

## Alcohols, Phenols and Ethers Class 12

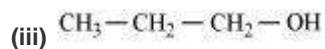
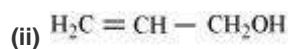
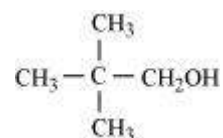
### Chapter 11 Alcohols, Phenols and Ethers Exercise Solutions

In text : Solutions of Questions on Page Number : 317

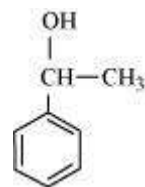
Q1 :

Classify the following as primary, secondary and tertiary alcohols:

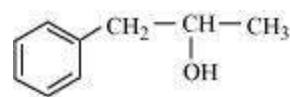
(i)



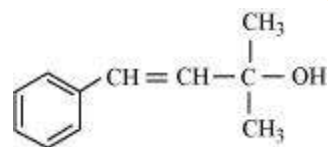
(iv)



(v)



(vi)



Answer :

Primary alcohol → (i), (ii), (iii)

Secondary alcohol → (iv), (v)

Tertiary alcohol → (vi)

Q2 :

Identify allylic alcohols in the above examples.

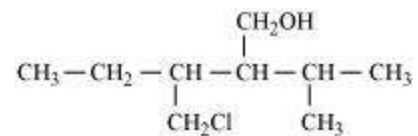
**Answer :**

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

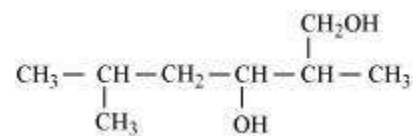
**Q3 :**

Name the following compounds according to IUPAC system.

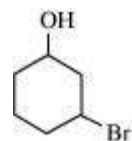
(i)



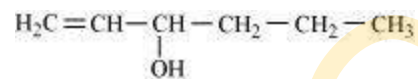
(ii)



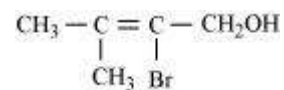
(iii)



(iv)



(v)



**Answer :**

(i) 3-Chloromethyl-2-isopropylpentan-1-ol

(ii) 2, 5-Dimethylhexane-1, 3-diol

(iii) 3-Bromocyclohexanol

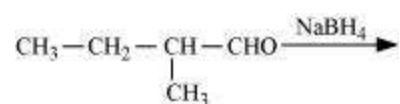
(iv) Hex-1-en-3-ol

(v) 2-Bromo-3-methylbut-2-en-1-ol

**Q4 :**

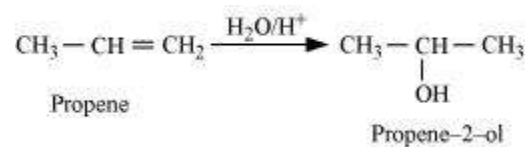


(iii)

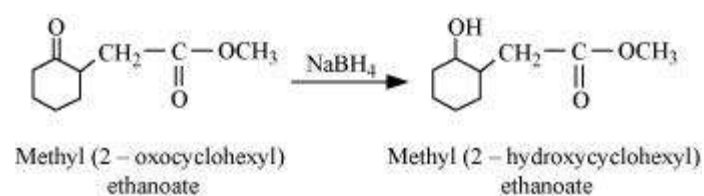


Answer :

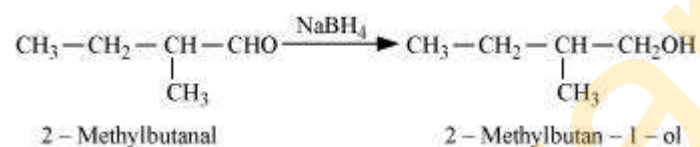
(i)



(ii)



(iii)



Q6 :

Give structures of the products you would expect when each of the following alcohol reacts with (a) HCl-ZnCl<sub>2</sub> (b) HBr and (c) SOCl<sub>2</sub>.

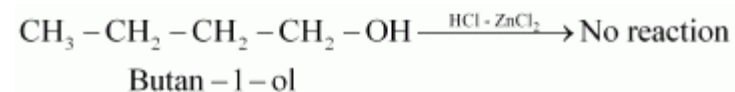
(i) Butan-1-ol

(ii) 2-Methylbutan-2-ol

Answer :

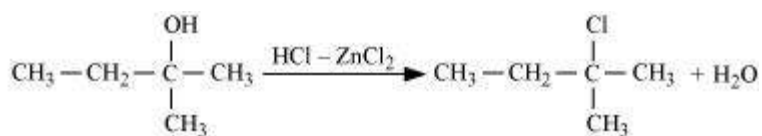
(a)

(i)



Primary alcohols do not react appreciably with Lucas' reagent (HCl-ZnCl<sub>2</sub>) at room temperature.

(ii)



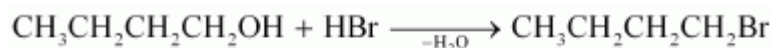
2 - Methylbutan - 2 - ol (3°)

2 - Chloro - 2 - Methylbutane  
(White turbidity)

Tertiary alcohols react immediately with Lucas' reagent.

(b)

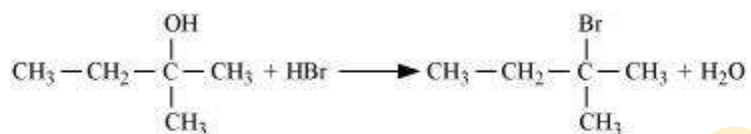
(i)



Butan - 1 - ol

1-Bromobutane

(ii)

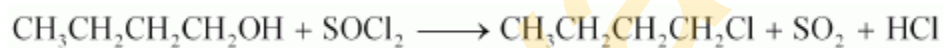


2 - Methylbutan - 2 - ol (3°)

2 - Bromo - 2 - Methylbutane

(c)

(i)



Butan-1-ol

1-chlorobutane

(ii)



2 - Methylbutan - 2 - ol

2 - Chloro - 2 - Methylbutane

Q7 :

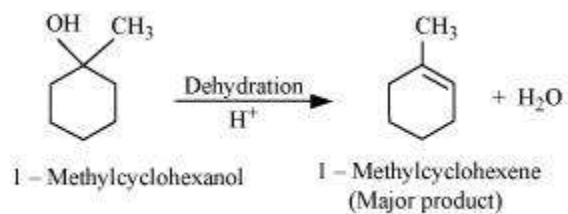
Predict the major product of acid catalysed dehydration of

(i) 1-Methylcyclohexanol and

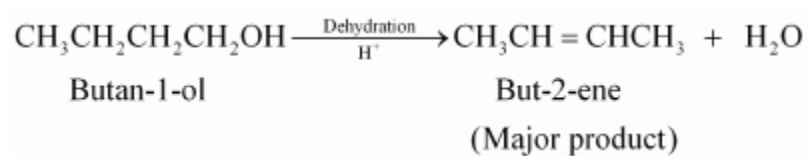
(ii) Butan-1-ol

Answer :

i.



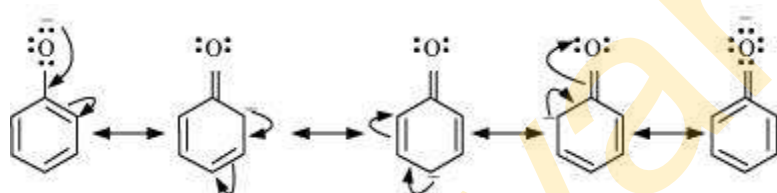
(ii)



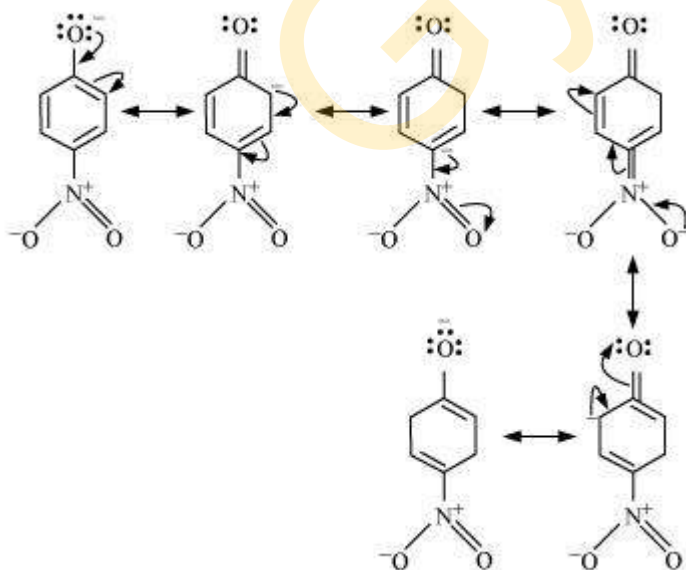
Q8 :

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

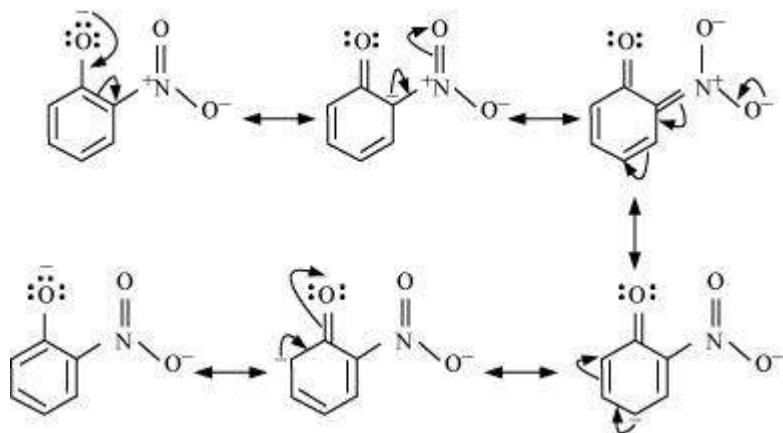
Answer :



Resonance structure of the phenoxide ion



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 phenoxide ion.

Q9 :

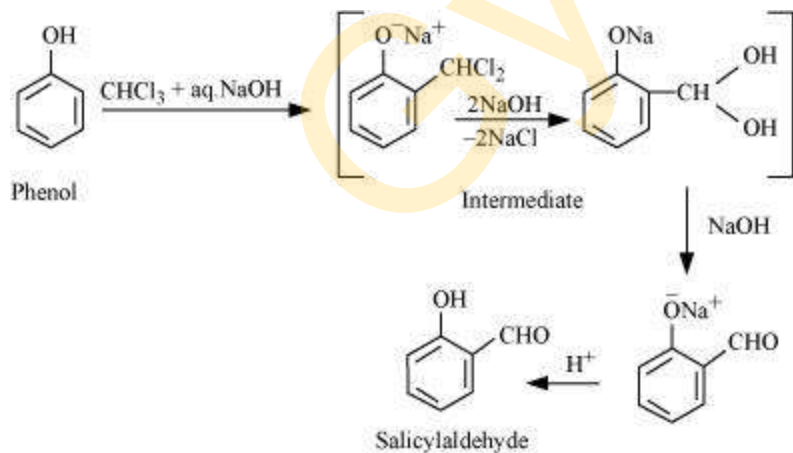
Write the equations involved in the following reactions:

(i) Reimer-Tiemann reaction

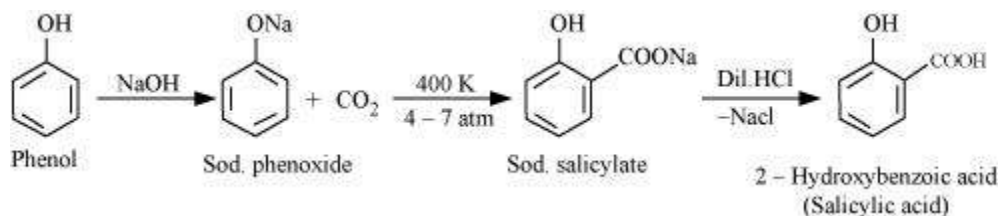
(ii) Kolbe's reaction

Answer :

i. Reimer-Tiemann reaction



ii. Kolbe's reaction

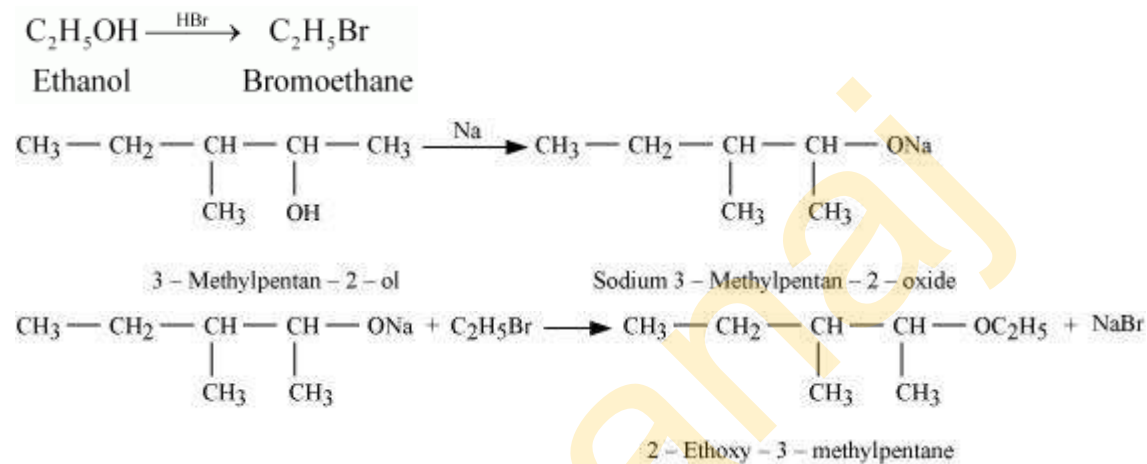


Q10 :

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

Answer :

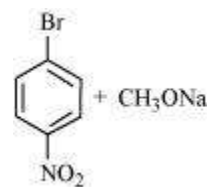
In Williamson synthesis, an alkyl halide reacts with an alkoxide ion. Also, it is an  $S_N2$  reaction. In the reaction, alkyl halides should be primary having the least steric hindrance. Hence, an alkyl halide is obtained from ethanol and alkoxide ion from 3-methylpentan-2-ol.



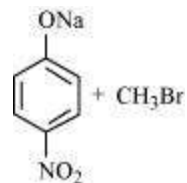
Q11 :

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

(i)



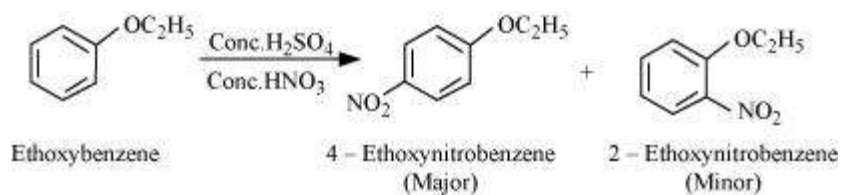
(ii)



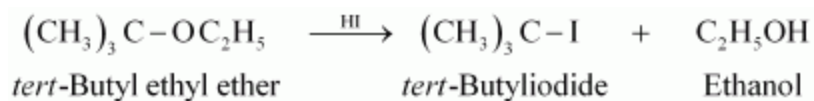
Answer :







(iv)



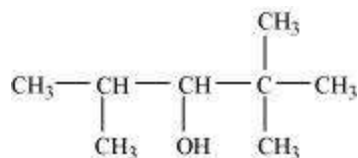
<< Previous Chapter 10 : Haloalkanes and Haloarenes Next Chapter 12 : Aldehydes, Ketones and Carboxylic Acids >>

Exercise : Solutions of Questions on Page Number : 344

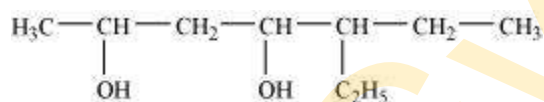
Q1 :

Write IUPAC names of the following compounds:

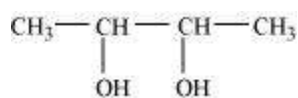
(i)



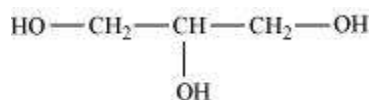
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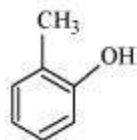
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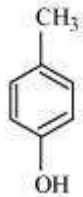
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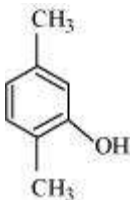
(v)



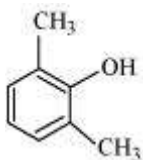
(vi)



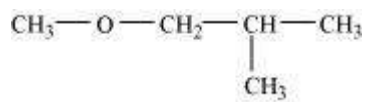
(vii)



(viii)



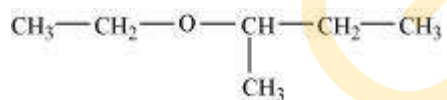
(ix)



(x)  $\text{C}_6\text{H}_5 - \text{O} - \text{C}_2\text{H}_5$

(xi)  $\text{C}_6\text{H}_5 - \text{O} - \text{C}_7\text{H}_{15} (\text{n-})$

(xii)



**Answer :**

(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

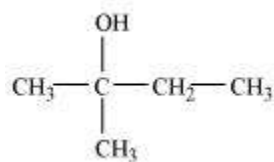
Q2 :

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

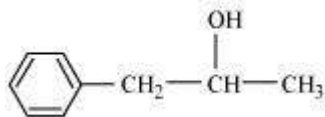
- (i) 2-Methylbutan-2-ol
- (ii) 1-Phenylpropan-2-ol
- (iii) 3,5-Dimethylhexane -1, 3, 5-triol
- (iv) 2,3 - Diethylphenol
- (v) 1 - Ethoxypropane
- (vi) 2-Ethoxy-3-methylpentane
- (vii) Cyclohexylmethanol
- (viii) 3-Cyclohexylpentan-3-ol
- (ix) Cyclopent-3-en-1-ol
- (x) 3-Chloromethylpentan-1-ol.

Answer :

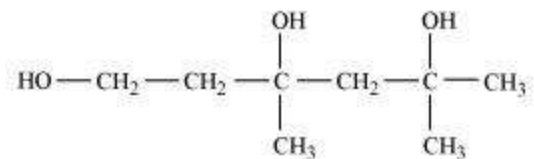
(i)



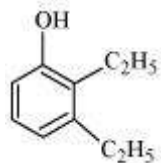
(ii)



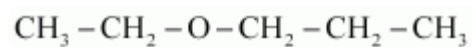
(iii)



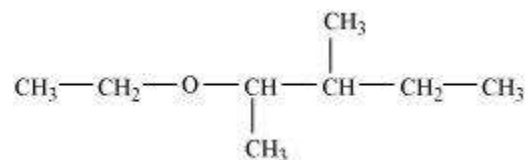
(iv)



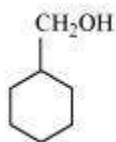
(v)



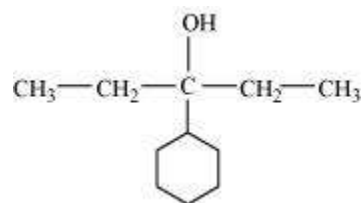
(vi)



(vii)



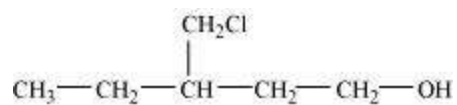
(viii)



(ix)



(x)



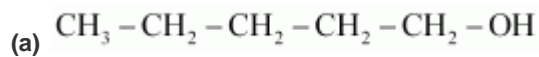
Q3 :

(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.

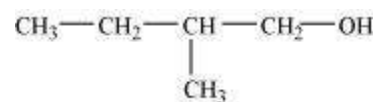
**Answer :**

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



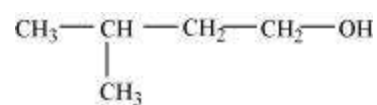
Pentan-1-ol ( $1^\circ$ )

(b)



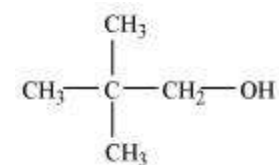
2-Methylbutan-1-ol ( $1^\circ$ )

(c)



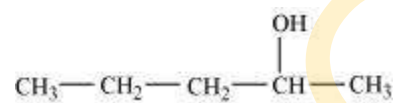
3-Methylbutan-1-ol ( $1^\circ$ )

(d)



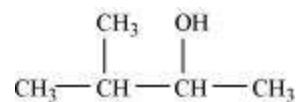
2, 2-Dimethylpropan-1-ol ( $1^\circ$ )

(e)



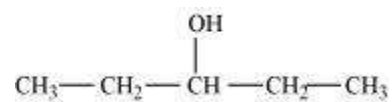
Pentan-2-ol ( $2^\circ$ )

(f)



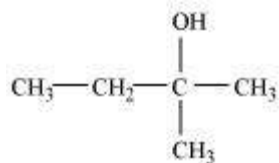
3-Methylbutan-2-ol ( $2^\circ$ )

(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

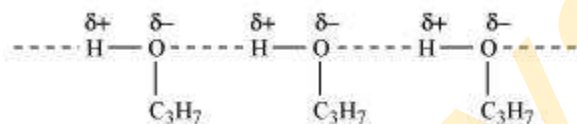
Tertiary alcohol: 2-methylbutan-2-ol

**Q4 :**

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

**Answer :**

Propanol undergoes intermolecular H-bonding because of the presence of -OH group. On the other hand, butane does not



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

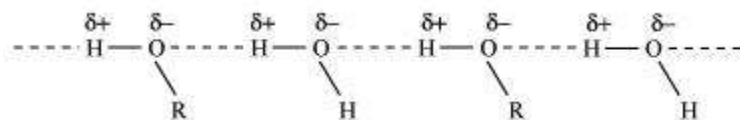
**Q5 :**

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

**Explain this fact.**

**Answer :**

Alcohols form H-bonds with water due to the presence of -OH group. However, hydrocarbons cannot form H-bonds with water.



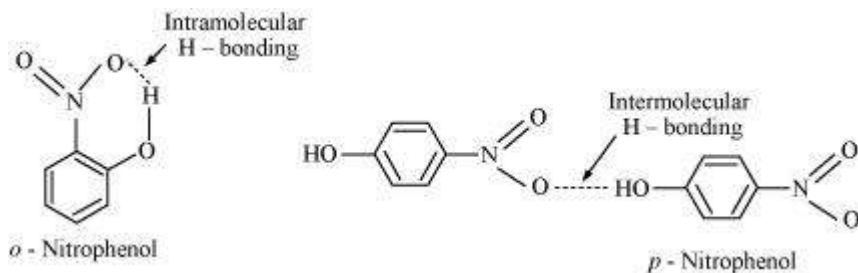
As a result, alcohols are comparatively more soluble in water than hydrocarbons of comparable molecular masses.





**Answer :**

Intramolecular H-bonding is present in *o*-nitrophenol. In *p*-nitrophenol, the molecules are strongly associated due to the presence of intermolecular bonding. Hence, *o*-nitrophenol is steam volatile.

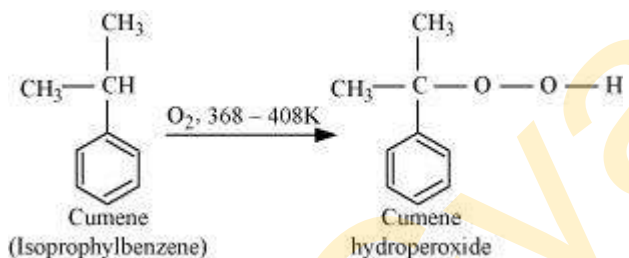


**Q9 :**

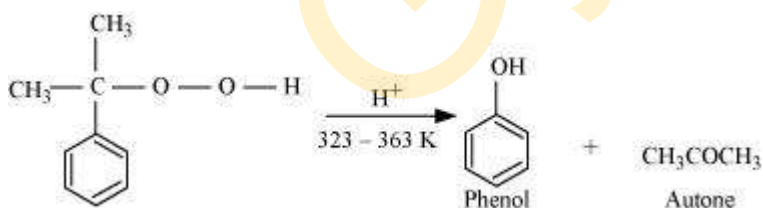
**Give the equations of reactions for the preparation of phenol from cumene.**

**Answer :**

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



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

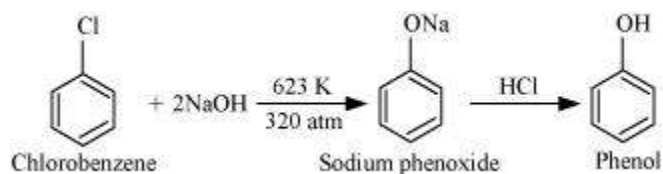


**Q10 :**

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

**Answer :**

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



Q11 :

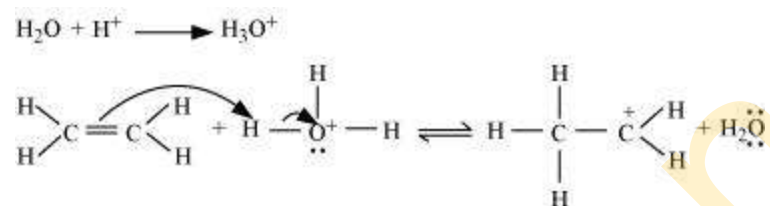
Write the mechanism of hydration of ethene to yield ethanol.

Answer :

The mechanism of hydration of ethene to form ethanol involves three steps.

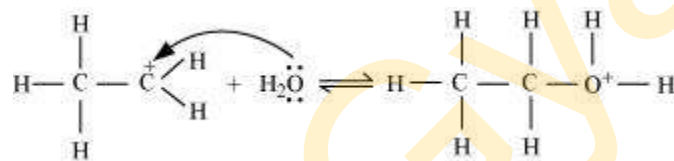
Step 1:

Protonation of ethene to form carbocation by electrophilic attack of  $\text{H}_3\text{O}^+$ :



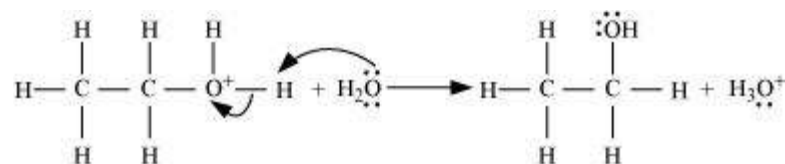
Step 2:

Nucleophilic attack of water on carbocation:



Step 3:

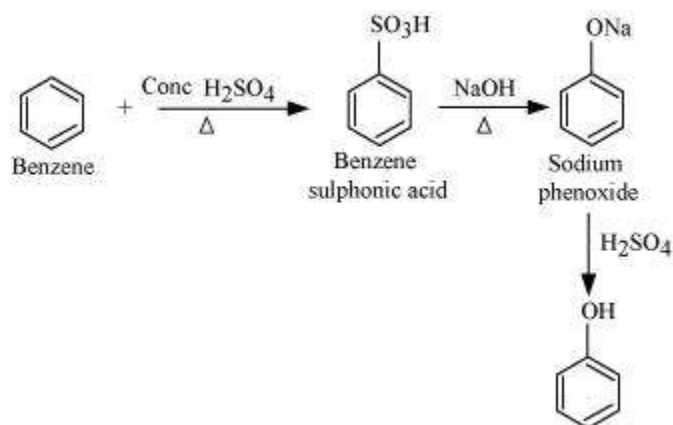
Deprotonation to form ethanol:



Q12 :

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

Answer :



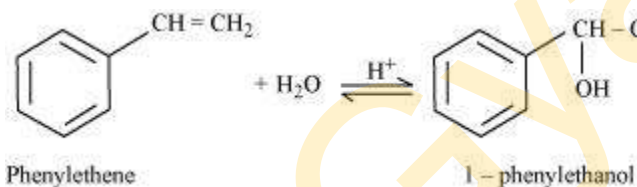
**Q13 :**

Show how will you synthesize:

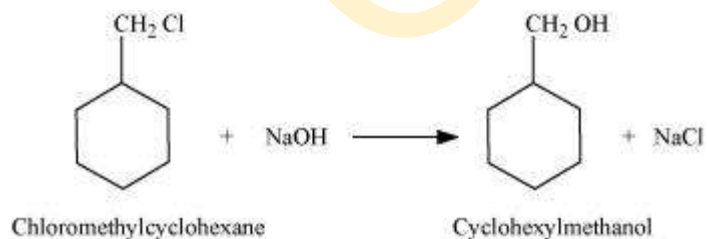
- 1-phenylethanol from a suitable alkene.
- cyclohexylmethanol using an alkyl halide by an  $\text{S}_{\text{N}}2$  reaction.
- pentan-1-ol using a suitable alkyl halide?

**Answer :**

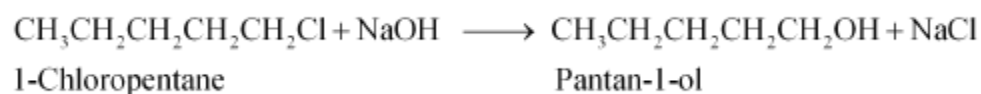
- (i) By acid-catalyzed hydration of ethylbenzene (styrene), 1-phenylethanol can be synthesized.



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



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



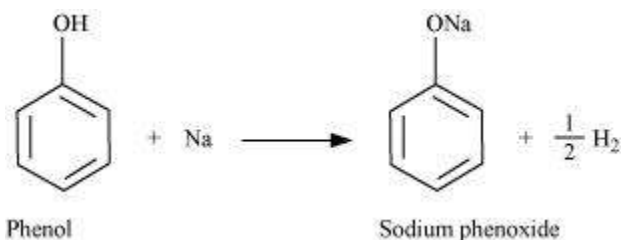
**Q14 :**

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

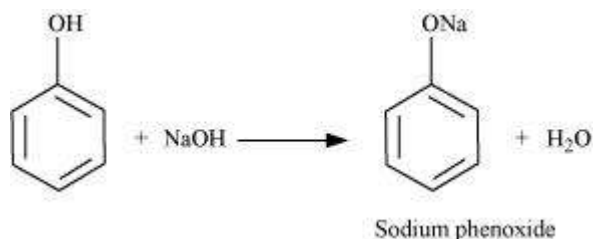
Answer :

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

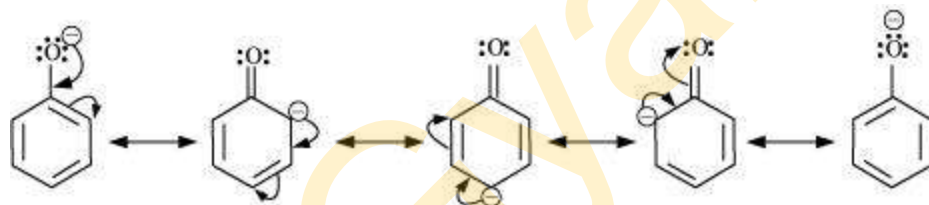
(i) Phenol reacts with sodium to give sodium phenoxide, liberating H<sub>2</sub>.



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



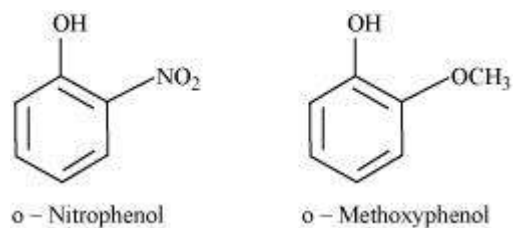
The acidity of phenol is more than that of ethanol. This is because after losing a proton, the phenoxide ion undergoes resonance and gets stabilized whereas ethoxide ion does not.



Q15 :

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

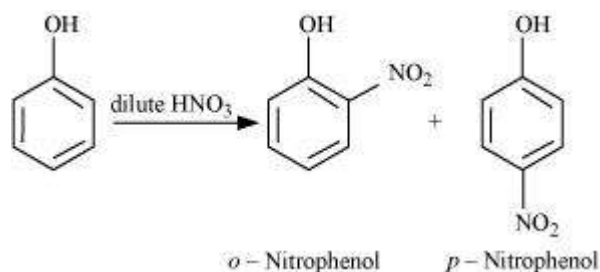
Answer :



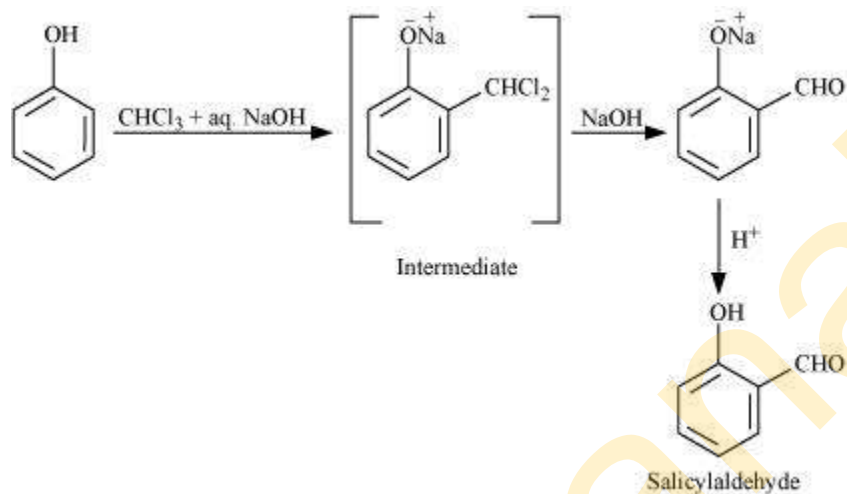
The nitro-group is an electron-withdrawing group. The presence of this group in the ortho position decreases the electron density in the O-H bond. As a result, it is easier to lose a proton. Also, the *o*-nitrophenoxide ion formed after the loss of protons is stabilized by resonance. Hence, *ortho* nitrophenol is a stronger acid.



(iii)



(iv)



Q18 :

Explain the following with an example.

(i) Kolbe's reaction.

(ii) Reimer-Tiemann reaction.

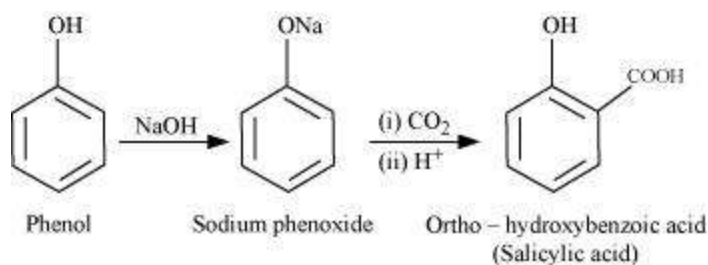
(iii) Williamson ether synthesis.

(iv) Unsymmetrical ether.

Answer :

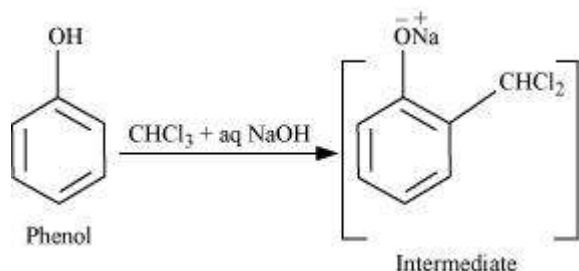
(i) Kolbe's reaction:

When phenol is treated with sodium hydroxide, sodium phenoxide is produced. This sodium phenoxide when treated with carbon dioxide, followed by acidification, undergoes electrophilic substitution to give ortho-hydroxybenzoic acid as the main product. This reaction is known as Kolbe's reaction.



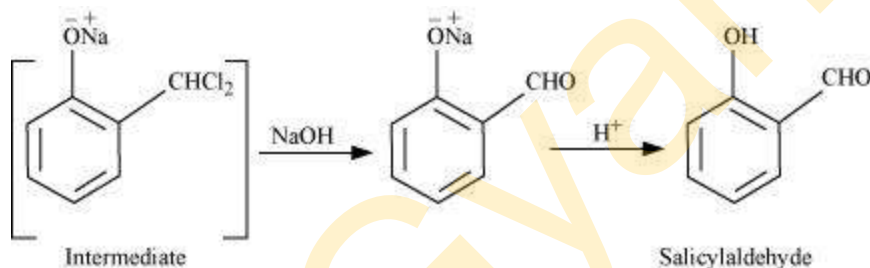
### (ii) Reimer-Tiemann reaction:

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



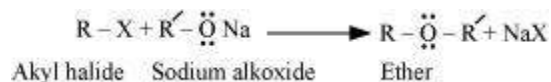
This reaction is known as the Reimer-Tiemann reaction.

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  $\text{S}_{\text{N}}2$  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 ( $\text{CH}_3\text{-O-CH}_2\text{CH}_3$ ).

**Q19 :**

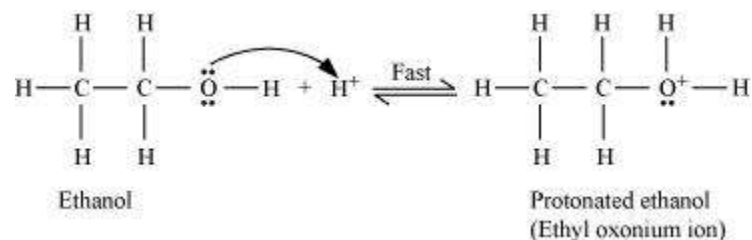
**Write the mechanism of acid-catalysed dehydration of ethanol to yield ethene.**

**Answer :**

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

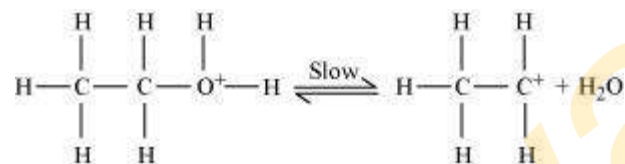
**Step 1:**

Protonation of ethanol to form ethyl oxonium ion:



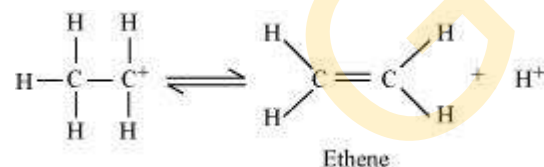
**Step 2:**

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.

**Q20 :**

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

(i) Propene → Propan-2-ol

(ii) Benzyl chloride → Benzyl alcohol

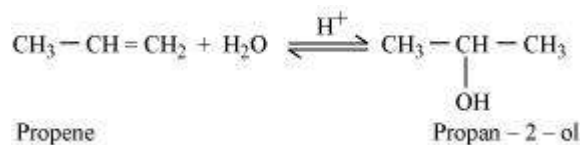
(iii) Ethyl magnesium chloride → Propan-1-ol.

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

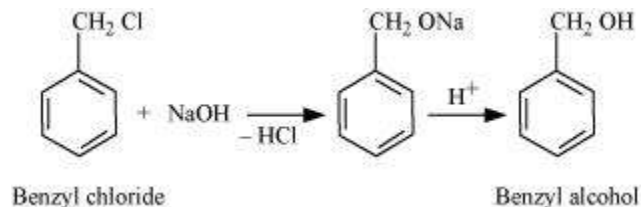


**Answer :**

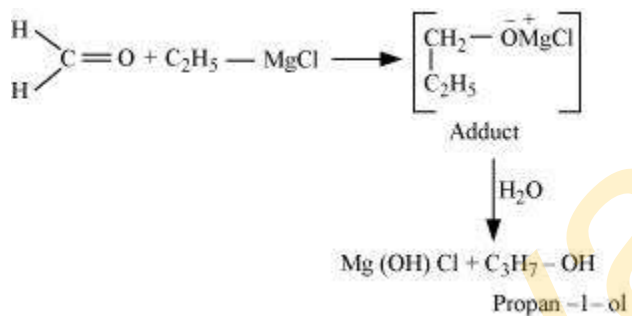
(i) If propene is allowed to react with water in the presence of an acid as a catalyst, then propan-2-ol is obtained.



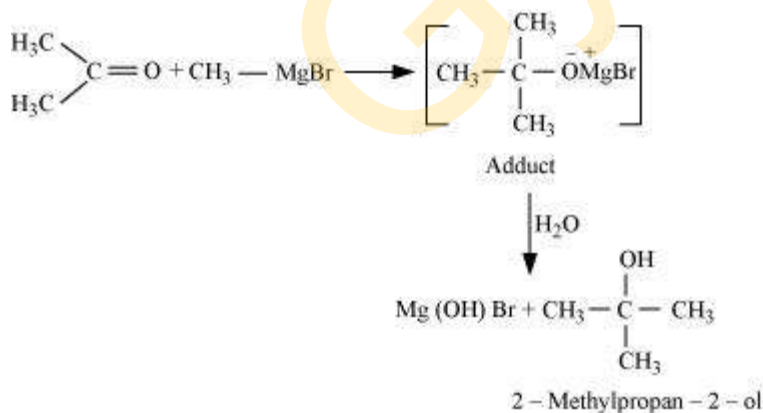
(ii) If benzyl chloride is treated with NaOH (followed by acidification) then benzyl alcohol is produced.



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



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



**Q21 :**

**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.

**Answer :**

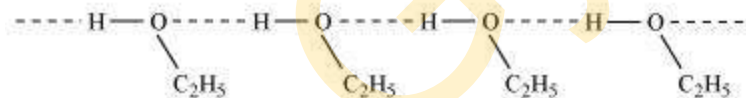
- (i) Acidified potassium permanganate
- (ii) Pyridinium chlorochromate (PCC)
- (iii) Bromine water
- (iv) Acidified potassium permanganate
- (v) 85% phosphoric acid
- (vi)  $\text{NaBH}_4$  or  $\text{LiAlH}_4$

**Q22 :**

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

**Answer :**

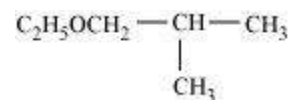
Ethanol undergoes intermolecular H-bonding due to the presence of -OH group, resulting in the association of molecules. Extra energy is required to break these hydrogen bonds. On the other hand, methoxymethane does not undergo H-bonding. Hence, the boiling point of ethanol is higher than that of methoxymethane.



**Q23 :**

**Give IUPAC names of the following ethers:**

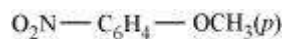
(i)



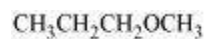
(ii)



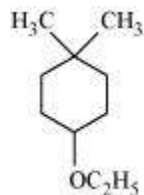
(iii)



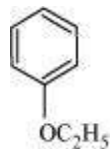
(iv)



(v)



(vi)



**Answer :**

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

**Q24 :**

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

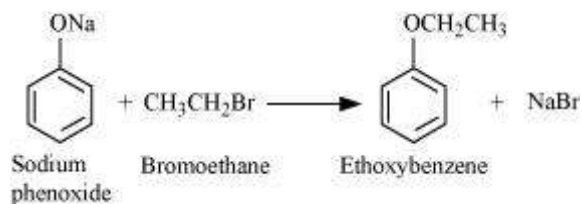
- (i) 1-Propoxypropane
- (ii) Ethoxybenzene
- (iii) 2-Methoxy-2-methylpropane
- (iv) 1-Methoxyethane

**Answer :**

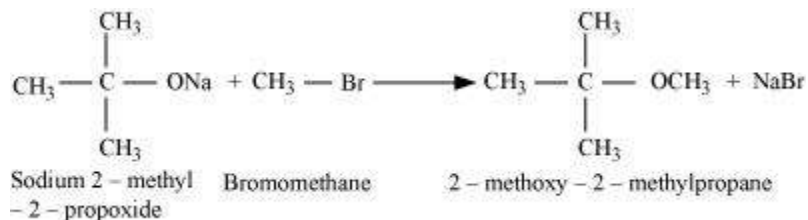


(i) Sodium propoxide    1-Bromopropane                      1- Propoxypropane

(ii)



(iii)



(iv)

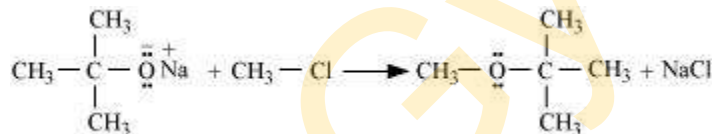


Q25 :

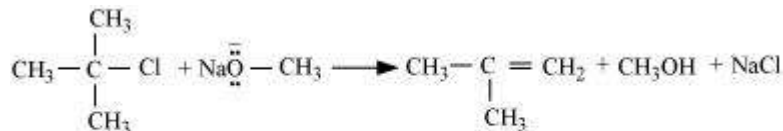
Illustrate with examples the limitations of Williamson synthesis for the preparation of certain types of ethers.

Answer :

The reaction of Williamson synthesis involves  $\text{S}_{\text{N}}2$  attack of an alkoxide ion on a primary alkyl halide.



But 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.



Tertiary alkyl halide

Alkene

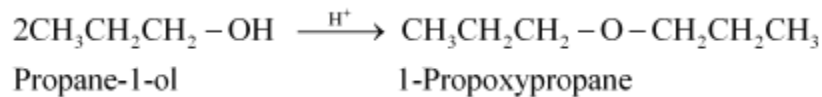
Q26 :

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

Answer :

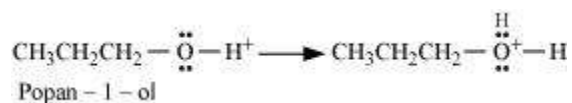
1-propoxypropane can be synthesized from propan-1-ol by dehydration.

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

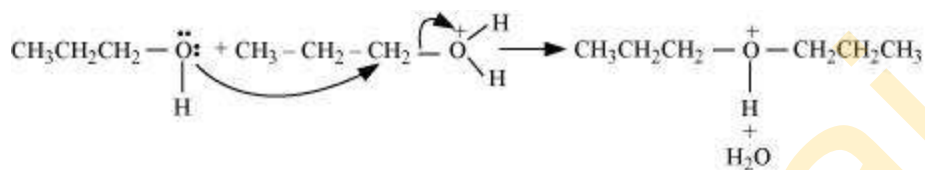


The mechanism of this reaction involves the following three steps:

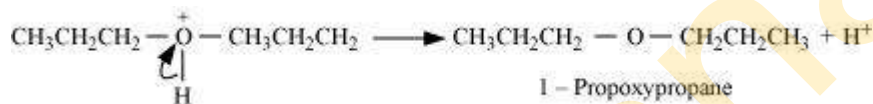
**Step 1: Protonation**



**Step 2: Nucleophilic attack**



**Step 3: Deprotonation**



**Q27 :**

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

**Answer :**

The formation of ethers by dehydration of alcohol is a bimolecular reaction ( $\text{S}_{\text{N}}2$ ) involving the attack of an alcohol molecule on a protonated alcohol molecule. 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.

**Q28 :**

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

**(i) 1-propoxypropane**

**(ii) Methoxybenzene and**

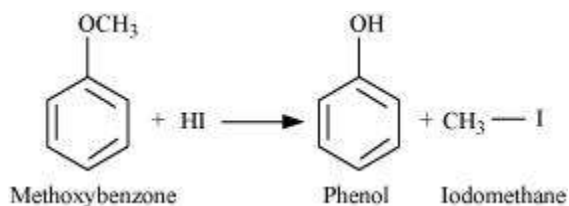
**(iii) Benzyl ethyl ether**

**Answer :**

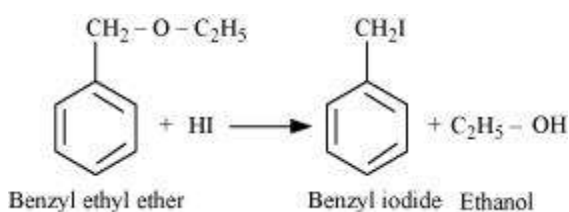
(i)



(ii)



(iii)



Q29 :

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.

Answer :

(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.

(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.

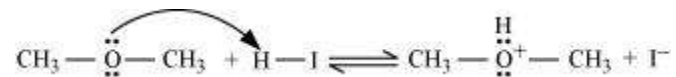
Q30 :

Write the mechanism of the reaction of HI with methoxymethane.

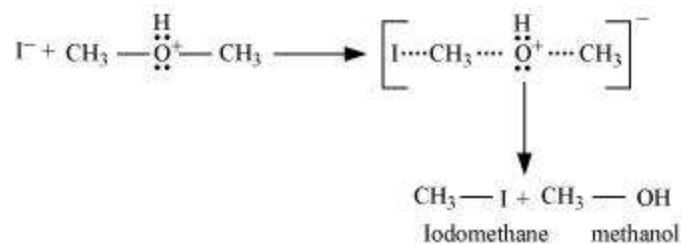
**Answer :**

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

**Step1:** Protonation of methoxymethane:

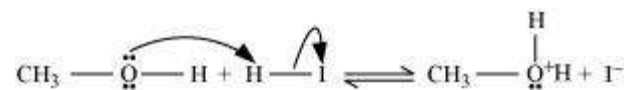


**Step2:** Nucleophilic attack of  $\text{I}^-$ :



**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



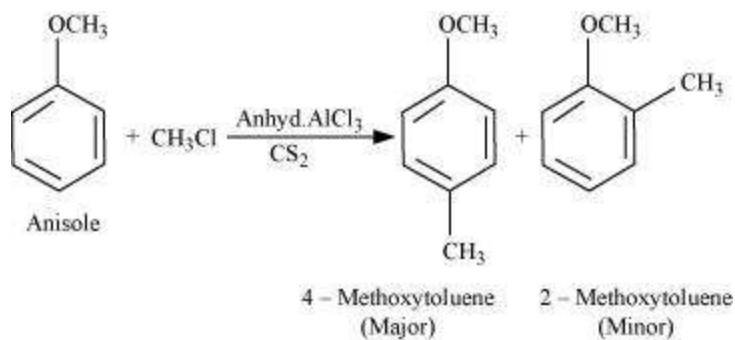
**Q31 :**

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.

**Answer :**

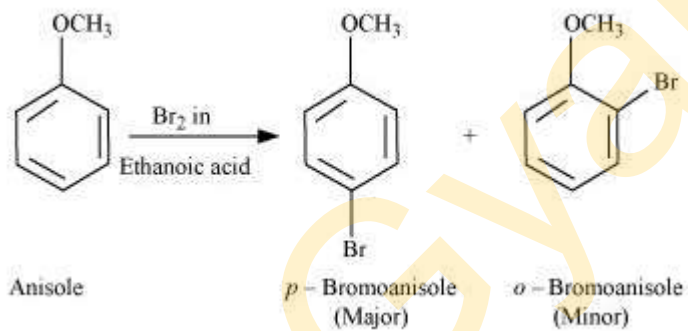
(i)



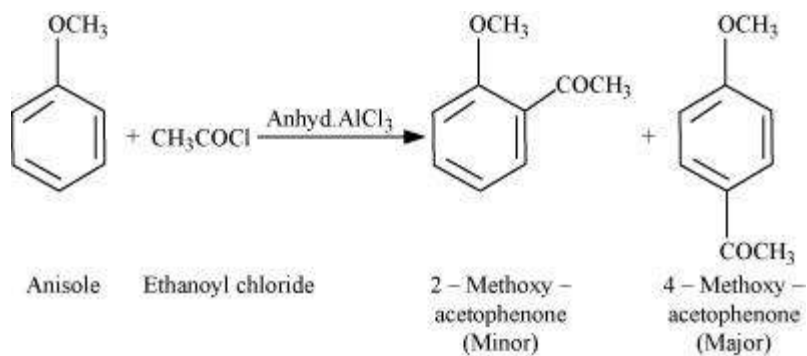
(ii)



(iii)



(iv)

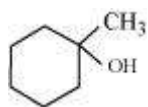


Q32 :

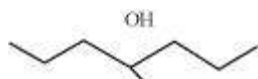


Show how would you synthesise the following alcohols from appropriate alkenes?

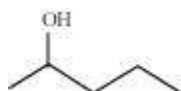
(i)



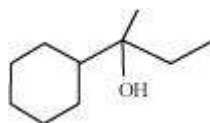
(ii)



(iii)



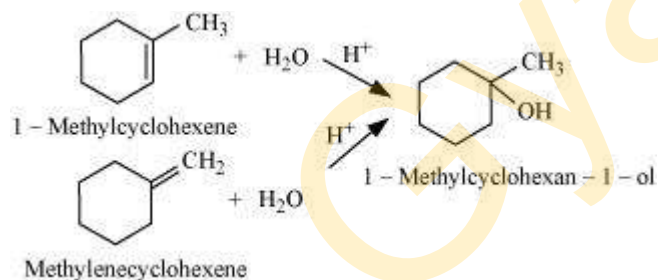
(iv)



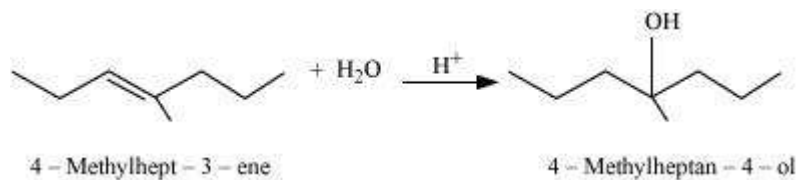
**Answer :**

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

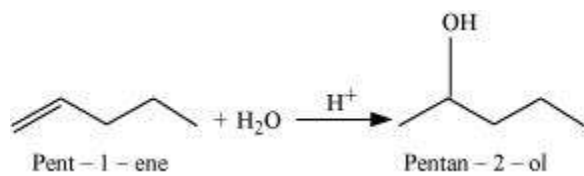
(i)



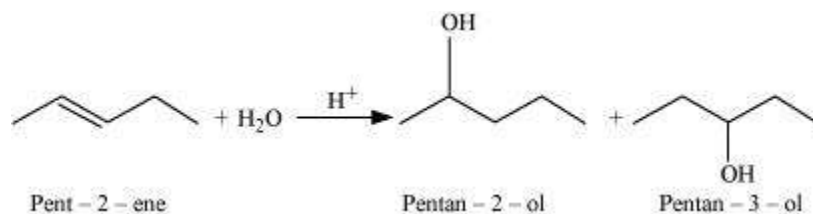
(ii)



(iii)

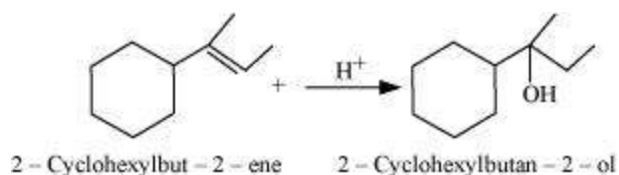


Acid-catalyzed hydration of pent-2-ene also produces pentan-2-ol but along with pentan-3-ol.



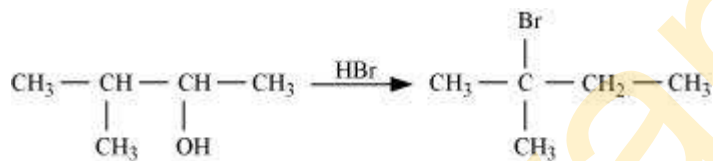
Thus, the first reaction is preferred over the second one to get pentan-2-ol.

(iv)



Q33 :

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



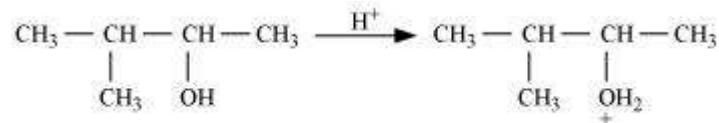
Give a mechanism for this reaction.

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

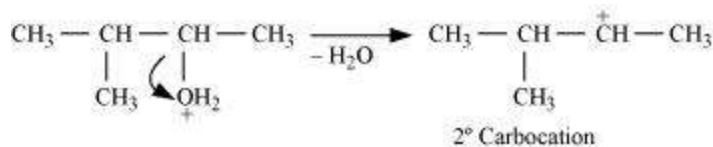
Answer :

The mechanism of the given reaction involves the following steps:

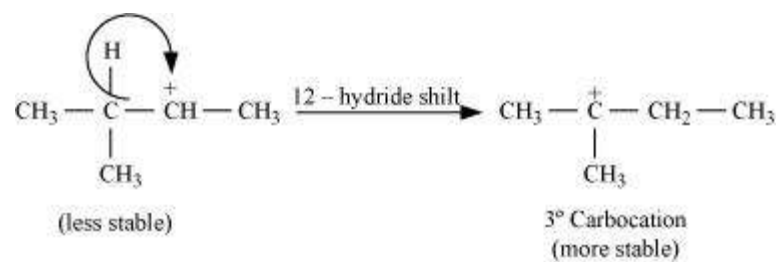
**Step 1:** Protonation



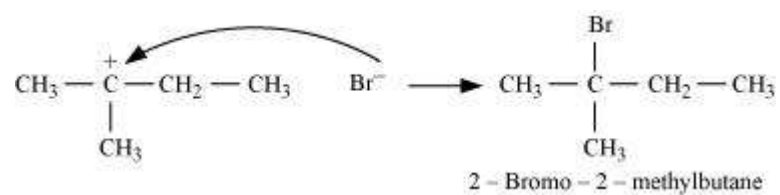
**Step 2:** Formation of 2° carbocation by the elimination of a water molecule



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



**Step 4: Nucleophilic attack**



Gyanajal