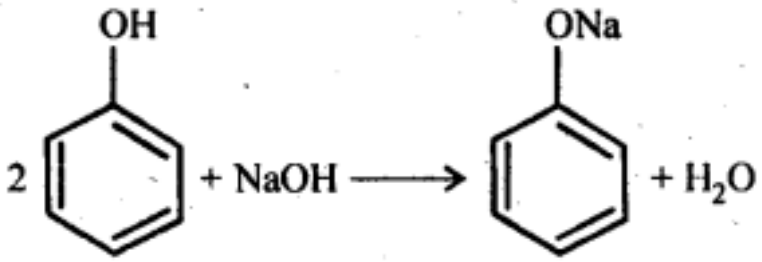
$$CH_3CH_2CH_2CH_2CH_2Br + NaOH \xrightarrow[S_N2,\text{Hydrolysis}]{\Delta} \underset{\text{Propan-1-ol}}{CH_3CH_2CH_2CH_2CH_2-OH} + NaBr$$

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.



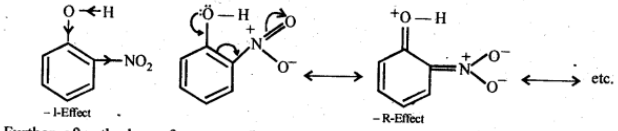
Phenol — Sodium phenoxide

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

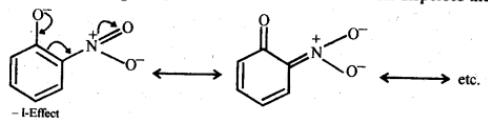


Phenol is more acidic than ethanol. This is due to the reason that phenoxide ion left after the loss of a proton from phenol is stabilized by resonance, while ethoxide ion left after less of a proton from ethanol, is not.

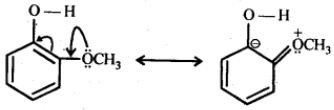
11.15. Explain why is ortho-nitrophenol more acidic than ortho-methoxyphenol?
Ans: Due to strong -R and - I-effect of the -NO_2 group, electron density of the O - H bond decreases and hence the loss of a proton becomes easy.



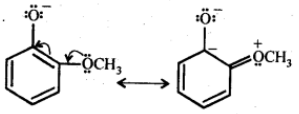
Further, after the loss of a proton, the o-nitrophenoxide ion left behind is stabilized by resonance and electron withdrawing –NO_2 group which withdraws electrons and disperses the negative charge.



In contrast, due to +R effect of the –OCH_3 group, it increases the electron density of the O– H bond thereby making the loss of proton difficult.

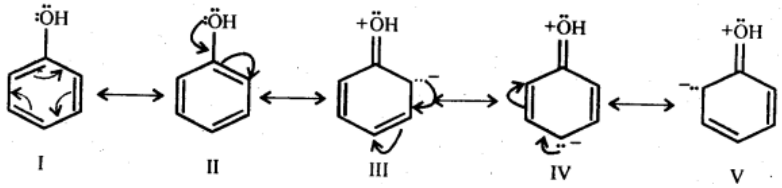


Further more, the *o*-methoxyphenoxide ion left after the loss of a proton is destabilized by resonance. The two negative charges repel each other thereby destabilizing the *o*-methoxy phenoxide ion.



Further the presence of electron donating –OCH_3 group intensifies the negative charge thereby destabilising the phenoxide ion. Thus, *o*-nitrophenol is more acidic than *o*-methoxyphenol.

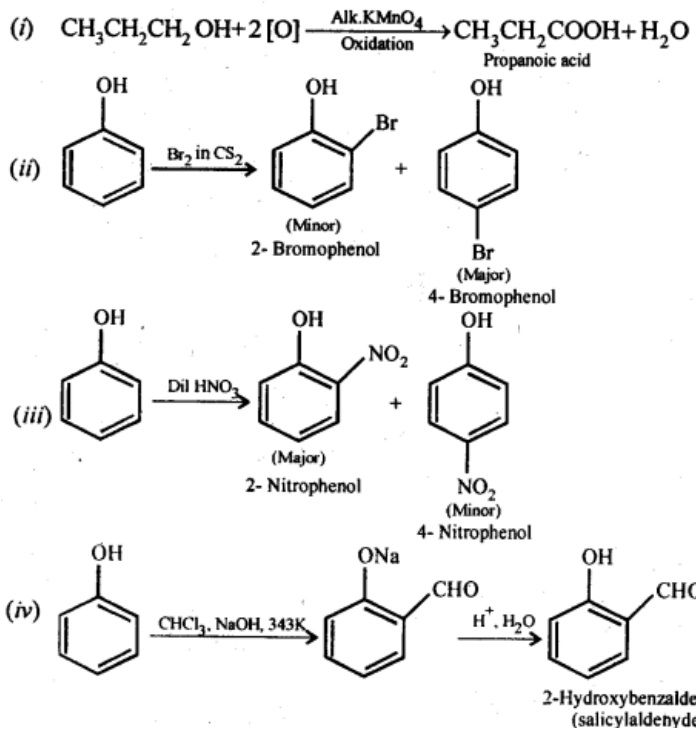
11.16. Explain how does the - OH group attached to a carbon of benzene ring activate it towards electrophilic substitution?
Ans: Phenol may be regarded as a resonance hybrid of structures I-V, shown below.



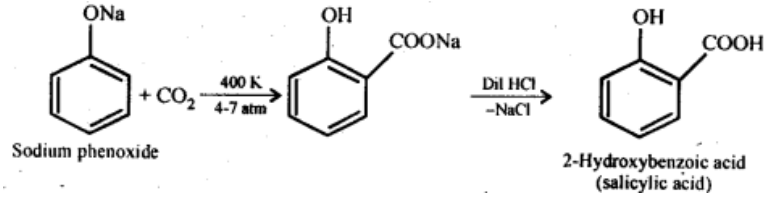
As a result of +R effect of the -OH group, the electron density in the benzene ring increases thereby facilitating the attack of an electrophile. In other words, presence of -OH group, activates the benzene ring towards electrophilic substitution reactions. Further, since the electron density is relatively 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 CS_2 with phenol.
(iii) Dilute HNO_3 acid with phehoL

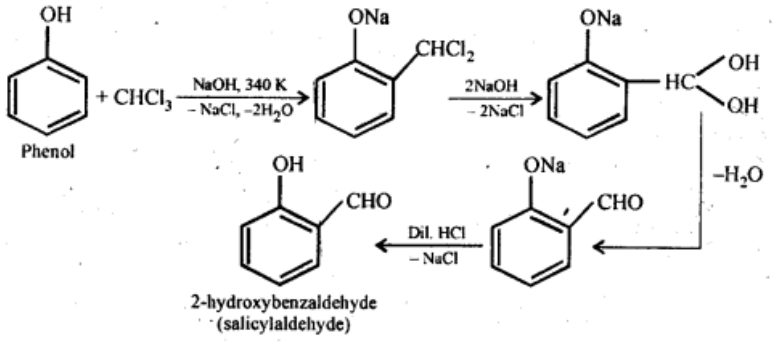
(iv) Treating phenol with chloroform in presence of aqueous NaOH.
Ans:



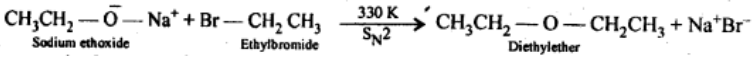
11.18 Explain the following with an example
(i) Kolbe's reaction
(ii) Reimer - Tiemann reaction -
(iii) Williamson ether synthesis
(iv) Unsymmetrical ether
Ans:
(i) Kolbe's reaction: Sodium phenoxide when heated with CO_2 at 400K under a pressure of 4-7 atmospheres followed by acidification gives 2-hydroxybenzoic 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.



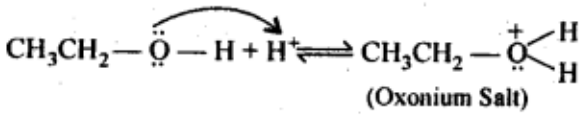
(iii) Williamson's ether synthesis: It involves the treatment of an alkyl halide with a suitable sodium alkoxide to obtain ethers. The sodium alkoxide needed for the purpose is prepared by the action of sodium on a suitable alcohol. In this reaction alkyl halide should primary. Secondary and tertiary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



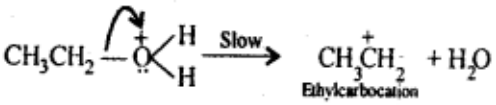
(iv) Unsymmetrical ether: If the alkyl or aryl groups attached to the oxygen atom are different, ethers are called unsymmetrical ethers. For example, ethylmethylether, methylphenylether, 4-chlorophenyl-4-nitrophenyl ether, etc.

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:

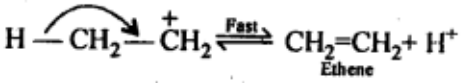
(a) Formation of protonated alcohol:



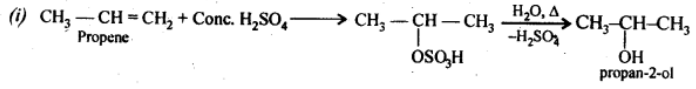
(b) Formation of carbocation :

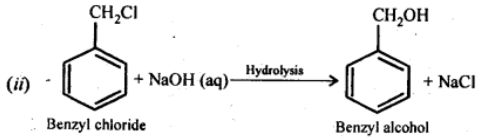


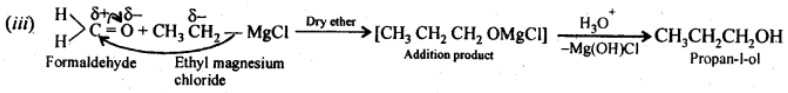
(c) Elimination of a proton to form ethene:

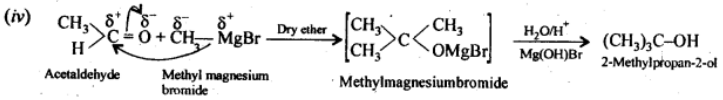


11.20. How are the following conversions carried out?
(i) Propene → Propan -2-ol
(ii) Benzyl chloride → Benzyl alcohol
(iii) Ethyl magnesium chloride → Propan-l-ol
(iv) Methyl magnesium bromide → 2-Methylpropan-2-ol
Ans:









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