

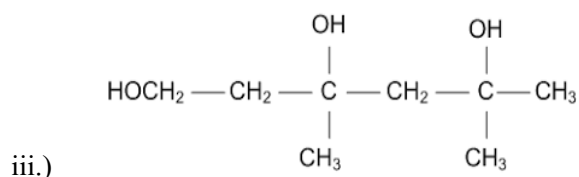
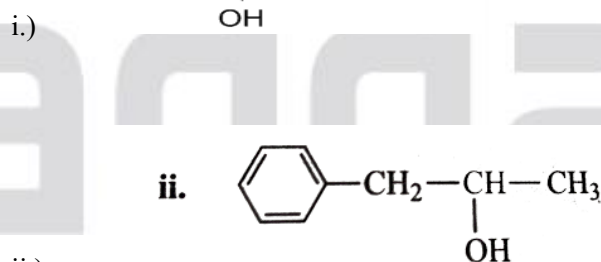
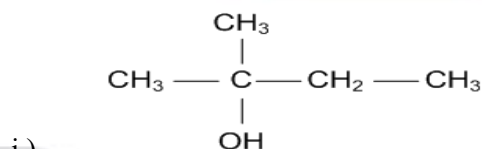
Chapter – 11 (Alcohols, Phenols and Ethers)

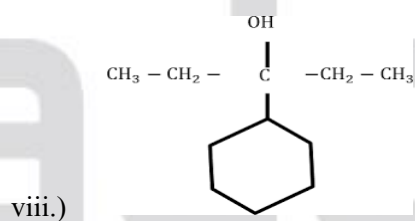
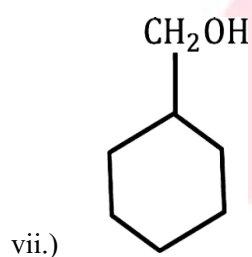
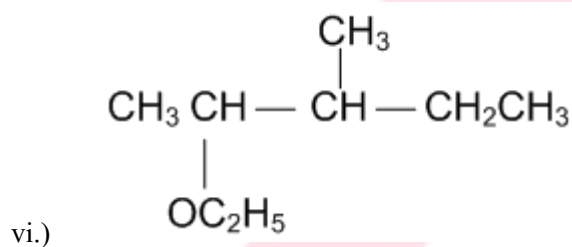
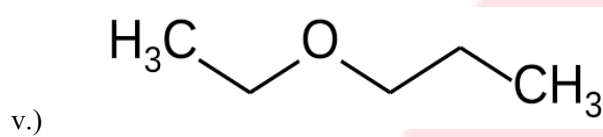
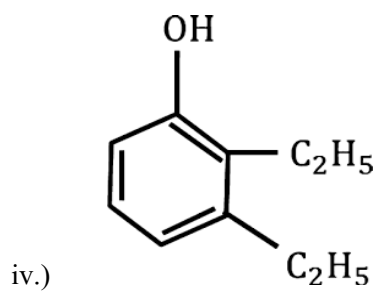
Exercise Questions:

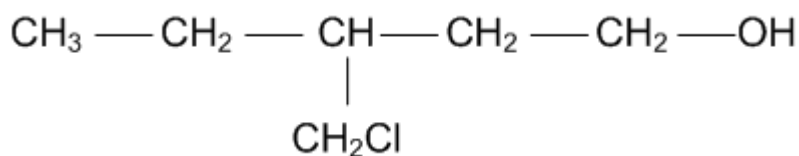
Question :1 Write structures of the compounds whose IUPAC names are as follows :

- 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:







x.)

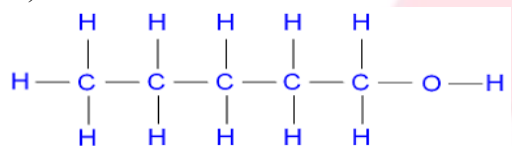
Question :2 I. Draw the structures of all isomeric alcohols of molecular formula $\text{C}_5\text{H}_{12}\text{O}$ and give their IUPAC names.

II. Classify the isomers of alcohols in question 2(I) as primary, secondary and tertiary alcohols

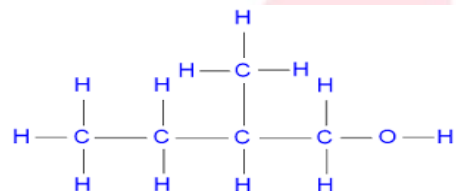
Answer:

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

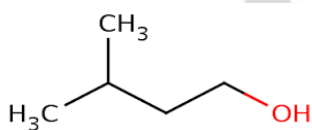
a.) Pentan-1-ol



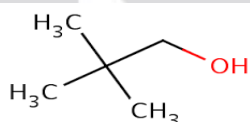
b.) 2-methylbutan-1-ol



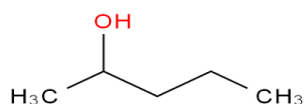
c.) 3-methylbutan-1-ol



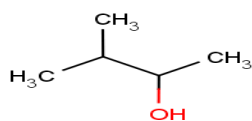
d.) 2,2-Dimethylpropan-1-ol



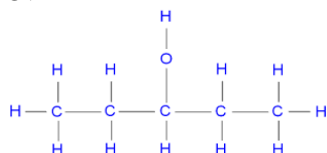
e.) Pentan-2-ol



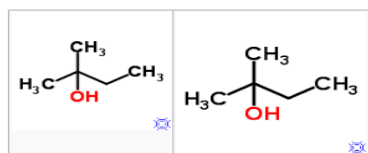
f.) 3-Methylbutan-2-ol



g.) Pentan-3-ol



h.) 2-Methylbutan-2-ol

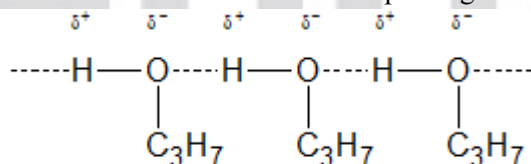


(ii) Primary alcohol: Pentan-1-ol; 2-Methylbutan-1-ol;
3-Methylbutan-1-ol; 2, 2 - Dimethylpropan-1-ol
Secondary alcohol: Pentan-2-ol; 3-Methylbutan-2-ol;
Pentan-3-ol
Tertiary alcohol: 2-methylbutan-2-ol

Question 3 Explain why propanal has higher boiling point than that of the hydrocarbon, butane?

Answer:

The presence of -OH group makes propanol undergo intermolecular H-bonding. Butane, while on the other side does not have the same privilege.

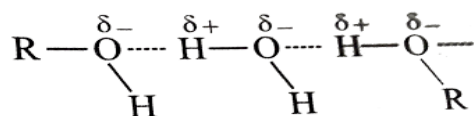


Hence, additional energy would be required to break the intermolecular hydrogen bonds. This is the reason why hydrocarbon butane has a lower boiling point than propanol.

Question :4 Alcohols are comparatively more soluble in water than hydrocarbons of comparable molecular masses. Explain this fact.

Answer:

Due to the presence of –OH group, alcohols form H-bonds with water.

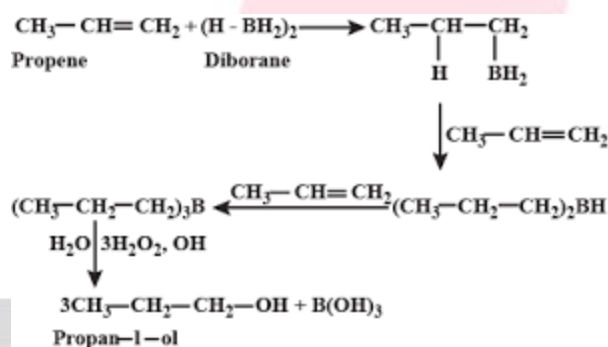


As a result, alcohols are comparatively more soluble in water than hydrocarbons of comparable molecular masses.

Question :5 What is meant by hydroboration – oxidation reaction? Illustrate it with an example.

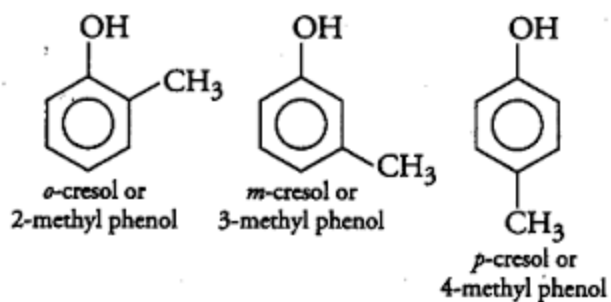
Answer:

The hydroboration – oxidation reaction is the reaction where borane is added in order for the oxidation to take place. For example, propan-1-ol is formed by making propene undergo the hydroboration – oxidation reaction. In the above reaction, the reaction between propene and diborane takes place in order to form trialkyl borane which acts an additional product. This additional product is oxidized to alcohol by hydrogen peroxide in the presence of aqueous sodium hydroxide.



Question :6 Give the structures and IUPAC names of monohydric phenols of molecular formula, C₇H₈O.

Answer:

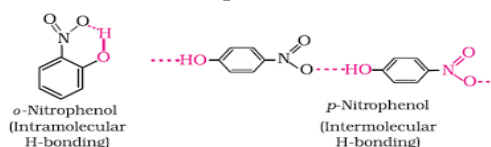


Question :7 While separating a mixture of ortho and para nitrophenols by steam distillation, name the isomer which will be steam volatile. Give reason.

Answer:

Intramolecular H – bonding is present in o- nitrophenol and p – nitrophenol. In p – nitrophenol, the molecules are strongly associated due to the existence of intermolecular bonding.

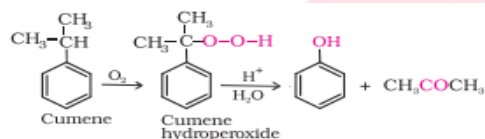
Therefore, o – nitrophenol is steam volatile.



Question :8 Give the equation of reactants for the preparation of phenol from cumene.

Answer:

To synthesize phenol, cumene is initially oxidized in the presence of air of cumene hydroperoxide. Followed by, treating cumene hydroxide with dilute acid to prepare phenol and acetone as by products.



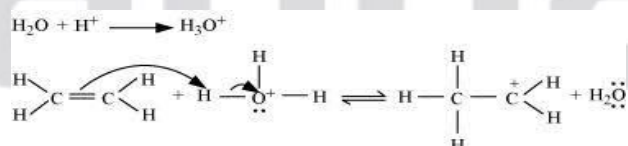
Question :9 Write the mechanism of hydration of ethene to yield ethanol.

Answer:

There are three steps that are involved in the mechanism of hydration of ethene to form ethanol. These steps are as follows:

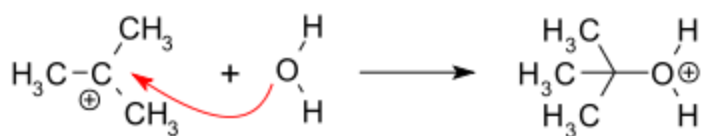
Step : 1

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



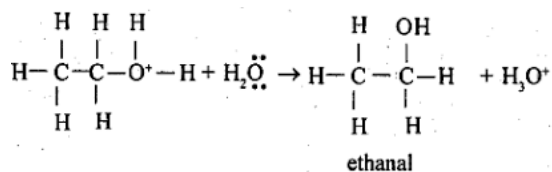
Step : 2

Nucleophilic attack of water on carbocation.



Step : 3

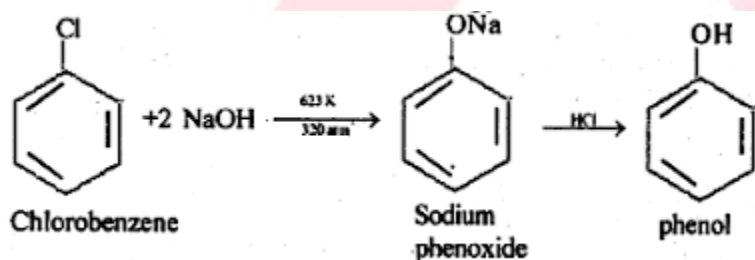
Deprotonation to form ethanol:



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

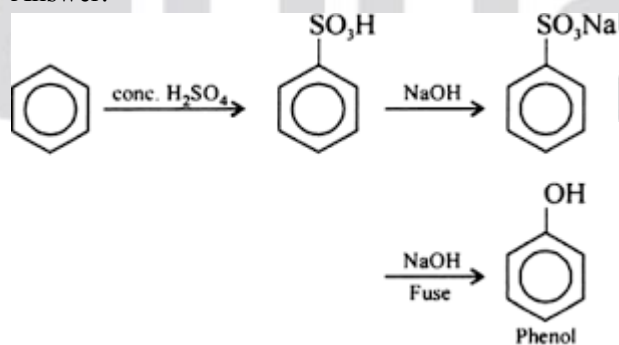
Answer:

Chlorobenzene is combined with NaOH to prepare sodium phenoxide, resulting in phenol on acidification.



Question :11 You are given benzene, conc. H₂SO₄ and NaOH. Write the equations for the preparation of phenol using these reagents.

Answer:

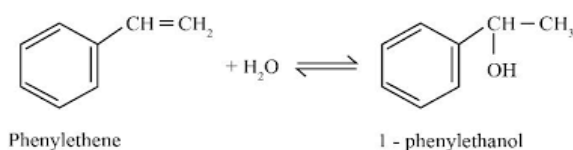


Question :12 Show how will you synthesise:

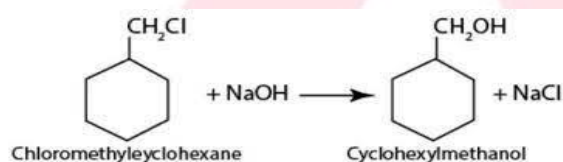
- I. 1-phenylethanol from a suitable Alkene
- II. Cyclohexylmethanol using an alkyl halide by an SN2 reaction.
- III. Pentan-1-ol using a suitable alkyl halogen?

Answer:

- i.) By acid – catalysed hydration of ethylbenzene, 1 – phenylethanol can be synthesised.



- ii.) When chloromethyl cyclohexane is treated with sodium hydroxide, cyclohexyl methanol is obtained.



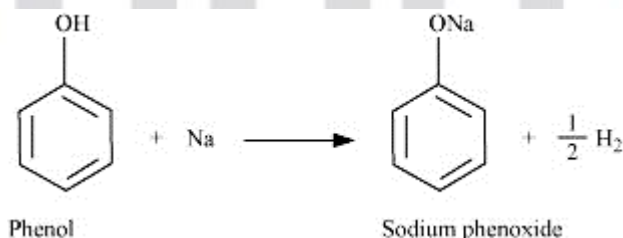
- iii.) When 1 – chloropentane is treated with NaOH, pentan – 1- ol is produced.
 $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl} + \text{NaOH} \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH} + \text{NaCl}$

Question :13 Give two reactions that show the acidic nature of phenol. Compare acidity of phenol with that of ethanol.

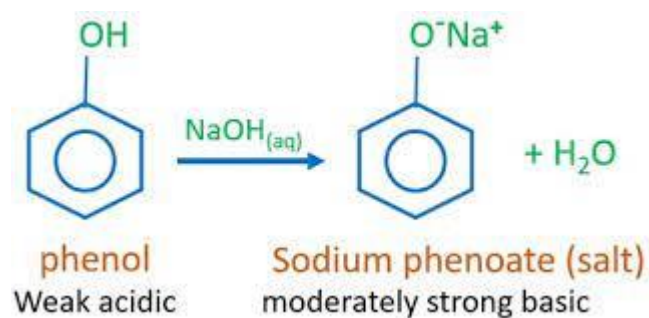
Answer:

The acidic nature of phenol can be proven with two reactions given below:

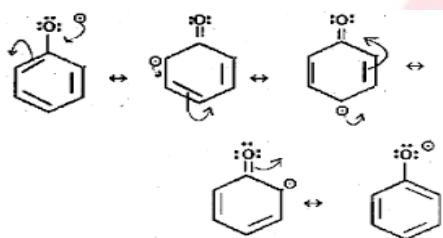
- i.) Phenol reacts with sodium to give sodium phenoxide, liberating H₂.



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

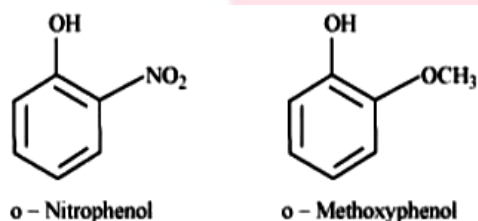


The acidity of phenol is more than that of ethanol. This is because after losing a proton, the phenoxide ion undergoes resonance and get stabilized whereas ethoxide ion does not.



Question :14 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.

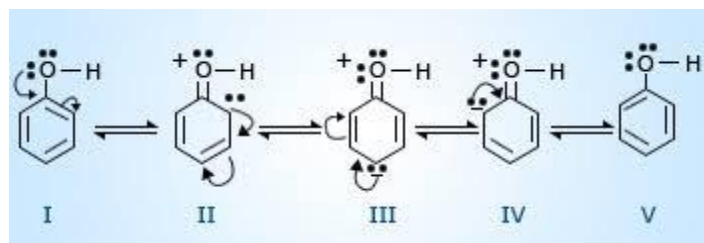
On the other hand, methoxy group is an electron-releasing group. Thus, it increases the electron density in the O-H bond and hence, the proton cannot be given out easily.

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

Question :15 Explain how does the -OH group attached to a carbon of benzene ring activate it towards electrophilic substitution?

Answer:

The density of the electron increases in the benzene ring as the -OH group acts as an electron - donating group. This is clearly shown in the resonance structure of phenol given here.

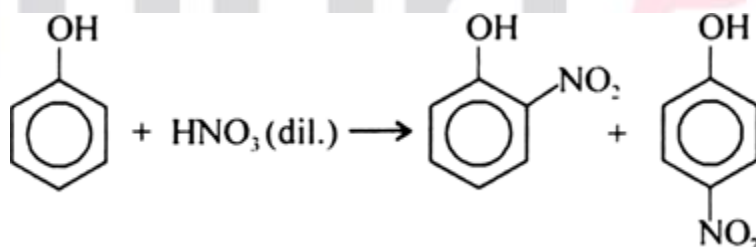
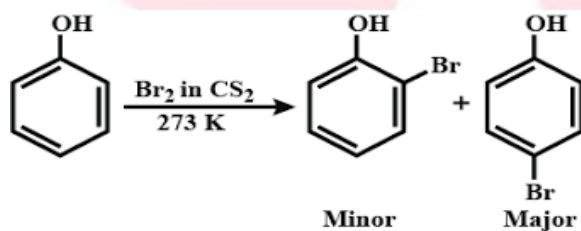
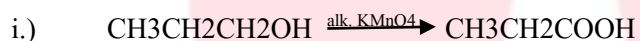


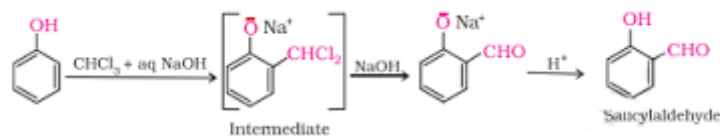
As a result, the benzene ring is activated towards electrophilic substitution.

Question :16 Give equations of the following reactions :

- I. Oxidation of propan-1-ol with alkaline KMnO_4 solution.
- II. Bromine in CS_2 with phenol.
- III. Dilute HNO_3 with phenol.
- IV. Treating phenol with chloroform in presence of aqueous NaOH .

Answer:





iv.)

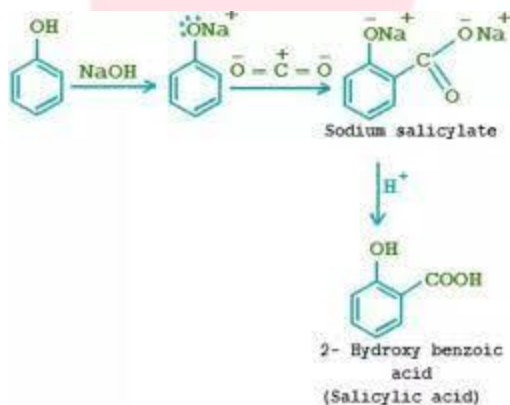
Question :17 Explain the following with an example.

- I. Kolbe's reaction.
- II. Reimer -Tiemann reaction.
- III. Williamson ether synthesis
- IV. Unsymmetrical ether.

Answer:

i.) Kolbe's reaction:

Sodium phenoxide is formed when phenol is treated with sodium hydroxide. Ortho – hydroxybenzoic acid as the main product when sodium phenoxide is treated with carbon dioxide, followed by acidification, it undergoes electrophilic substitution. This reaction is known as Kolbe's reaction.

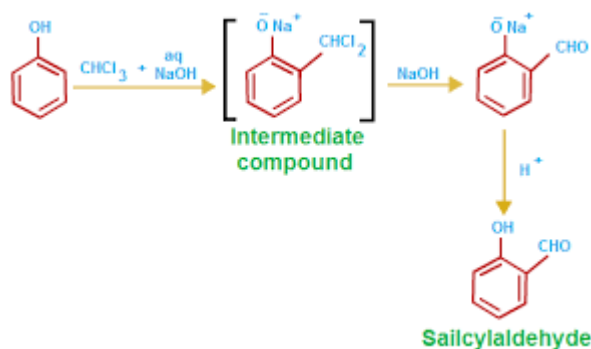


ii.) Reimer – Tiemann reaction:

A –CHO group is introduced at the ortho position of the benzene ring when phenol is treated with chloroform in the presence of sodium hydroxide.

This reaction is known as Reimer – Tiemann reaction.

Salicylaldehyde is produced when the intermediate is hydrolysed in the presence of alkalis.

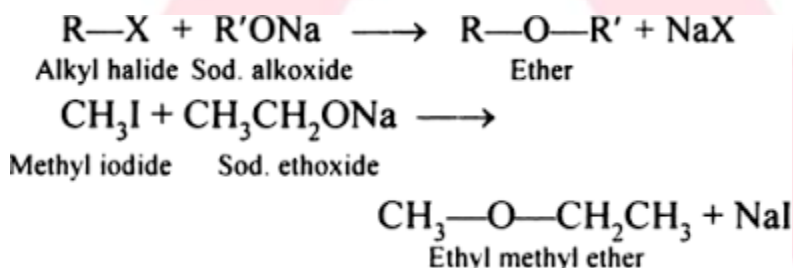


iii.) Williamson ether synthesis:

A chemical method to synthesize symmetrical and unsymmetrical ethers by making alkyl halides to react with sodium alkoxides is called Williamson ether synthesis.

The above reaction includes S_N2 attack of the alkoxide ion on the alkyl halide. In the case of primary alkyl halides, better results are obtained.

Only if the alkyl halide is tertiary or secondary, in that case, elimination competes over substitution.



iv.) Unsymmetrical ether:

When an oxygen atom has two groups on its two sides, it is called Unsymmetrical ether.

For example: ethyl methyl ether ($\text{CH}_3\text{-O-CH}_2\text{CH}_3$).

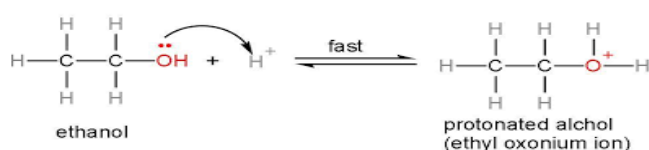
Question :18 Write the mechanism of acid dehydration of ethanol to yield ethene.

Answer:

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

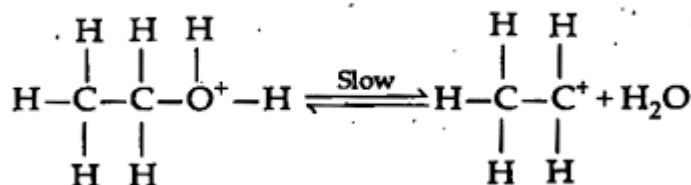
Step 1:

Formation of ethyl oxonium by protonation of ethanol:



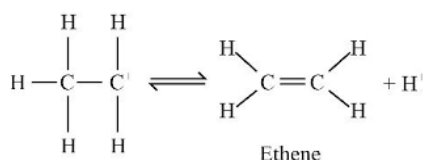
Step 2:

A carbocation is formed (rate determining step) :



Step 3:

Ethene is formed by elimination of proton:



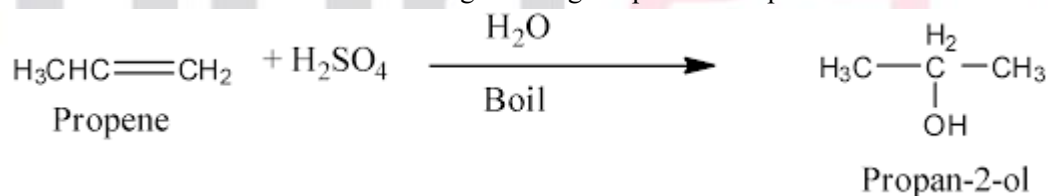
The acid is released in Step 3 which was being consumed in Step 1. It is removed to shift the equilibrium in a forward direction, after ethene is formed.

Question :19 How are the following conversions carried out?

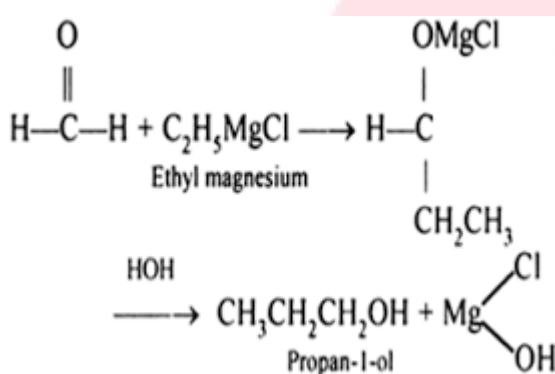
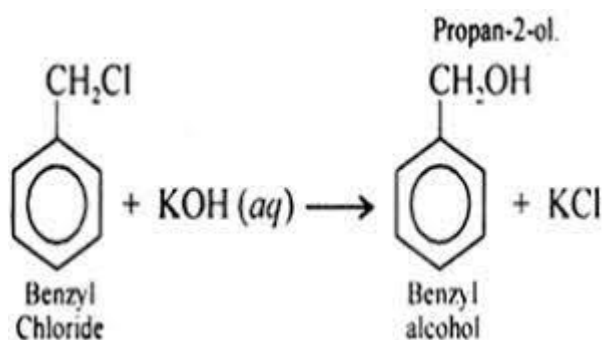
- I. Propene to propan-2-ol.
- II. Benzyl chloride to Benzyl alcohol.
- III. Ethyl magnesium chloride to Propan-1-ol.
- IV. Methyl magnesium bromide to 2-Methylpropan-2-ol.

Answer;

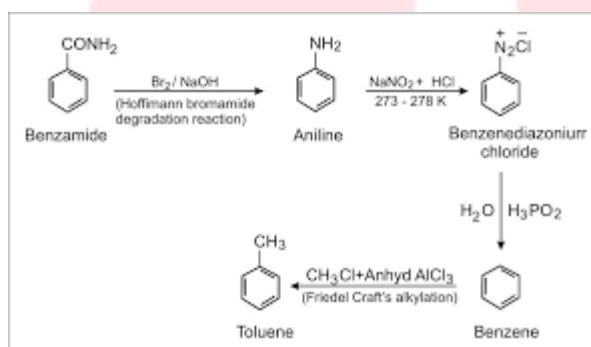
- i.) We can convert Propene to Propan-2-ol by reaction of the propene with acid. Propene reacts with acid in presence of water to produce Propan-2-ol. Step 3: In this step protonated alcohol reacts with the water molecule generating the product Propan-2-ol.



- ii.) Benzyl chloride undergoes a substitution reaction when reacting with aqueous potassium hydroxide to give benzyl alcohol.



iii.)



iv.)

Question :20 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.

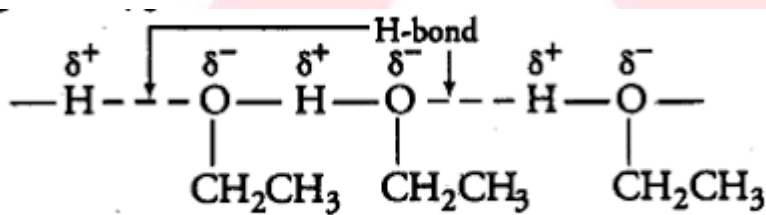
Answer:

- i.) NaBH_4 or LiAlH_4 to acidified KMnO_4
- ii.) Pyridinium chlorochromate (PCC)
- iii.) Bromine water
- iv.) Acidified potassium permanganate
- v.) Concentrated H_2SO_4 or H_3PO_4
- vi.) Catalytic hydrogenation or sodium borohydride or lithium aluminium hydride (LiAlH_4)

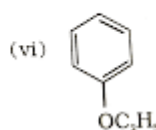
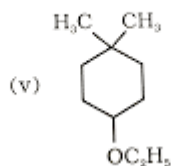
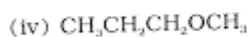
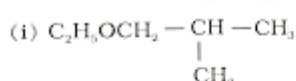
Question :21 Give reason for the higher boiling point of ethanol in comparison to methoxymethane.

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.



Question: 22 Give IUPAC names of the following ethers:



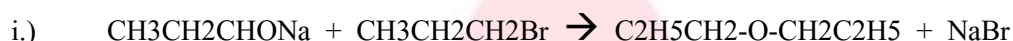
Answer:

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

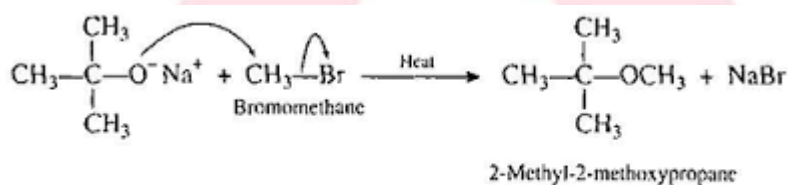
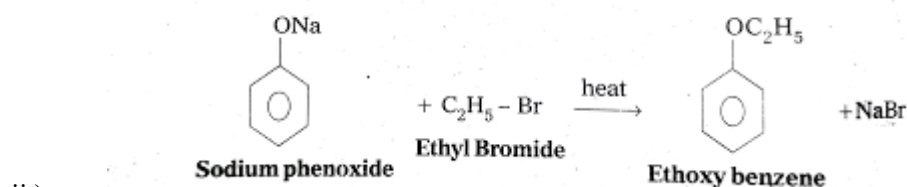
Question :23 Write the names of reagents and equations for the preparation of the following ethers by Williamson's synthesis:

- I. 1-Propoxypropane
- II. Ethoxybenzene
- III. 2-Methoxy-2-methylpropane
- IV. 1-Methoxyethane

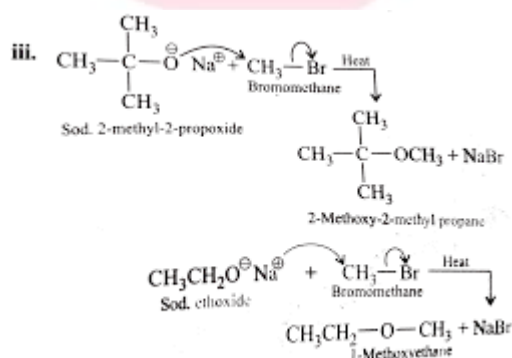
Answer:



ii) Preparation of Ethoxybenzene :



iii.)

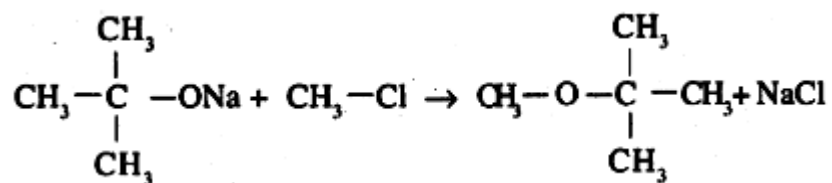


iv.)

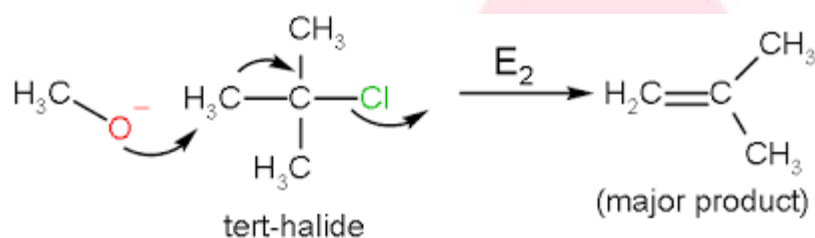
Question :24 Illustrate with examples the limitations of Williamson synthesis for the preparation of certain types of ether.

Answer:

The reaction of Williamson synthesis involves SN2 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.

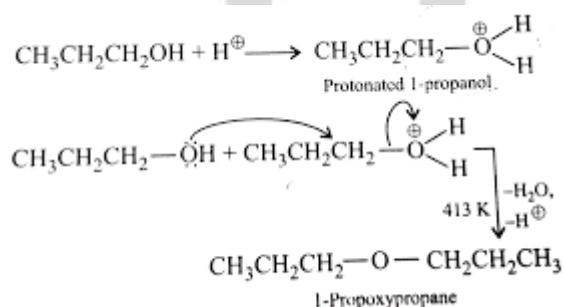


Question :25 How is 1-propoxypropane synthesised from propan-1-ol? Write mechanism of this reaction.

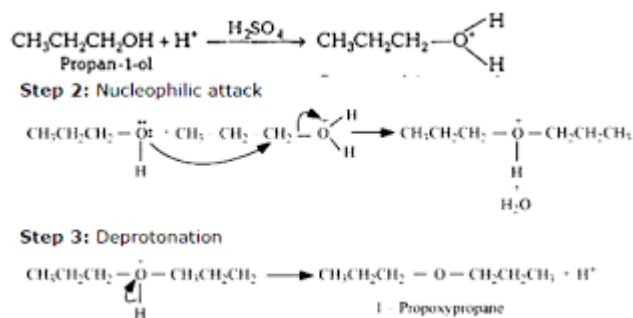
Answer:

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

Propan-1-ol undergoes dehydration in the presence of protic acids (such as H_2SO_4 , H_3PO_4) to give 1-propoxypropane.



The mechanism of this reaction involves the following steps:



Question :26 Preparation of ethers by acid dehydration of secondary or tertiary alcohols is not a suitable method. Give reason.

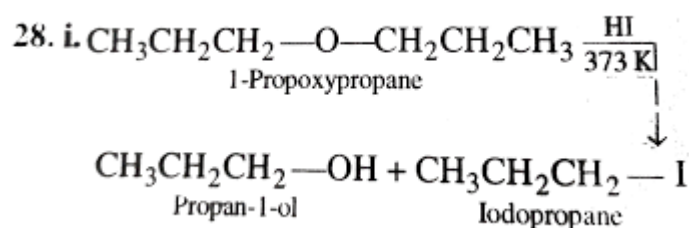
Answer:

The formation of ethers by dehydration of alcohol is a bimolecular reaction (SN₂) 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

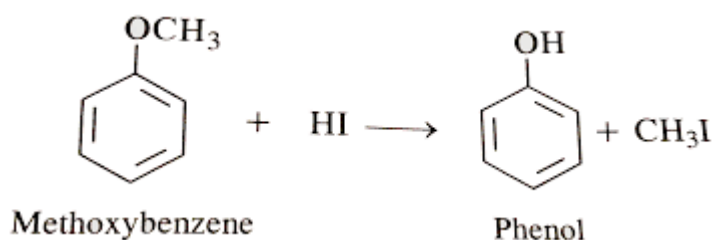
Question :27 Write the equation of the reaction of hydrogen iodide with :

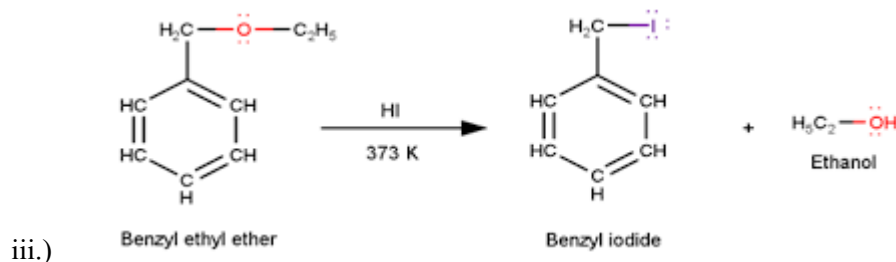
- I. 1-propoxypropane
- II. Methoxybenzene
- III. Benzyl ethyl ether.

Answer:



i.)



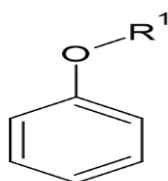


Question :28 Explain the fact that in aryl alkyl ethers

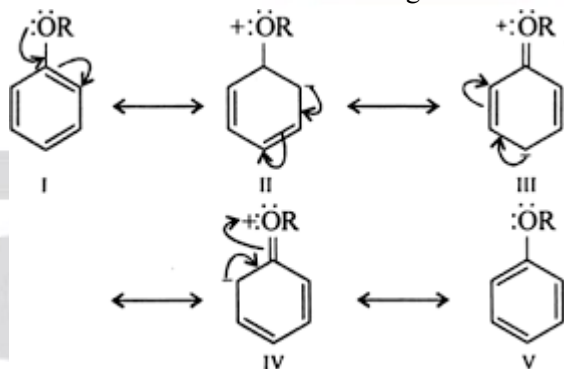
- I. The alkoxy group activates the benzene ring towards electrophilic substitution and
- II. It directs the incoming substituents to ortho and para positions in benzene ring.

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

Question :29 Write the mechanism of the reaction of HI with methoxymethane.

Answer:

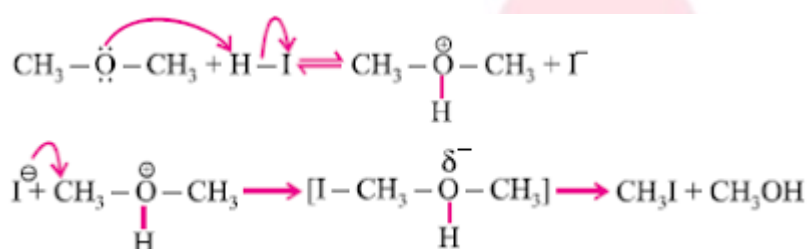
The steps of the reaction of methoxymethane with HI are given below:

Step 1:

Protonation of methoxymethane:

Step 2:

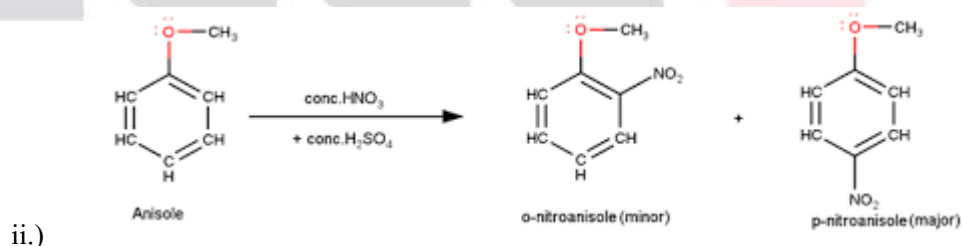
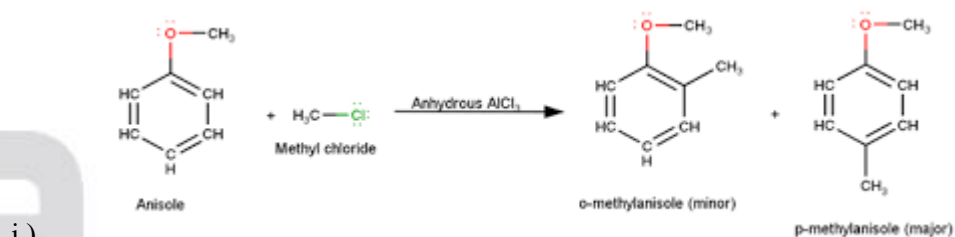
Nucleophilic attack of I⁻:

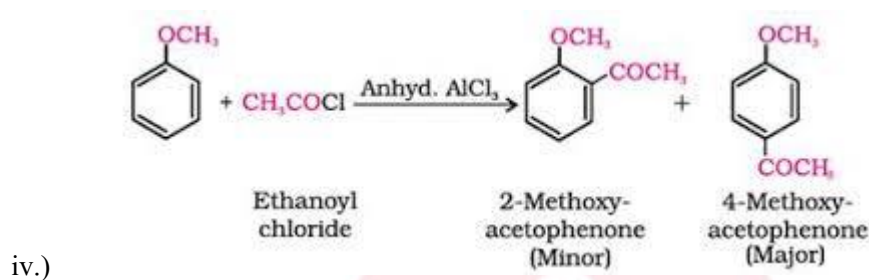
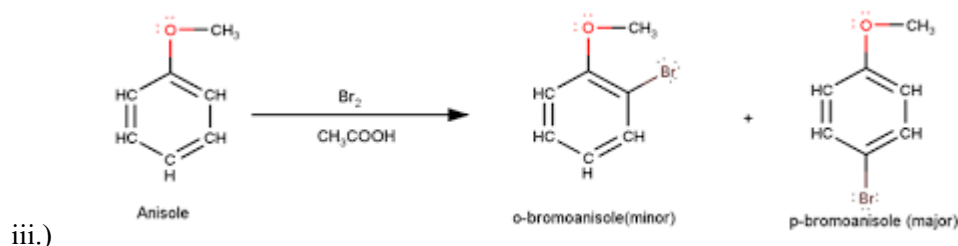


Question :30 Write equations of the following reactions :

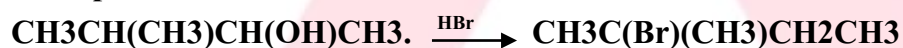
- I. Friedel – Crafts reaction – alkylation of anisole.
- II. Nitration of anisole.
- III. Bromination of anisole in ethanoic acid medium.
- IV. Freidel – Craft’s acetylation of anisole.

Answer:





Question :31 When 3-methylbutan-2-ol is treated with HBr , the following reaction takes place:



Give a mechanism for this reaction.

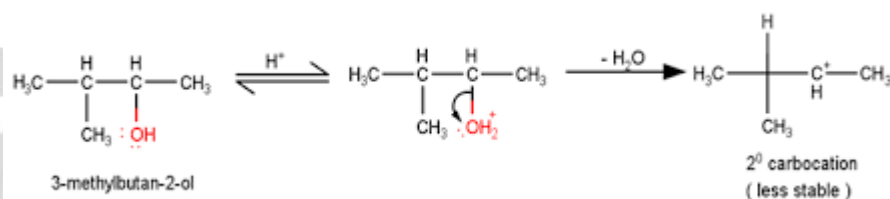
Answer:

The steps of the reaction given above involve the following procedure:

Step 1: protonation

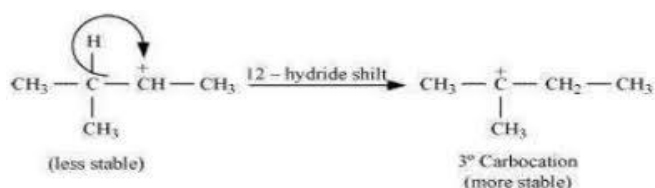
Step 2:

Forming 2° carbocation by eliminating the water molecule.



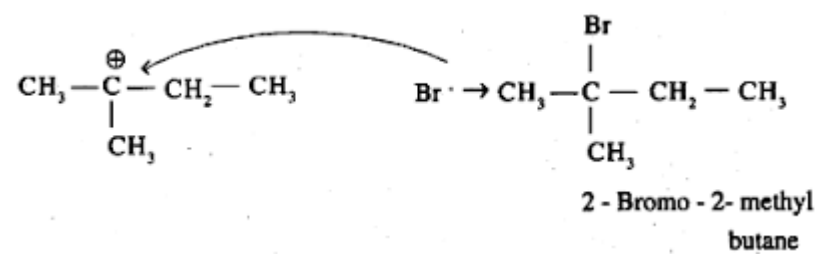
Step 3:

Re-arranging by the shifting hydride – ion



Step 4:

Nucleophilic attack.



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