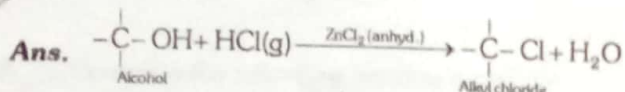


ALCOHOLS, PHENOLS AND ETHERS

SOLVED SUBJECTIVE EXERCISE

Very Short Answer Type Questions (1 mark)

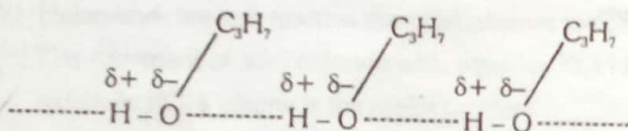
1. What is the function of anhydrous $ZnCl_2$ in the Lucas test of alcohols?



Anhydrous $ZnCl_2$ is a dehydrating agent and absorbs molecules of H_2O formed in the reaction, this enables the reaction to proceed in the forward direction.

2. Explain why is propanol higher boiling than butane?

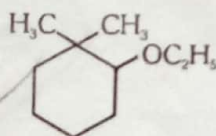
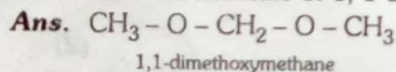
Ans. Propan-1-ol and butane are of comparable molecular masses 60 u and 58 u respectively but the boiling point of propanol is higher because of the presence of intermolecular hydrogen bonding in the molecules. However, it is not present in butane due to the absence of polar OH group. The only attractive forces are weak van der Waal's forces. Therefore, the boiling point of propanol (391 K) is more than that of butane (309 K).



3. An ether possesses dipole moment even if the alkyl groups present in it are identical. Explain.

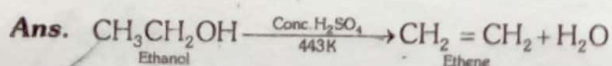
Ans. The dipole moment of ethers is because of their bent structure in which $C-O-C$ bond angle is nearly 110° . Now, the bond polarities do not cancel out even if the alkyl groups are the same. Therefore, an ether has always a specific dipole moment value.

4. Give the structure of 1, 1-dimethoxymethane and 2-ethoxy-1, 1-dimethylcyclohexane.



2-ethoxy-1, 1-dimethyl cyclohexane

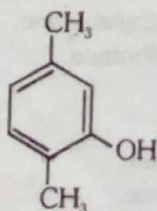
5. How would you convert from ethanol to ethene?



6. Why diethyl ether does not react with sodium?

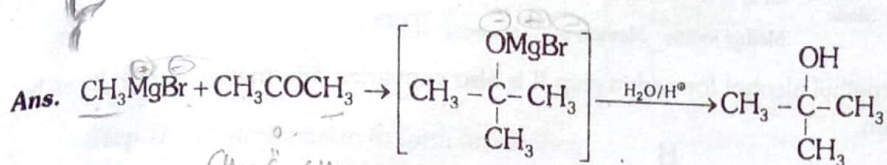
Ans. Diethyl ether does not react with sodium because diethyl ether does not contain an active H-attached to oxygen like alcohols and phenols.

7. Write IUPAC name of



Ans. 2, 5-dimethylphenol

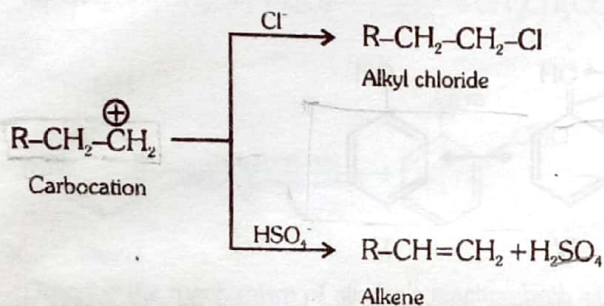
8. How is the following conversion carried out.
Methyl magnesium bromide \rightarrow 2-methylpropan-2-ol.



Short Answer Type Questions (2 mark)

9. Dehydration of alcohol to form an alkene is always carried out with concentrated H_2SO_4 and not with concentrated HCl or HNO_3 . Explain.

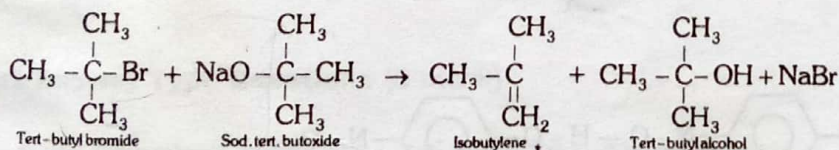
Ans. Under the acidic conditions, alcohol is initially protonated and then loses H_2O to form a carbocation. If HCl is used, then Cl^- ion being a strong nucleophile will result in nucleophilic substitution to form alkyl chloride. However, HSO_4^- ion released by H_2SO_4 is a very weak nucleophile and cannot participate in the nucleophilic substitution. It will rather act as a base and eliminate a proton to form alkene as the product as follows:



Concentrated HNO_3 is a powerful oxidising agent. It will cause oxidation of alcohol to aldehyde and then to acid. Thus, out of the mineral acids listed, dehydration is carried by concentrated H_2SO_4 . Even phosphoric acid can be used.

10. Why is it not possible to prepare ditertiary butyl ether by Williamson's synthesis ?

Ans. Ditertiary butyl ether is to be prepared by the reaction between tertiary butyl bromide and sodium tertiary butoxide. But under the reaction conditions, tertiary butyl bromide prefers to undergo elimination to form isobutylene and tertiary butyl alcohol.

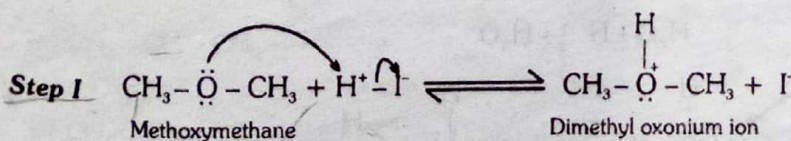


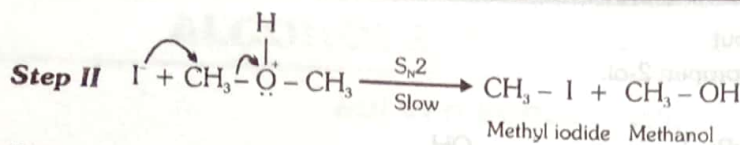
11. Give the name of the alkyl halide and sodium alkoxide used to synthesis tert-butyl ethyl ether.

Ans. Ethyl bromide and sodium tert-butoxide.

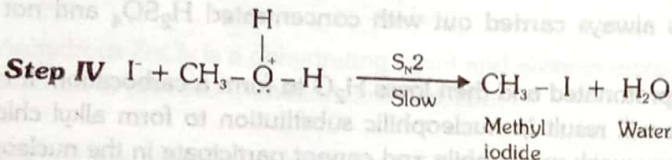
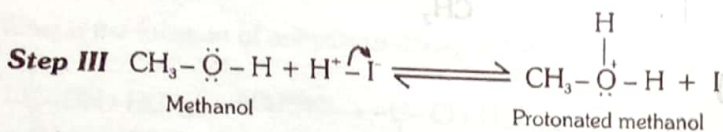
12. Write the mechanism of the reaction of HI with methoxymethane.

Ans. With equimolar amounts of HI and methoxymethane, a mixture of methyl alcohol and methyl iodide is obtained. the mechanism as follows

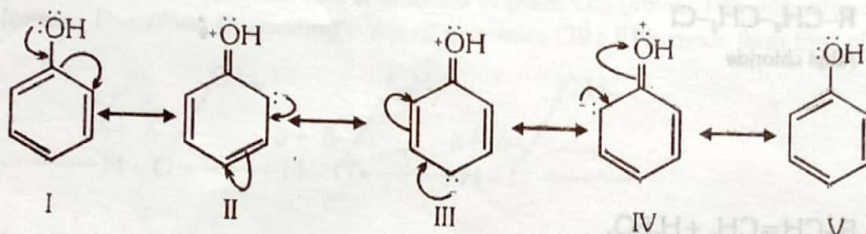




If however, excess of HI is used methyl alcohol formed in step II is also converted into methyl iodide. It can be explained by following mechanism.



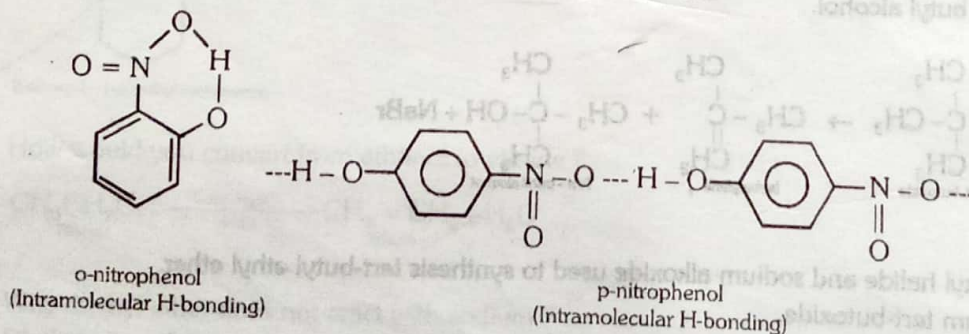
13. Explain how does -OH group attached to a carbon of benzene ring activate it towards electrophilic substitution?
 Ans. Phenol can be regarded as resonating hybrid of structures.



Therefore, due to +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. Now, since the electron density is relatively higher of the two o-and p-position, electrophilic substitution occurs mainly at o-and p-position.

14. While separating a mixture of ortho and para nitrophenols by steam distillation, name the isomer which will be steam volatile. Give reason.

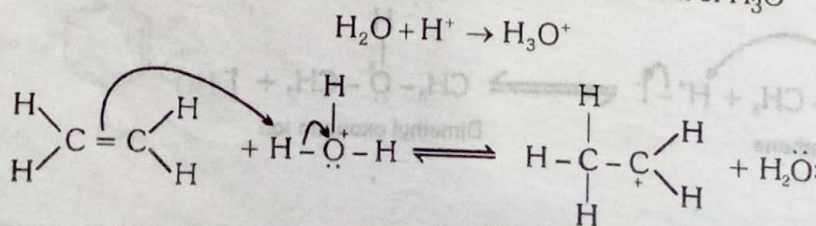
Ans. o-nitrophenol is steam volatile because of chelation thus it can be separated by steam distillation from p-nitrophenol which is not steam volatile due to intermolecular H-bonding.



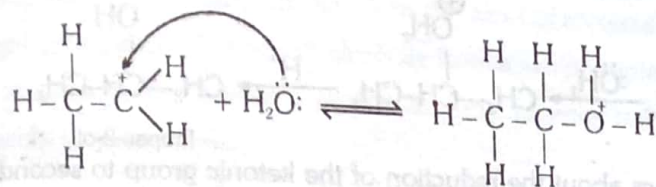
15. Write the mechanism of hydration of ethene to yield ethanol.

Ans. The mechanism of the reaction involves the following three steps.

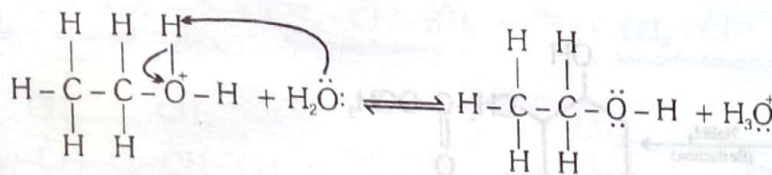
Step I Protonation to ethene of form carbocation by electrophilic attack of H_3O^+



Step II Nucleophilic attack of water on carbocation

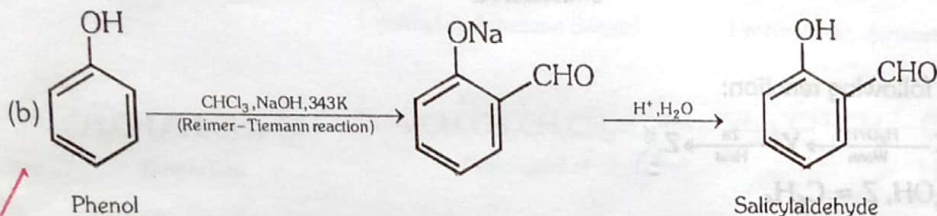
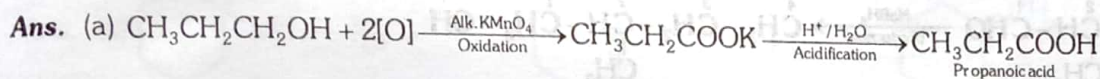


Step II Deprotonation to form an alcohol



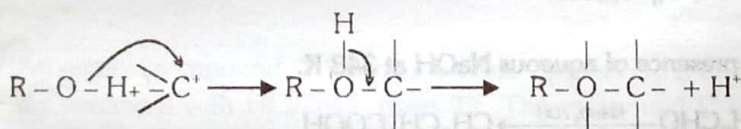
16. Give equations of the following reactions

- (a) Oxidation of propan-1-ol with alkaline KMnO_4 solution.
 (b) Treating phenol with chloroform in the presence of aqueous NaOH .

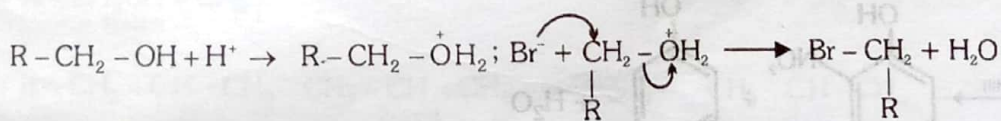


17. Describe the mechanism of alcohols reacting both as nucleophiles and as electrophiles in their reactions.

Ans. Alcohols as nucleophiles



Alcohols as electrophiles Protonated alcohols act as electrophiles

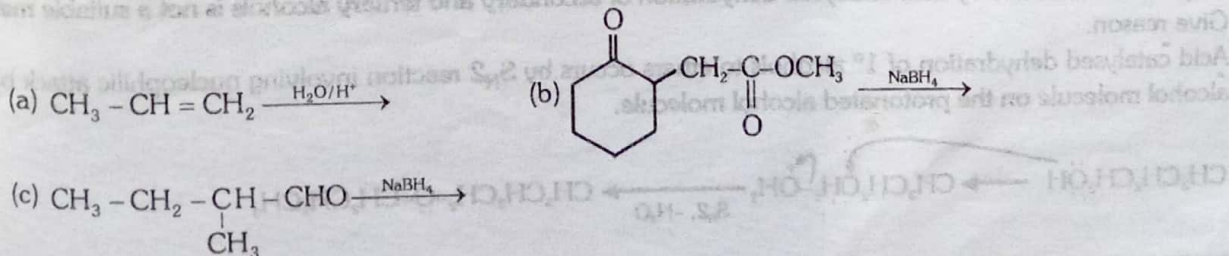


Short Answer Type Questions (3 mark)

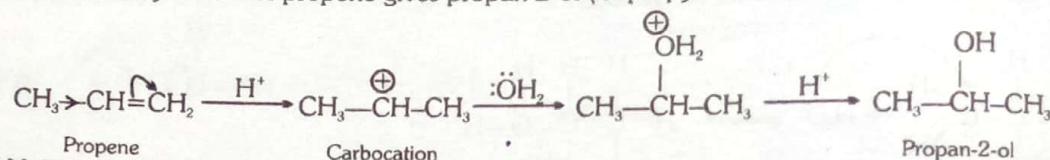
18. Name the reagents which can be used for the following conversions :
 (a) A primary alcohol to an aldehyde (b) Butan-2-one to butan-2-ol (c) Phenol to picric acid.

- Ans.** (a) Pyridinium chlorochromate
 (b) Lithium aluminium hydride
 (c) Nitrating mixture of conc. HNO_3 and conc. H_2SO_4 .

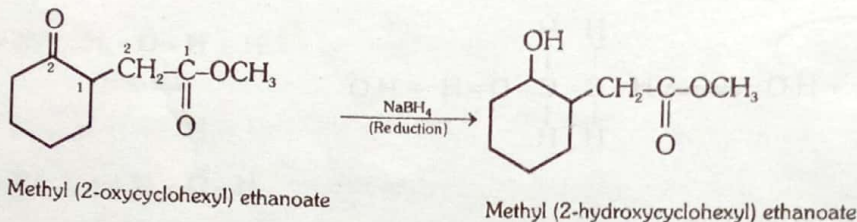
19. Write the structures of the products of the following reactions :



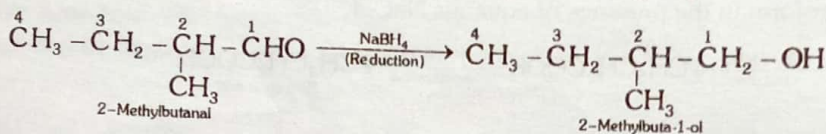
Ans. (a) The acidic hydration of propene gives propan-2-ol (isopropyl alcohol)



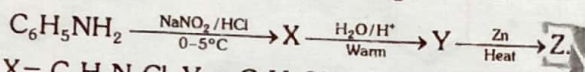
(b) NaBH_4 is a weak reducing agent. It brings about the reduction of the ketonic group to secondary alcoholic group. However, it does not affect ester group.



(c) NaBH_4 reduces aldehydic group to a primary alcoholic group.



20. Identify X, Y and Z in the following reaction:



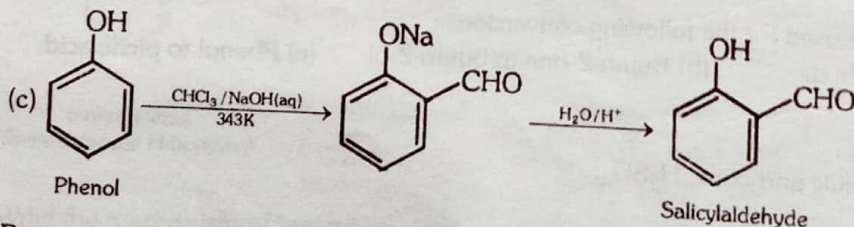
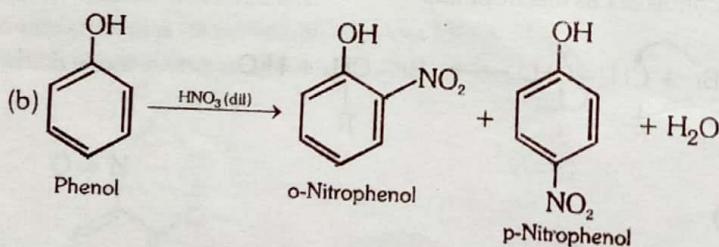
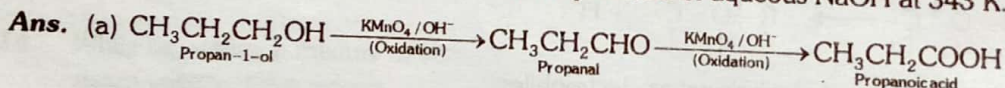
Ans. X = $\text{C}_6\text{H}_5\text{N}_2\text{Cl}$, Y = $\text{C}_6\text{H}_5\text{OH}$, Z = C_6H_6

21. Give equations for the following chemical reactions :

(a) Oxidation of propan-1-ol with alkaline KMnO_4 solution.

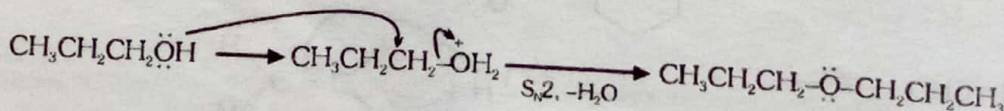
(b) Action of dilute HNO_3 on phenol

(c) Treating phenol with chloroform in the presence of aqueous NaOH at 343 K.

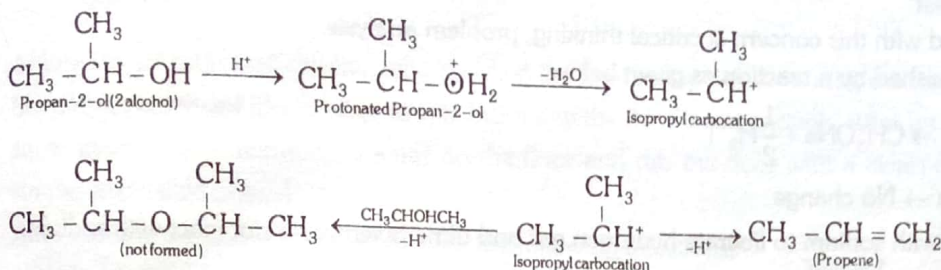


22. Preparation of ethers by acid-catalysed dehydration of secondary and tertiary alcohols is not a suitable method. Give reason.

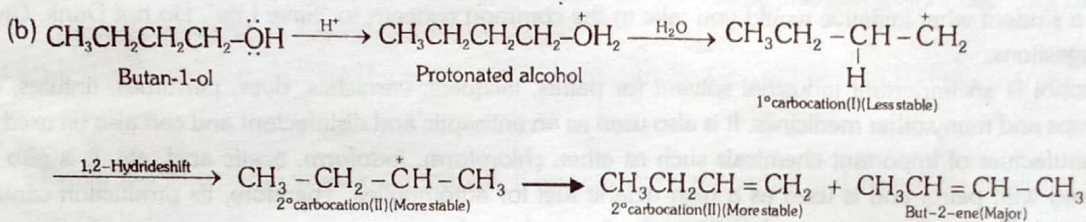
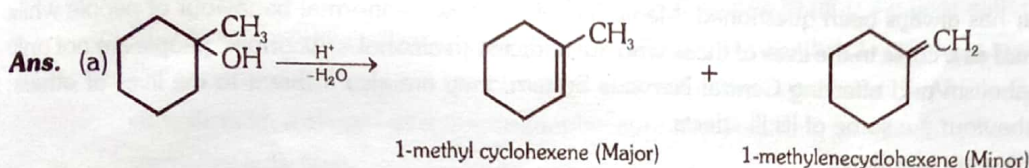
Ans. Acid catalysed dehydration of 1° alcohols to ethers occurs by $\text{S}_\text{N}2$ reaction involving nucleophilic attack by the alcohol molecule on the protonated alcohol molecule.



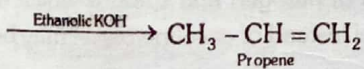
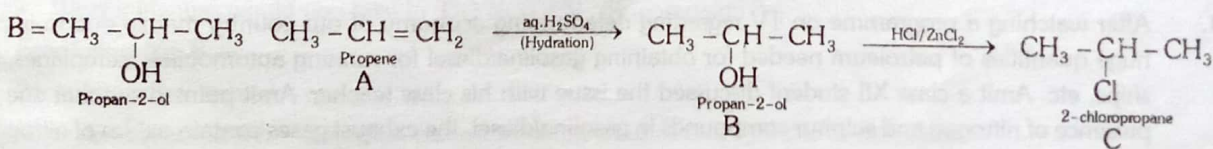
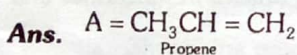
Under these conditions, 2° and 3° alcohols, however give alkenes rather than ethers. The reason is that due to steric hinderance, nucleophilic attack by the alcohol molecule on the protonated alcohol molecule does not occur. Instead protonated 2° and 3° alcohols lose a water molecule to form stable 2° and 3° carbocations. These carbocations prefer to lose a proton to form alkenes rather than undergoing nucleophilic attack by alcohol molecule to form ethers.



23. Predict the major product of acid catalysed dehydration of (a) 1-methyl cyclohexanol (b) butan-1-ol.



24. An organic compound 'A' having molecular formula C₃H₆ on the treatment with aqueous H₂SO₄ gives 'B' which on treatment with HCl/ZnCl₂ gives 'C'. The compound C on treatment with ethanolic KOH gives back the compound 'A'. Identify the compounds A, B, C.



EXERCISE-1

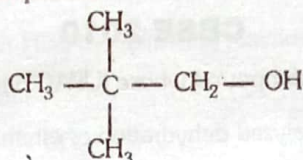
PREVIOUS YEARS BOARD PROBLEMS

CBSE 2016

- Write the chemical equations involved in the following reactions:
 - Kolbe's reaction
 - Friedel-Crafts acetylation of anisole.
- How do you convert:
 - Phenol to toluene
 - Formaldehyde to Ethanol
- Give reasons for the following:
 - Protonation of Phenols is difficult whereas ethanol easily undergoes protonation.
 - Boiling point of ethanol is higher than that of dimethyl ether.
 - Anisole on reaction with HI gives phenol and $\text{CH}_3\text{-I}$ as main products and not iodobenzene and CH_3OH .

CBSE 2015

- Write the IUPAC name of the given compound :

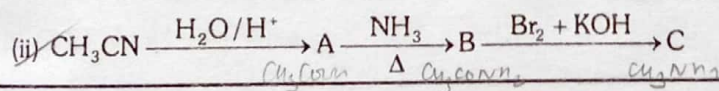
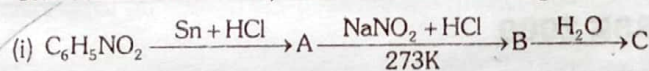


- Give reasons for the following :
 - p-nitrophenol is more acidic than p-methylphenol.
 - Bond length of C - O bond in phenol is shorter than that in methanol.
 - $(\text{CH}_3)_3\text{C - Br}$ on reaction with sodium methoxide ($\text{Na}^+ \text{OCH}_3^-$). Gives alkene as the main product and not an ether.

CBSE 2014

- Write the mechanism of the following reaction :

$$\text{CH}_3\text{CH}_2\text{OH} \xrightarrow{\text{HBr}} \text{CH}_3\text{CH}_2\text{Br} + \text{H}_2\text{O}$$
- Write the equations involved in the following reactions :
 - Reimer - Tiemann reaction
 - Williamson synthesis
- Give the structures of A, B and C in the following reactions :



CBSE 2013

- Explain the mechanism of the following reaction?

$$\text{CH}_3 - \text{CH}_2 - \text{OH} \xrightarrow[443\text{K}]{\text{H}^+} \text{CH}_2 = \text{CH}_2 + \text{H}_2\text{O}$$
- Write the equation involved in the reaction Williamson's ether synthesis.

CBSE 2012

- Write the equations involved in the following reaction :
Reimer-Tiemann reaction
- Explain the following behaviours.
 - Alcohols are more soluble in water than the hydrocarbons of comparable molecular masses.
 - Ortho-nitrophenol is more acidic than ortho-methoxyphenol.
- Explain the mechanism of acid catalysed hydration of an alkene to form corresponding alcohol.
- Acid catalysed hydration of an alkene forming an alcohol.

CBSE 2011

- How could you convert ethanol to ethene? $C-C-OH \rightarrow C=C$
- Draw the structure of 2, 6-dimethyl phenol.
- Write Reimer-Tiemann reaction giving an example. $C-C-X \xrightarrow{aq. KOH} C-C-OH$ *alk. brn*
- How would you obtain the following?
 - Benzoquinone from phenol.
 - 2-methylpropan-2-ol from methyl magnesium bromide
 - Propan-2-ol from propene
- A compound A (C_2H_6O) on oxidation by PCC gave B, which on treatment with aqueous alkali and subsequent heating furnished C. B on oxidation by $KMnO_4$, forms a monobasic carboxylic acid with molar mass 60 g mol^{-1} . Deduce the structure of A, B and C.
- Describe the mechanism of hydration of ethene to yield ethanol.
 - Write Kolbe's reaction with an example. NO_2, CO_2, H^+

CBSE 2010

- Write the structure of the molecule of compound whose IUPAC name is 1-phenyl propan-2-ol.
- Describe the mechanism of acid catalyzed dehydration of ethanol to yield ethene.
 - Describe the chemical test to distinguish between ethanol and phenol.
- How would you convert
 - phenol to benzoquinone
 - propanone to 2-methylpropan-2-ol
 - propene to propan-2-ol.
- Explain the mechanism of the following reactions.

Acid catalyzed dehydration of an alcohol forming an alkene.
- Illustrate the following reaction by giving a chemical equation for each.
 - Kolbe's reaction *alkene, alcohol*
 - Williamson's synthesis *alkene, alcohol*

CBSE 2009

- Explain the following giving one example for each.
 - Reimer-Tiemann reaction
 - Friedel-Crafts acetylation of anisole
- Give IUPAC name of the following compound.

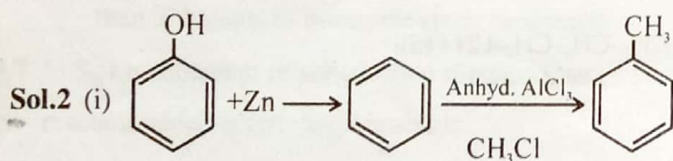
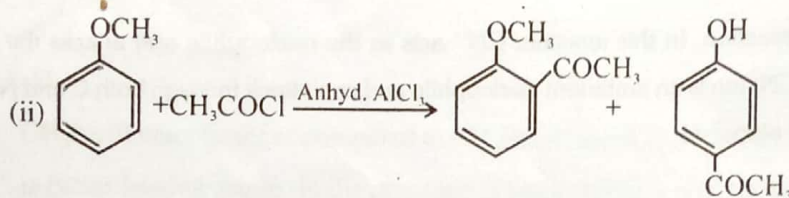
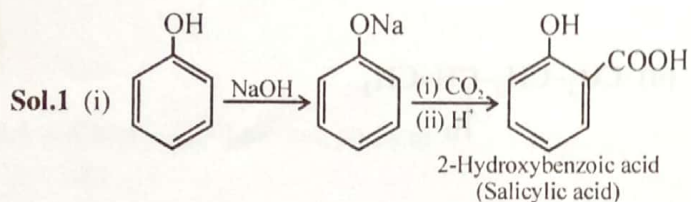
$$H_2C = CH - \underset{\substack{| \\ OH}}{CH} - CH_2 - CH_2 - CH_3$$
- Account for the following.
 - The boiling point of ethanol is higher than that of methanol.
 - Phenol is a stronger acid than an alcohol.
 - The boiling point of ethers are lower than isomeric alcohols.
- Explain the following observations:
 - The boiling point of ethanol is higher than of methoxy methane
 - Phenol is more acidic than ethanol.
 - o- and p-nitro phenols are more acidic than phenol.

EXERCISE-1

SOLUTION PREVIOUS YEARS BOARD PROBLEMS

ALCOHOL, PHENOL AND ETHER

CBSE 2016



Sol.3 (a) In phenols lone pair of electron on oxygen are delocalized over benzene ring due to resonance but in alcohol lone pair of electron on oxygen are localized & hence available for protonation / + R- effect in phenol but not in ethanol.

(b) Due to intermolecular Hydrogen bonding

(c) Weaker (O-CH₃) bond and stronger(O-C₆H₅) bond, due to resonance / carbon in benzene is sp² hybridized due to which partial double bond character.

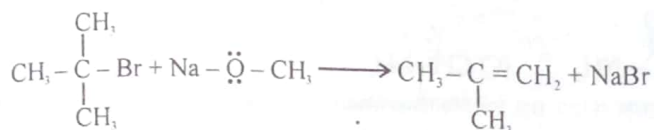
CBSE 2015

Sol.1 2,2-Dimethylpropan-1-ol

Sol.2 (i) Due to -I / -R effect of -NO₂ group & +I / +R effect of -CH₃ group or 4-nitrophenoxide ion is more stable than 4-methylphenoxide ion

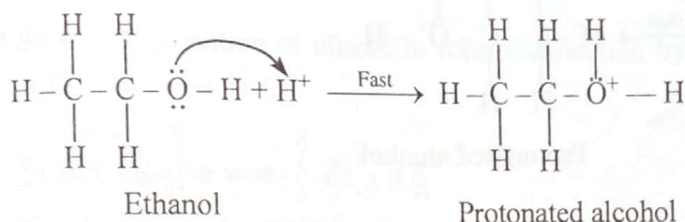
(ii) Due to +R effect of -OH group in phenol / due to sp² hybridization of C-atom in C-OH group in phenol whereas sp³ hybridization of C-atom in C-OH group in methanol.

(ii) Williamson's synthesis is not applicable for tertiary alkyl halides as they yield alkenes instead of ethers. The reaction of CH₃ONa with (CH₃)₃C-Br gives exclusively 2-methyl propene.

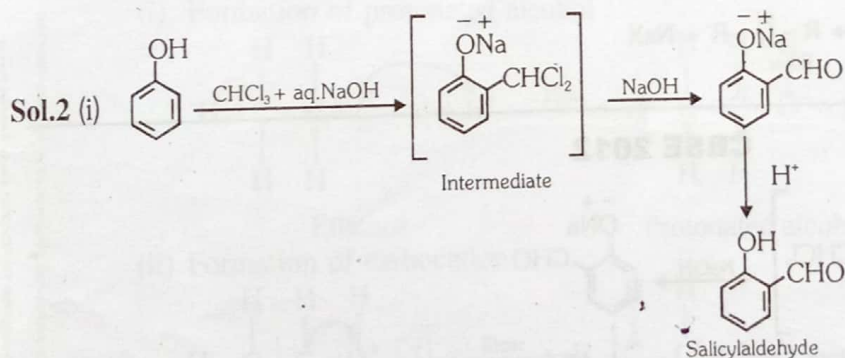
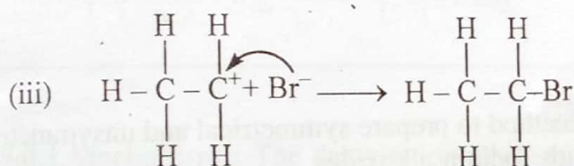
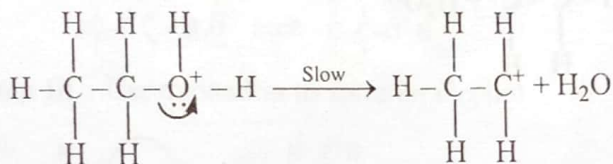


CBSE 2014

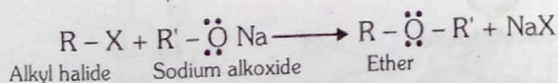
Sol.1 (i) Formation of protonated alcohol :



(ii) Formation of carbocation :



(ii) Williamson ether synthesis is a laboratory method to prepare symmetrical and unsymmetrical ethers by allowing alkyl halides to react with sodium alkoxides.

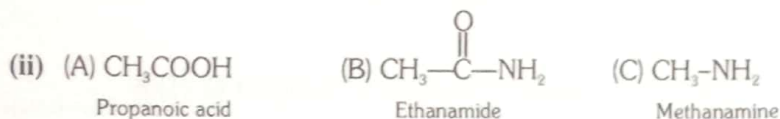


Sol.3

(i) (A) $\text{C}_6\text{H}_5\text{NH}_2$
Aniline

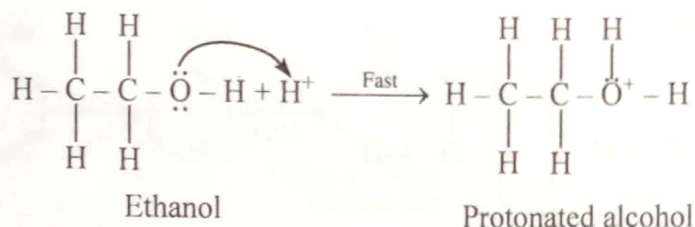
(B) $\text{C}_2\text{H}_5\text{N}^+ \equiv \text{NCl}^-$
Benzenediazonium Chloride

(C) $\text{C}_6\text{H}_5\text{OH}$
Phenol

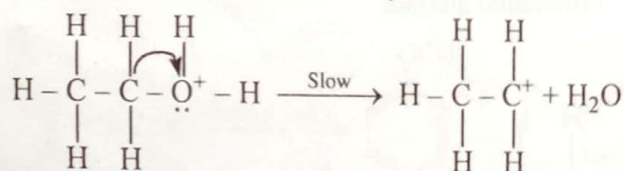
**CBSE 2013**

Sol.1 Mechanism : The dehydration of ethanol involves the following steps :

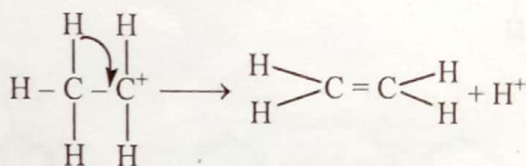
(i) Formation of protonated alcohol :



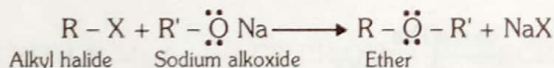
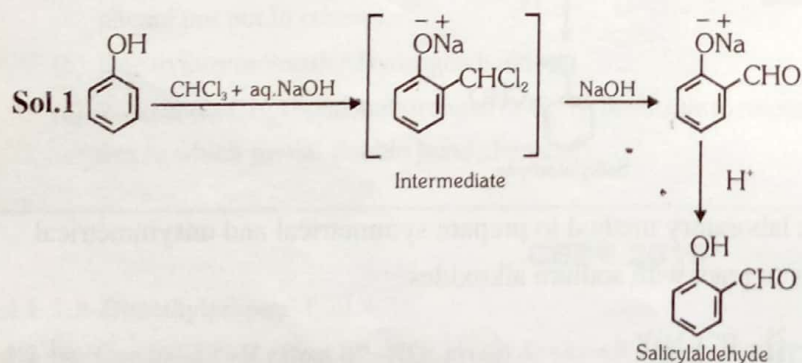
(ii) Formation of carbocation :



(iii) Formation of ethene :



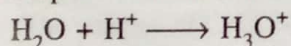
Sol.2 (ii) Williamson ether synthesis is a laboratory method to prepare symmetrical and unsymmetrical ethers by allowing alkyl halides to react with sodium alkoxides.

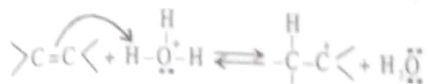
**CBSE 2012**

Sol.2 (i) Due to formation of intermolecular H-bonding with water.

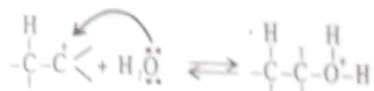
(ii) Nitro is withdrawing group which decrease the e^- density and stabilised the intermediate phenoxide ion which makes the equilibrium shifts in forward direction.

Sol.3 Step I : Protonation of alkene to form carbocation by electrophilic attack of H_3O^+ .

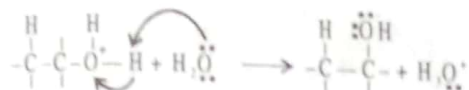




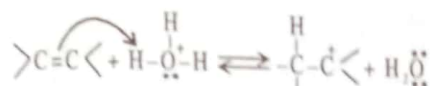
Step II : Nucleophilic attack of water on carbocation.



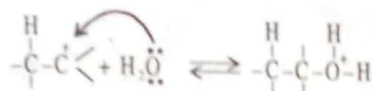
Step III : Deprotonation to form an alcohol.



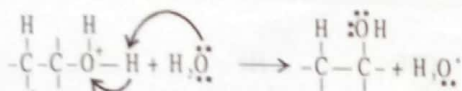
Sol.4 Step I : Protonation of alkene to form carbocation by electrophilic attack of H_3O^+ .



Step II : Nucleophilic attack of water on carbocation.



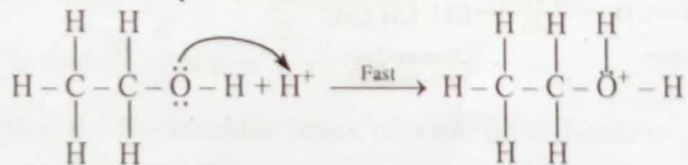
Step III : Deprotonation to form an alcohol.



CBSE 2011

Sol.1 Mechanism : The dehydration of ethanol involves the following steps :

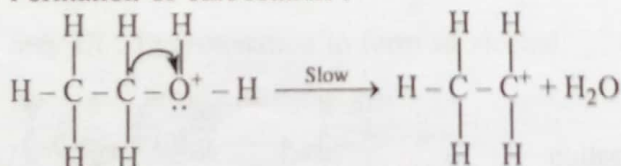
(i) Formation of protonated alcohol :



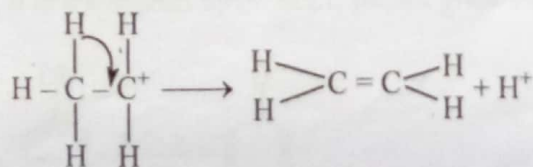
Ethanol

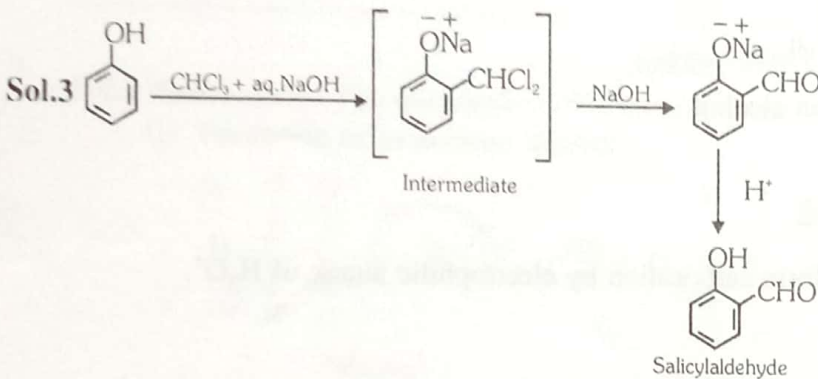
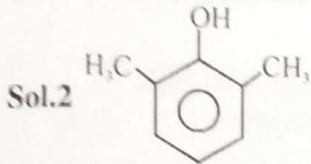
Protonated alcohol

(ii) Formation of carbocation :

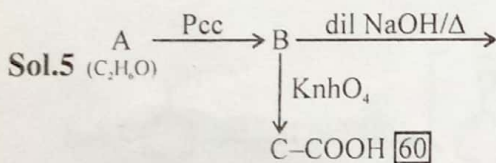
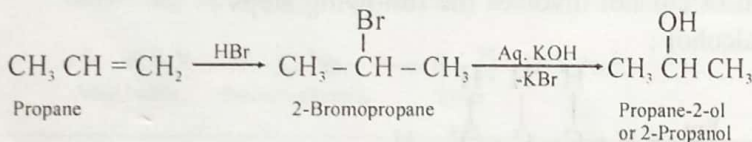
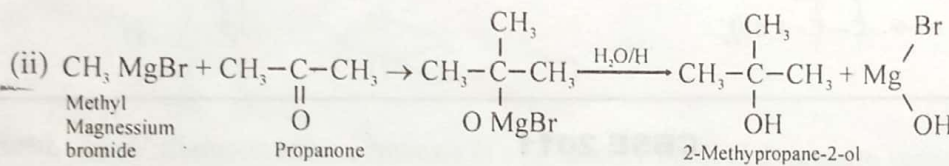
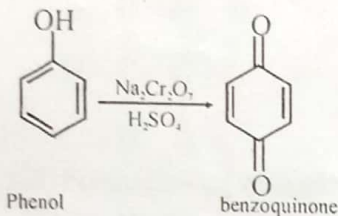


(iii) Formation of ethene :



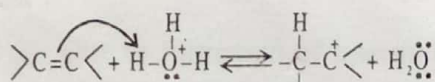
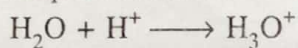


Sol.4 (i) Benzoquinone from phenol

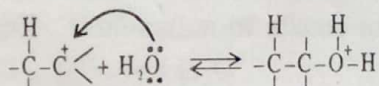


- A \Rightarrow C-C-OH
- B \Rightarrow C-CHO By oxidation
- C \Rightarrow C-C=C-CHO By Aldol condensation.

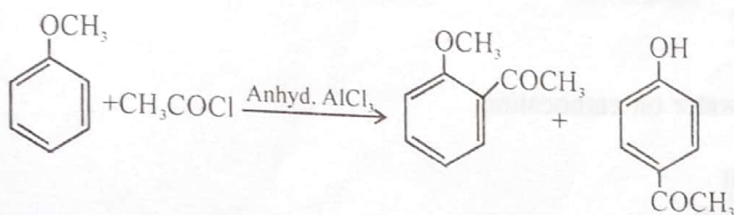
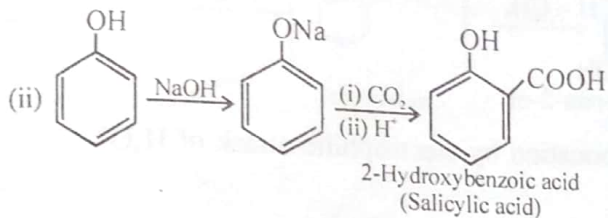
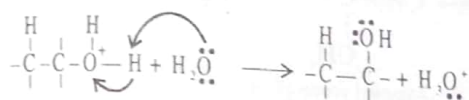
Sol.6 (i) Step I : Protonation of alkene to form carbocation by electrophilic attack of H_3O^+ .



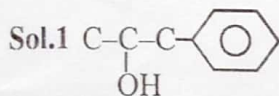
Step II : Nucleophilic attack of water on carbocation.



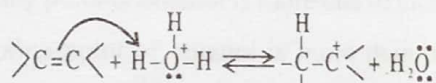
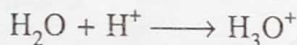
Step III : Deprotonation to form an alcohol.



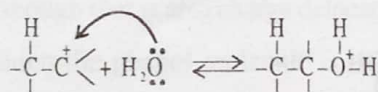
CBSE 2010



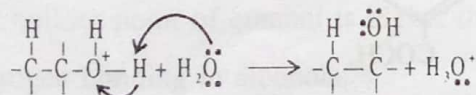
Sol.2 (i) Step I : Protonation of alkene to form carbocation by electrophilic attack of H_3O^+ .



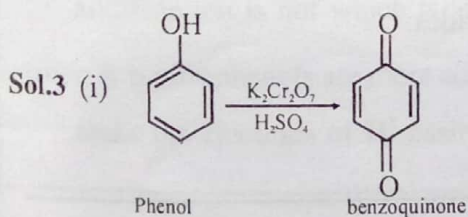
Step II : Nucleophilic attack of water on carbocation.

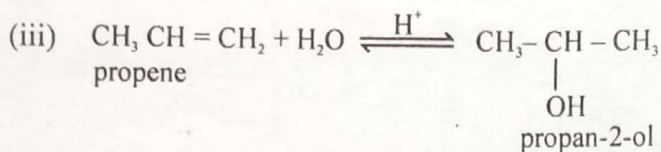
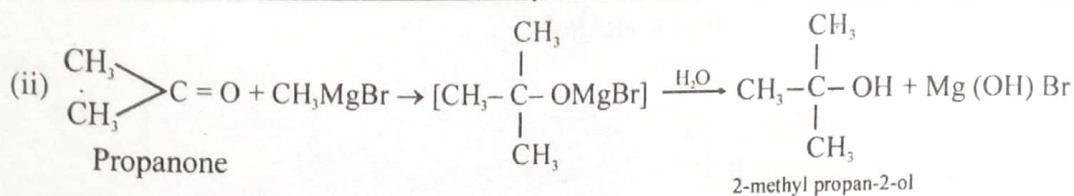


Step III : Deprotonation to form an alcohol.

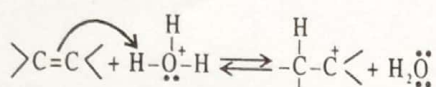
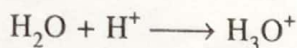


(ii) It is distinguished by N. FeCl_3 phenol gives violet ppt with N. FeCl_3 while ethanol does not give.

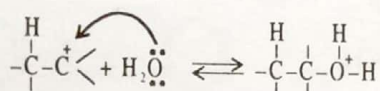




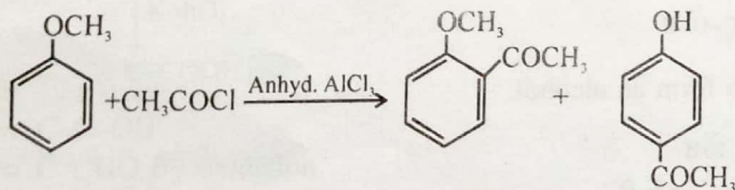
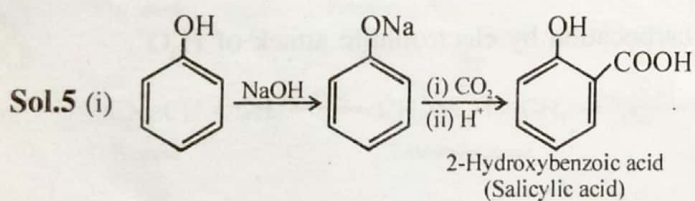
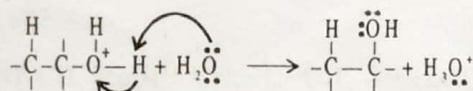
Sol.4 Step I : Protonation of alkene to form carbocation by electrophilic attack of H_3O^+ .



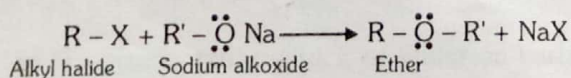
Step II : Nucleophilic attack of water on carbocation.

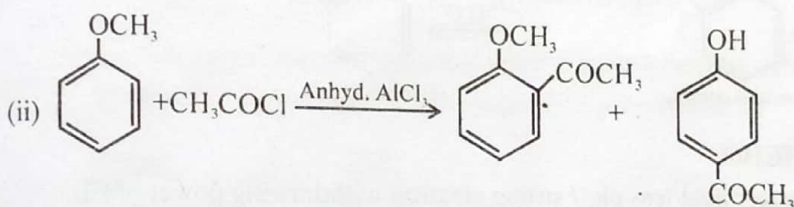
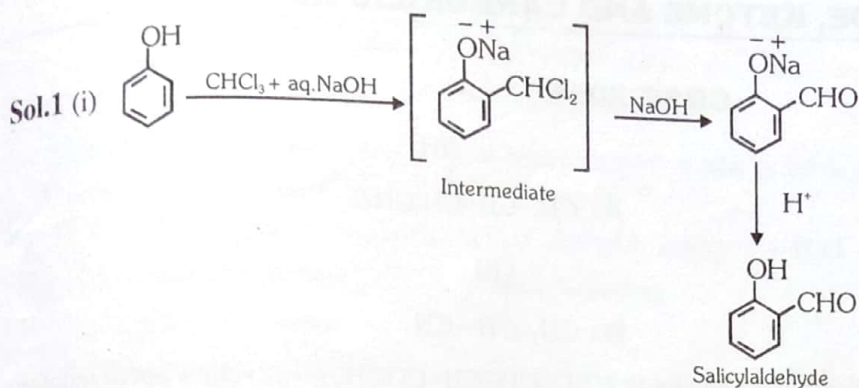


Step III : Deprotonation to form an alcohol.



(ii) Williamson ether synthesis is a laboratory method to prepare symmetrical and unsymmetrical ethers by allowing alkyl halides to react with sodium alkoxides.





Sol.2 Hex-1-en-3-ol

Sol.3 (i) Boiling point of ethanol is more due to increasing surface area wondervall's force of attraction increases. as boling point of ethanol is more than of methonal.

(ii) Due to formation of stable phenoxide ion, phenoxide ion more stable and favours the ionisation of phenol although ther is also charge delocatisation in phenol, its resonance structures have charge separation due to which the phenol molecule is less stable than phenoxide ion.

(ii) Alochol forms inter molecular H-bonding so, its boiling point is more than that of corresponding ether.

Sol.4 (i) The boiling point of ethanol is higher than that of methoxymethane due to the presence of hydrogen bonding in alcohols.

(ii) Since the phenoxide ion left after the removal of a proton is stabilized by resonance where as alkoxide ion is not which is left after the removal of a proton found alcohol.

(iii) o & p-nitrophenols are more acidic then phenol due to -M effect of NO₂ at from o & p position make the ejections of H⁺ easity & secondly stabilized the conjugate base.