

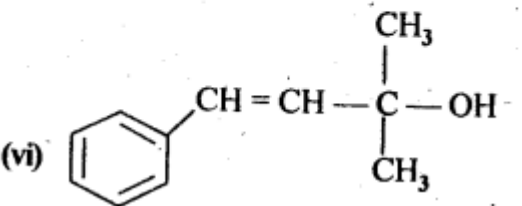
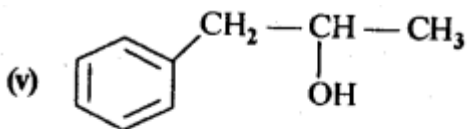
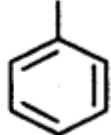
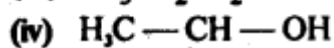
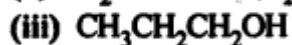
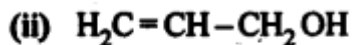
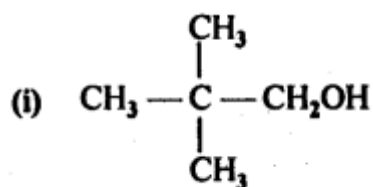
## CHAPTER 7

### ALCOHOLS, PHENOLS & ETHERS

#### QUESTION AND ANSWERS

#### 2 MARKS

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



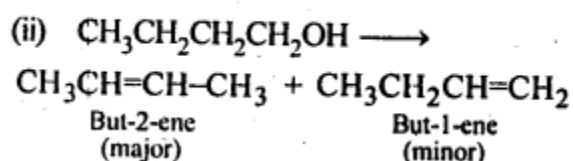
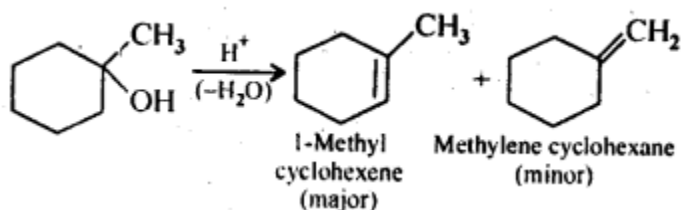
**Ans:** Primary alcohols: (i), (ii), (iii)

Secondary alcohols: (iv), (v)

Tertiary alcohols: (vi)

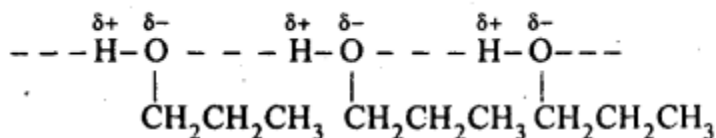
2. Predict the major product of acid catalysed dehydration of  
 (i) 1-methylcyclohexanol  
 (ii) butan-1-ol

**Ans:**



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

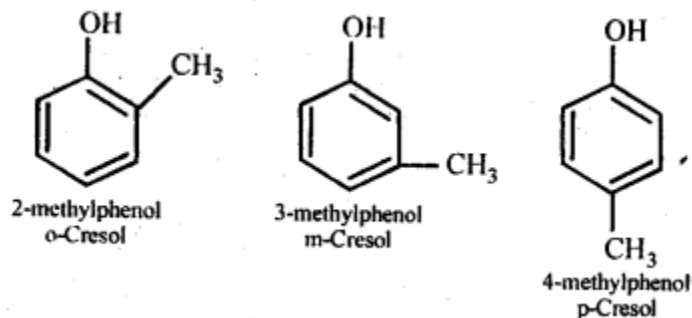
**Ans:** The molecules of butane are held together by weak van der Waal's forces of attraction while those of propanol are held together by stronger intermolecular hydrogen bonding.



Therefore, the boiling point of propanol is much higher than that of butane.

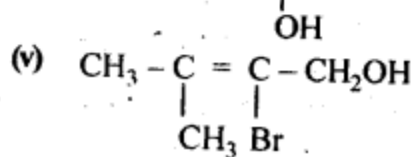
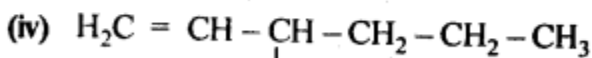
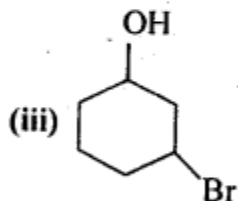
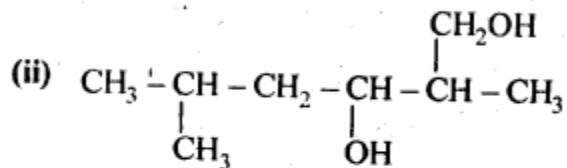
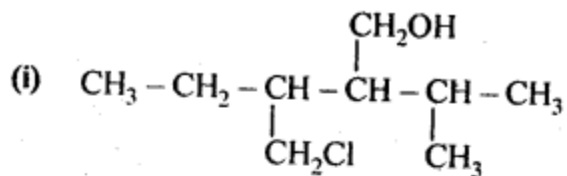
4. Give the structures and IUPAC names of monohydric phenols of molecular formula,  $\text{C}_7\text{H}_8\text{O}$ .

**Ans:** The three isomers are:

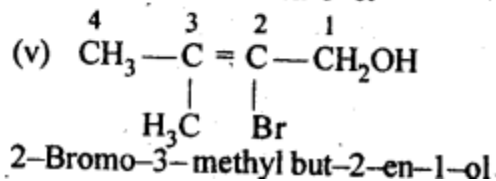
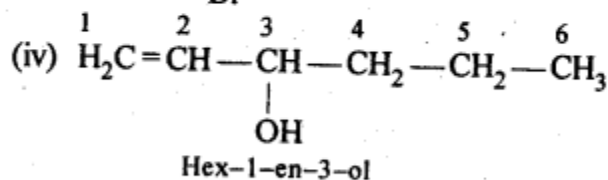
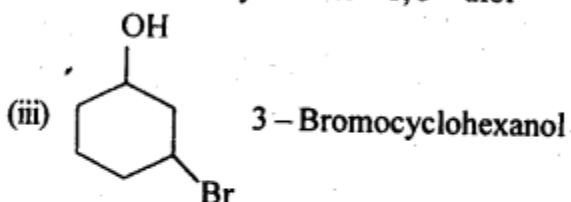
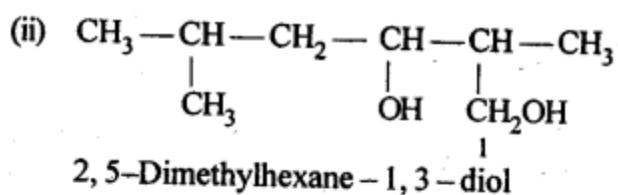
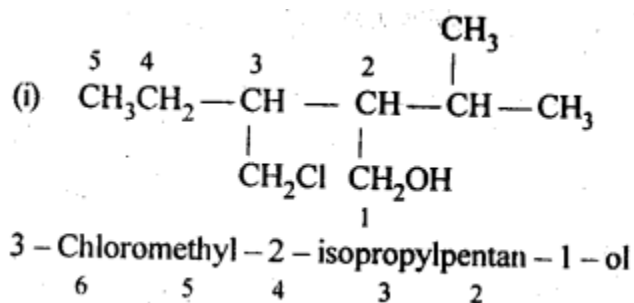


## 5MARKS

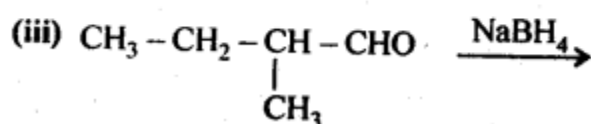
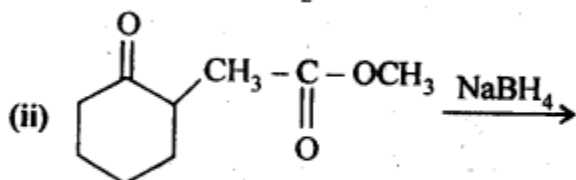
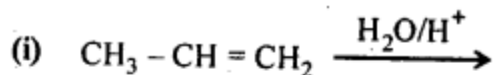
**1. Name the following compounds according to IUPAC system.**



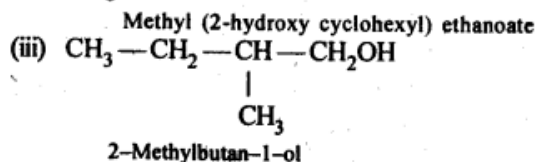
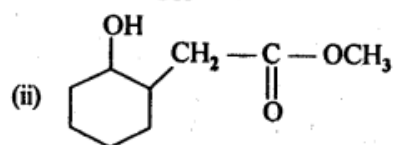
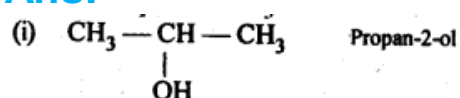
Ans:



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



**Ans:**



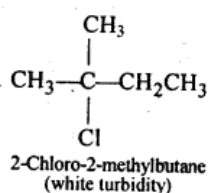
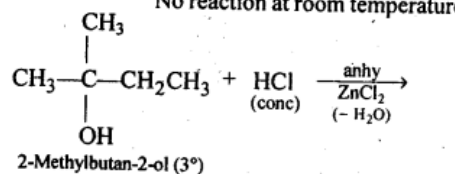
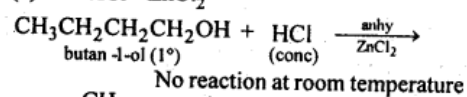
3. Give structures of the products you would expect when each of the following alcohol reacts with (a) HCl- $\text{ZnCl}_2$  (b) HBr and (c)  $\text{SOCl}_2$

(i) Butan-1-ol

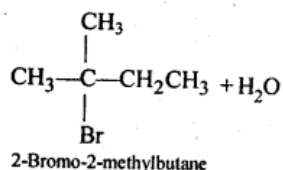
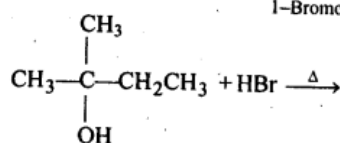
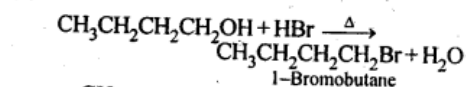
(ii) 2-Methylbutan-2-ol

**Ans:**

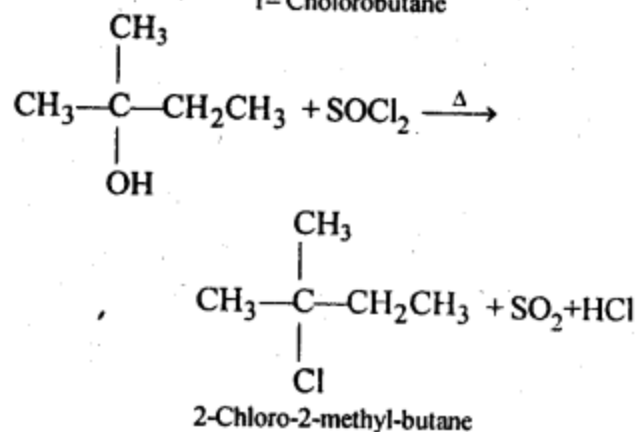
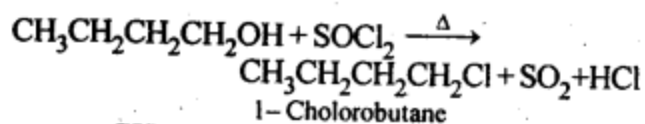
(a) with HCl -  $\text{ZnCl}_2$



(b) with HBr



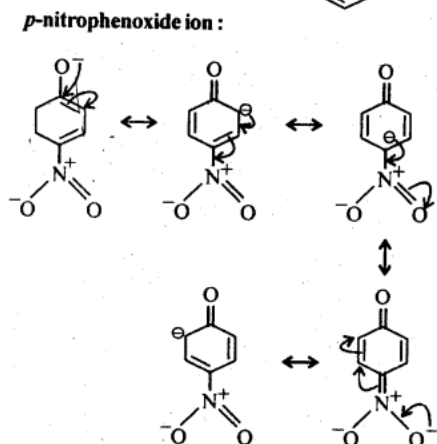
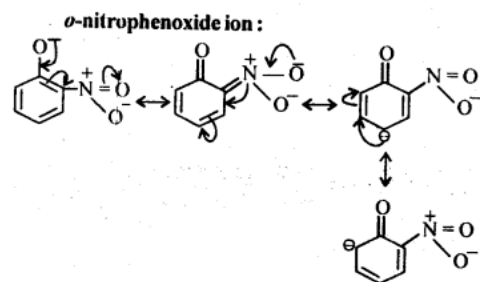
(c) with  $\text{SOCl}_2$



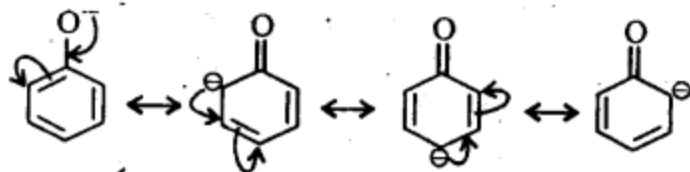
**4. Ortho and para nitrophenols are more acidic than phenol. Draw the resonance structures of the corresponding phenoxide ions.**

**Ans:**

The resonance structures of o- and p- nitrophenoxide ions and phenoxide ion are given below:



**phenoxide ion :**



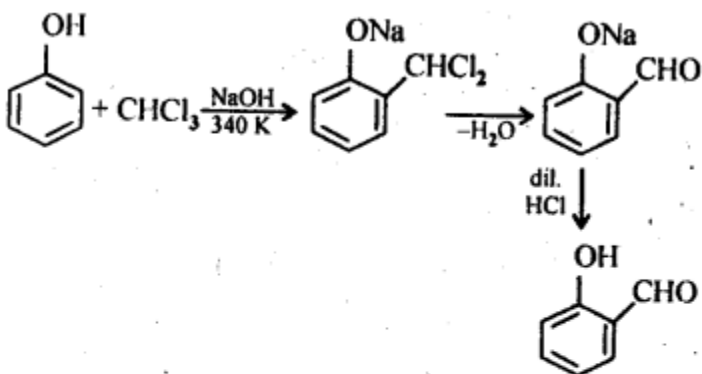
Due to  $-R$  effect of  $-NO_2$  group,  $o$ - and  $p$ -nitrophenoxide are more stable than phenoxide ion. As a result,  $o$ - and  $p$ -nitrophenols are more acidic than phenol.

**5; Write the equations involved in the following reactions:**

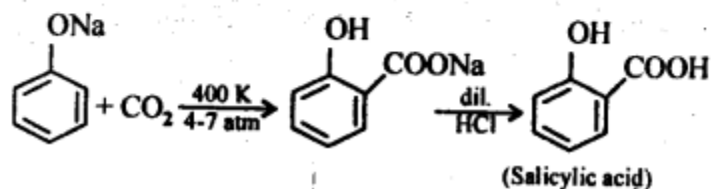
**(i) Reimer-Tiemann reaction**

**(ii) Kolbe's reaction**

**Ans:** (i) Reimer-Tiemann reaction



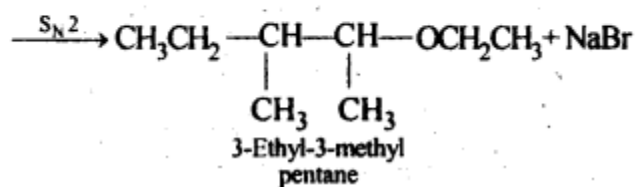
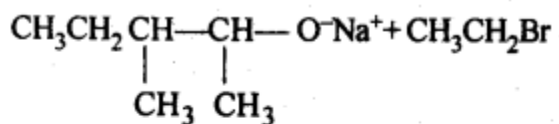
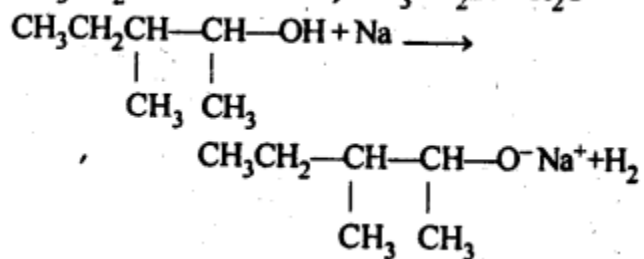
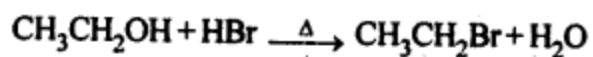
**(ii) Kolbe's reaction**



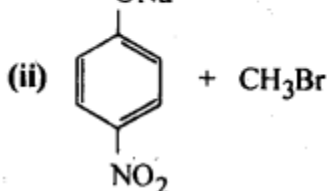
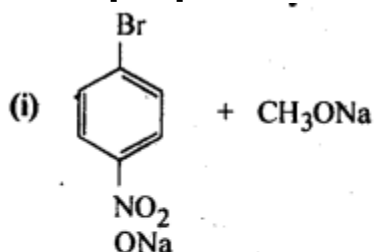
**6. Write the reactions of Williamson synthesis of 2-ethoxy-3-methylpentane starting from ethanol and 3-methylpentan-2-ol.**

**Ans:** In Williamson's synthesis, the alkyl halide should be primary. Thus, the alkyl halide should be derived from ethanol and the alkoxide ion from 3-methylpentan-2-ol. The synthesis is as

follows



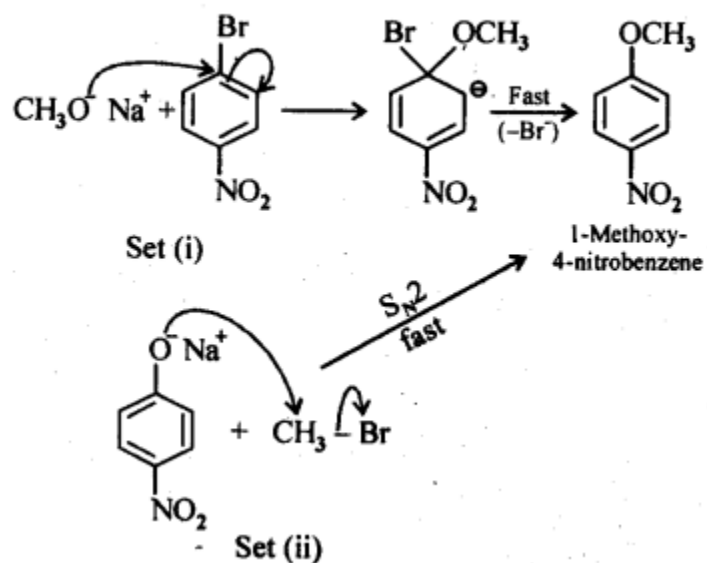
7. Which of the following is an appropriate set of reactants for the preparation of 1-methoxy-4-nitrobenzene and why?





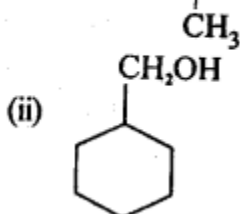
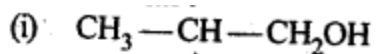
Ans:

Chemically, both sets are equally probable.

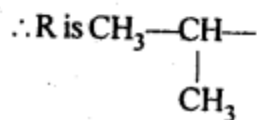
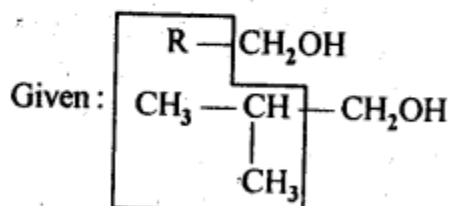
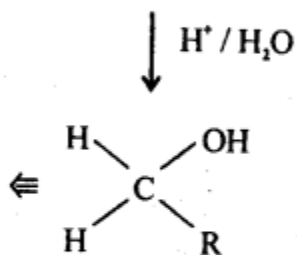
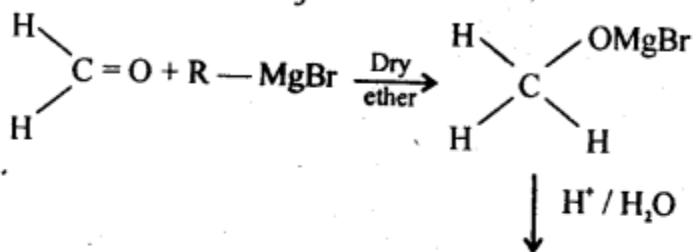
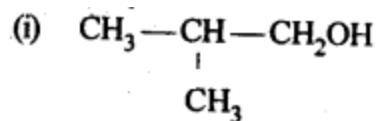


## 7MARKS

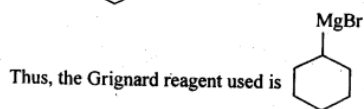
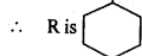
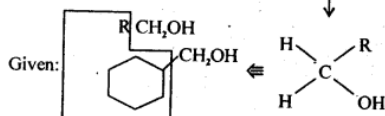
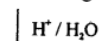
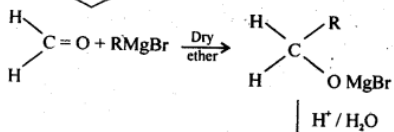
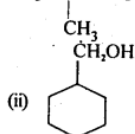
1. Show how are the following alcohols prepared by the reaction of a suitable Grignard reagent on methanal ?



Ans:



Thus, Grignard reagent used is  $\text{CH}_3-\underset{\text{CH}_3}{\text{CH}}-\text{MgBr}$



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

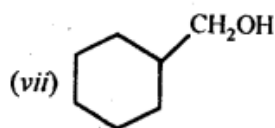
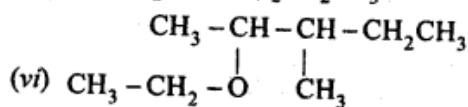
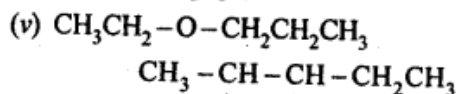
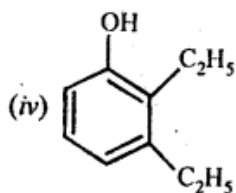
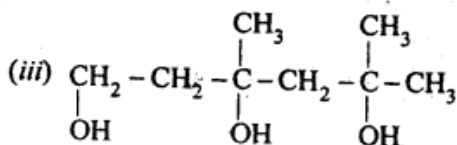
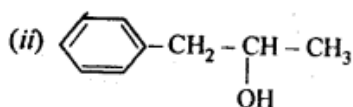
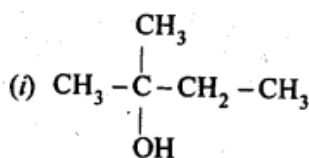
(vii) Cyclohexylmethanol

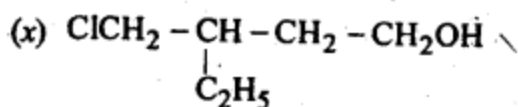
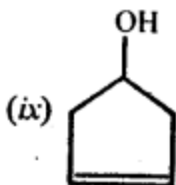
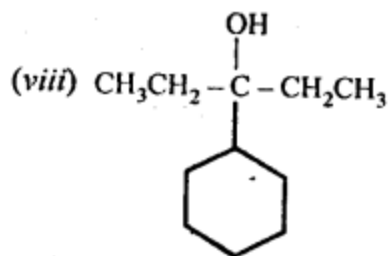
(viii) 3-Cyclohexylpentan-3-ol

(ix) Cyclopent-3-en-1-ol

(x) 4-Chloro-3-ethylbutan-1-ol

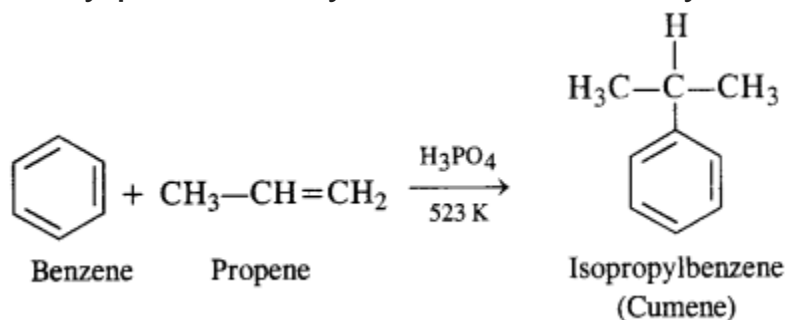
Ans:





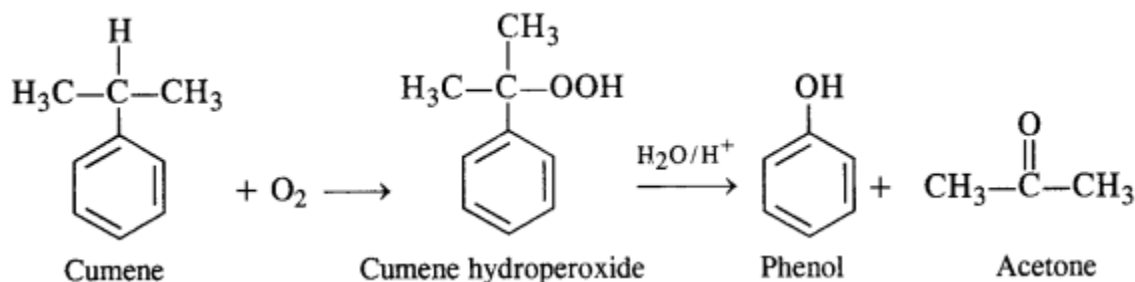
**3. Give the equations of the reaction for the preparation of phenol from cumene.**

**Ans:** This process has a great industrial importance because it gives the preparation of two very useful compounds i.e. phenol and acetone. The raw materials are benzene and propene and it initially proceeds by Friedel Crafts alkylation of benzene.



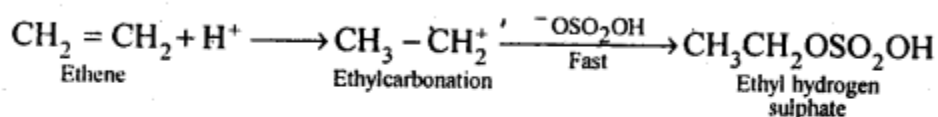
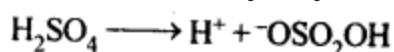
Oxygen is bubbled through the above solution to form cumene hydroperoxide which is decomposed with aqueous acid

solution to form phenol and acetone as follows:

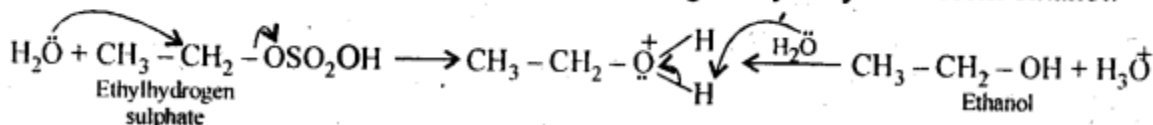


#### 4. Write the mechanism of hydration of ethene to yield ethanol.

**Ans:** Direct addition of  $\text{H}_2\text{O}$  to ethene in presence of an acid does not occur. Indirectly, ethene is first passed through concentrated  $\text{H}_2\text{SO}_4$ , when ethyl hydrogen sulphate is formed.



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



#### 5. Show how will you synthesise

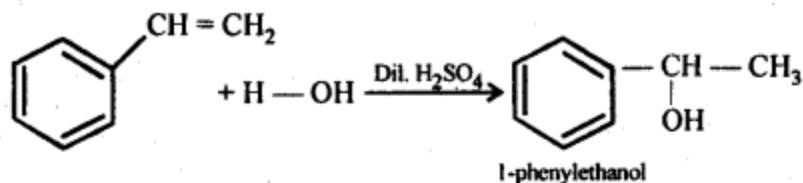
(i) 1 -phenylethanol from a suitable alkene.

(ii) cyclohexylmethanol using an alkyl halide by an  $\text{S}_{\text{N}}2$  reaction.

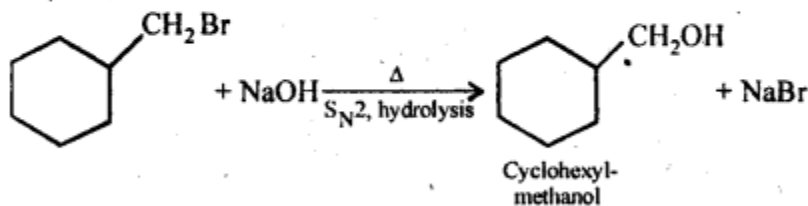
(iii) Pentan-1-ol using a suitable alkyl halide?

**Ans:**

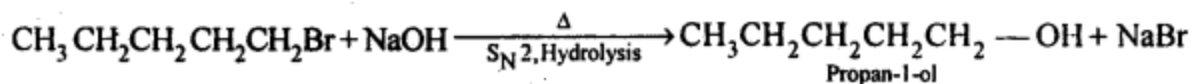
(i) Addition of  $\text{H}_2\text{O}$  to ethenylbenzene in presence of dil  $\text{H}_2\text{SO}_4$ .



(ii) Hydrolysis of cyclohexylmethyl bromide by aqueous  $\text{NaOH}$  gives cyclohexylmethanol.



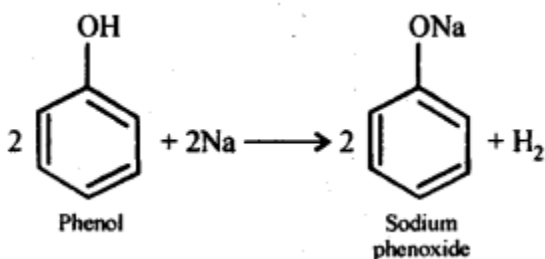
(iii) Hydrolysis of 1-bromopentane by aqueous  $\text{NaOH}$  gives pentan-1-ol.



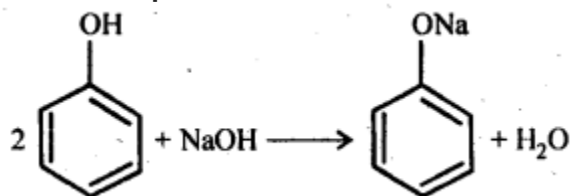
**6. Give two reactions that show the acidic nature of phenol. Compare its acidity with that of ethanol.**

**Ans:** The reactions showing acidic nature of phenol are:

(a) Reaction with sodium: Phenol reacts with active metals like sodium to liberate  $\text{H}_2$  gas.



(b) Reaction with  $\text{NaOH}$ : Phenol dissolves in  $\text{NaOH}$  to form sodium phenoxide and water.



Phenol is more acidic than ethanol. This is due to the reason that phenoxide ion left after the loss of a proton from phenol is

stabilized by resonance, while ethoxide ion left after loss of a proton from ethanol, is not.

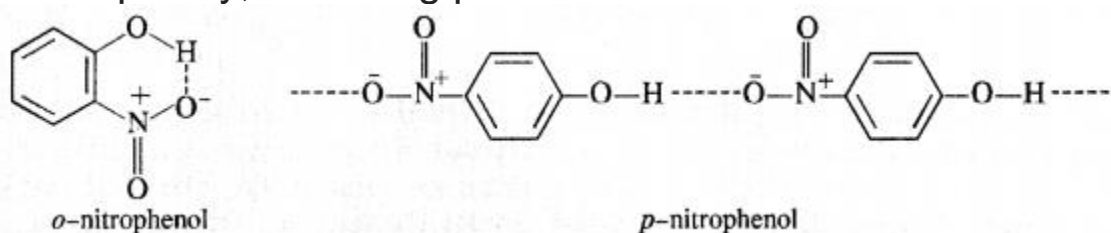
### 7. Explain why is orthonitrophenol more acidic than orthomethoxyphenol?

**Ans:** Nitro ( $\text{NO}_2$ ) group is an electron withdrawing group while methoxy ( $\text{OCH}_3$ ) group is electron releasing in nature. The release of  $\text{H}^+$  ion is therefore, easier from o-nitrophenol while it is quite difficult from o-methoxyphenol. Apart from that, o-nitrophenoxide ion is stabilised due to resonance o-nitrophenol is steam volatile while p-nitrophenol is not. This is on account of intramolecular hydrogen bonding in the molecules of o-nitrophenol. As a result, its boiling point is less than that of p-nitrophenol in which the molecules are linked by intermolecular hydrogen bonding.

It is interesting to note that in the substituted phenols, the nature and position of the substituent influences the boiling point of phenol.

For example: o-nitrophenol is steam volatile while p-nitrophenol is not. This is supported by the fact that the boiling point temperature of o-nitrophenol ( $100^\circ\text{C}$ ) is less than that of p-nitrophenol, ( $279^\circ\text{C}$ ). In o-nitrophenol, there is intramolecular hydrogen bonding in OH and  $\text{NO}_2$  groups placed in adjacent positions. However, these are linked by intermolecular hydrogen bonding in the p-isomers. It is quite obvious that extra energy is needed to cleave the hydrogen bonds in the p-isomer.

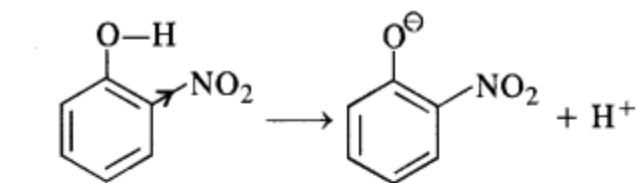
Consequently, its boiling point is more.



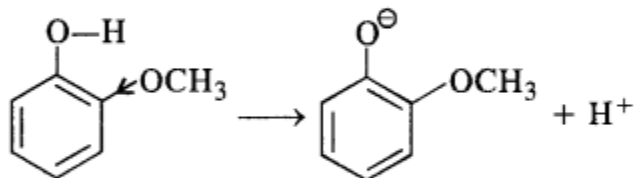
o-nitrophenol with lower boiling point is steam volatile while p-nitrophenol is not. This helps in the separation of the two isomers present in the liquid mixture. On passing steam, o-nitrophenol

volatilises and its vapours rise alongwith steam and after condensation, collect in the receiver p-nitrophenol is left behind in the distillation flask. e-nkrophenol p-nnrophenol.

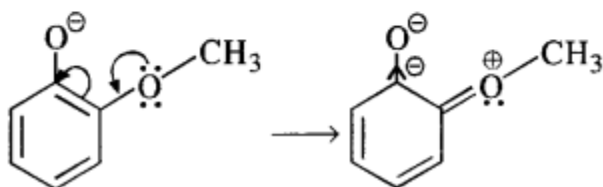
On the contrary, o-methoxyphenoxide is destabilised since the electron density on the negatively charged oxygen tends to increase due to the electron releasing tendency of the methoxy( $\text{OCH}_3$ ) group.



*o*-nitrophenol



*o*-methoxyphenol



In the light of the above discussion, we may conclude that o-nitrophenol is a stronger acid ( $\text{pK}_a = 7.23$ ) than o-methoxyphenol ( $\text{pK}_a = 9.98$ )



## SUMMARY

**1.** Alcohols and phenols may be classified as monohydric, dihydric, trihydric or polyhydric according to number of hydroxyl groups they contain one, two, three or many respectively in their molecules.

**2. Primary ( $1^\circ$ ), secondary ( $2^\circ$ ) and tertiary ( $3^\circ$ ) alcohols** are those in which as the OH group is attached to a primary, secondary and tertiary carbon atoms respectively.

**3. Ethers are classified as simple or symmetrical** ethers if the alkyl or aryl groups attached to the oxygen atom are same, and mixed or unsymmetrical ethers if the two groups are different.

### **4. Preparation of Alcohols**

#### **(a) From alkenes:**

(i) By acid catalyzed hydration: The addition reaction takes place in accordance with Markovnikov's rule.

(ii) By hydroboration-oxidation

#### **(b) From carbonyl compounds**

(i) By reduction of aldehydes and ketones: On reduction, aldehydes give  $1^\circ$  alcohols and ketones give  $2^\circ$  alcohols.

(ii) By reduction of carboxylic acids and esters

(iii) From Grignard reagents

### **5. Phenols may be prepared by substitution of halogen in**

(a) Haloarenes

(b) Sulphonic acid group in benzene sulphonic acid

(c) From hydrolysis of diazonium salts

(d) Industrially from Cumene: