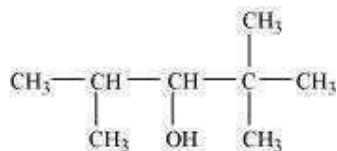


## Chapter 11: Alcohols Phenols and Ethers

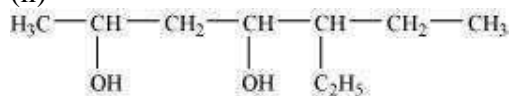
### Exercise

11.1. Write IUPAC names of the following compounds:

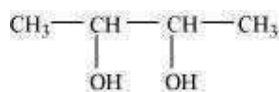
(i)



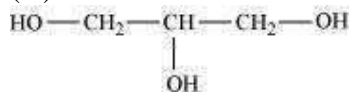
(ii)



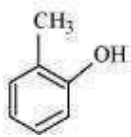
(iii)



(iv)



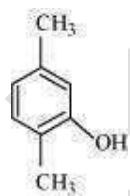
(v)



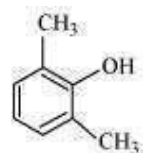
(vi)



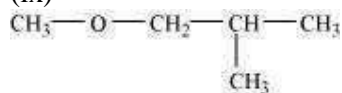
(vii)

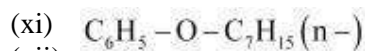
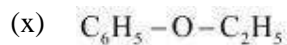


(viii)

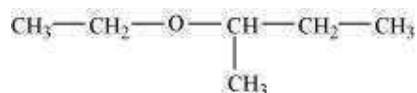


(ix)





(xii)



**Solution:**

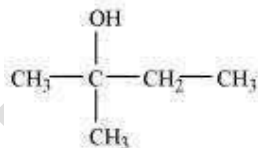
- (i) 2, 2, 4-Trimethylpentan-3-ol
- (ii) 5-Ethylheptane-2, 4-diol
- (iii) Butane-2, 3-diol
- (iv) Propane-1, 2, 3-triol
- (v) 2-Methylphenol
- (vi) 4-Methylphenol
- (vii) 2, 5-Dimethylphenol
- (viii) 2, 6-Dimethylphenol
- (ix) 1-Methoxy-2-methylpropane
- (x) Ethoxybenzene
- (xi) 1-Phenoxyheptane
- (xii) 2-Ethoxybutane

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

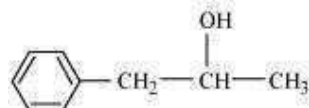
- (i) 2-Methylbutan-2-ol
- (ii) 1-Phenylpropan-2-ol
- (iii) 3,5-Dimethylhexane -1, 3, 5-triol
- (iv) 2,3 - Diethylphenol
- (v) 1 - Ethoxypropane
- (vi) 2-Ethoxy-3-methylpentane
- (vii) Cyclohexylmethanol
- (viii) 3-Cyclohexylpentan-3-ol
- (ix) Cyclopent-3-en-1-ol
- (x) 3-Chloromethylpentan-1-ol.

**Solution:**

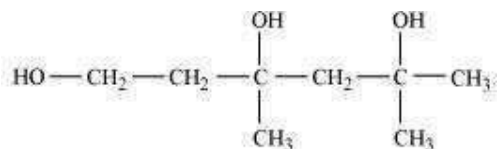
(i)



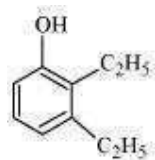
(ii)



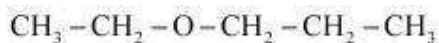
(iii)



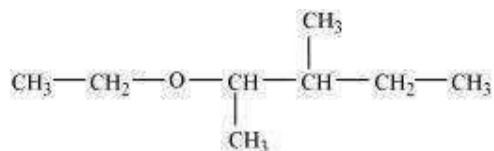
(iv)



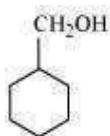
(v)



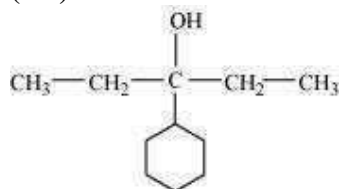
(vi)



(vii)



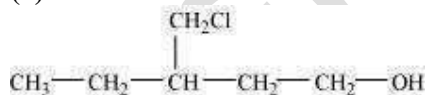
(viii)



(ix)



(x)



11.3. (i) Draw the structures of all isomeric alcohols of molecular formula  $\text{C}_5\text{H}_{12}\text{O}$  and give their IUPAC names.

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

**Solution:**

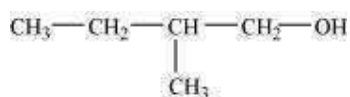
(i) The structures of all isomeric alcohols of molecular formula,  $\text{C}_5\text{H}_{12}\text{O}$  are shown below:

(a)



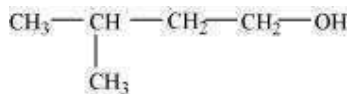
Pentan-1-ol ( $1^\circ$ )

(b)



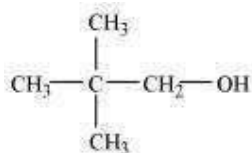
2-Methylbutan-1-ol ( $1^\circ$ )

(c)



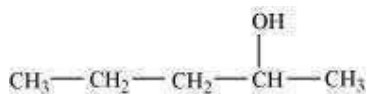
3-Methylbutan-1-ol ( $1^\circ$ )

(d)



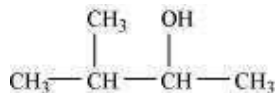
2, 2-Dimethylpropan-1-ol ( $1^\circ$ )

(e)



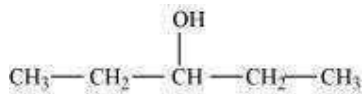
Pentan-2-ol ( $2^\circ$ )

(f)



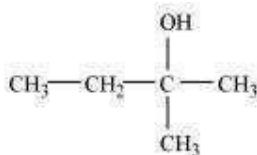
3-Methylbutan-2-ol ( $2^\circ$ )

(g)



Pentan-3-ol ( $2^\circ$ )

(h)



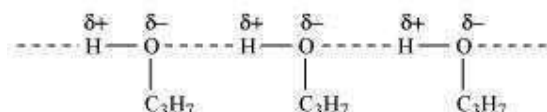
2-Methylbutan-2-ol ( $3^\circ$ )

(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

**11.4.** Explain why propanol has higher boiling point than that of the hydrocarbon, butane? **Solution:** Since the presence of the hydroxide group, propanol undergoes intermolecular hydrogen-bonding. Butane, on the other hand, does not.

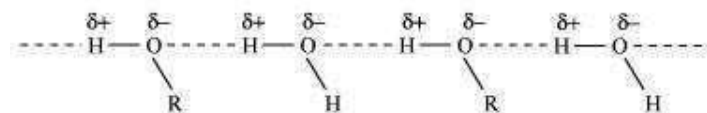


As a result, additional energy is required to break hydrogen bonds. Propanol has a higher boiling point than the hydrocarbon butane as a result.

**11.5.** Alcohols are comparatively more soluble in water than hydrocarbons of comparable molecular

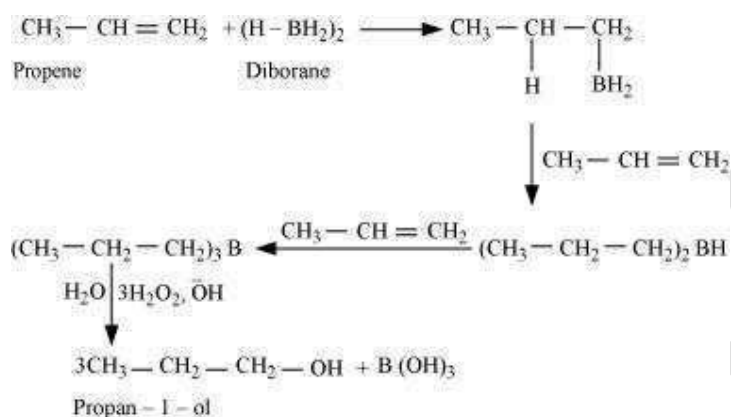
masses. Explain this fact.

**Solution:** Because of the presence of the hydroxide group, alcohols form H-bonds with water. Hydrocarbons, on the other hand, cannot form H-bonds with water.

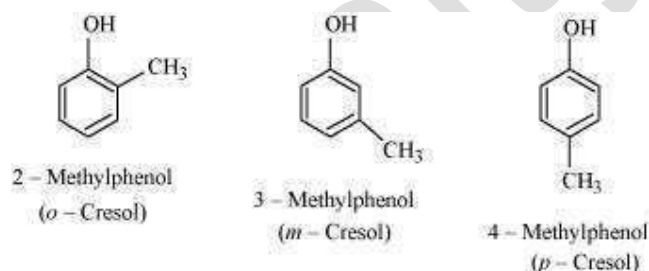


As a result, alcohols are more soluble in water than comparable molecular mass hydrocarbons.

**11.6.** What is meant by hydroboration-oxidation reaction? Illustrate it with an example. **Solution:** The hydroboration-oxidation reaction is defined as the addition of borane followed by oxidation. Propan-1-ol, for example, is produced by the hydroboration-oxidation reaction of propene. Propene reacts with diborane  $(\text{BH}_3)_2$  to form trialkyl borane as an addition product in this reaction. In the presence of aqueous sodium hydroxide, hydrogen peroxide oxidizes this addition product to alcohol.

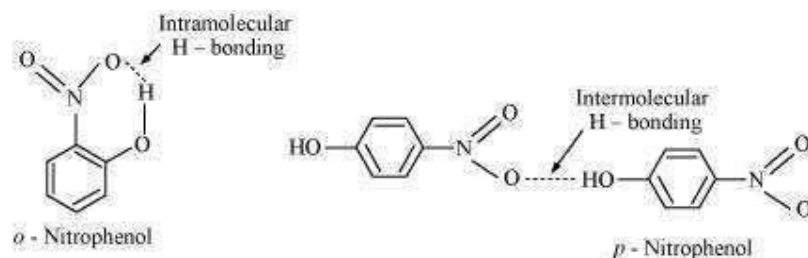


**11.7.** Give the structures and IUPAC names of monohydric phenols of molecular formula,  $\text{C}_7\text{H}_8\text{O}$ . **Solution:**



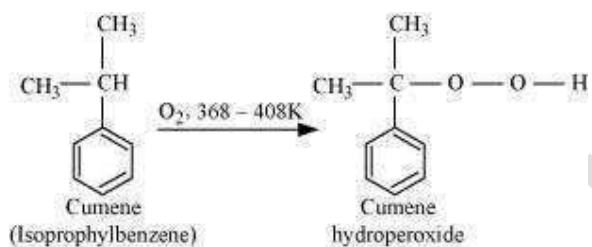
**11.8.** While separating a mixture of *ortho* and *para* nitrophenols by steam distillation, name the isomer which will be steam volatile. Give reason.

**Solution:** O-nitrophenol and p-nitrophenol contain intramolecular H-bonding. Because of the presence of intermolecular bonding, the molecules in p-nitrophenol are strongly associated. As a result, o-nitrophenol is steam volatile.

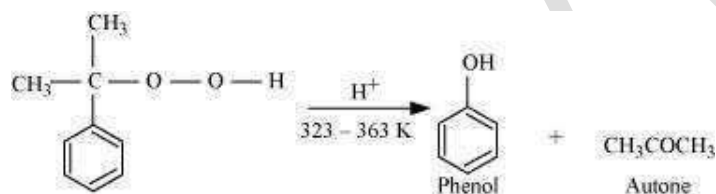


**11.9.** Give the equations of reactions for the preparation of phenol from cumene.

**Solution:** Cumene is first oxidized in the presence of air to produce cumene hydroperoxide, which is then used to make phenol.



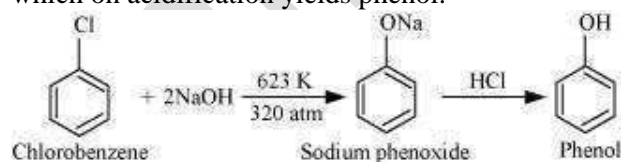
Cumene hydroperoxide is then treated with dilute acid to produce phenol and acetone as byproducts.



**11.10.** Write chemical reaction for the preparation of phenol from chlorobenzene.

**Solution:**

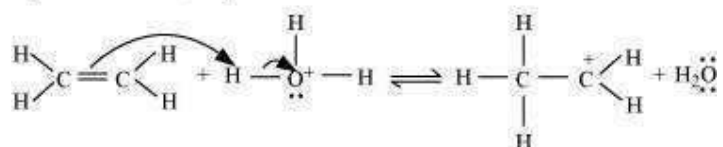
Chlorobenzene is fused with NaOH (at 623 K and 320 atm pressure) to produce sodium phenoxide, which on acidification yields phenol.



**11.11.** Write the mechanism of hydration of ethene to yield ethanol.

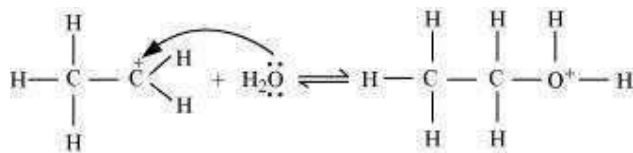
**Solution:** Three steps are involved in the hydration of ethene to form ethanol.

**Step 1:** Electrophilic attack of H<sub>3</sub>O<sup>+</sup> on ethene to form carbocation:



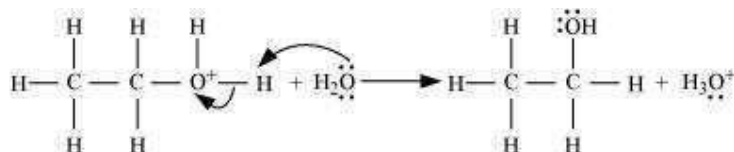
**Step 2:**

Nucleophilic attack of water on carbocation:



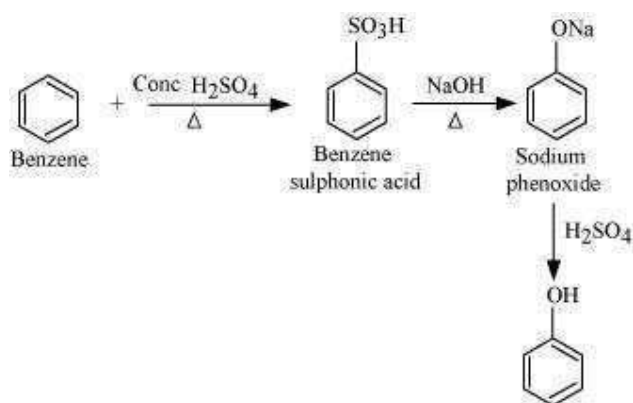
**Step 3:**

Deprotonation to form ethanol:



**11.12.** You are given benzene, conc.  $\text{H}_2\text{SO}_4$  and  $\text{NaOH}$ . Write the equations for the preparation of phenol using these reagents.

**Solution:**

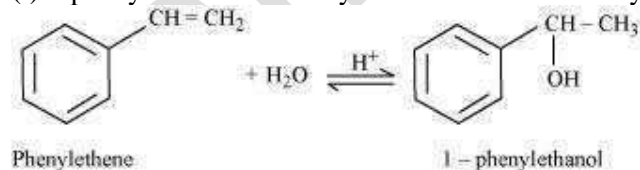


**11.13.** Show how will you synthesize:

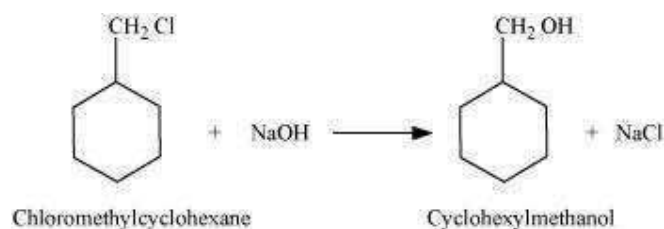
- 1-phenylethanol from a suitable alkene.
- cyclohexylmethanol using an alkyl halide by an  $\text{S}_{\text{N}}2$  reaction.
- pentan-1-ol using a suitable alkyl halide?

**Solution:**

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



(ii) Cyclohexylmethanol is formed when chloromethylcyclohexane is treated with sodium hydroxide.



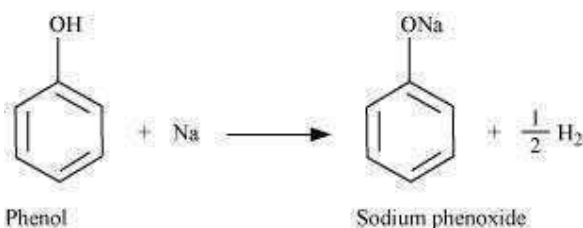
(iii) When 1-chloropentane is treated with NaOH, pentan-1-ol is produced.



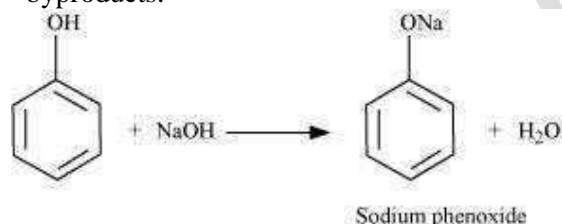
**11.14.** Give two reactions that show the acidic nature of phenol. Compare acidity of phenol with that of ethanol.

**Solution:** The acidic nature of phenol can be represented by the two reactions listed below:

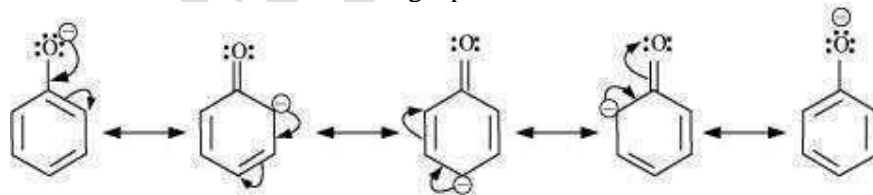
(i) Phenol reacts with sodium to form sodium phenoxide, which releases  $\text{H}_2$ .



(ii) When phenol reacts with sodium hydroxide, sodium phenoxide and water are produced as byproducts.

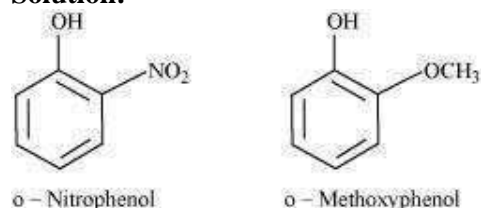


Phenol has a higher acidity than ethanol. This is because the phenoxide ion undergoes resonance and becomes stabilized after losing a proton, whereas the ethoxide ion does not.



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

**Solution:**



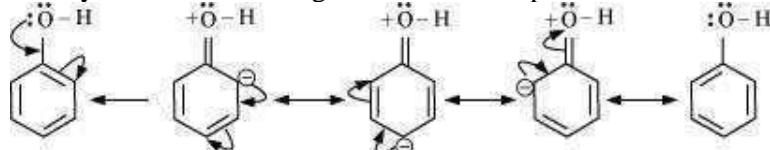
The nitro-group is a group that draws electrons. This group's presence in the *ortho* position reduces the electron density in the OH bond. As a result, losing a proton is easier. Furthermore, resonance stabilizes the *o*-nitrophenoxide ion formed after proton loss. As a result, *ortho* nitrophenol is a more potent acid.



Methoxy group, on the other hand, is an electron-releasing group. As a result, the electron density in the OH bond increases, and the proton cannot be easily given out. As a result, ortho-nitrophenol has a higher acidity than ortho-methoxyphenol.

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

**Solution:** The -OH group is a group that donates electrons. As a result, it increases the electron density in the benzene ring, as shown in the phenol resonance structure.



As a result, the benzene ring is primed for electrophilic substitution.

**11.17.** Give equations of the following reactions:

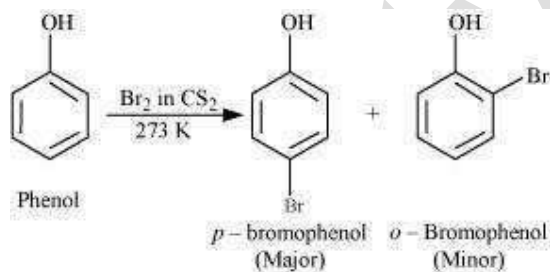
- (i) Oxidation of propan-1-ol with alkaline  $\text{KMnO}_4$  solution.
- (ii) Bromine in  $\text{CS}_2$  with phenol.
- (iii) Dilute  $\text{HNO}_3$  with phenol.
- (iv) Treating phenol with chloroform in presence of aqueous  $\text{NaOH}$ .

**Solution:**

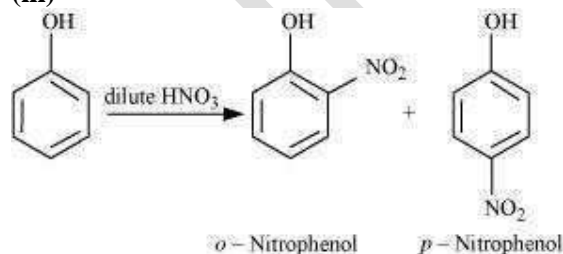


(i) Propan-1-ol Propanoic acid

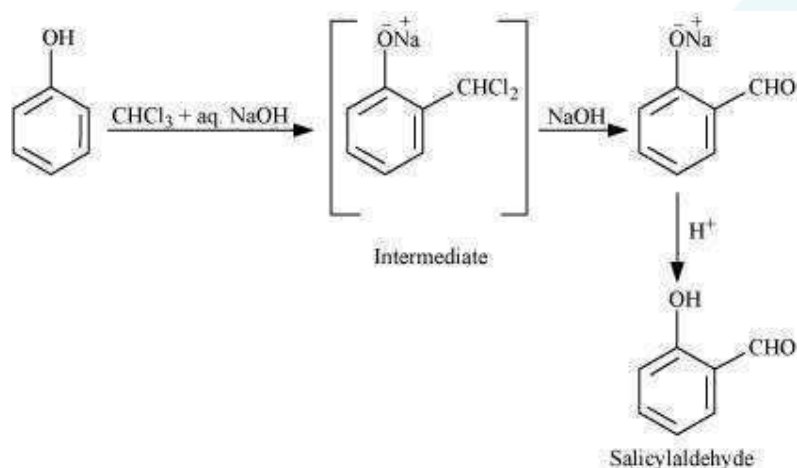
(ii)



(iii)



(iv)



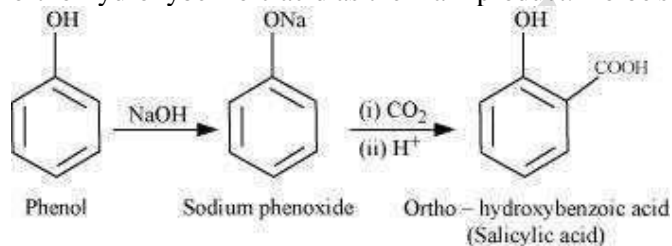
11.18. Explain the following with an example.

- (i) Kolbe's reaction.
- (ii) Reimer-Tiemann reaction.
- (iii) Williamson ether synthesis.
- (iv) Unsymmetrical ether.

**Solution:**

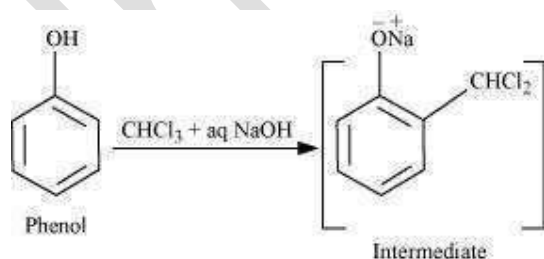
(i) **Kolbe's reaction:**

Sodium phenoxide is produced when phenol is treated with sodium hydroxide. When treated with carbon dioxide and acidified, sodium phenoxide undergoes electrophilic substitution, yielding ortho-hydroxybenzoic acid as the main product. Kolbe's reaction is the name given to this reaction.



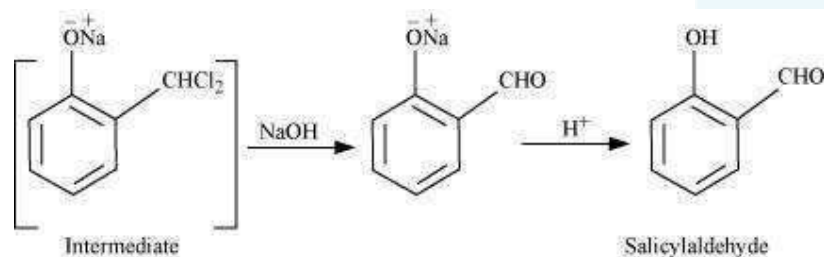
(ii) **Reimer-Tiemann reaction:**

A -CHO group is introduced at the ortho position of the benzene ring when phenol is treated with chloroform ( $\text{CHCl}_3$ ) in the presence of sodium hydroxide.



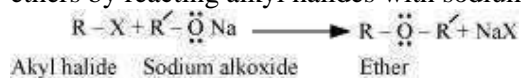
This reaction is known as the Reimer-Tiemann reaction

In the presence of alkali, the intermediate is hydrolyzed to produce salicylaldehyde..

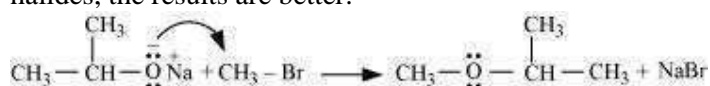


**(iii) Williamson ether synthesis:**

Williamson ether synthesis is a laboratory technique for producing symmetrical and unsymmetrical ethers by reacting alkyl halides with sodium alkoxides.



The alkoxide ion is attacked by  $\text{S}_{\text{N}}2$  on the alkyl halide in this reaction. In the case of primary alkyl halides, the results are better.



When the alkyl halide is secondary or tertiary, elimination takes precedence over substitution.

**(iv) Unsymmetrical ether:**

An unsymmetrical ether is one in which the two groups on opposite sides of an oxygen atom differ (i.e., have an unequal number of carbon atoms). For example: ethyl methyl ether ( $\text{CH}_3\text{-O-CH}_2\text{CH}_3$ ).

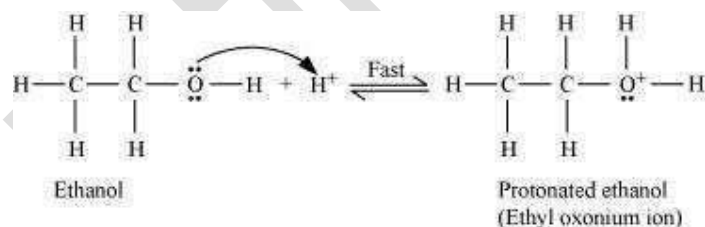
**11.19.** Write the mechanism of acid-catalysed dehydration of ethanol to yield ethene.

**Solution:**

The following three steps are involved in the mechanism of acid dehydration of ethanol to yield ethene:

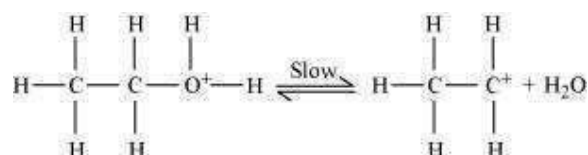
**Step 1:**

Protonation of ethanol to form ethyl oxonium ion:



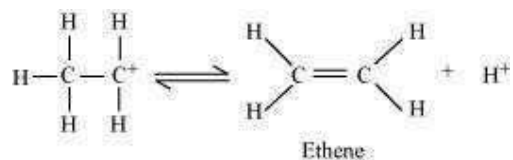
**Step 2:**

Formation of carbocation (rate determining step):



**Step 3:**

Elimination of a proton to form ethene:



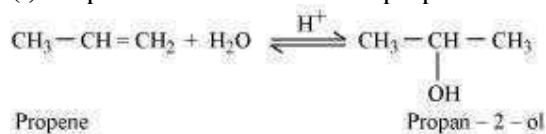
Step 3 releases the acid that was consumed in Step 1. Following the formation of ethene, it is removed to shift the equilibrium forward.

**11.20.** How are the following conversions carried out?

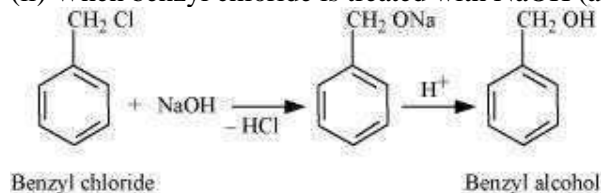
- (i) Propene  $\rightarrow$  Propan-2-ol
- (ii) Benzyl chloride  $\rightarrow$  Benzyl alcohol
- (iii) Ethyl magnesium chloride  $\rightarrow$  Propan-1-ol.
- (iv) Methyl magnesium bromide  $\rightarrow$  2-Methylpropan-2-ol.

**Solution:**

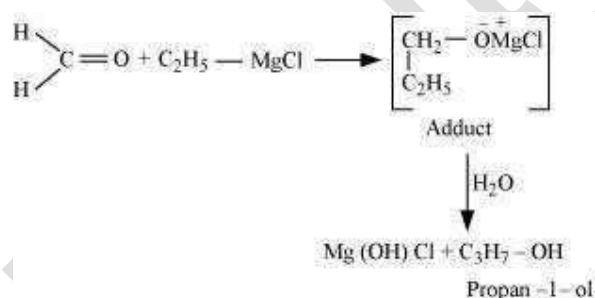
(i) Propan-2-ol is formed when propene reacts with water in the presence of an acid as a catalyst.



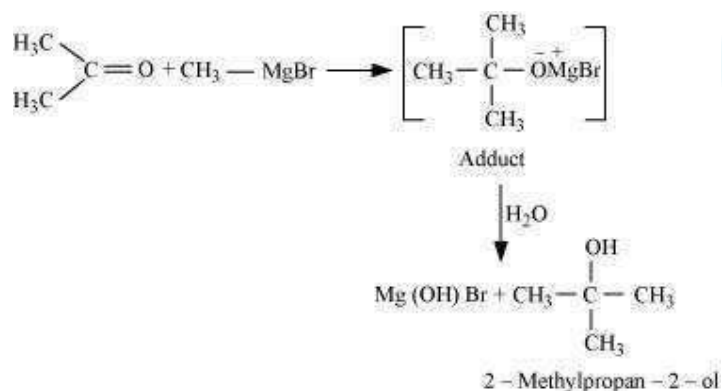
(ii) When benzyl chloride is treated with NaOH (and then acidified), benzyl alcohol is formed.



(iii) When ethyl magnesium chloride is treated with methanal, an adduct is formed that when hydrolyzed yields propan-1-ol.



(iv) When methyl magnesium bromide is treated with propane, an adduct is formed, which when hydrolyzed yields 2-methylpropan-2-ol.



11.21. 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.

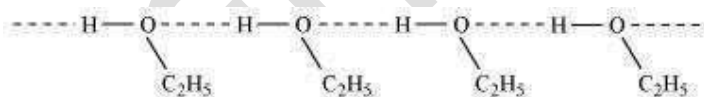
**Solution:**

- (i) Acidified potassium permanganate
- (ii) Pyridinium chlorochromate (PCC)
- (iii) Bromine water
- (iv) Acidified potassium permanganate
- (v) 85% phosphoric acid
- (vi)  $\text{NaBH}_4$  or  $\text{LiAlH}_4$

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

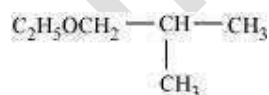
**Solution:** Because of the presence of the hydroxide group, ethanol undergoes intermolecular H-bonding, resulting in the association of molecules. Breaking these hydrogen bonds necessitates the use of additional energy. Methoxymethane, on the other hand, does not form H-bonds.

As a result, ethanol has a higher boiling point than methoxymethane.

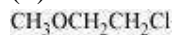


11.23. Give IUPAC names of the following ethers:

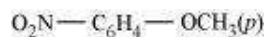
(i)



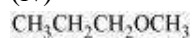
(ii)



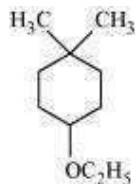
(iii)



(iv)



(v)



(vi)



**Solution:**

- (i) 1-Ethoxy-2-methylpropane
- (ii) 2-Chloro-1-methoxyethane
- (iii) 4-Nitroanisole
- (iv) 1-Methoxypropane
- (v) 1-Ethoxy-4,4-dimethylcyclohexane
- (vi) Ethoxybenzene

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

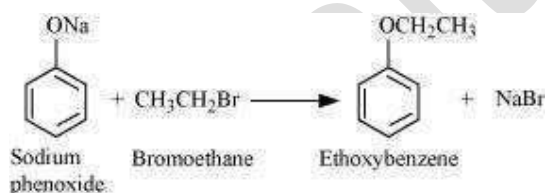
- (i) 1-Propoxypropane
- (ii) Ethoxybenzene
- (iii) 2-Methoxy-2-methylpropane
- (iv) 1-Methoxyethane

**Solution:**

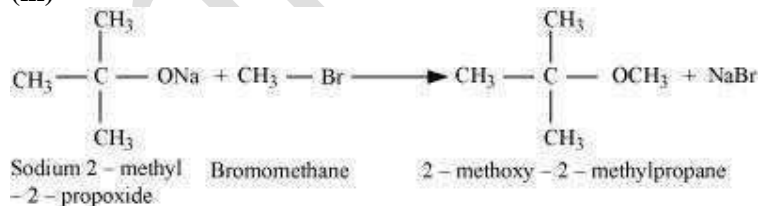


(i) Sodium propoxide    1-Bromopropane                      1- Propoxypropane

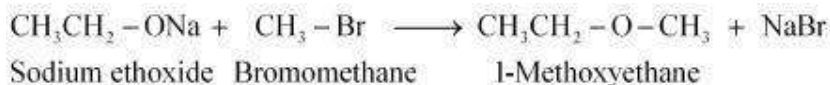
(ii)



(iii)

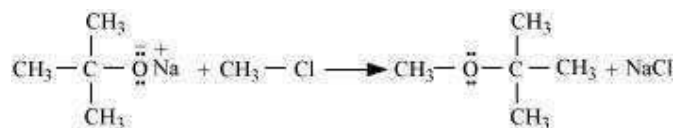


(iv)

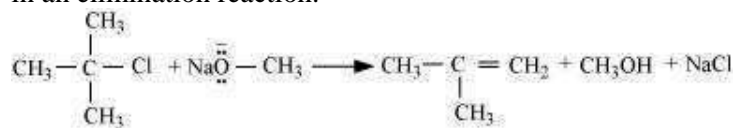


**11.25.** Illustrate with examples the limitations of Williamson synthesis for the preparation of certain types of ethers.

**Solution:** The Williamson synthesis reaction involves the SN2 attack of an alkoxide ion on a primary alkyl halide.



However, if secondary or tertiary alkyl halides are substituted for primary alkyl halides, elimination will win out over substitution. Alkenes would be produced as a result. This is due to the fact that alkoxides are both nucleophiles and strong bases. As a result, they react with alkyl halides, resulting in an elimination reaction.



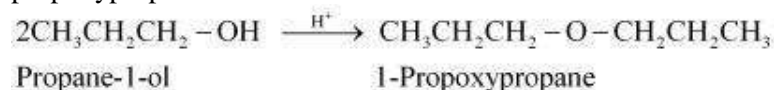
Tertiary alkyl halide

Alkene

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

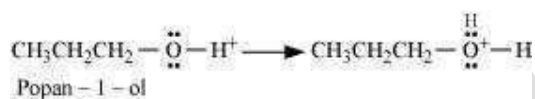
**Solution:** Dehydration can be used to produce 1-propoxypropane from propan-1-ol.

In the presence of protic acids (such as  $\text{H}_2\text{SO}_4$ ,  $\text{H}_3\text{PO}_4$ ), propan-1-ol dehydrates to give 1-propoxypropane..

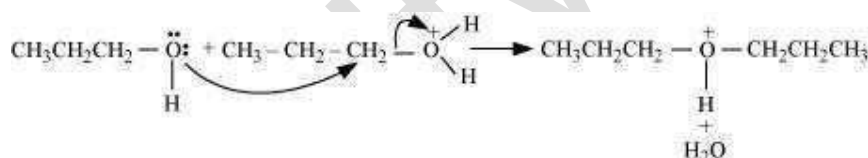


The mechanism of this reaction involves the following three steps:

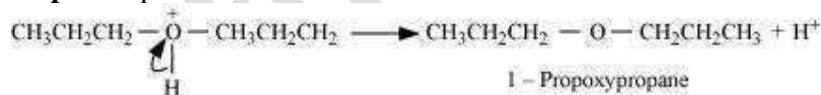
**Step 1: Protonation**



**Step 2: Nucleophilic attack**



**Step 3: Deprotonation**



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

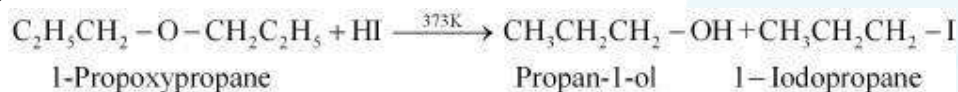
**Solution:** Dehydration of alcohol results in the formation of ethers, which is a bimolecular reaction ( $\text{S}_{\text{N}}2$ ) involving the attack of an alcohol molecule on a protonated alcohol molecule. The alkyl group should be unhindered in the method. The alkyl group is hindered in secondary or tertiary alcohols. As a result, elimination triumphs over substitution. As a result, alkenes are formed instead of ethers.

**11.28.** Write the equation of the reaction of hydrogen iodide with:

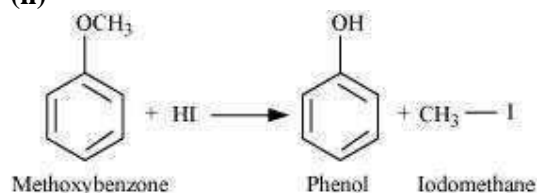
- (i) 1-propoxypropane
- (ii) Methoxybenzene and
- (iii) Benzyl ethyl ether

**Solution:**

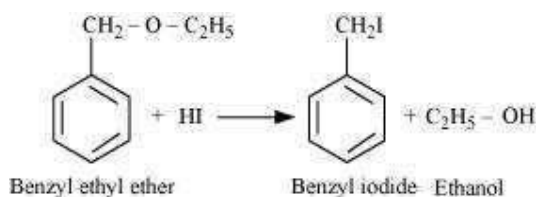
(i)



(ii)



(iii)

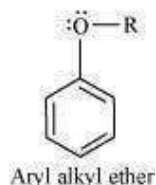


**11.29.** Explain the fact that in aryl alkyl ethers

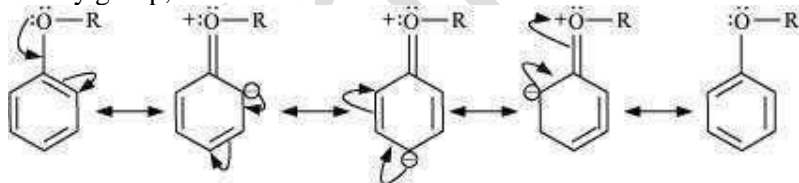
- (i) The alkoxy group activates the benzene ring towards electrophilic substitution and
- (ii) It directs the incoming substituents to ortho and para positions in benzene ring.

**Solution:**

(i)



The electron density in the benzene ring increases in aryl alkyl ethers due to the +R effect of the alkoxy group, as shown in the resonance structure below.



As a result, the alkoxy group activates benzene towards electrophilic substitution.

- (ii) The resonance structures also show 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 benzene ring's ortho and para positions.

**11.30.** Write the mechanism of the reaction of HI with methoxymethane.

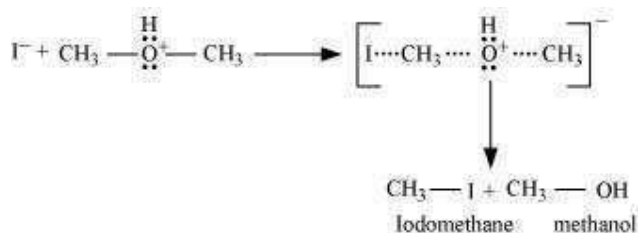
**Solution:** The following steps are involved in the mechanism of the reaction of HI with methoxymethane:

**Step1:** Protonation of methoxymethane:



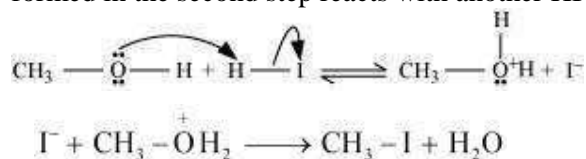
**Step2:** Nucleophilic attack of  $\text{I}^-$





**Step3:**

When there is an excess of HI and the reaction is carried out at a high temperature, the methanol formed in the second step reacts with another HI molecule, converting it to methyl iodide.

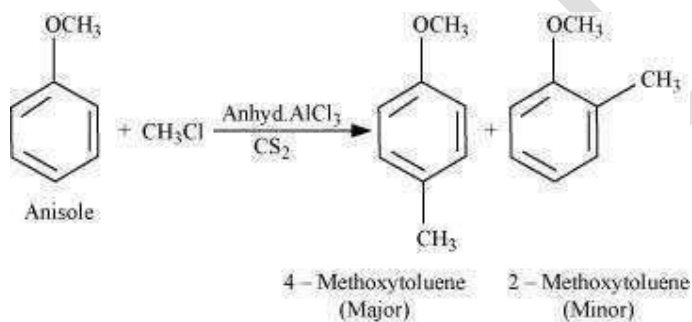


**11.31.** Write equations of the following reactions:

- (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.

**Solution:**

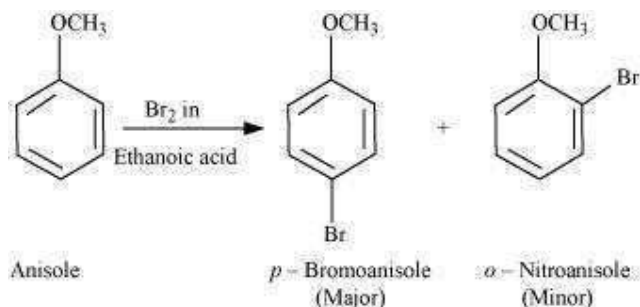
(i)



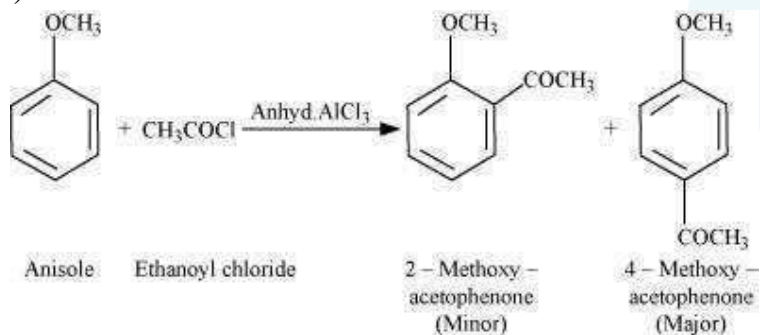
(ii)



(iii)

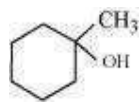


(iv)

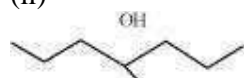


11.32. Show how would you synthesise the following alcohols from appropriate alkenes?

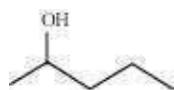
(i)



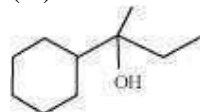
(ii)



(iii)



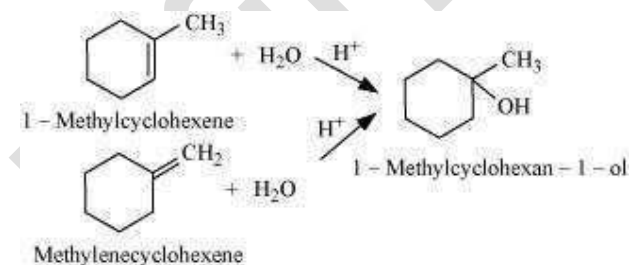
(iv)



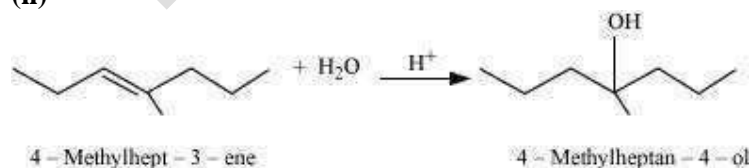
**Solution:**

Markovnikov's rule of acid-catalyzed hydration of appropriate alkenes can be used to synthesize the given alcohols.

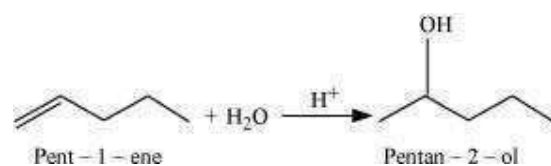
(i)



(ii)

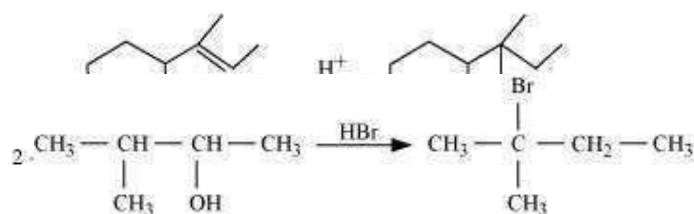
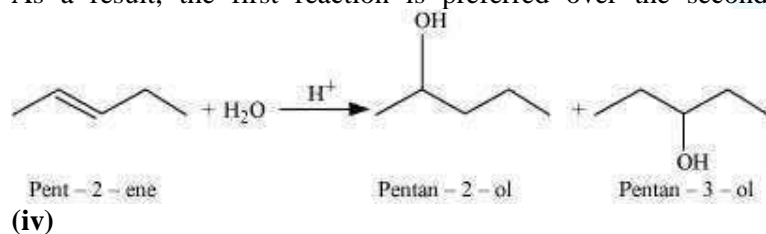


(iii)



The acid-catalyzed hydration of pent-2-ene yields pentan-2-ol as well as pentan-3-ol.

As a result, the first reaction is preferred over the second in order to obtain pentan-2-ol.



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

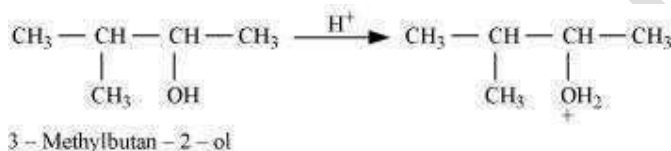
Give a mechanism for this reaction.

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

**Solution:**

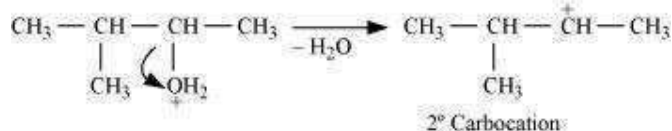
The mechanism of the given reaction involves the following steps:

**Step 1: Protonation**



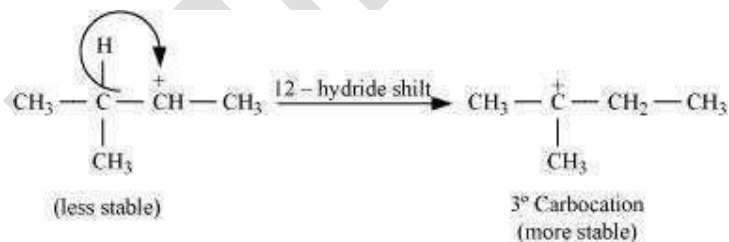
3-Methylbutan-2-ol

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



2° Carbocation

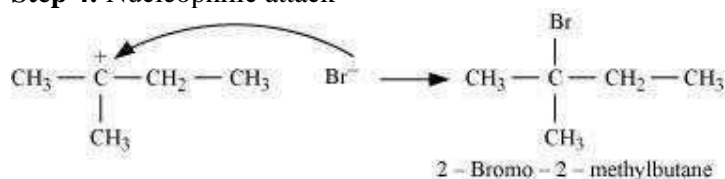
**Step 3: Re-arrangement by the hydride-ion shift**



(less stable)

3° Carbocation  
(more stable)

**Step 4: Nucleophilic attack**



2-Bromo-2-methylbutane