

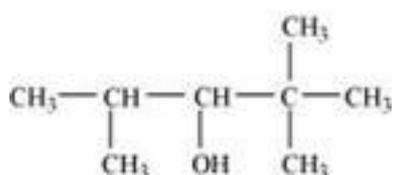
CBSE Class-12 Subject Chemistry
NCERT Solutions
Chapter – 11 Alcohol Phenol and Ether

Chapter End Question

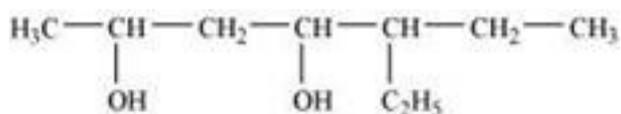
Part-1

1. Write IUPAC names of the following compounds:

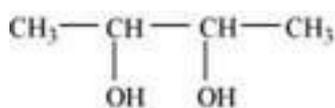
(i)



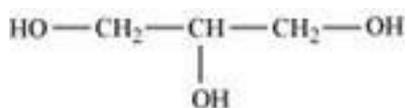
(ii)



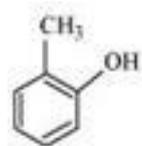
(iii)



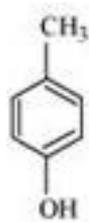
(iv)



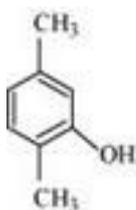
(v)



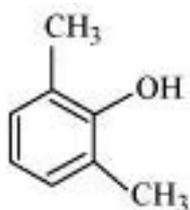
(vi)



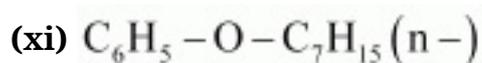
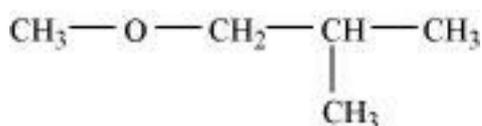
(vii)



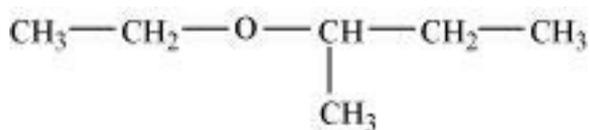
(viii)



(ix)



(xii)



Ans. (i) 2, 2, 4-Trimethylpentan-3-ol

(ii) 5-Ethylheptane-2, 4-diol

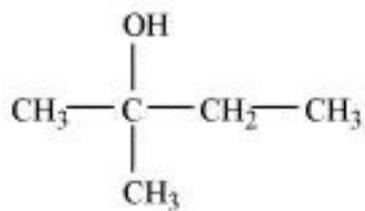
(iii) Butane-2, 3-diol

- (iv) Propane-1, 2, 3-triol
 - (v) 2-Methylphenol
 - (vi) 4-Methylphenol
 - (vii) 2, 5-Dimethylphenol
 - (viii) 2, 6-Dimethylphenol
 - (ix) 1-Methoxy-2-methylpropane
 - (x) Ethoxybenzene
 - (xi) 1-Phenoxyheptane
 - (xii) 2-Ethoxybutane
-

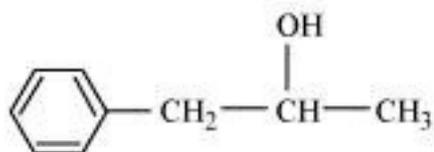
2. Write structures of the compounds whose IUPAC names are as follows:

- (i) 2-Methylbutan-2-ol
- (ii) 1-Phenylpropan-2-ol
- (iii) 3,5-Dimethylhexane -1, 3, 5-triol
- (iv) 2,3 - Diethylphenol
- (v) 1 - Ethoxypropane
- (vi) 2-Ethoxy-3-methylpentane
- (vii) Cyclohexylmethanol
- (viii) 3-Cyclohexylpentan-3-ol
- (ix) Cyclopent-3-en-1-ol
- (x) 3-Chloromethylpentan-1-ol.

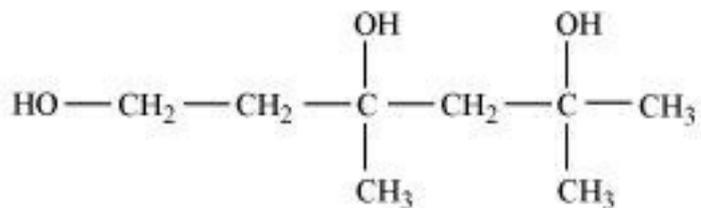
Ans. (i)



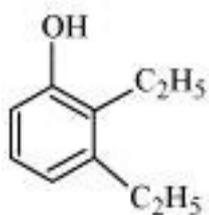
(ii)



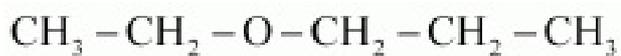
(iii)



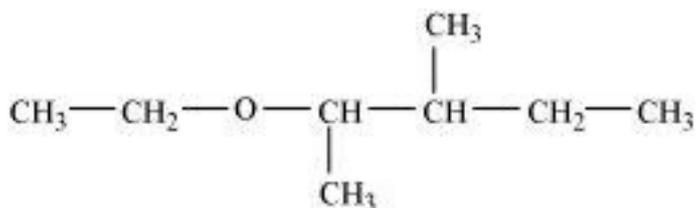
(iv)



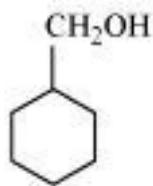
(v)



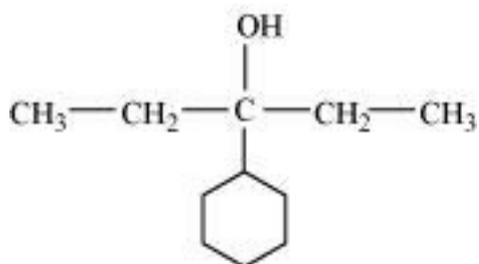
(vi)



(vii)



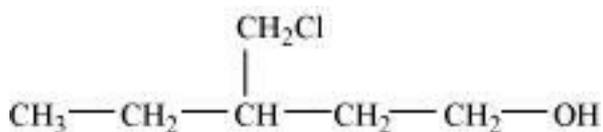
(viii)



(ix)



(x)



3. (i) Draw the structures of all isomeric alcohols of molecular formula $C_5H_{12}O$ and give their IUPAC names.

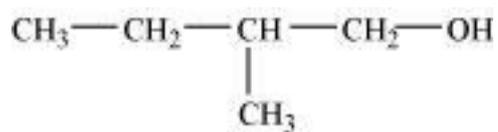
(ii) Classify the isomers of alcohols in question 11.3 (i) as primary, secondary and tertiary alcohols.

Ans. (i) The structures of all isomeric alcohols of molecular formula, $C_5H_{12}O$ are shown below:



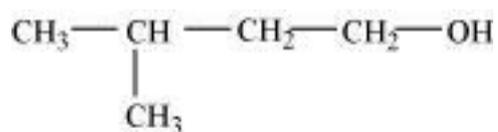
Pentan-1-ol (1°)

(b)



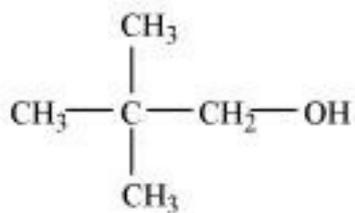
2-Methylbutan-1-ol (1°)

(c)



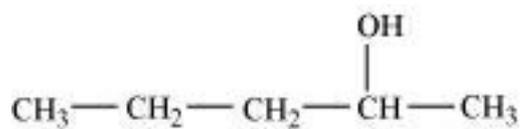
3-Methylbutan-1-ol (1°)

(d)



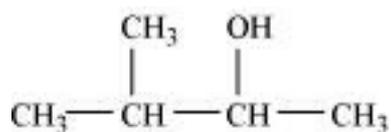
2, 2-Dimethylpropan-1-ol (1°)

(e)



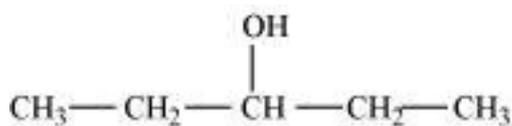
Pentan-2-ol (2°)

(f)



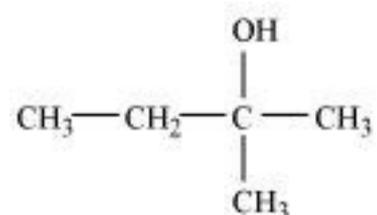
3-Methylbutan-2-ol (2°)

(g)



Pentan-3-ol (2°)

(h)



2-Methylbutan-2-ol (3°)

(ii) Primary alcohol: Pentan-1-ol; 2-Methylbutan-1-ol;

3-Methylbutan-1-ol; 2, 2 - Dimethylpropan-1-ol

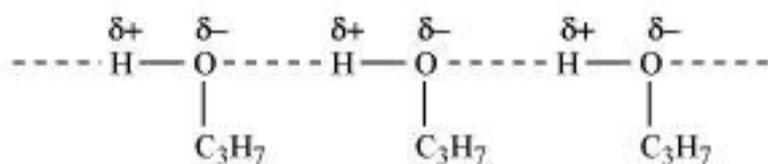
Secondary alcohol: Pentan-2-ol; 3-Methylbutan-2-ol;

Pentan-3-ol

Tertiary alcohol: 2-methylbutan-2-ol

4. Explain why propanol has higher boiling point than that of the hydrocarbon, butane?

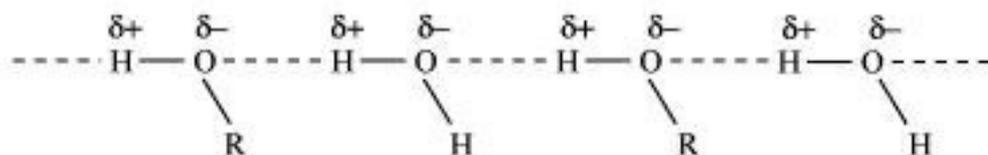
Ans. Propanol undergoes intermolecular H-bonding due to which its boiling point is higher than butane which is non-polar and held by weak van der Waals forces of attraction, and it is so because of the presence of -OH group.



Therefore, extra energy is required to break hydrogen bonds. For this reason, propanol has a higher boiling point than hydrocarbon butane.

5. Alcohols are comparatively more soluble in water than hydrocarbons of comparable molecular masses. Explain this fact.

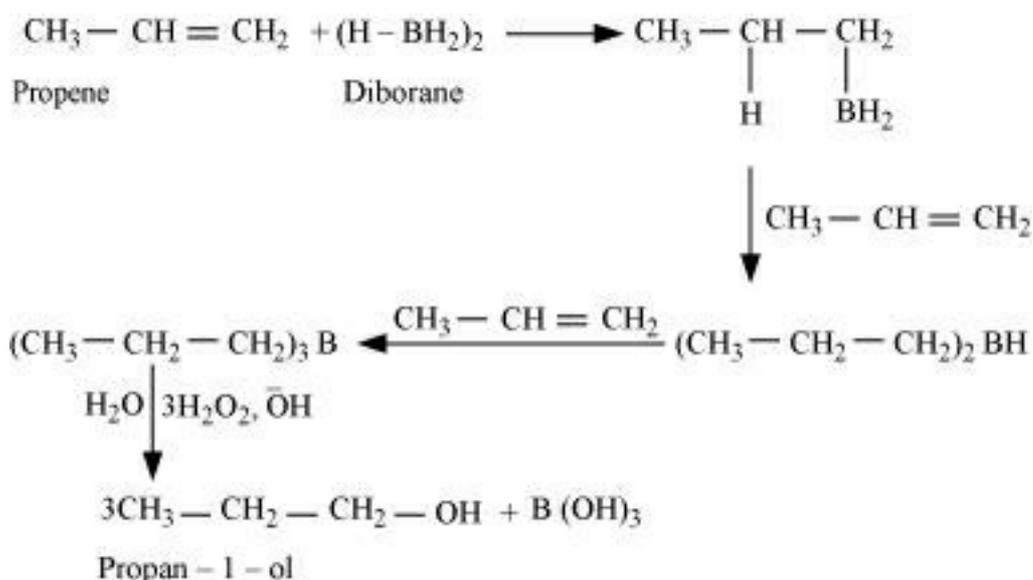
Ans. Alcohols form H-bonds with water due to the presence of -OH group which prevails formation of H-bonding with water. However, hydrocarbons cannot form H-bonds with water as they are non-polar.



As a result, alcohols are comparatively more soluble in water than hydrocarbons of comparable molecular masses.

6. What is meant by hydroboration-oxidation reaction? Illustrate it with an example.

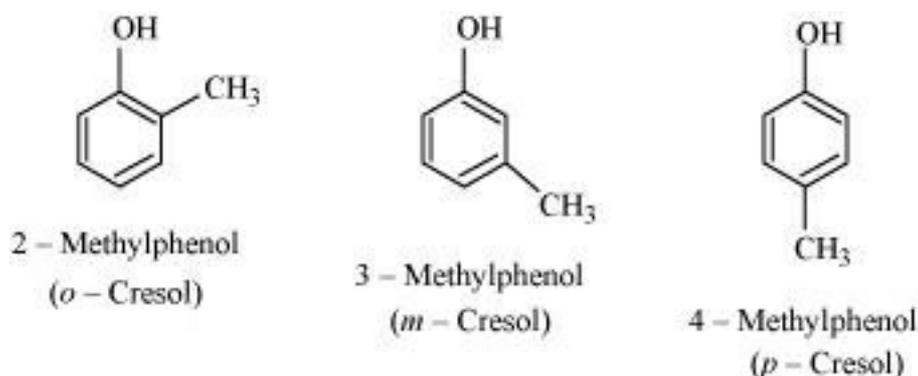
Ans. The addition of borane B_2H_6 followed by oxidation to form propan-1-ol, and is known as the hydroboration-oxidation reaction. For example, propan-1-ol is produced by the hydroboration-oxidation reaction of propene. In this reaction, propene reacts with diborane $(BH_3)_2$ to form trialkyl borane as an addition product. This addition product is oxidized to alcohol by hydrogen peroxide in the presence of aqueous sodium hydroxide.



7. Give the structures and IUPAC names of monohydric phenols of molecular formula,

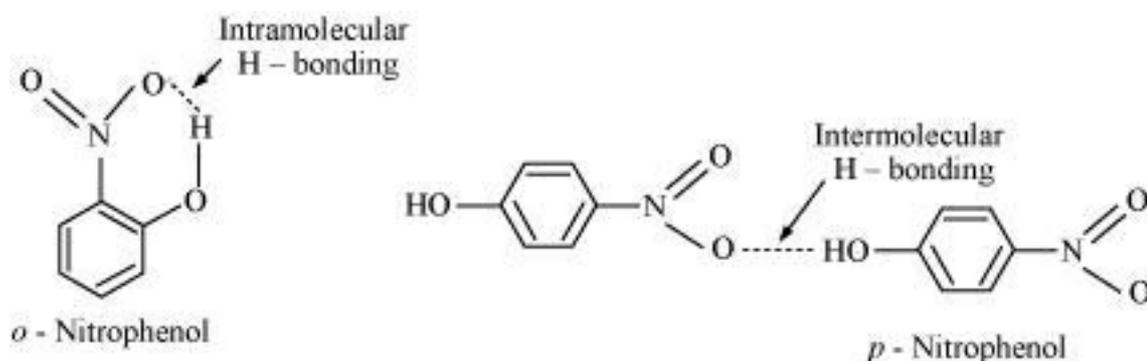
C_7H_8O .

Ans.



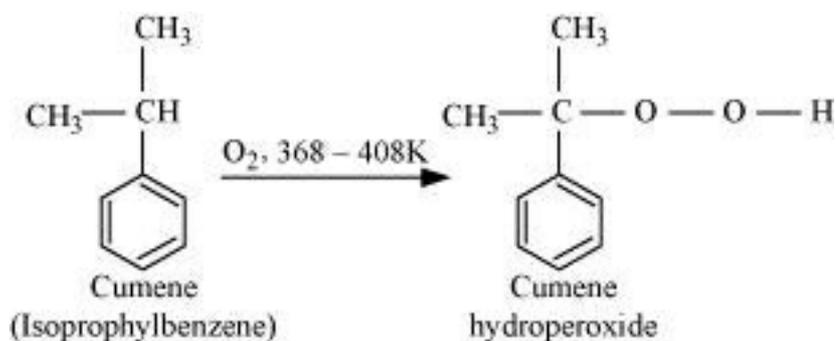
8. While separating a mixture of *ortho* and *para* nitrophenols by steam distillation, name the isomer which will be steam volatile. Give reason.

Ans. Intramolecular H-bonding is present in *o*-nitrophenol. *O*-Nitrophenol is steam volatile because of weak intra molecular H-Bonding. In *p*-nitrophenol, the molecules are strongly associated due to the presence of intermolecular bonding. Hence, *o*-nitrophenol is steam volatile whereas *p*-nitrophenol is not.

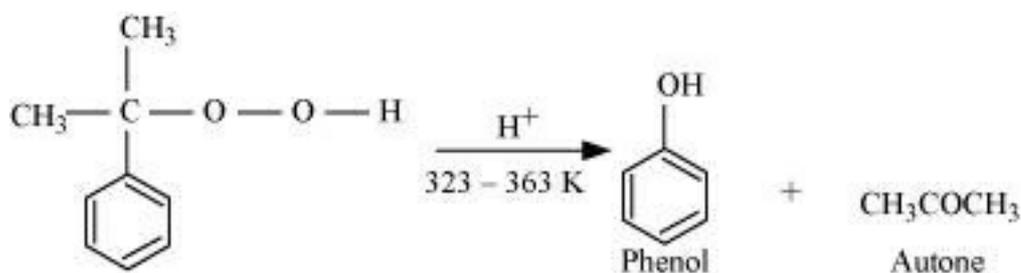


9. Give the equations of reactions for the preparation of phenol from cumene.

Ans. To prepare phenol, cumene is first oxidized in the presence of air to form cumene hydro-peroxide.

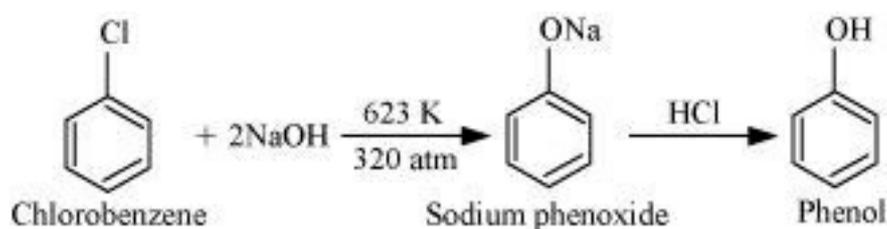


Then, cumene hydroperoxide is treated with dilute acid to prepare phenol and acetone as by-products.



10. Write chemical reaction for the preparation of phenol from chlorobenzene.

Ans. Chlorobenzene is fused with NaOH (at 623 K and 320 atm pressure) to produce sodium phenoxide, which gives phenol on acidification by nucleophilic substitution reaction.

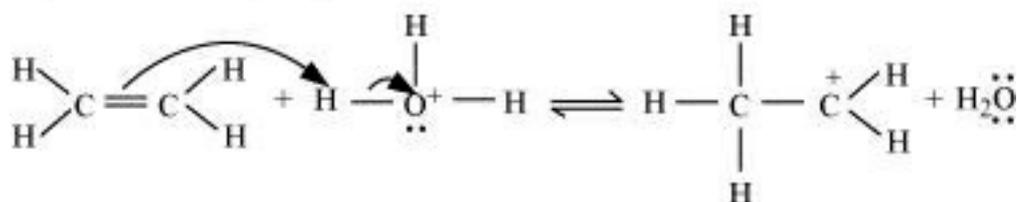


11. Write the mechanism of hydration of ethene to yield ethanol.

Ans. The mechanism of hydration of ethene to form carbocation by electrophilic attack of hydronium ion involves three steps.

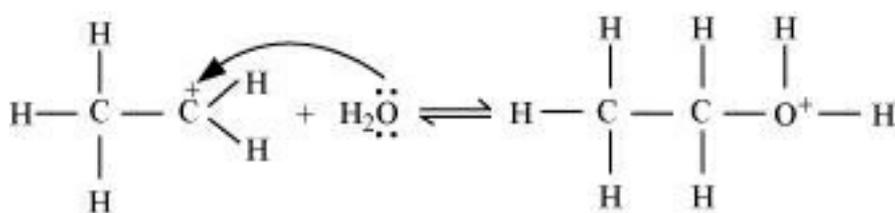
Step 1:

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



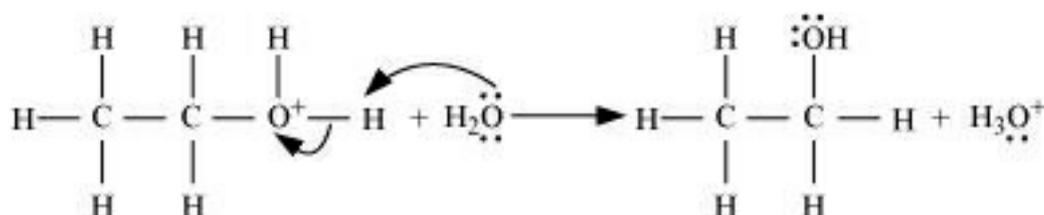
Step 2:

Nucleophilic attack of water on carbocation:



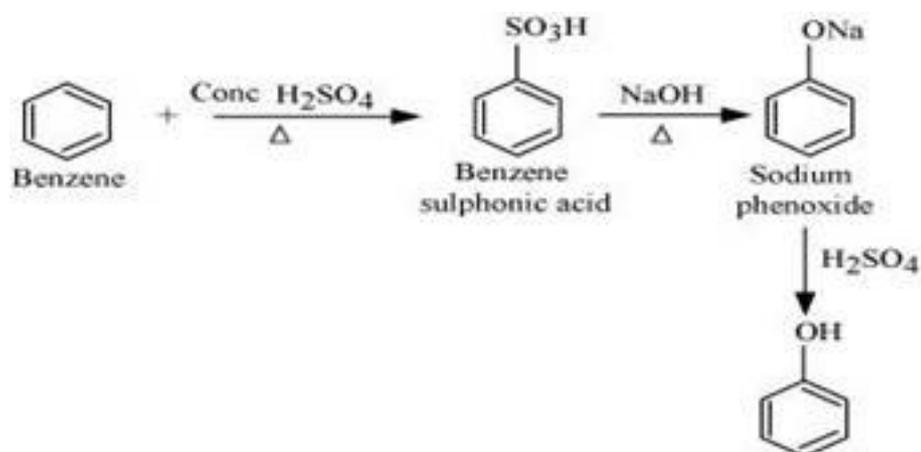
Step 3:

Deprotonation to form ethanol:



12. You are given benzene, conc. H_2SO_4 and NaOH. Write the equations for the preparation of phenol using these reagents.

Ans.



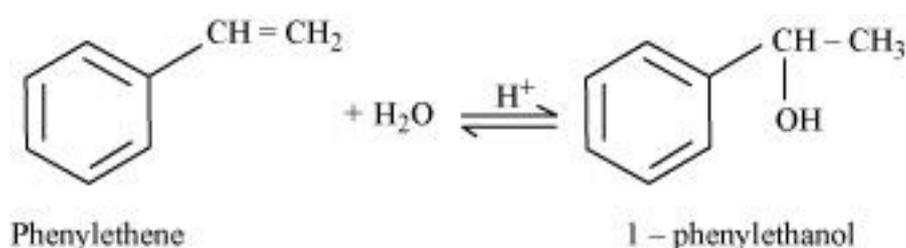
13. Show how will you synthesize:

(i) 1-phenylethanol from a suitable alkene.

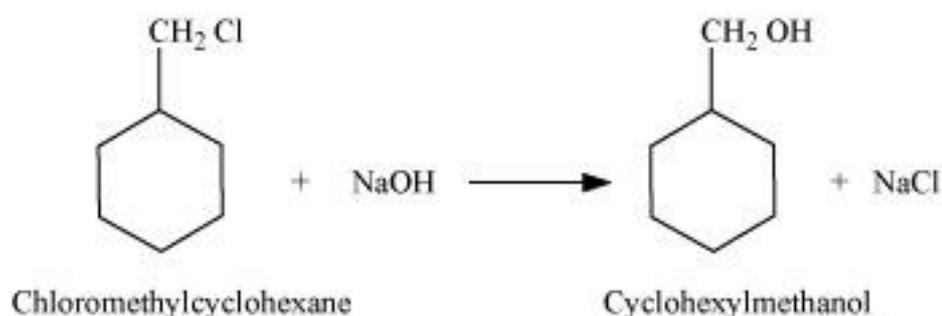
(ii) cyclohexylmethanol using an alkyl halide by an SN2 reaction.

(iii) pentan-1-ol using a suitable alkyl halide?

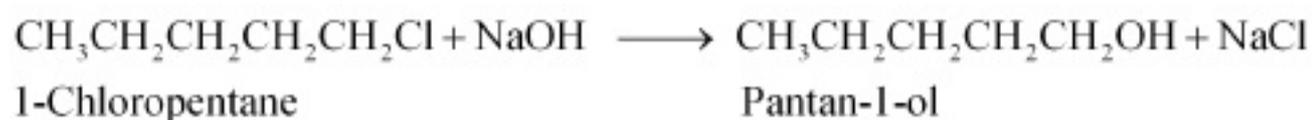
Ans. (i) By acid-catalyzed hydration of ethylbenzene (styrene), 1-phenylethanol can be synthesized.



(ii) When chloromethylcyclohexane is treated with sodium hydroxide, cyclohexylmethanol is obtained.



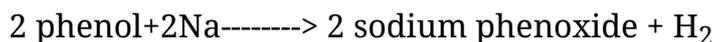
(iii) When 1-chloropentane is treated with NaOH, pentan-1-ol is produced.



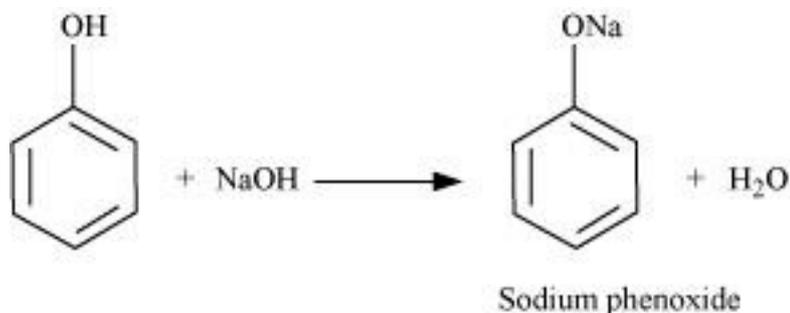
14. Give two reactions that show the acidic nature of phenol. Compare acidity of phenol with that of ethanol.

Ans. The acidic nature of phenol can be represented by the following two reactions:

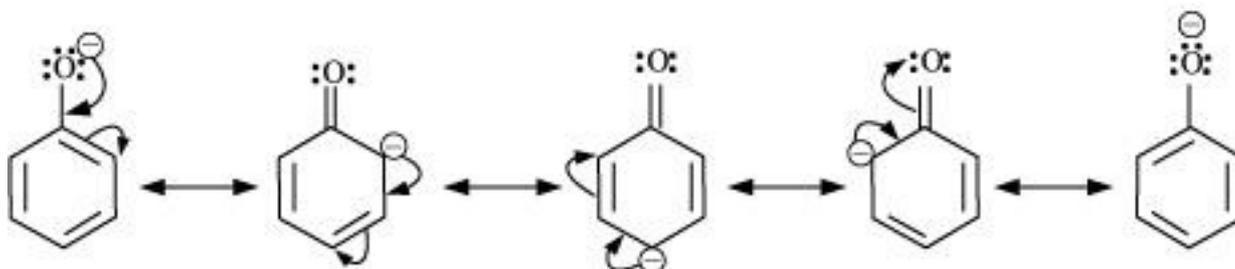
(i) Phenol reacts with sodium to give sodium phenoxide and release H₂ gas as by-product.



(ii) Phenol reacts with sodium hydroxide to give sodium phenoxide and water as by-product.

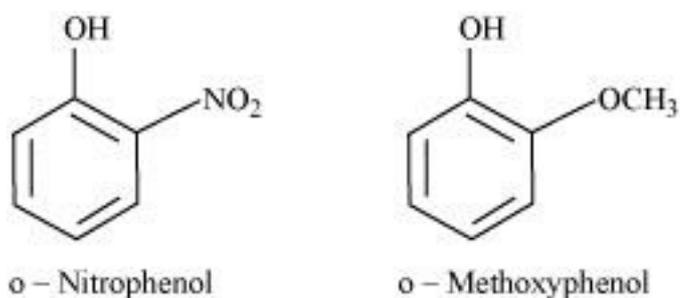


The acidity of phenol is more than that of ethanol. This is because after losing a proton, the phenoxide ion undergoes resonance and gets stabilized whereas ethoxide ion does not undergo resonance. Resonance leads to distribution of charge due to which the compound gets stable unlike concentration of charge at single point like in case of ethoxide ion which promotes instability.



15. Explain why is *ortho* nitrophenol more acidic than *ortho* methoxyphenol?

Ans.



The nitro-group is an electron-withdrawing group. The presence of this group in the ortho position decreases the electron density in the O-H bond and increase positive charge on Oxygen. As a result, it is easier to lose a proton. Also, the *o*-nitrophenoxide ion formed after

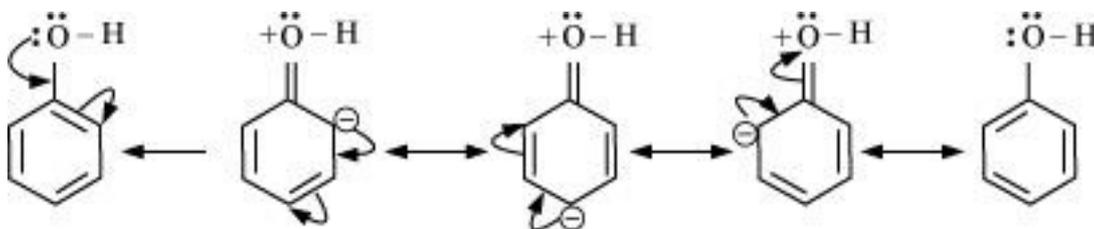
the loss of protons is stabilized by resonance. Hence, *ortho* nitrophenol is a stronger acid.

On the other hand, methoxy group is an electron-releasing group and it decreases positive charge on oxygen. Thus, it increases the electron density in the O-H bond and hence, the proton cannot be given out easily. It makes it less acidic.

For this reason, *ortho*-nitrophenol is more acidic than *ortho*-methoxyphenol.

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

Ans. The -OH group is an electron-donating group. Thus, it increases the electron density in the benzene ring as shown in the given resonance structure of phenol.



As a result, the benzene ring is activated towards electrophilic substitution.

17. Give equations of the following reactions:

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

(ii) Bromine in CS_2 with phenol.

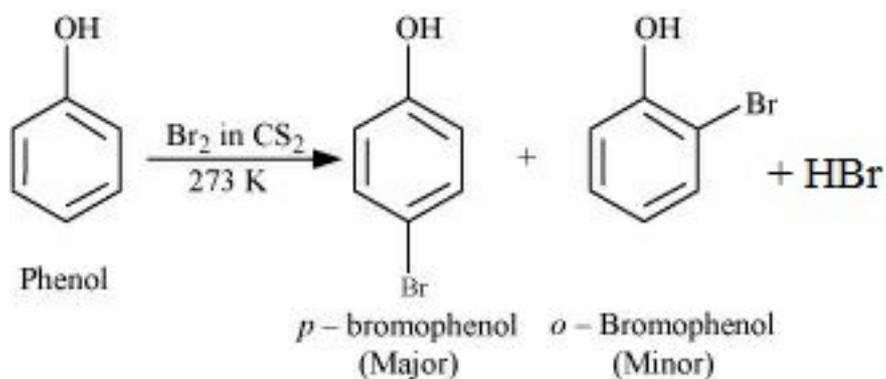
(iii) Dilute HNO_3 with phenol.

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

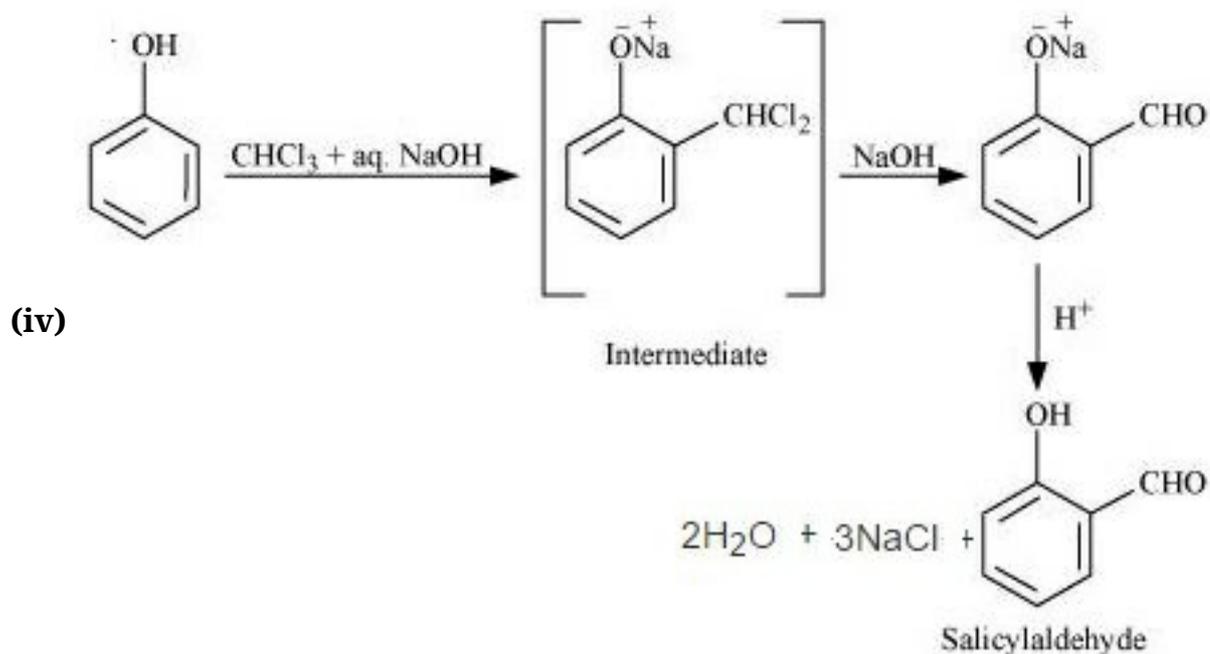
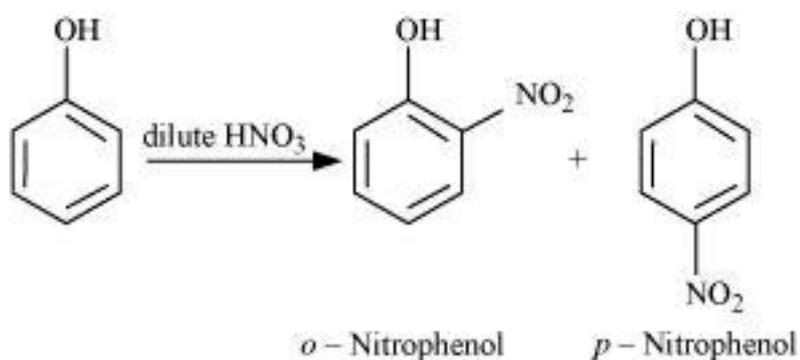
Ans. Propan-1-ol is treated with alcoholic $KMnO_4$ followed by hydrolysis to form propanoic acid as follows-



(ii)



(iii) By the process of nitration, as follows-



18. Explain the following with an example.

(i) Kolbe's reaction.

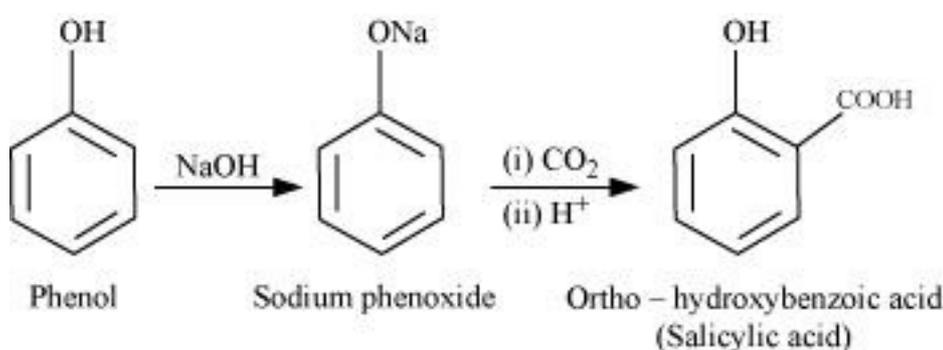
(ii) Reimer-Tiemann reaction.

(iii) Williamson ether synthesis.

(iv) Unsymmetrical ether.

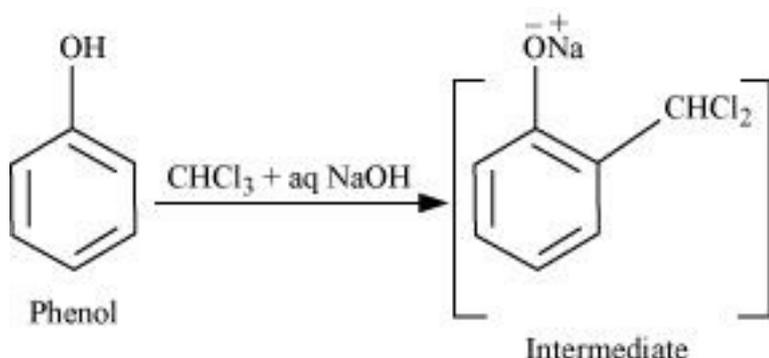
Ans. (i) Kolbe's reaction:

When phenol is treated with sodium hydroxide, sodium phenoxide is produced. This sodium phenoxide when treated with carbon dioxide, at 400K under 3-7 atm. pressure followed by acidification, undergoes electrophilic substitution to give ortho-hydroxybenzoic acid as the main product also known as salicylic acid. This reaction is known as Kolbe's reaction.



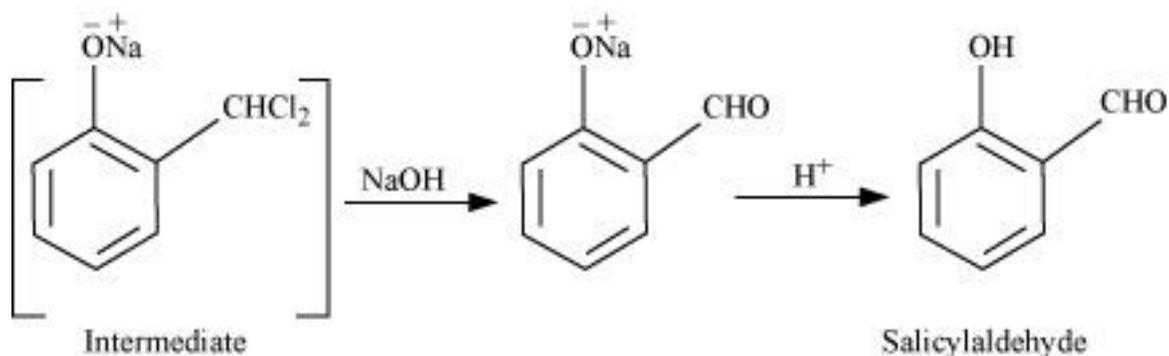
(ii) Reimer-Tiemann reaction:

When phenol is treated with chloroform (CHCl_3) in the presence of sodium hydroxide or potassium hydroxide, a $-\text{CHO}$ group is introduced at the ortho position of the benzene ring and 3KCl and 2 molecules of water are formed as by product.



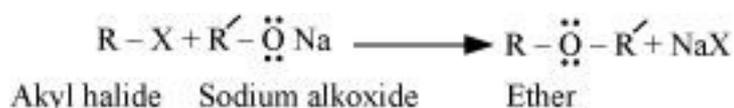
This reaction is known as the Reimer-Tiemann reaction.

The intermediate is hydrolyzed in the presence of alkalis to produce salicylaldehyde.



(iii) Williamson ether synthesis:

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



This reaction involves SN2 attack of the alkoxide ion on the alkyl halide. Better results are obtained in case of primary alkyl halides.



If the alkyl halide is secondary or tertiary, then elimination competes over substitution.

(iv) Unsymmetrical ether:

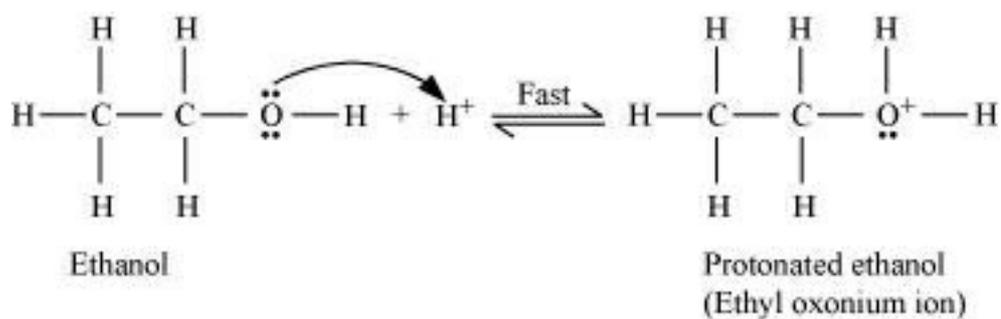
An unsymmetrical ether is an ether where two groups on the two sides of an oxygen atom differ (i.e., have an unequal number of carbon atoms). For example: ethyl methyl ether (CH₃-O-CH₂CH₃).

19. Write the mechanism of acid-catalysed dehydration of ethanol to yield ethene.

Ans. The mechanism of acid dehydration of ethanol to yield ethene involves the following three steps:

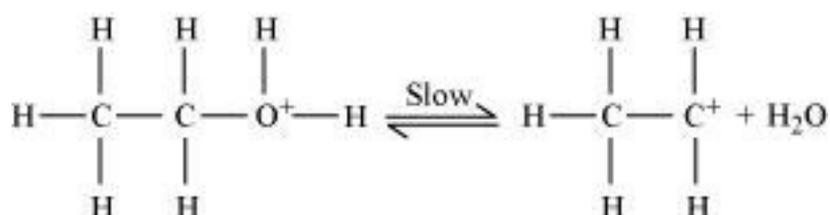
Step 1:

Protonation of ethanol to form ethyl oxonium ion:



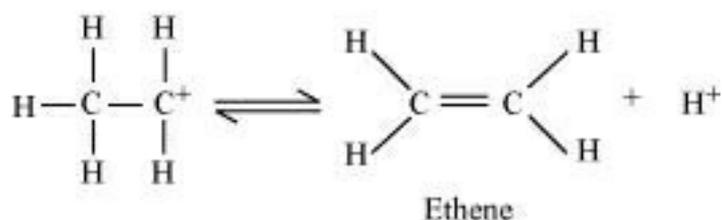
Step 2:

Formation of carbocation (rate determining step):



Step 3:

Elimination of a proton to form ethene:



The acid consumed in step 1 is released in Step 3. After the formation of ethene, it is removed to shift the equilibrium in a forward direction.

20. How are the following conversions carried out?

(i) Propene → Propan-2-ol

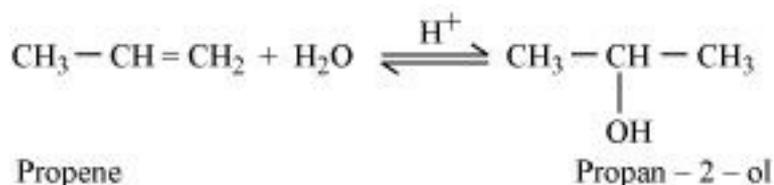
(ii) Benzyl chloride → Benzyl alcohol

(iii) Ethyl magnesium chloride → Propan-1-ol.

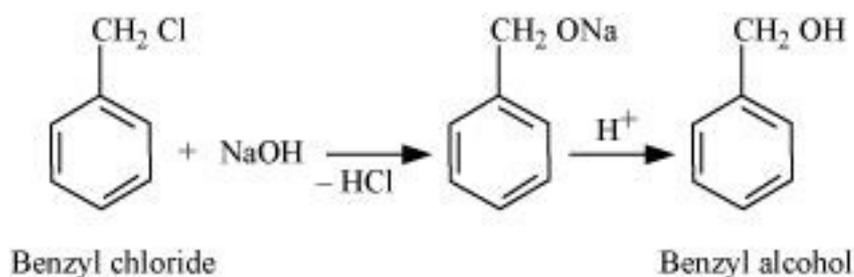
(iv) Methyl magnesium bromide → 2-Methylpropan-2-ol.

Ans. (i) If propene is allowed to react with water in the presence of an acid as a catalyst, then

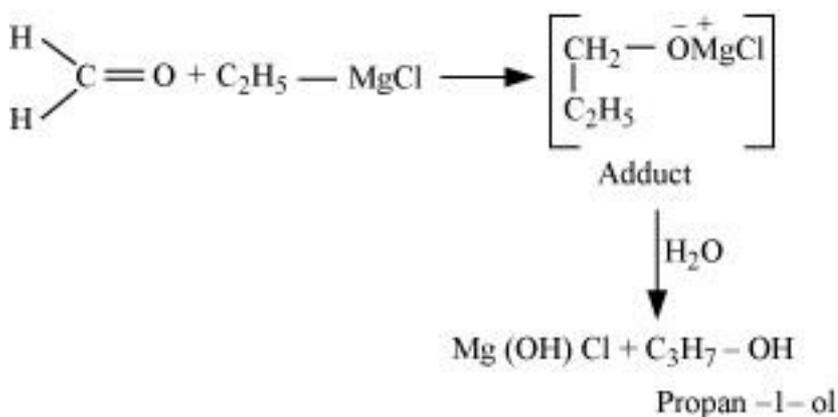
propan-2-ol is obtained.



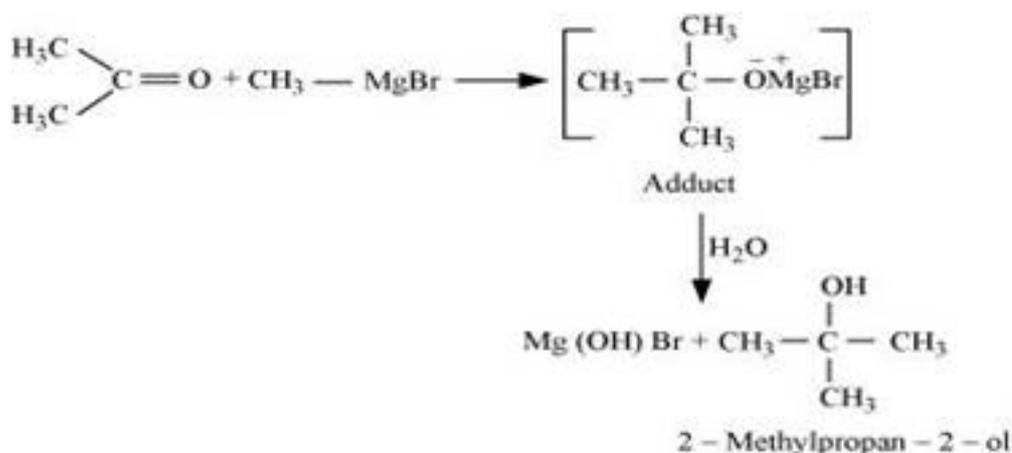
(ii) If benzyl chloride is treated with NaOH (followed by acidification) then benzyl alcohol is produced.



(iii) When ethyl magnesium chloride is treated with methanal, an adduct is the produced which gives propan-1-ol and MgClOH on hydrolysis.



(iv) When methyl magnesium bromide is treated with propane, an adduct is the product which gives 2-methylpropan-2-ol on hydrolysis.



21. Name the reagents used in the following reactions:

(i) Oxidation of a primary alcohol to carboxylic acid.

(ii) Oxidation of a primary alcohol to aldehyde.

(iii) Bromination of phenol to 2,4,6-tribromophenol.

(iv) Benzyl alcohol to benzoic acid.

(v) Dehydration of propan-2-ol to propene.

(vi) Butan-2-one to butan-2-ol.

Ans. (i) Acidified potassium permanganate

(ii) Pyridinium chlorochromate (PCC)

(iii) Bromine water

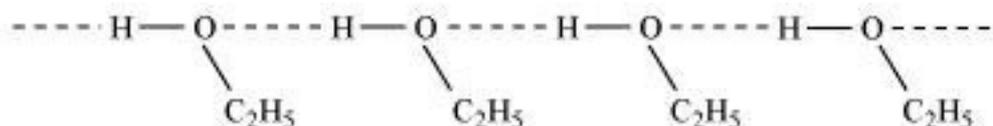
(iv) Acidified potassium permanganate

(v) 85% phosphoric acid or conc. Sulphuric acid at 443K.

(vi) NaBH_4 or LiAlH_4 or H_2/Ni

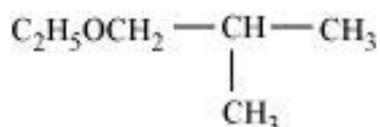
22. Give reason for the higher boiling point of ethanol in comparison to methoxymethane.

Ans. Ethanol undergoes intermolecular H-bonding due to the presence of -OH group, resulting in the association of molecules. Extra energy is required to break these hydrogen bonds. On the other hand, methoxymethane does not undergo intermolecular H-bonding. Hence, the boiling point of ethanol is higher than that of methoxymethane.



23. Give IUPAC names of the following ethers:

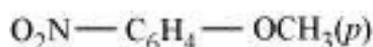
(i)



(ii)



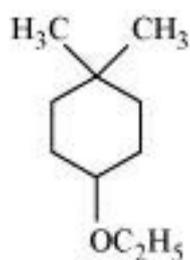
(iii)



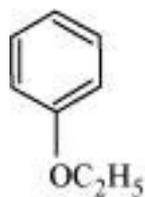
(iv)



(v)



(vi)

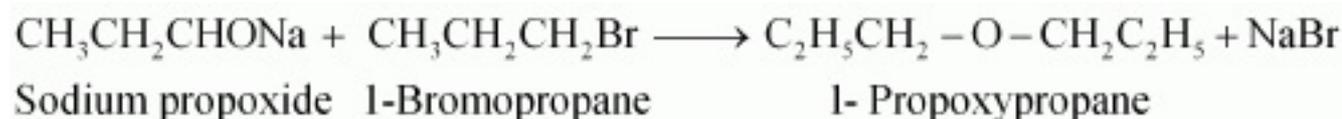


- Ans. (i)** 1-Ethoxy-2-methylpropane
(ii) 2-Chloro-1-methoxyethane
(iii) 4-Nitro-1-methoxybenzene
(iv) 1-Methoxypropane
(v) 1-Ethoxy-4,4-dimethylcyclohexane
(vi) Ethoxybenzene

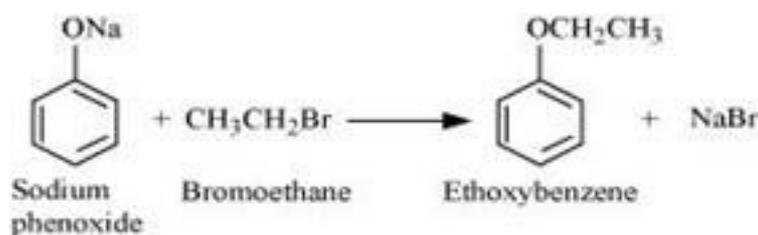
24. Write the names of reagents and equations for the preparation of the following ethers by Williamson's synthesis:

- (i)** 1-Propoxypropane
(ii) Ethoxybenzene
(iii) 2-Methoxy-2-methylpropane
(iv) 1-Methoxyethane

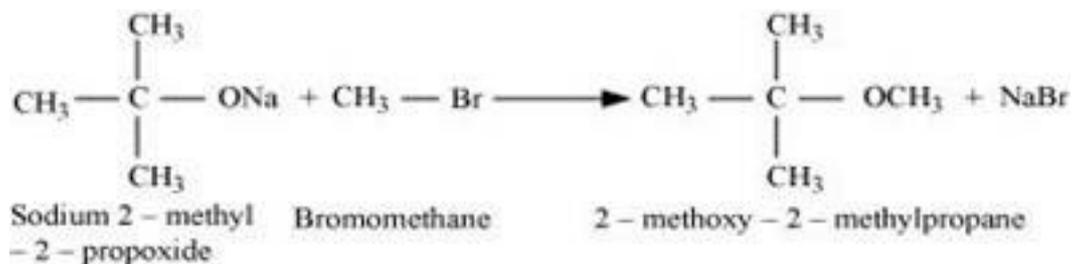
Ans. **(i)**



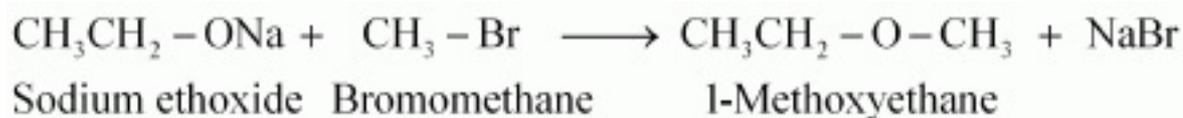
(ii)



(iii)

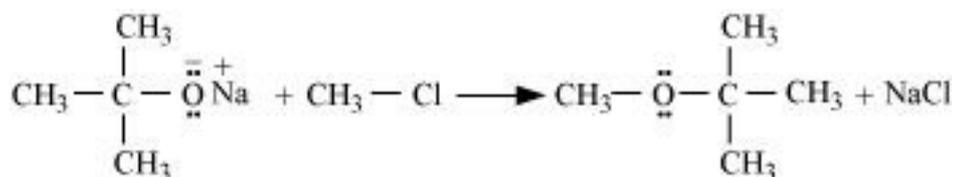


(iv)

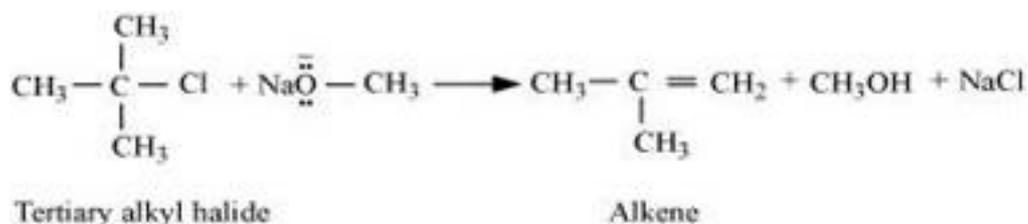


25. Illustrate with examples the limitations of Williamson synthesis for the preparation of certain types of ethers.

Ans. The reaction of Williamson synthesis involves SN₂ attack of an alkoxide ion on a primary alkyl halide because tertiary halide undergoes elimination reaction instead of substitution reaction.



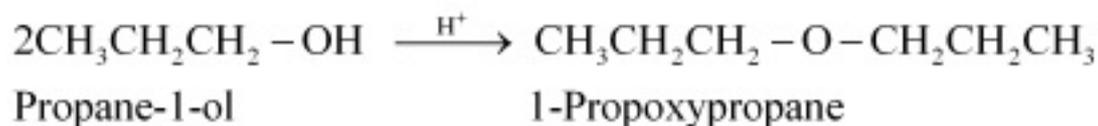
That's why if secondary or tertiary alkyl halides are taken in place of primary alkyl halides, then elimination would compete over substitution. As a result, alkenes would be produced. This is because alkoxides are nucleophiles as well as strong bases. Hence, they react with alkyl halides, which results in an elimination reaction.



26. How is 1-propoxypropane synthesised from propan-1-ol? Write mechanism of this reaction.

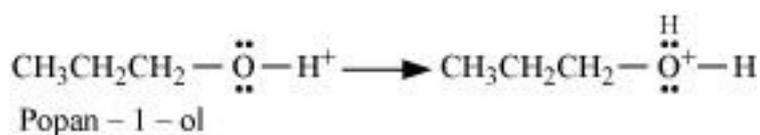
Ans. 1-propoxypropane can be synthesized from propan-1-ol by dehydration.

Propan-1-ol undergoes dehydration in the presence of protic acids (such as H₂SO₄, H₃PO₄) to give 1-propoxypropane.

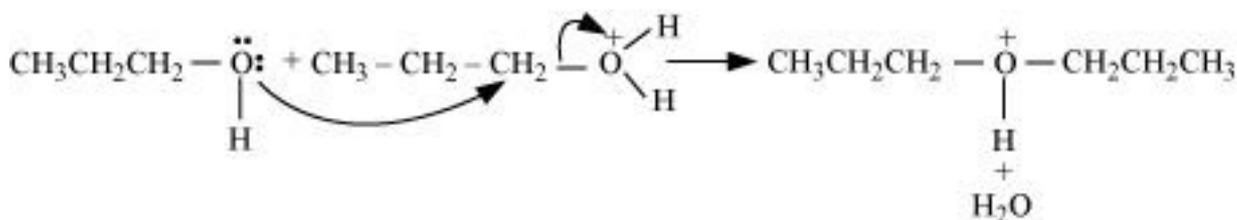


The mechanism of this reaction involves the following three steps:

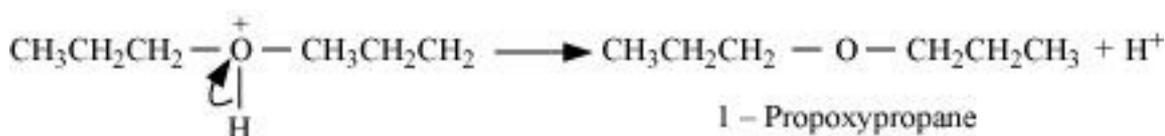
Step 1: Protonation



Step 2: Nucleophilic attack



Step 3: Deprotonation



27. Preparation of ethers by acid dehydration of secondary or tertiary alcohols is not a suitable method. Give reason.

Ans. The formation of ethers by dehydration of secondary or tertiary alcohol is a bimolecular reaction (S_N2) involving the attack of an alcohol molecule on a protonated alcohol molecule very quickly. In the method, the alkyl group should be unhindered. In case of secondary or tertiary alcohols, the alkyl group is hindered. As a result, elimination dominates substitution. Hence, in place of ethers, alkenes are formed.

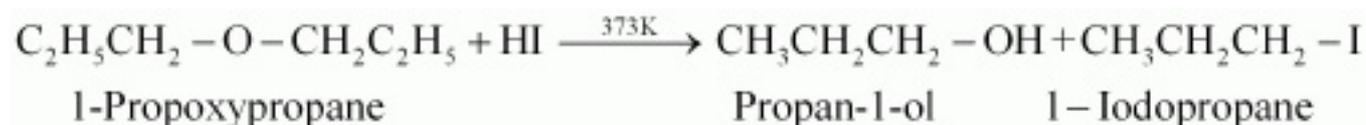
28. Write the equation of the reaction of hydrogen iodide with:

(i) 1-propoxypropane

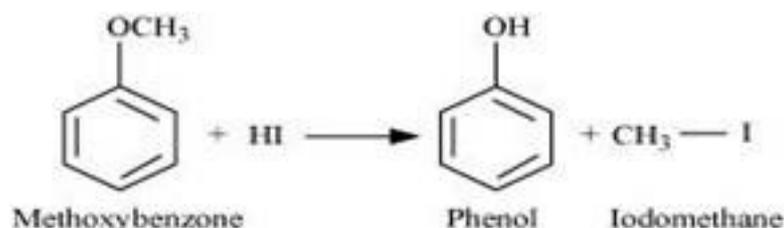
(ii) Methoxybenzene and

(iii) Benzyl ethyl ether

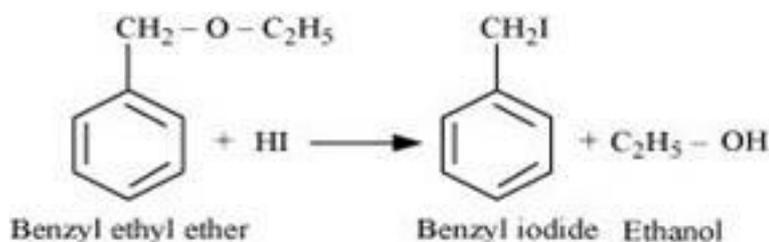
Ans. (i)



(ii)



(iii)



29. Explain the fact that in aryl alkyl ethers

(i) The alkoxy group activates the benzene ring towards electrophilic substitution and

(ii) It directs the incoming substituents to ortho and para positions in benzene ring.

Ans. (i) In aryl alkyl ethers, due to the +R effect of the alkoxy group, the electron density in the benzene ring increases as shown in the following resonance structure.

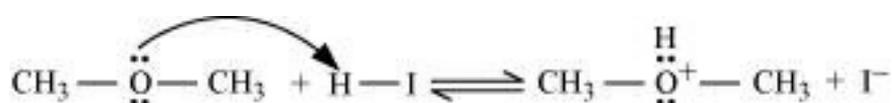
Thus, benzene is activated towards electrophilic substitution by the alkoxy group and electrophile will attack at O- and p- positions.

(ii) It can also be observed from the resonance structures that the electron density increases more at the ortho and para positions than at the meta position. As a result, the incoming substituents are directed to the ortho and para positions in the benzene ring.

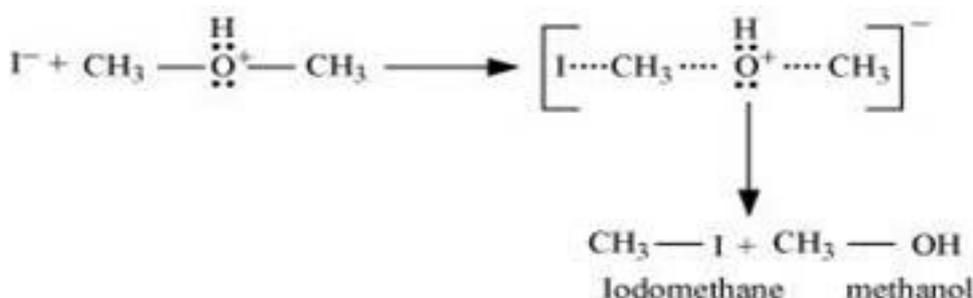
30. Write the mechanism of the reaction of HI with methoxymethane.

Ans. The mechanism of the reaction of HI with methoxymethane involves the following steps:

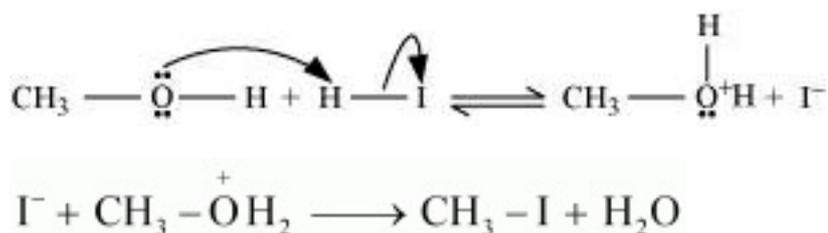
Step1: Protonation of methoxymethane:



Step2: Nucleophilic attack of I⁻:



Step3: When HI is in excess and the reaction is carried out at a high temperature, the methanol formed in the second step reacts with another HI molecule and gets converted to methyl iodide



31. Write equations of the following reactions:

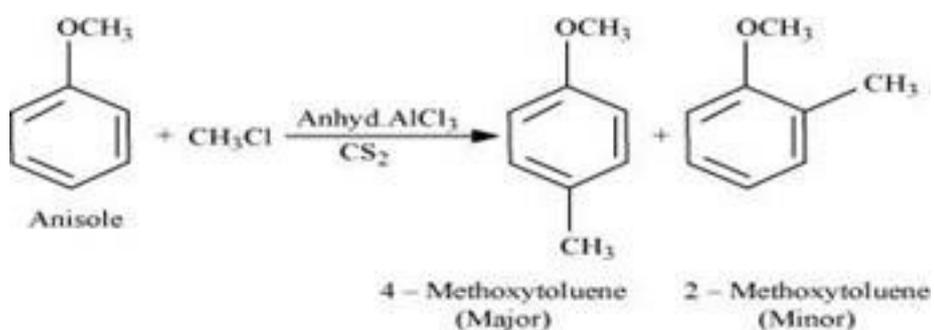
(i) Friedel-Crafts reaction-alkylation of anisole.

(ii) Nitration of anisole.

(iii) Bromination of anisole in ethanoic acid medium.

(iv) Friedel-Craft's acetylation of anisole.

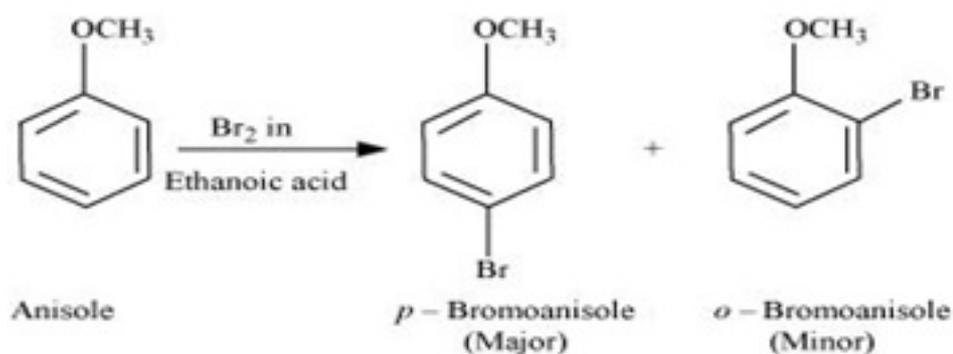
Ans. (i)



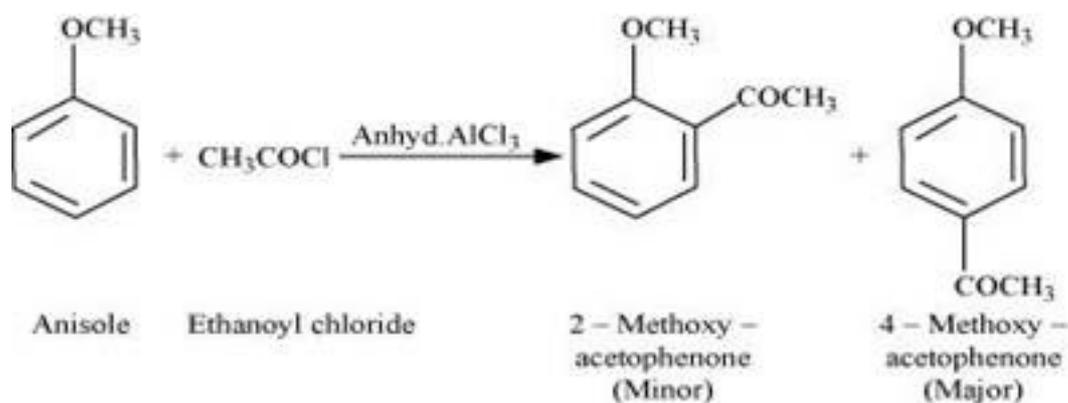
(ii)



(iii)

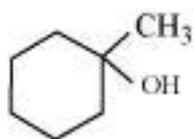


(iv)

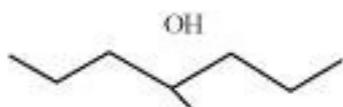


32. Show how would you synthesise the following alcohols from appropriate alkenes?

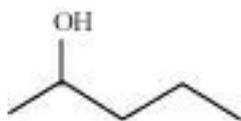
(i)



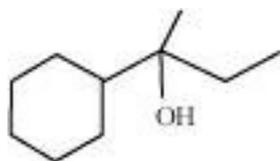
(ii)



(iii)

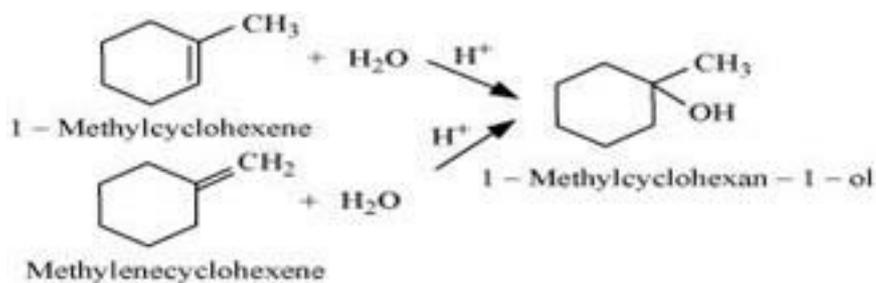


(iv)

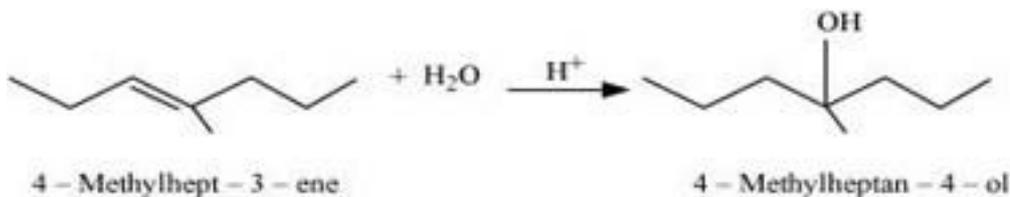


Ans. The given alcohols can be synthesized by applying Markovnikov's rule of acid-catalyzed hydration of appropriate alkenes.

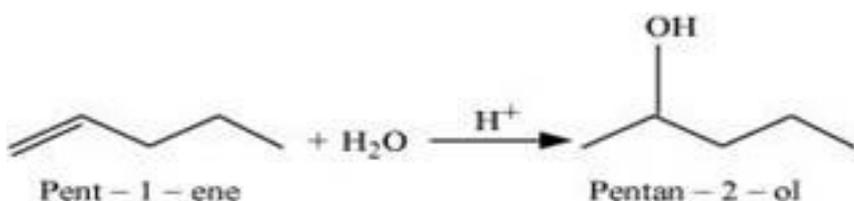
(i)



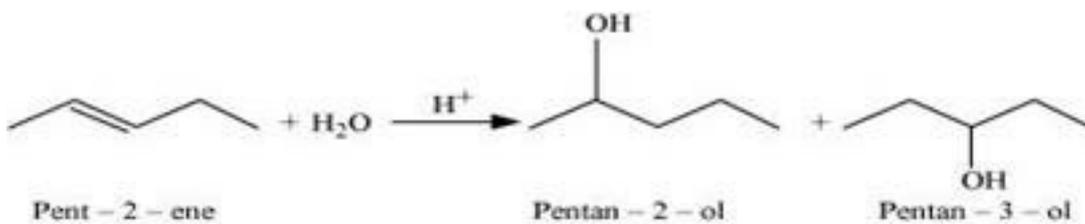
(ii)



(iii)

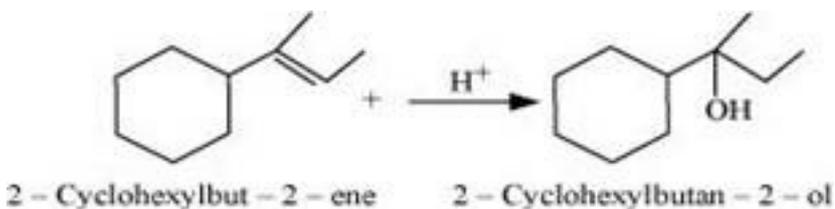


Acid-catalyzed hydration of pent-2-ene also produces pentan-2-ol but along with pentan-3-ol.

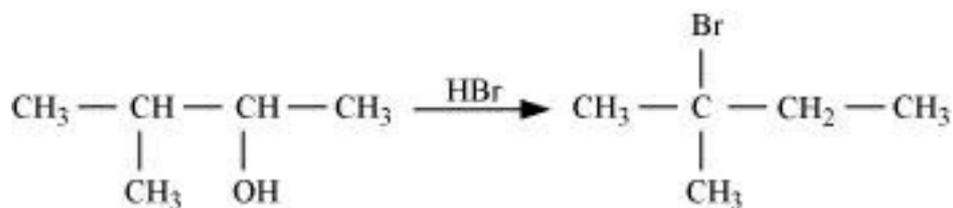


Thus, the first reaction is preferred over the second one to get pentan-2-ol.

(iv)



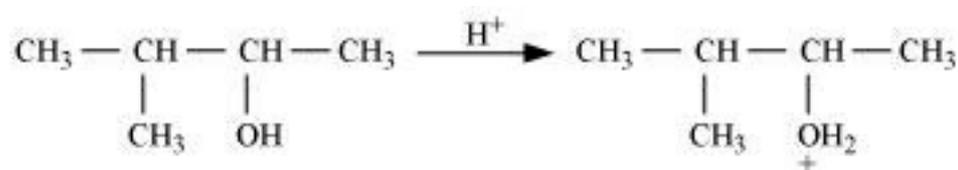
33. When 3-methylbutan-2-ol is treated with HBr, the following reaction takes place:



Give a mechanism for this reaction. (Hint: The secondary carbocation formed in step II rearranges to a more stable tertiary carbocation by a hydride ion shift from 3rd carbon atom.)

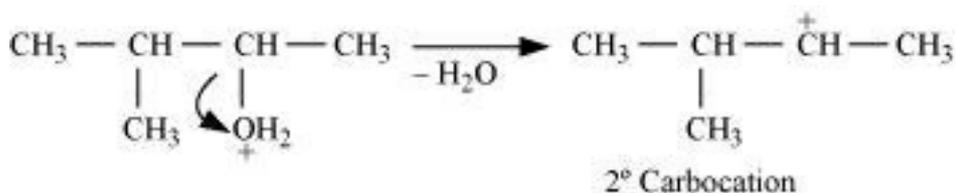
Ans. The mechanism of the given reaction involves the following steps:

Step 1: Protonation

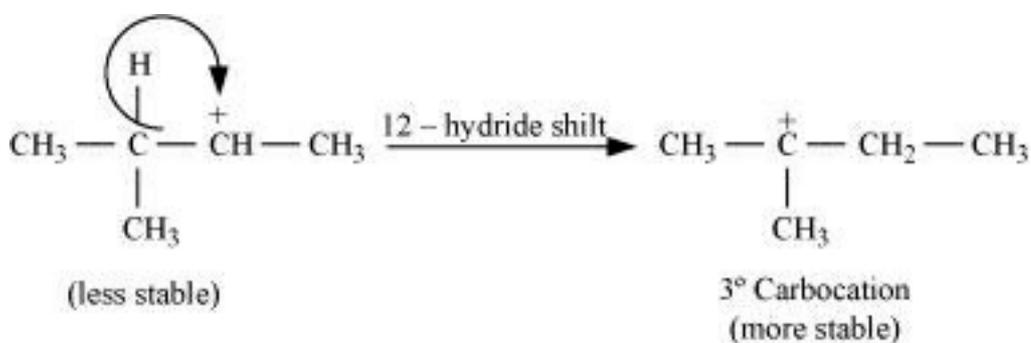


3 - Methylbutan - 2 - ol

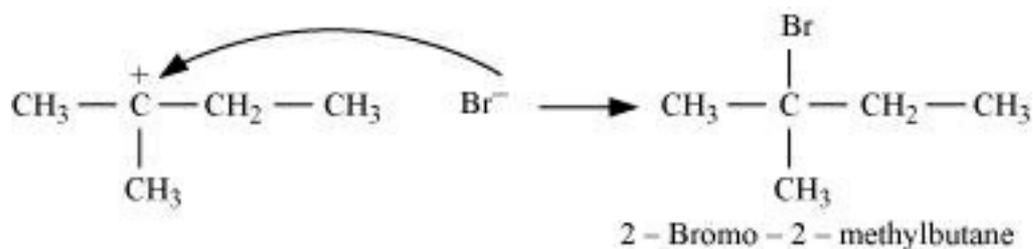
Step 2: Formation of 2° carbocation by the elimination of a water molecule



Step 3: Re-arrangement by the hydride-ion shift



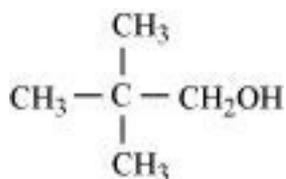
Step 4: Nucleophilic attack



In-text question

1. Classify the following as primary, secondary and tertiary alcohols:

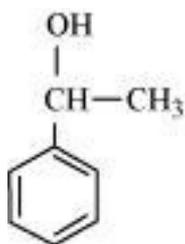
(i)



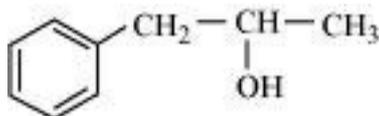
(ii) $\text{H}_2\text{C} = \text{CH} - \text{CH}_2\text{OH}$

(iii) $\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{OH}$

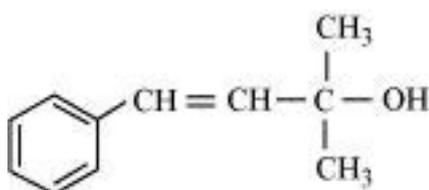
(iv)



(v)



(vi)



Ans. Primary alcohol → (i), (ii) (iii)

Secondary alcohol → (iv), (v)

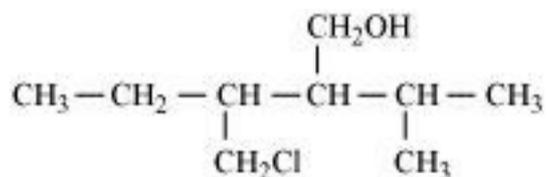
Tertiary alcohol → (vi)

2. Identify allylic alcohols in the above examples.

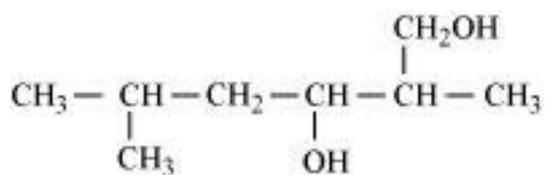
Ans. The alcohols given in (ii) and (vi) are allylic alcohols.

3. Name the following compounds according to IUPAC system.

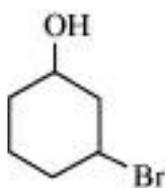
(i)



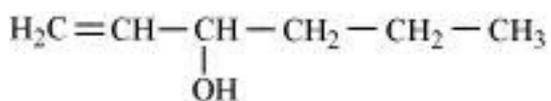
(ii)



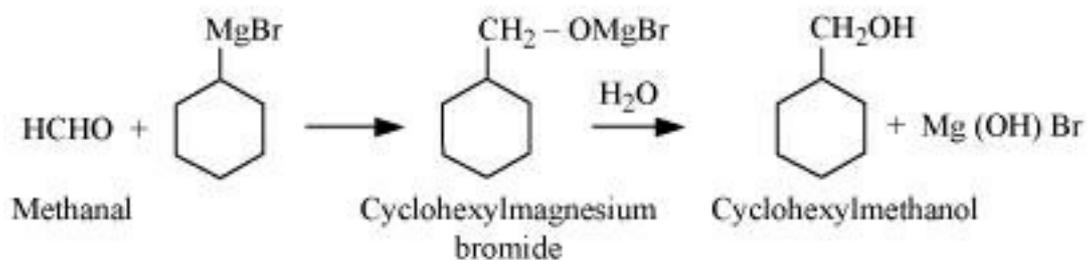
(iii)



(iv)

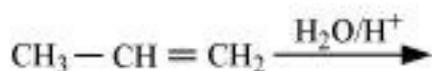


(v)

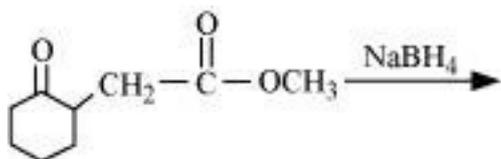


5. Write structures of the products of the following reactions:

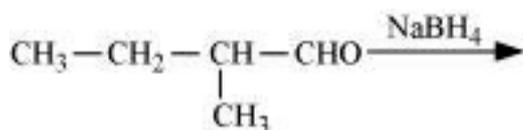
(i)



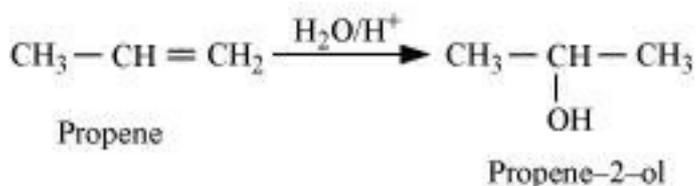
(ii)



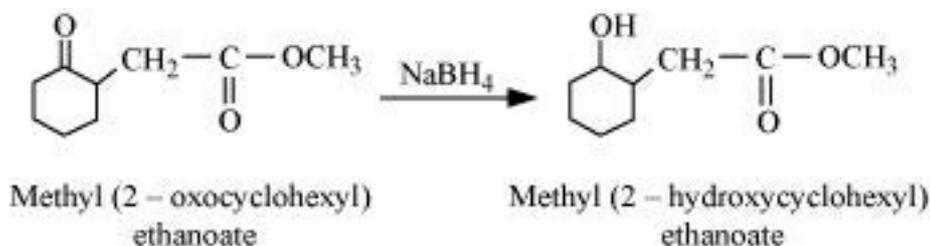
(iii)



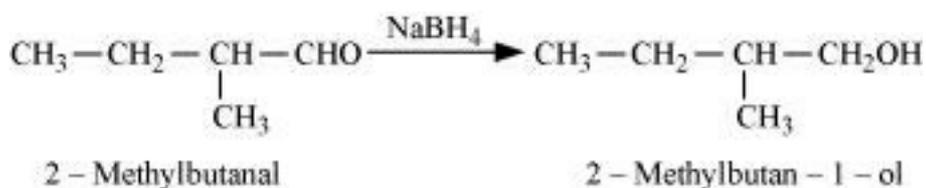
Ans. (i)



(ii)



(iii)

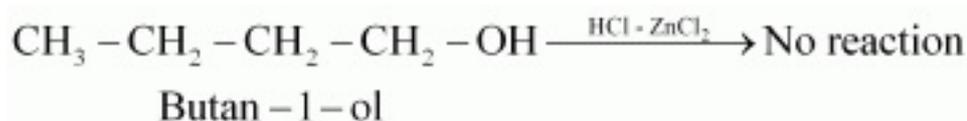


6. Give structures of the products you would expect when each of the following alcohol reacts with (a) $\text{HCl} - \text{ZnCl}_2$ (b) HBr and (c) SOCl_2 .

(i) Butan-1-ol

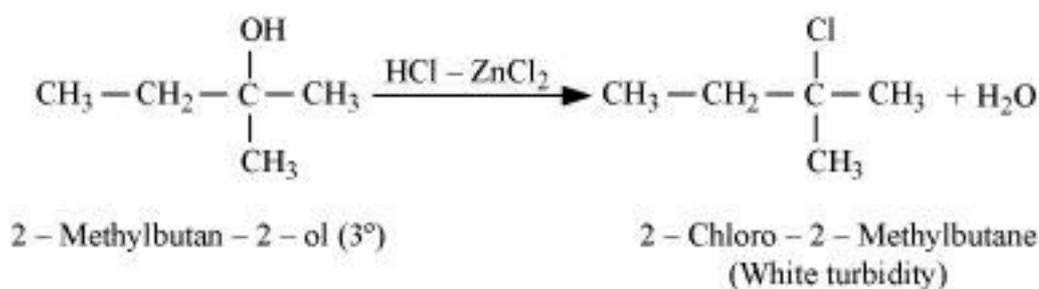
(ii) 2-Methylbutan-2-ol

Ans. (a)(i)



Primary alcohols do not react appreciably with Lucas' reagent ($\text{HCl} - \text{ZnCl}_2$) at room temperature.

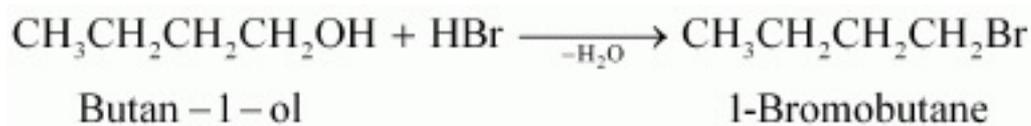
(ii)



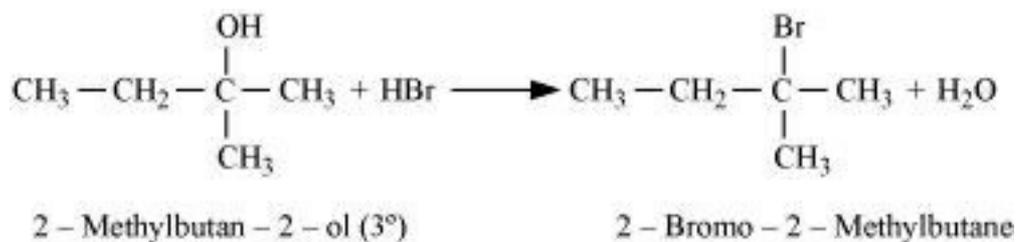
Tertiary alcohols react immediately with Lucas' reagent.

(b)

(i)

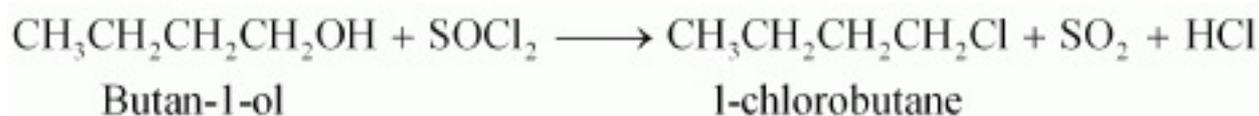


(ii)

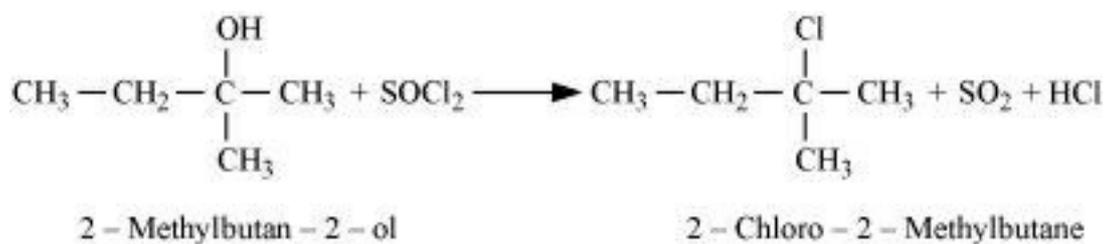


(c)

(i)



(ii)

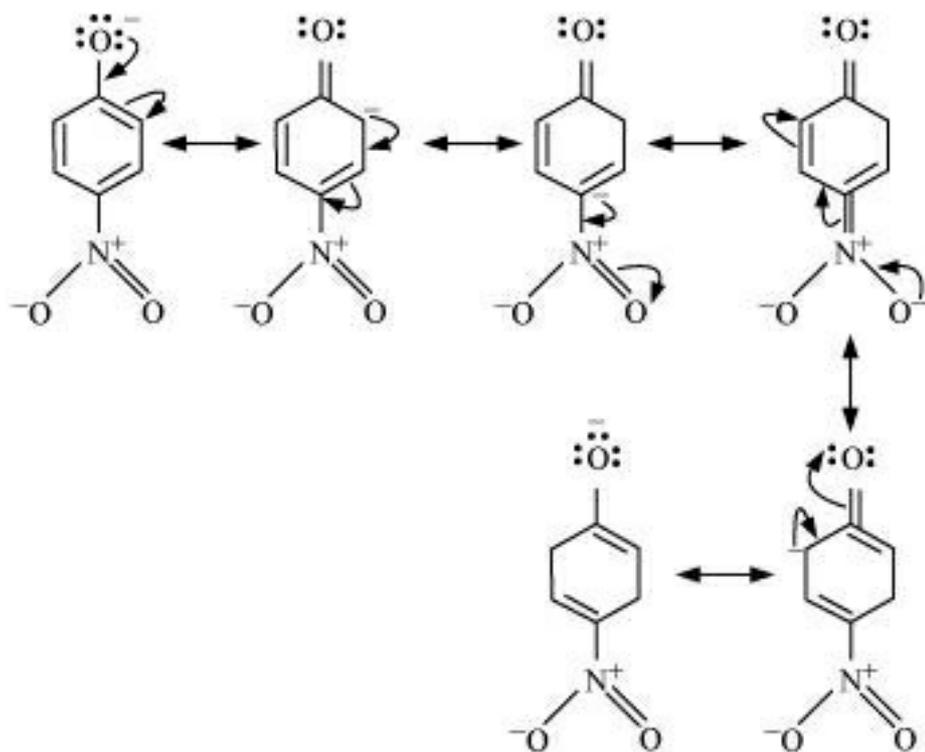


7. Predict the major product of acid catalysed dehydration of

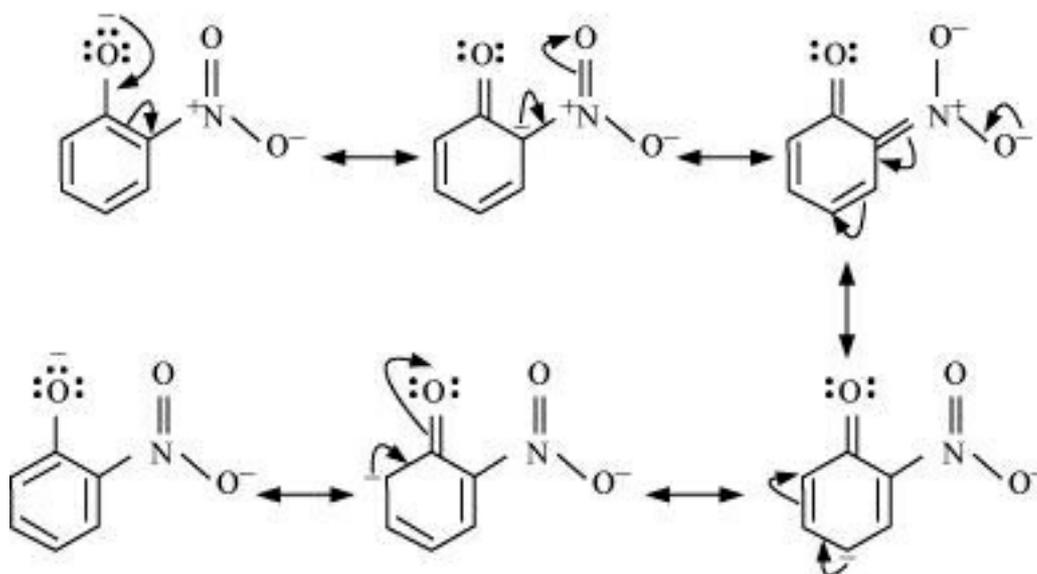
(i) 1-Methylcyclohexanol and

(ii) Butan-1-ol

Ans. (i)



Resonance structures of *p*-nitrophenoxide ion



Resonance structures of *o*-nitrophenoxide ion

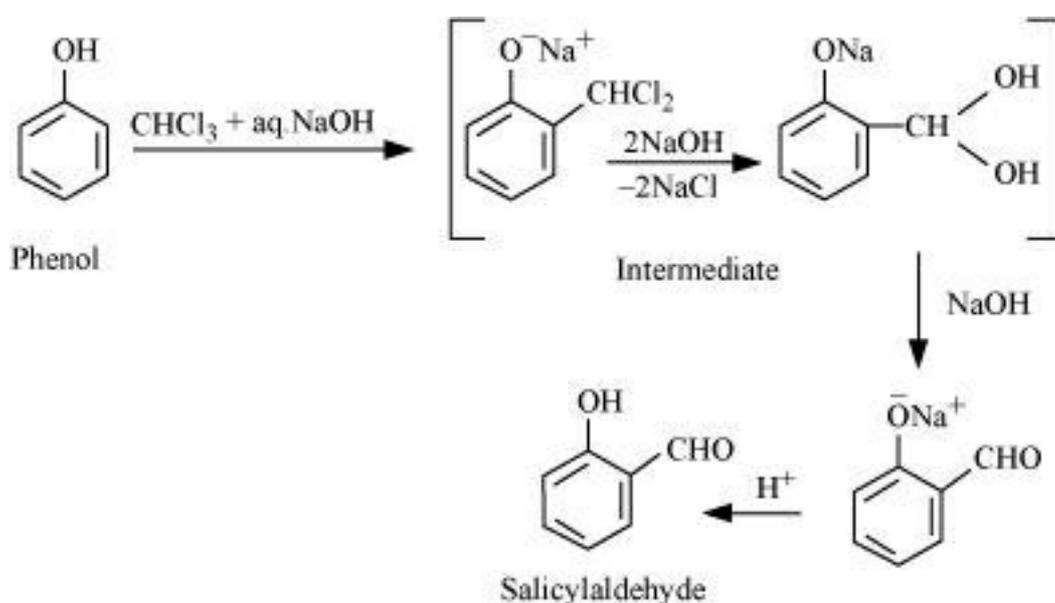
It can be observed that the presence of nitro groups increases the stability of *o*- and *p*-nitrophenoxide ion or phenolate ion as compared to phenoxide ion.

9. Write the equations involved in the following reactions:

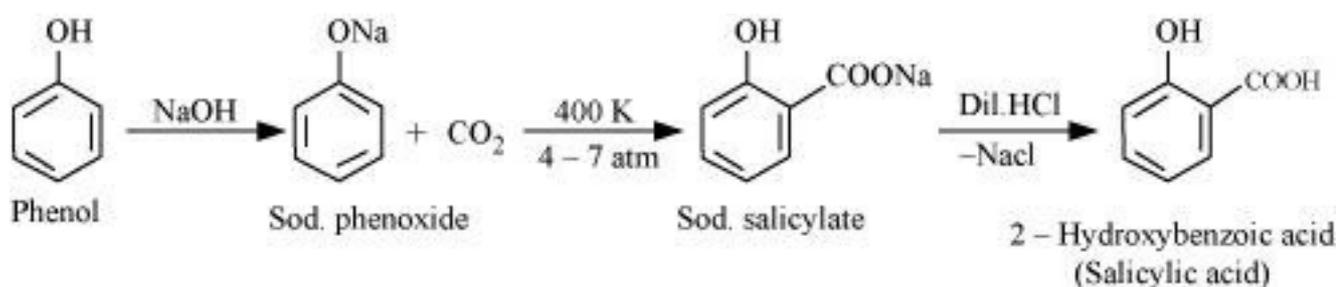
(i) Reimer-Tiemann reaction

(ii) Kolbe's reaction

Ans. (i) Reimer-Tiemann reaction: when phenol reacts with CHCl_3 and KOH at 60°C , salicylaldehyde is formed.

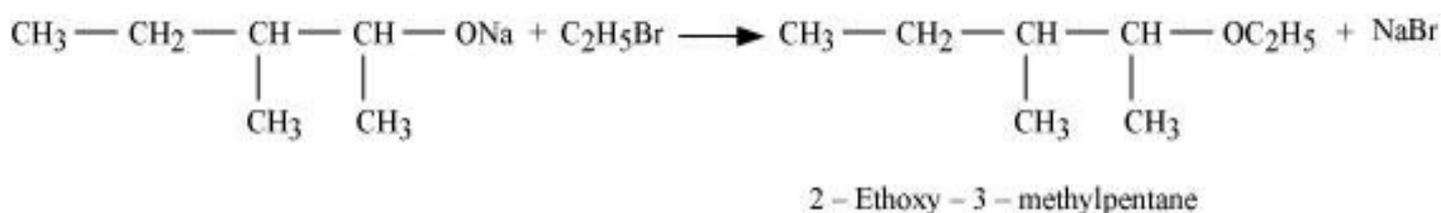
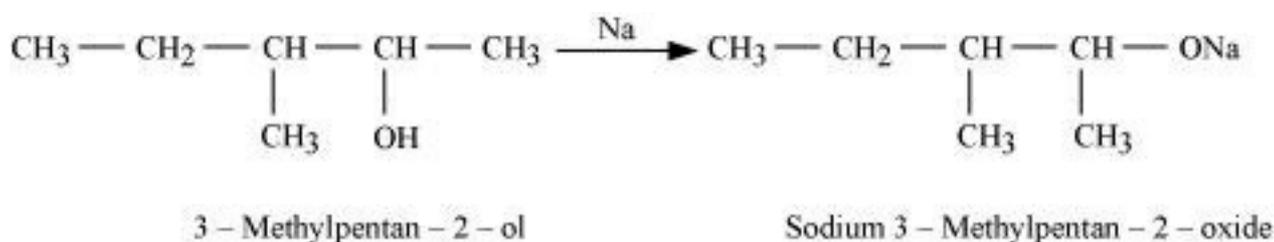
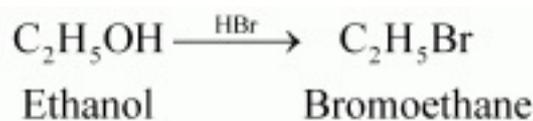


(ii) Kolbe's reaction: when sodium phenoxide reacts with CO_2 at high pressure, on heating sodium salicylate is formed which on acidification gives salicylic acid.



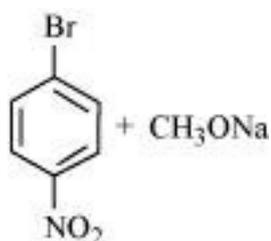
10. Write the reactions of Williamson synthesis of 2-ethoxy-3-methylpentane starting from ethanol and 3-methylpentan-2-ol.

Ans. In Williamson synthesis, an alkyl halide reacts with an alkoxide ion. Also, it is an $\text{S}_{\text{N}}2$ reaction. In the reaction, alkyl halides should be primary having the least steric hindrance. Hence, an alkyl halide is obtained from ethanol and alkoxide ion from 3-methylpentan-2-ol.

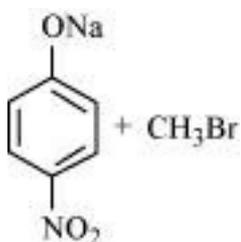


11. Which of the following is an appropriate set of reactants for the preparation of 1-methoxy-4-nitrobenzene and why?

(i)

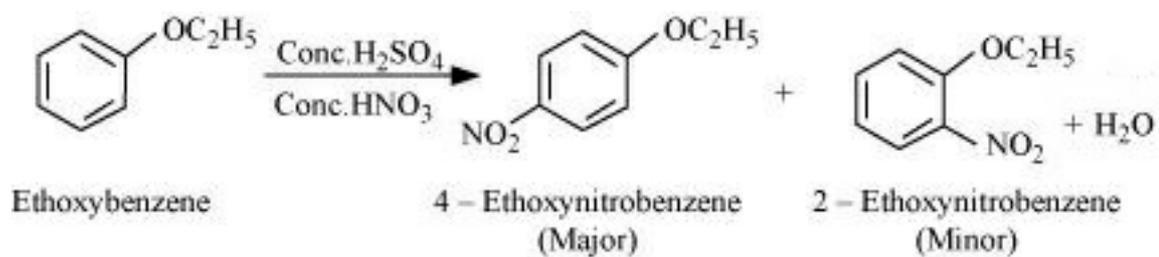


(ii)



Ans. Set (ii) is an appropriate set of reactants for the preparation of 1-methoxy-4-nitrobenzene.

(iii)



(iv)

