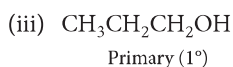
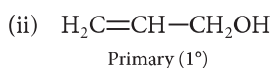
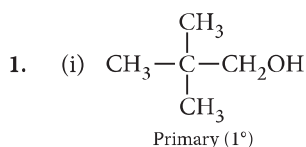


1.

ALCOHOL, PHENOL AND ETHER

Detailed Solutions



2. 2-Phenylethanol

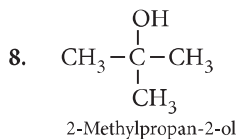
3. 2,5-Dinitrophenol

4. 2-Methylprop-2-en-1-ol

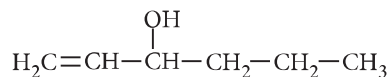
5. 3-methylbut-2-en-1-ol

6. Butan-2-ol

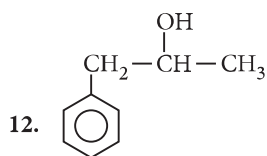
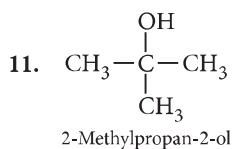
7. Propane-1,2,3-triol



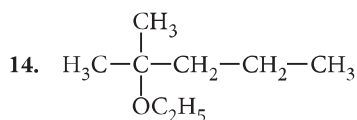
9. Hex-1-en-3-ol



10. 2-Bromo-3-methylbut-2-en-1-ol



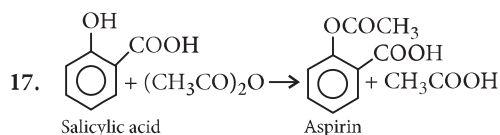
13. Hex-1-en-3-ol



15. 1-methoxy-2-methylbutane

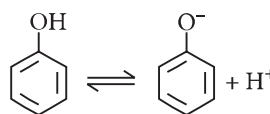
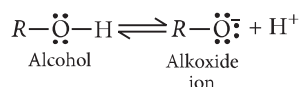
16. Due to resonance C—O bond acquires some partial double bond character.

So, in phenol C—O bond length is smaller than ethanol.



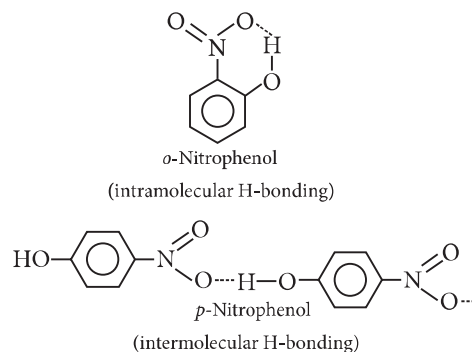
18. Phenols are more acidic than alcohols. It can be explained on the basis that alcohol on losing  $\text{H}^+$  ions form alkoxide ion and phenol forms phenoxide ion.

The greater acidity of phenol is due to the stability of the phenoxide ion which is resonance stabilized as shown below.



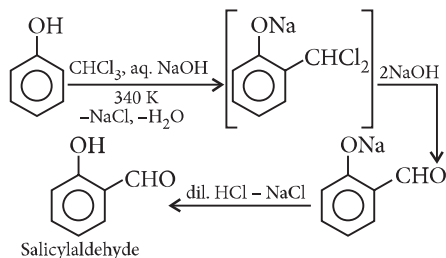
On the other hand, alkoxide ion shows no such resonance stabilisation and is unstable.

19. *o*-Nitrophenol is more steam volatile than *p*-Nitrophenol due to the presence of intramolecular H-bonding. *p*-nitrophenol shows intermolecular H-bonding.

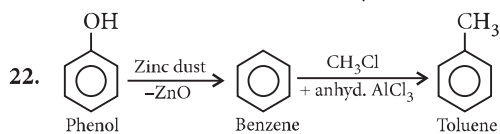
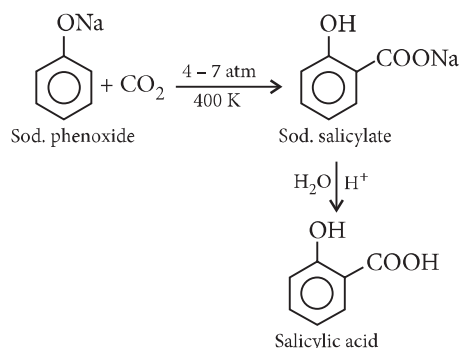


That's why *o*-nitrophenol has lower boiling point than *p*-nitrophenol.

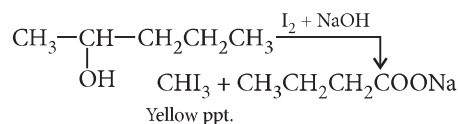
### 20. Reimer-Tiemann reaction



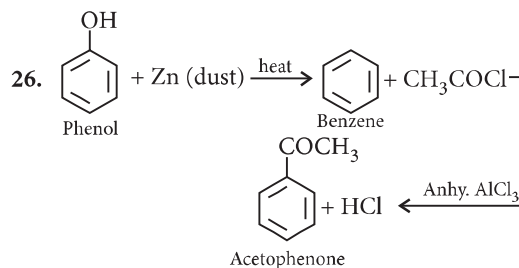
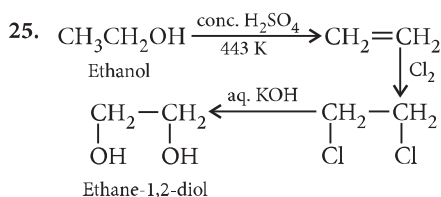
21. **Kolbe's reaction** : When sodium phenoxide is heated with carbon dioxide under pressure, it gives salicylic acid.



23. On adding  $I_2$  and  $NaOH$ , 2-pentanol will give yellow precipitate of iodoform whereas 3-pentanol will not give yellow precipitate.



24.  $R$  is alkyl group and  $R'$  is aryl group.  $R$  must be a group having more electron density than  $H$ . i.e., having  $+I$  effect whereas  $R'$  must be having  $-I$  effect.



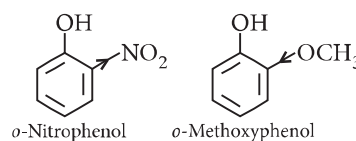
27. Refer to answer 19.

28. Benzoic acid gives brisk effervescence of  $CO_2$  on addition of  $NaHCO_3$  while phenol does not.

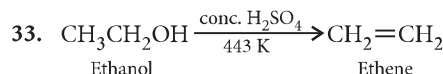
29. Refer to answer 20.

30. 2-propanol will give yellow precipitate of iodoform on addition of  $I_2$  and  $NaOH$  while 2-methyl-2-propanol will not.

31. As we know that the electron withdrawing groups enhance the acidic character of phenols because they help in the stabilisation of phenoxide ion by dispersing negative charge. Nitro group is an electron withdrawing group whereas methoxy group destabilises the phenoxide ion by intensifying the negative charge. Thus, *o*-nitrophenol is more acidic than *o*-methoxyphenol.



32. Refer to answer 20.

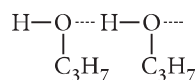


34. Refer to answer 21.

35. On adding  $I_2$  and  $NaOH$  2-Propanol will give yellow ppt. of iodoform, whereas 1-propanol will not give yellow ppt.

36. Refer to answer 21.

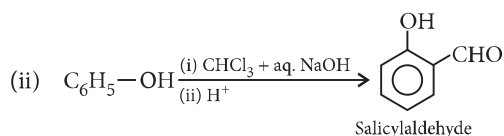
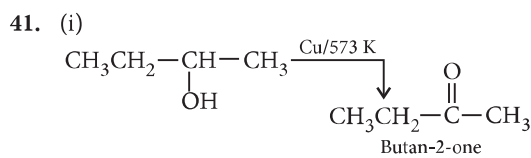
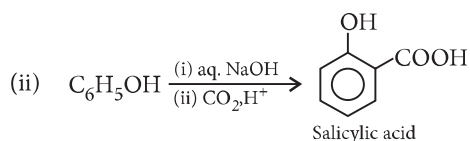
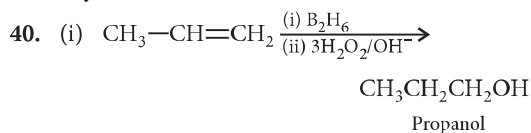
37. The molecules of butane are held together by weak van der Waals forces of attraction while those of propanol are held together by stronger intermolecular hydrogen bonding.



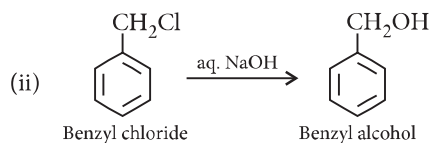
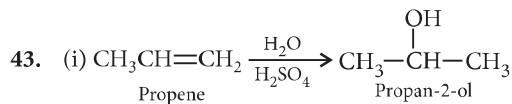
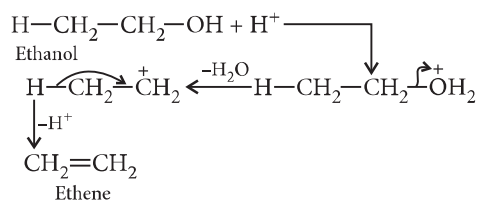
3.

38. Due to electron withdrawing effect of phenyl group the electron density on the oxygen atom of -OH group in phenol is less. Hence, phenols do not undergo protonation.

39. Refer to answer 18.

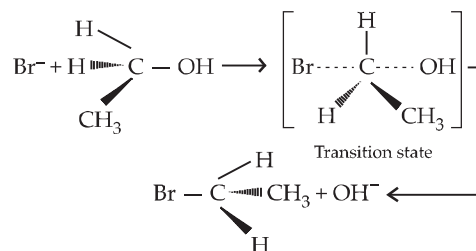


42. Acid catalysed dehydration of alcohols at high temperature takes place with formation of an alkene.



44. Refer to answer 42.

45. The reaction proceeds through nucleophilic substitution bimolecular ( $\text{S}_{\text{N}}2$ ) mechanism, as shown below :

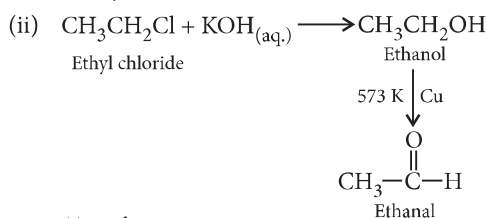


Inversion of configuration takes place during the reaction.

46. (i) Bromine water, ( $\text{Br}_{2(\text{aq})}$ )  
(ii) Lithium aluminium hydride, ( $\text{LiAlH}_4$ ) or  $\text{H}_2/\text{Ni}$   
(iii) Alkyl halide in the presence of anhydrous aluminium chloride,  $\text{CH}_3\text{Cl}$  and  $\text{AlCl}_3$  (anhy.)  
(iv) Acidified potassium permanganate,  $\text{KMnO}_4$ ,  $\text{H}_3\text{O}^+$

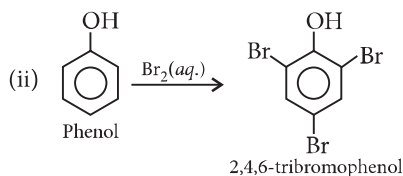
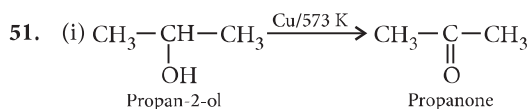
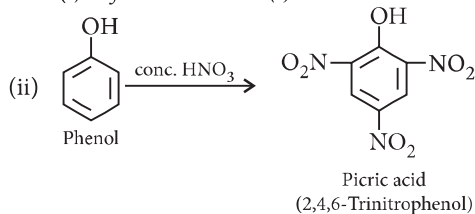
47. (i) Zinc dust  
(ii) Concentrated  $\text{H}_2\text{SO}_4$   
(iii) Refer to answer 46(iii).  
(iv)  $\text{Cu}/573 \text{ K}$

48. (i) Refer to answer 43(i).

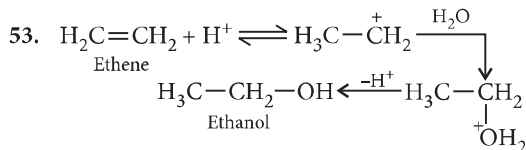


49. (i) Refer to answer 21.  
(ii) Refer to answer 20.

50. (i) Refer to answer 43(i).



52. Refer to answer 42.

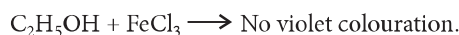
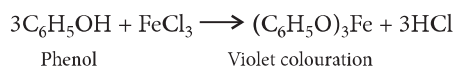


54. (i) The solubility of alcohols in water is due to their ability to form hydrogen bonds with water molecules. Hydrocarbons cannot form such hydrogen bonds, hence they are insoluble in water.

(ii) Refer to answer 31.

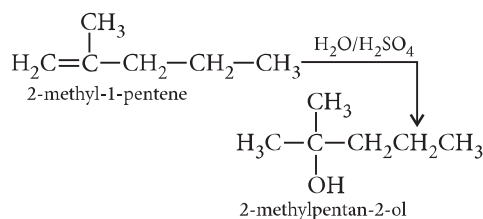
55. (i) Distinction between ethanol and phenol.

**FeCl<sub>3</sub> test :** Phenol gives a violet colouration with FeCl<sub>3</sub> solution while ethanol does not.



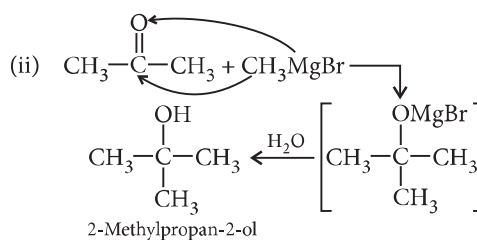
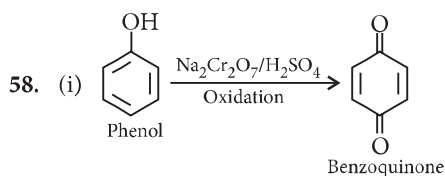
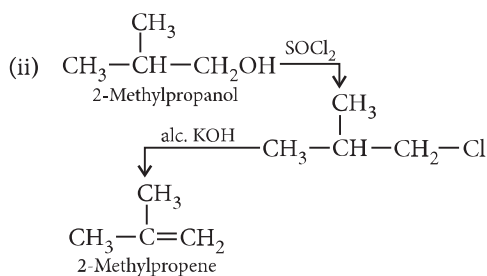
(ii) Refer to answer 26.

56. (i)



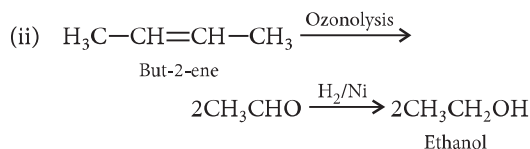
(ii) Refer to answer 26.

57. (i) Refer to answer 51(ii).



(iii) Refer to answer 43(i).

59. (i) Cu at 573 K



60. (i) Refer to answer 37.

(ii) Refer to answer 31.

61. (i) It is due to higher molecular weight, more surface area, more van der Waal's forces of attraction in C<sub>2</sub>H<sub>5</sub>OH than CH<sub>3</sub>OH.

(ii) Refer to answer 18.

62. Refer to answer 20.

63. (i) Refer to answer 43(ii).

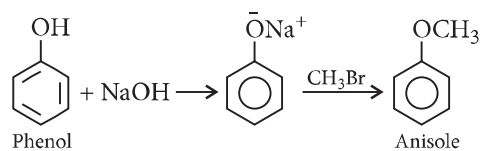
(ii) Refer to answer 58(i).

64. Refer to answer 53.

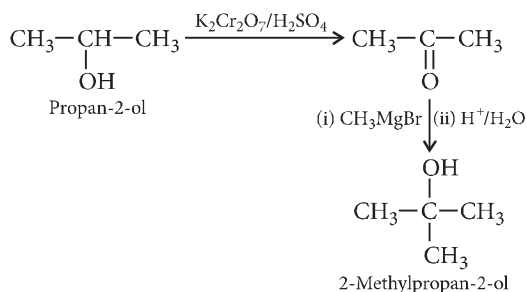
65. (i) Refer to answer 55(i).

(ii) Refer to answer 35.

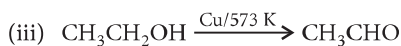
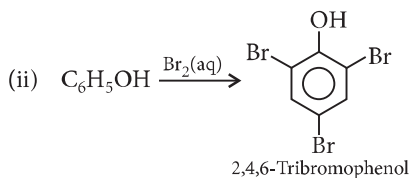
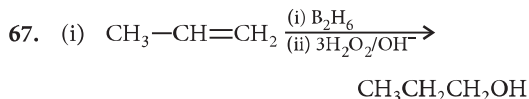
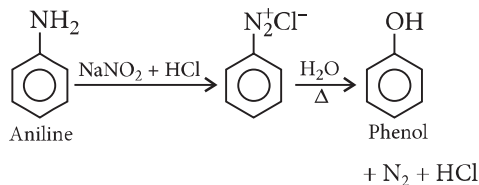
66. (i) Phenol to anisole



(ii) Propan-2-ol to 2-methylpropan-2-ol

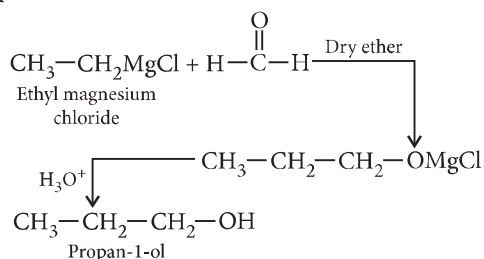


(iii) Aniline to phenol



68. (i) Refer to answer 43(ii).

(ii) Ethyl magnesium chloride on addition to formaldehyde followed by hydrolysis gives propan-1-ol.



(iii) Refer to answer 43(i).

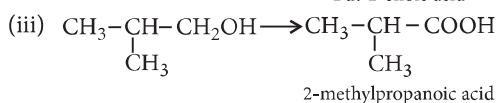
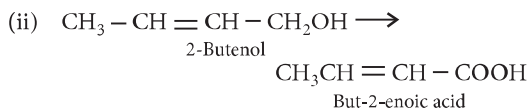
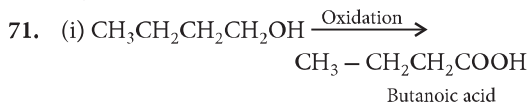
69. (i) Refer to answer 46.

(ii) Refer to answer 20.

70. (a) (i) Refer to answer 23.

(ii) Refer to answer 55(i).

(b) Refer to answer 31.

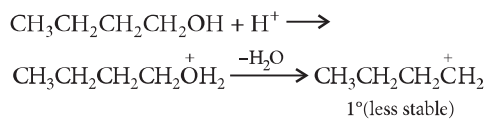
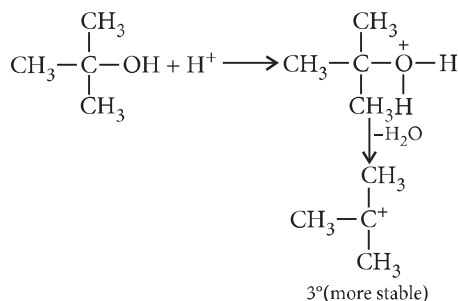


72. (a) Refer to answer 53.

(b) Refer to answer 21.

73. Acid catalysed dehydration of alcohols follows carbocation mechanism.

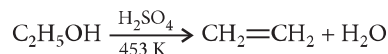
Hence, dehydration of *t*-butanol which form 3° carbocation is faster than *n*-butanol which form primary carbocation.



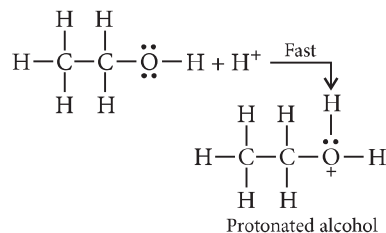
74. (i) Refer to answer 58(i).

(ii) Refer to answer 58(ii).

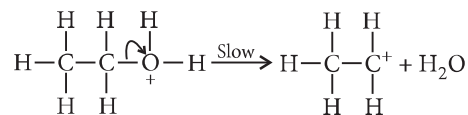
(iii) Refer to answer 43(i).

75. (i) Ethanol undergoes dehydration by heating it with concentrated  $\text{H}_2\text{SO}_4$  at 453 K.**Mechanism** : The dehydration of ethanol involves the following steps :

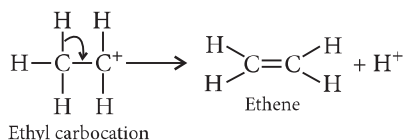
(a) Formation of protonated alcohol.



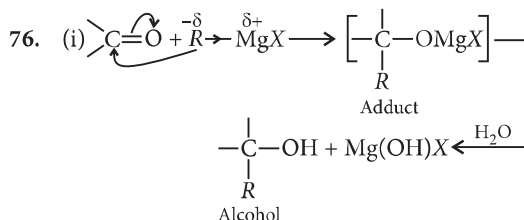
(b) Formation of carbocation.



(c) Formation of ethene.



(ii) Refer to answer 55(i).



(ii) Refer to answer 42.

(iii) Refer to answer 53.

77. (i) Copper at 573 K

(ii) Sodium borohydride ( $\text{NaBH}_4$ )

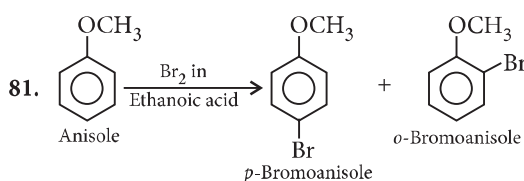
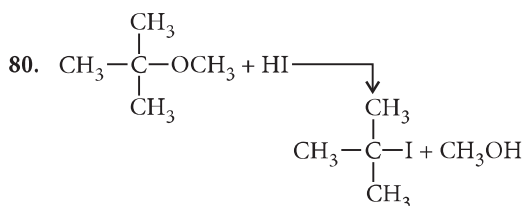
(iii) Bromine water ( $\text{Br}_2(\text{aq})$ )

78. (a) 2,5-Dimethylphenol

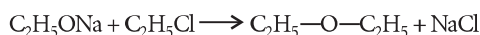
(b) (i) Refer to answer 18.

(ii) Refer to answer 54(i).

79. **Phenol**: 0.2% solution of phenol is an antiseptic while 2% solution is used as disinfectant.



82. **Williamson ether synthesis** : Alkyl halide when treated with sodium alkoxide gives dialkyl ether.

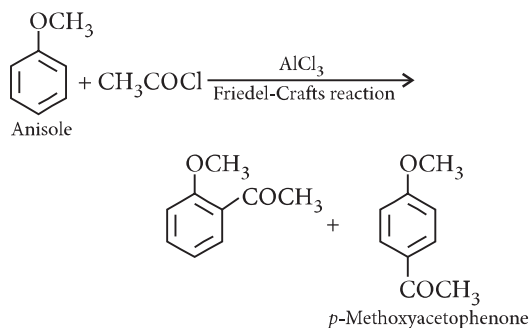


83. Refer to answer 82.

84. Refer to answer 82.

85. 1-Ethoxy-2-nitrocyclohexane.

86. **Reagents** : Acetyl chloride and Lewis acid catalyst.

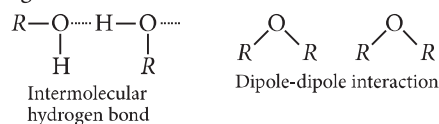


87. Acid dehydration of 2° and 3° alcohols give alkenes rather than ethers.

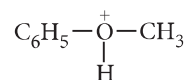
Due to steric hindrance the nucleophilic attack by the alcohol molecule on the protonated alcohol molecule does not occur.

The protonated 2° and 3° alcohols lose water molecules to form stable 2° and 3° carbocations.

88. The boiling points of ethers are much lower than, those of alcohol of comparable molar masses because like alcohols they cannot form intermolecular hydrogen bonds.



89. Protonation of anisole (Phenyl methyl ether) gives methyl phenyl oxonium ion.



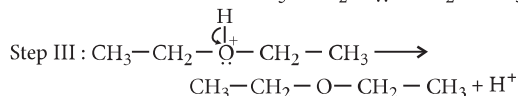
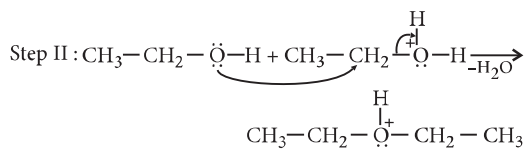
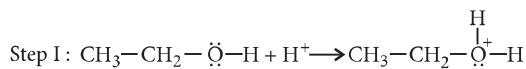
In this ion, the stronger bond is  $\text{O}-\text{C}_6\text{H}_5$ . Therefore, attack by  $\text{I}^-$  ion exclusively breaks the weaker  $\text{O}-\text{CH}_3$  bond forming methyl iodide and phenol. The phenol formed does not react further to give aryl halides.

90. **Unsymmetrical ether** : Ethers in which two alkyl groups are different are known as unsymmetrical ether. e.g.,  $\text{CH}_3\text{OCH}_2\text{CH}_3$  Methoxyethane.

91. Refer to answer 87.

92. Refer to answer 88.

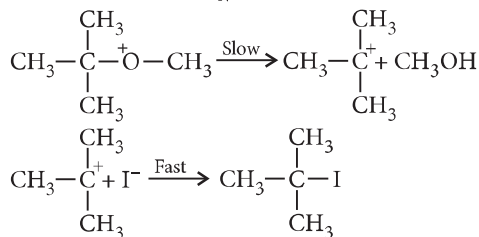
93. **Mechanism** : The formation of ether is nucleophilic bimolecular reaction.



94. (i) Ethanol has higher boiling point because of strong intermolecular hydrogen bonding whereas in methoxymethane, molecules are held by dipole-dipole interaction.

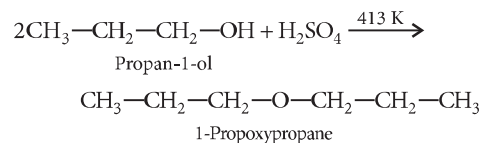
(ii) When one alkyl group is a tertiary group the halide formed is tertiary halide.

In step II the departure of leaving group ( $\text{CH}_3-\text{OH}$ ) creates a more stable carbocation ( $3^\circ$ ) and the reaction follows  $\text{S}_{\text{N}}1$  mechanism.



95. Refer to answer 93.

96. Propan-1-ol on treatment with conc.  $\text{H}_2\text{SO}_4$  at 413 K would yield 1-propoxypropane. In this method, the alcohol is continuously added to keep its concentration in excess.



Mechanism :

