Chapter 11

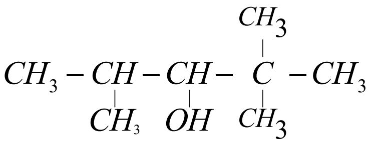
Alcohols phenols and ethers

NCERT Exercise

Question 1:

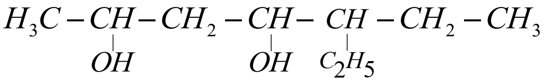
Write IUPAC names of the following compounds.

(i)



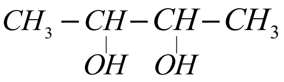
$$CH_3-\underset{CH_3}{\underset{|}{CH}}-\underset{OH}{\underset{|}{CH}}-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-CH_3$$

(ii)



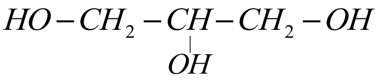
$$H_3C-\underset{OH}{\underset{|}{CH}}-CH_2-\underset{OH}{\underset{|}{CH}}-\underset{C_2H_5}{\underset{|}{CH}}-CH_2-CH_3$$

(iii)



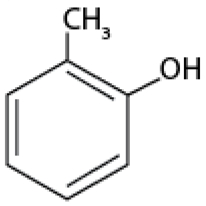
$$CH_3-\underset{OH}{\underset{|}{CH}}-\underset{OH}{\underset{|}{CH}}-CH_3$$

(iv)



$$HO-CH_2-\underset{OH}{\underset{|}{CH}}-CH_2-OH$$

(v)



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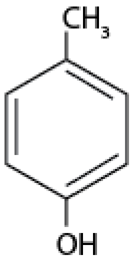

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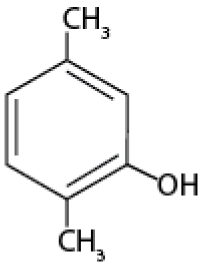

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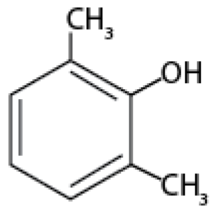
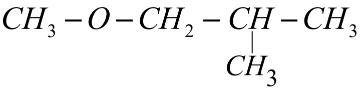
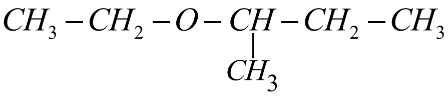


(ix) 
$CH_3-O-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3$

(x) $C_6H_5-O-C_2H_5$

(xi) C_6H_5-O-C_7H_{15}(n -)

(xii) 
$CH_3-CH_2-O-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-CH_3$

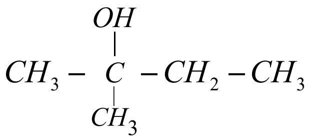
Solution 1:

(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

Question 2:

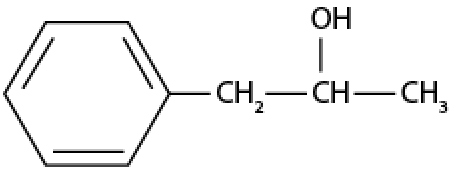
Write structures of the compounds whose IUPAC names are as follows:
(i) 2-Methylbutan-2-ol
(ii) 1-Phenylpropan-2-ol
(iii) 3,5-Dimethylhexane -1, 3, 5-triol
(iv) 2,3 -Diethylphenol
(v) 1 -Ethoxypropane
(vi) 2-Ethoxy-3-methylpentane
(vii) Cyclohexylmethanol
(viii) 3-Cyclohexylpentan-3-ol
(ix) Cyclopent-3-en-1-ol
(x) 3-Chloromethylpentan- 1-ol.

Solution 2:

(i)


$CH_3-\overset{OH}{\underset{CH_3}{C}}-CH_2-CH_3$

(ii)



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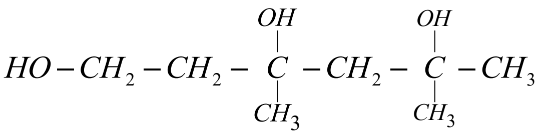
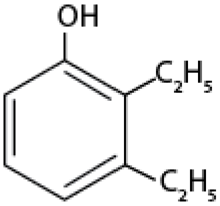
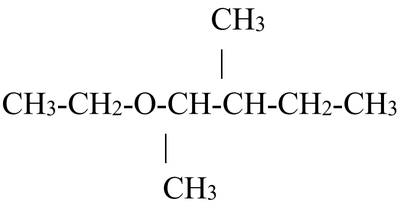


$HO-CH_2-CH_2-\overset{OH}{\underset{CH_3}{C}}-CH_2-\overset{OH}{\underset{CH_3}{C}}-CH_3$

(iv)

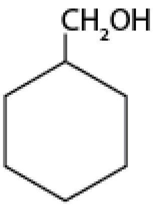


(v) $CH_3-CH_2-O-CH_2-CH_2-CH_3$

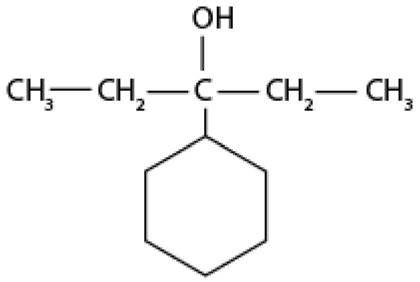
(VI)


$CH_3-CH_2-O-\underset{CH_3}{CH}-\overset{CH_3}{CH}-CH_2-CH_3$

(vii)



(viii)



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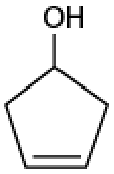
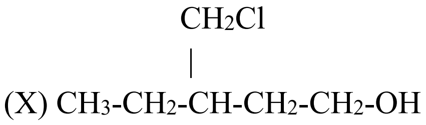




(X) $CH_3{-}CH_2{-}\overset{\overset{CH_2Cl}{|}}{CH}{-}CH_2{-}CH_2{-}OH$

Question 3:

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

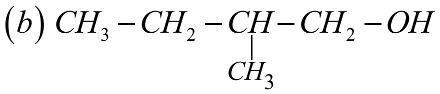
(ii) Classify the isomers of alcohols in question 11.3 (i) as primary, secondary and tertiary alcohols.

Solution 3:

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

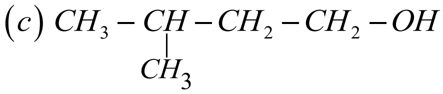
$(a)\ CH_3-CH_2-CH_2-CH_2-CH_2-OH$

Pentan-1-ol $(1°)$



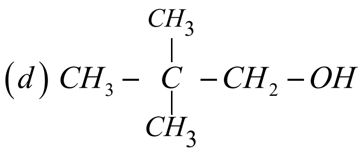
$(b)\ CH_3-CH_2-\underset{\underset{CH_3}{|}}{CH}-CH_2-OH$

2-Methylbutan-1-ol $(1°)$



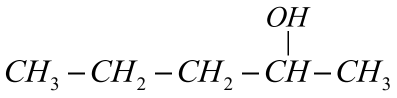
$(c)\ CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2-CH_2-OH$

3-Methlbutan-1-ol $(1°)$

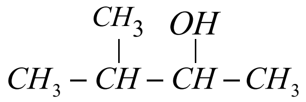


$(d)\ CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-OH$

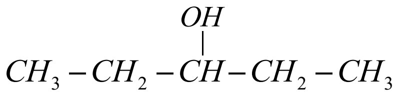
2, 2-Dimethylpropan-1-ol $(1°)$

(e)

$$CH_3-CH_2-CH_2-\overset{OH}{\overset{|}{C}H}-CH_3$$

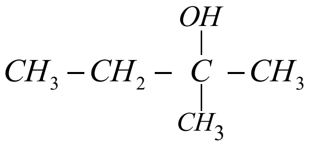
Pentan-2-ol $(2°)$

(f)

$$CH_3-\overset{CH_3}{\overset{|}{C}H}-\overset{OH}{\overset{|}{C}H}-CH_3$$

3-Methylbutan-2-ol $(2°)$

(g)

$$CH_3-CH_2-\overset{OH}{\overset{|}{C}H}-CH_2-CH_3$$

Pentan-3-ol $(2°)$

(h)

$$CH_3-CH_2-\underset{CH_3}{\underset{|}{\overset{OH}{\overset{|}{C}}}}-CH_3$$

2-Methylbutan-2-ol $(3°)$

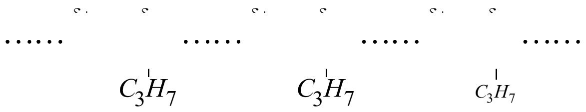
(ii) Primary alcohol: Pentan-1-ol; 2-Methylbutan-1-ol;
3-Methylbutan-1-ol; 2, 2—Dimethylpropan- 1-ol
Secondary alcohol: Pentan-2-ol; 3-Methylbutan-2-ol;
Pentan-3-ol
Tertiary alcohol: 2-methylbutan-2-ol

Question 4:

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

Solution 4:

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



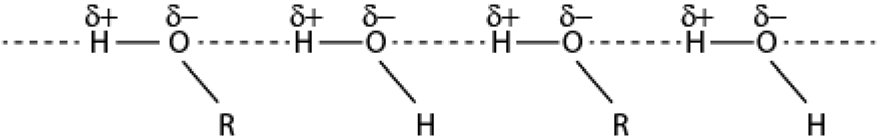
Therefore, extra energy is required to break hydrogen bonds. For this reason, propanol has a higher boiling point than hydrocarbon butane.

Question 5:

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

Solution 5:

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



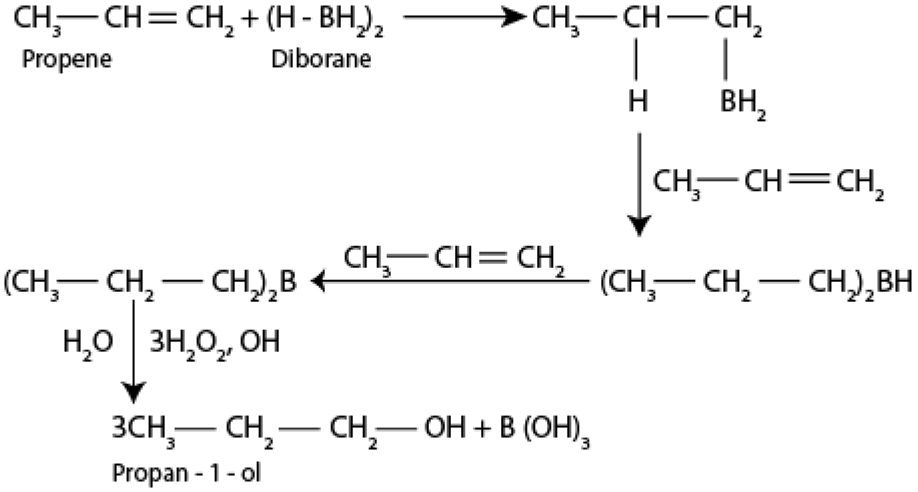
As a result, alcohols are comparatively more soluble in water than hydrocarbons of Comparable molecular masses.

Question 6:

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

Solution 6:

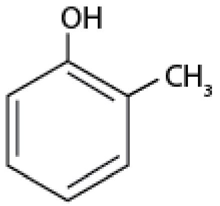
The addition of borane followed by oxidation is known as the hydroboration-oxidation reaction, For example, propan-l-ol is produced by the hydroboration-oxidation reaction of propene. In this reaction, propene reacts with diborane $(BH_3)_2$ to form trialkylborane as an addition product. This addition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



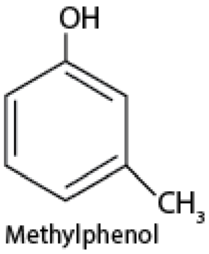
Question 7:

Give the structures and IUPAC names of monohydric phenols of molecular formula, C_7H_8O .

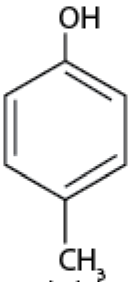
Solution 7:



2 - Methylphenol
(*o*-Cresol)



3 - Methylphenol
(*m*-Cresol)



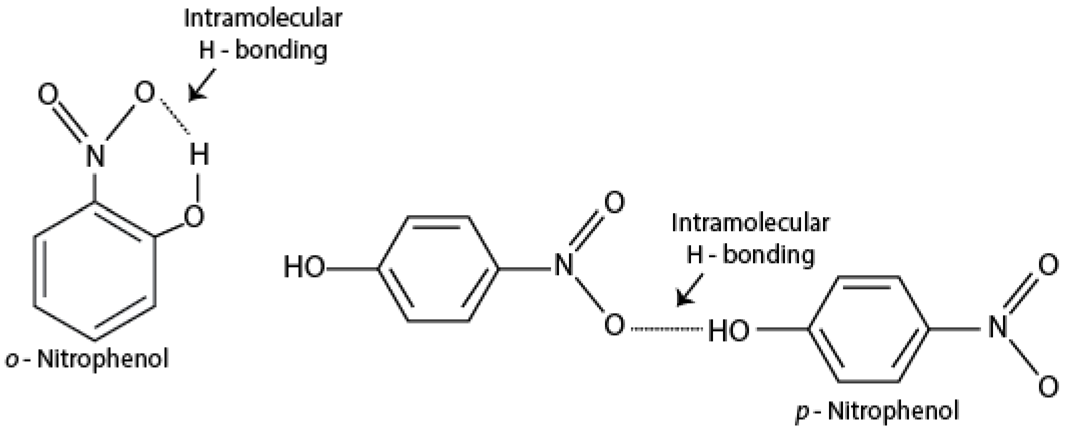
4 - Methylphenol
(*p*-Cresol)

Question 8:

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

Solution 8:

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

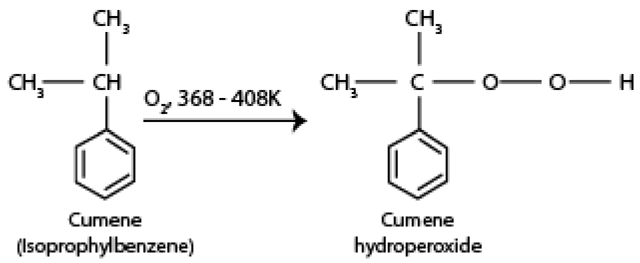


Question 9:

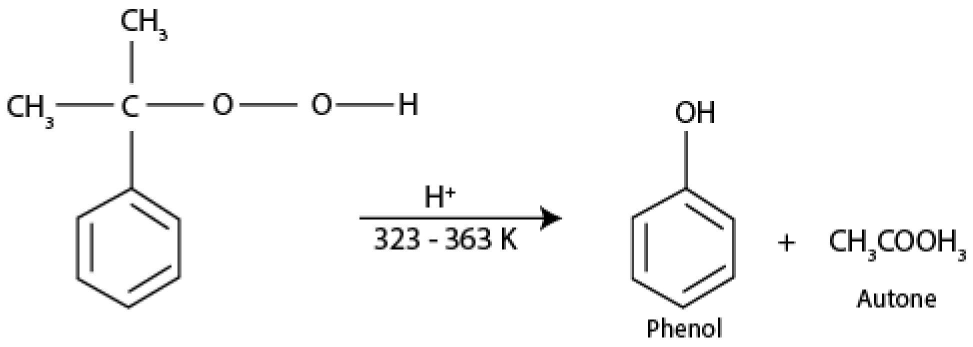
Give the equations of reactions for the preparation of phenol from cumene.

Solution 9:

To prepare phenol, cumene is first oxidized in the presence of air of cumene hydroperoxide.



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

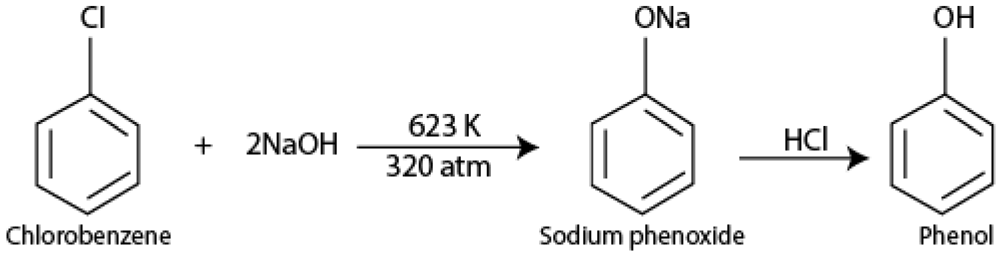


Question 10:

Write chemical reaction for the preparation of phenol from chlorobenzene.

Solution 10:

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



Question 11:

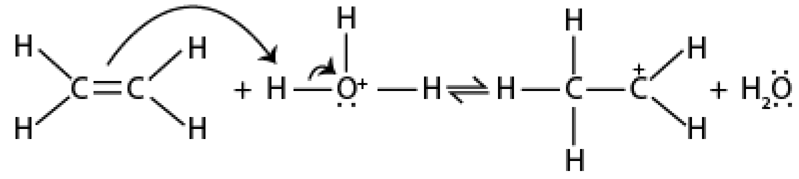
Write the mechanism of hydration of ethene to yield ethanol.

Solution 11:

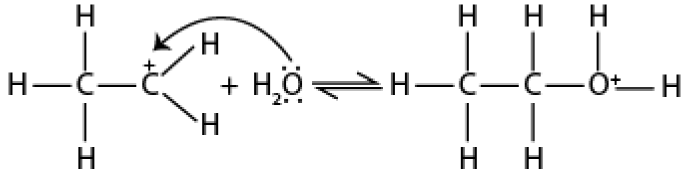
The mechanism of hydration of ethene to form ethanol involves three steps.

Step 1: Protonation of ethene to form carbocation by electrophilic attack of H_3O^+:

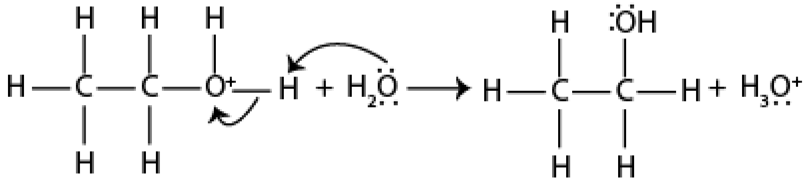
$$H_2O + H^+ \longrightarrow H_3O^+$$



Step 2: Nucleophilic attack of water on carbocation:



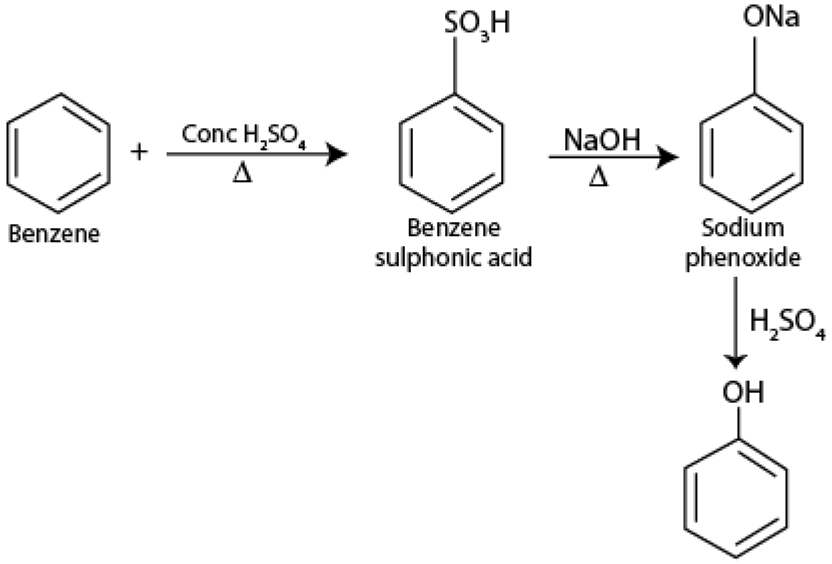
Step 3: Deprotonation to form ethanol :



Question 12:

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

Solution 12:



Question 13:

Show how will you synthesize:

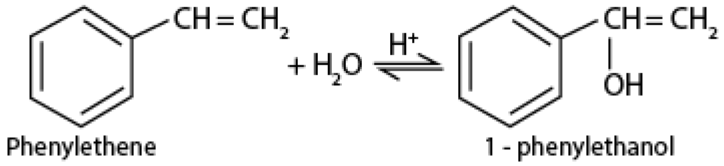
(I) 1-phenylethanol from a suitable alkene.

(ii) cyclohexylmethanol using an alkyl halide by an S_N^2 reaction.

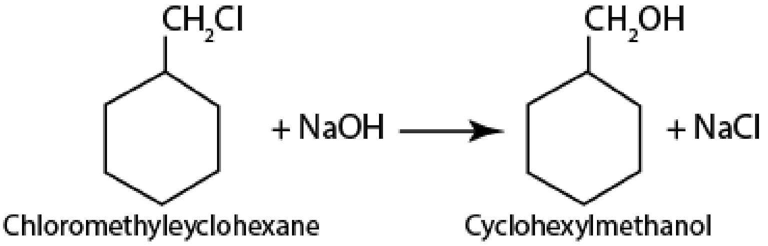
(iii) pentan-1-ol using a suitable alkyl halide?

Solution 13:

(i) By acid-catalysed 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.

$$\underset{1-Chloropentane}{CH_3CH_2CH_2CH_2CH_2Cl} + NaOH \longrightarrow \underset{Pantan-1-ol}{CH_3CH_2CH_2CH_2CH_2OH} + NaCl$$

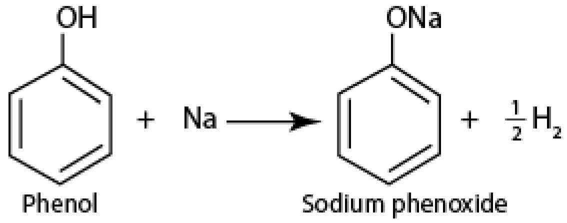
Question 14:

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

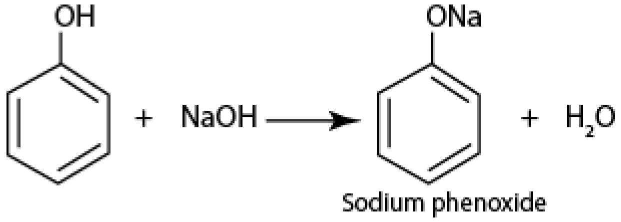
Solution 14:

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

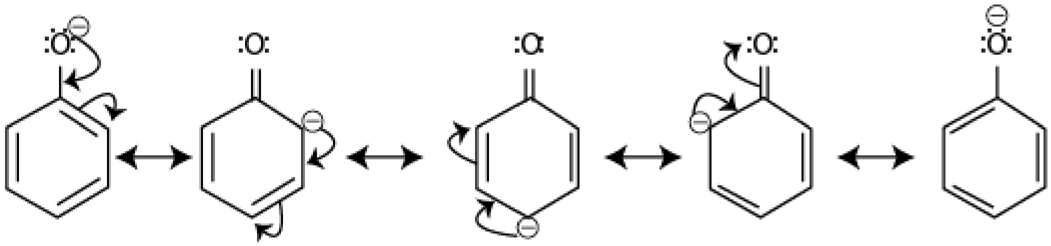
(i) Phenol reacts with sodium to give sodium phenoxide, liberating H_2.



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



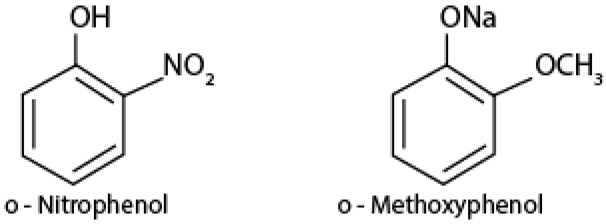
The acidity of phenol is more than that of ethanol. This is because after losing a proton, the phenoxide ion undergoes resonance and gets stabilized whereas ethoxide ion does not.



Question 15:

Explain why is ortho nitrophenol more acidic than ortho methoxyphenol?

Solution 15:



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.

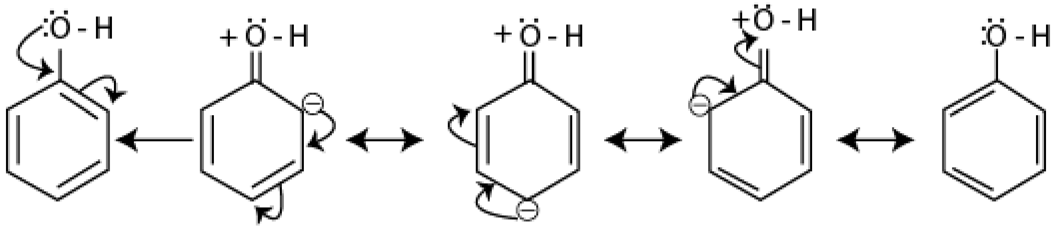
On the other hand, methoxy group is an electron-releasing group. Thus, it increases the electron density in the O—H bond and hence, the proton cannot be given out easily. For this reason, ortho-nitrophenol is more acidic than ortho-methoxyphenol.

Question 16:

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

Solution 16:

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



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

Question 17:

Give equations of the following reactions:

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

(ii) Bromine in CS_2 with phenol.

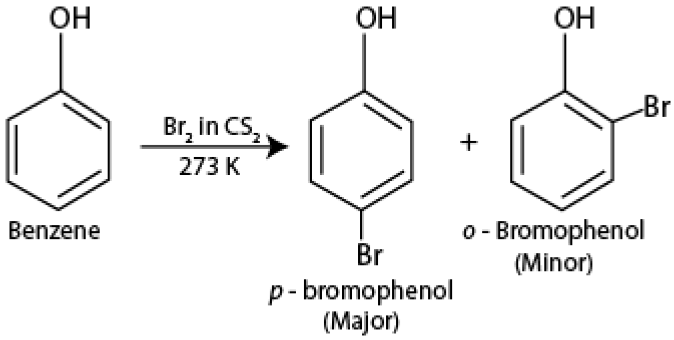
(iii) Dilute HNO_3 with phenol.

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

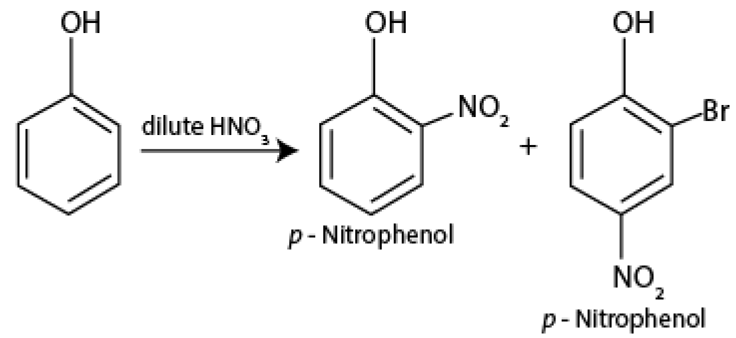
Solution 17:

$$\underset{\text{Propan-l-ol}}{CH_3CH_2CH_2OH} \xrightarrow{alk\ KmnO_4} \underset{\text{Propanic acid}}{CH_3CH_2COOH}$$

(ii)



(iii)



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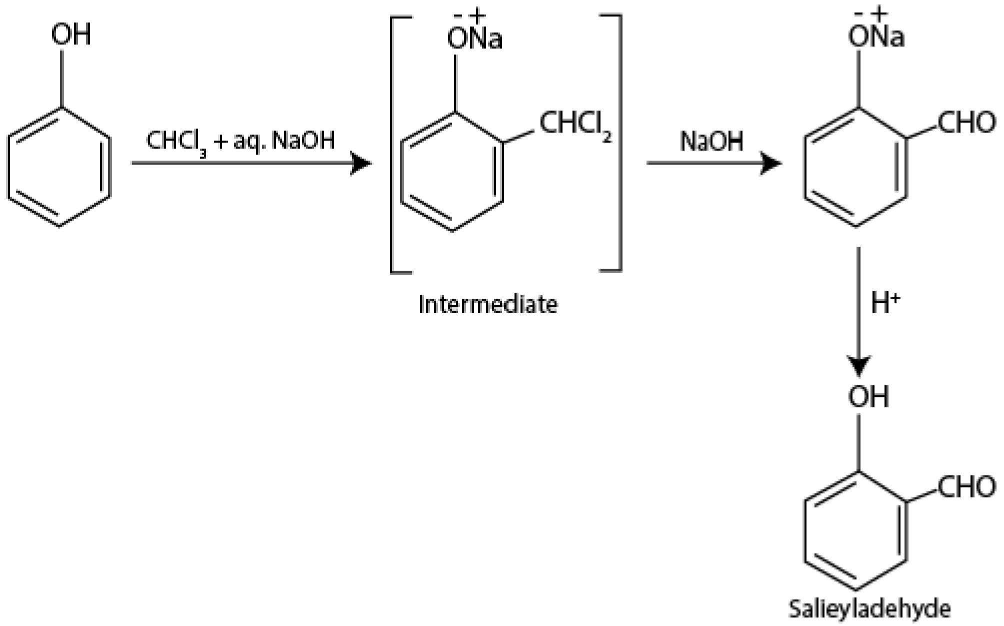


Question 18:

Explain the following with an example.

(i) Kolbe's reaction.

(ii) Reimer-Tiemann reaction.

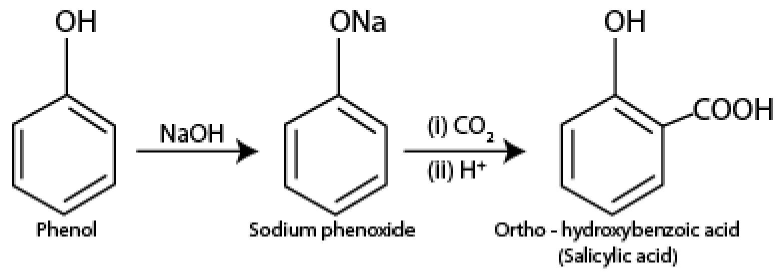
(iii) Williamson ether synthesis.

(iv) Unsymmetrical ether

Solution 18:

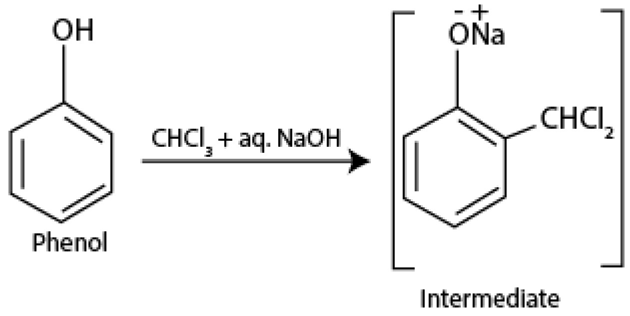
(i) Kolbe's reaction:

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.



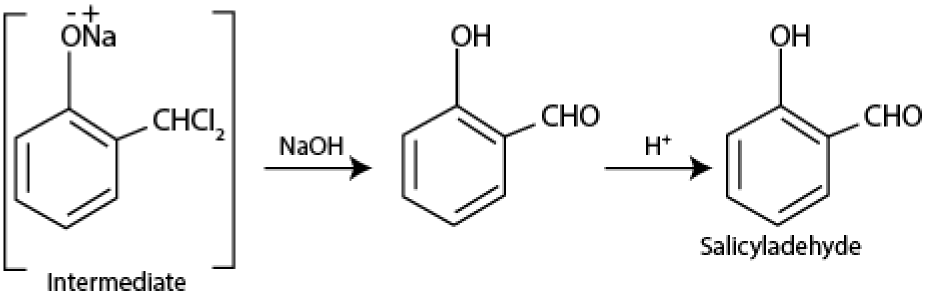
(ii) Reimer-Tiemann reaction:

When phenol is treated with chloroform ($CHCl_3$) in the presence of sodium hydroxide, a-CHO group is introduced at the ortho position of the benzene ring.



This reaction is known as the Reimer-Tiemann reaction.

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



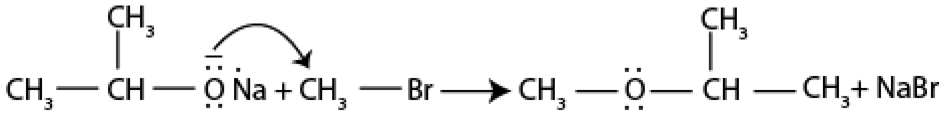
(iii) Williamson ether synthesis

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

$R - X + R' -$ aX

Alkl halide *Sodium*

This reaction involves S_N2 attack of the alkoxide ion on the alkyl halide. Better results are obtained in case of primary alkyl halides.



$$CH_3-\underset{}{\overset{CH_3}{\overset{|}{C}H}}-\ddot{O}\,Na+CH_3-Br\longrightarrow CH_3-\ddot{O}-\overset{CH_3}{\overset{|}{C}H}-CH_3+NaBr$$

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 $(CH_3-O-CH_2CH_3)$.

Question 19:

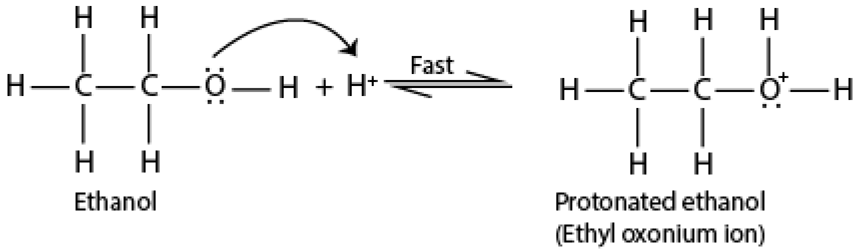
Write the mechanism of acid-catalyzed dehydration of ethanol to yield ethene.

Solution 19:

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

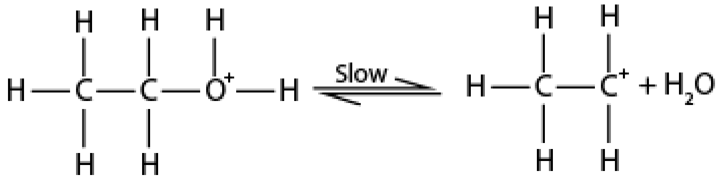
Step 1:

Protonation of ethanol to form ethyl oxonium ion:



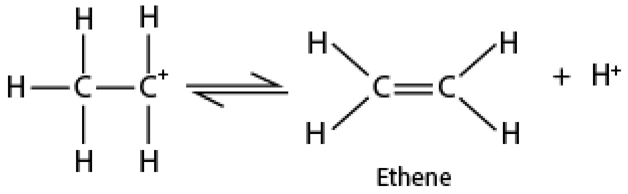
Step 2:

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.

Question 20:

How are the following conversions carried Out?

(i) Propene → Propan-2-ol

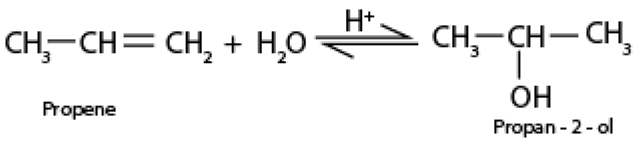
(ii) Benzyl chloride. →Benzyl alcohol

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

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

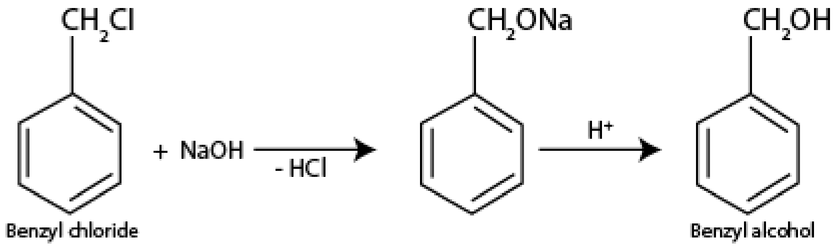
Solution 20:

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

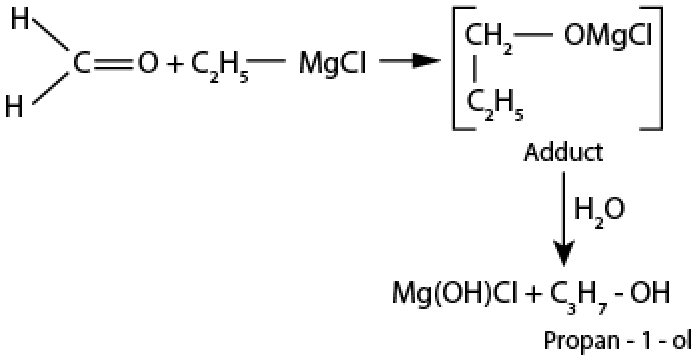


$$CH_3-CH=CH_2 + H_2O \overset{H^+}{\rightleftharpoons} CH_3-\underset{OH}{\underset{|}{CH}}-CH_3$$

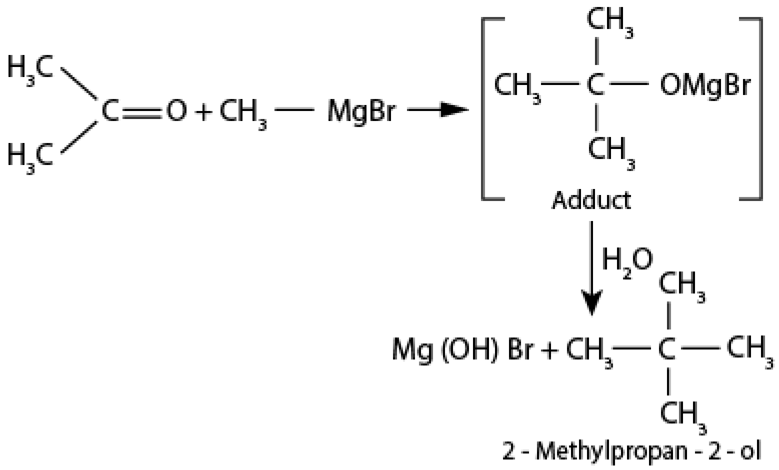
(ii) If benzyl chloride is treated with $NaOH$ (followed by acidification) then benzyl alcohol is produced.



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



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



Question 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 21:

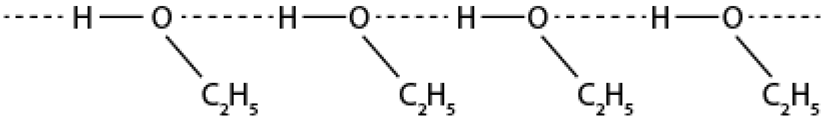
(i) Acidified potassium permanganate
(ii) Pyridinium chlorochromate (PCC)
(iii) Bromine water
(iv) Acidified potassium permanganate
(v) 85% phosphoric acid at 440 K
(vi) $NaBH_4 \text{ or } LiAlH_4$

Question 22:

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

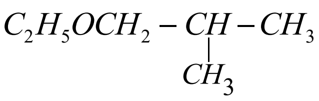
Solution 22:

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 23:

Give IUPAC names of the following ethers:

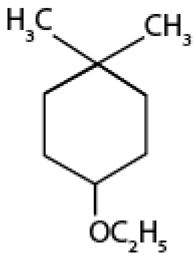
(i) 
$C_2H_5OCH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3$

(ii) $CH_3OCH_2CH_2Cl$

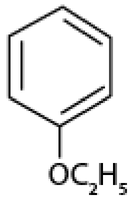
(iii) $O_2N-C_6H_4-OCH_{3(p)}$

(iv) $CH_3CH_2CH_2OCH_3$

(v)



(vi)



Solution 23:

(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 24:

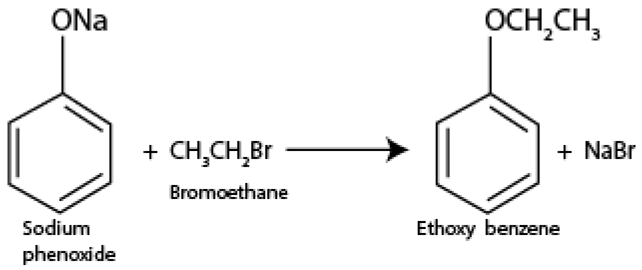
Write the names of reagents and equations for the preparation of the following ethers by Williamson's synthesis:

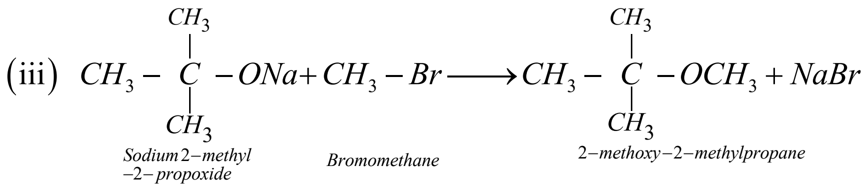
(I) 1-Propoxypropane
(ii) Ethoxybenzene
(iii) 2-Methoxy-2-methylpropane
(iv) 1-Methoxyethane

Solution 24:

(i) $\underset{Sodium\ propoxide}{CH_3CH_2CHONa} + \underset{1-Bromopropane}{CH_3CH_2CH_2Br} \longrightarrow \underset{1-Propoxypropane}{C_2H_5CH_2-O-CH_2C_2H_5} + NaBr$

(ii)



(iii)


$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-ONa+CH_3-Br\longrightarrow CH_3-\underset{CH_3}{\overset{CH_3}{C}}-OCH_3+NaBr$$

Sodium 2−methyl −2−propoxide; Bromomethane; 2−methoxy−2−methylpropane

(iv) $\underset{\text{Sodium ethoxide}}{CH_3CH_2-ONa}+\underset{\text{Bromomethane}}{CH_3-Br}\longrightarrow\underset{\text{1−Methoxyethane}}{CH_3CH_2-O-CH_3}+NaBr$

Question 25:

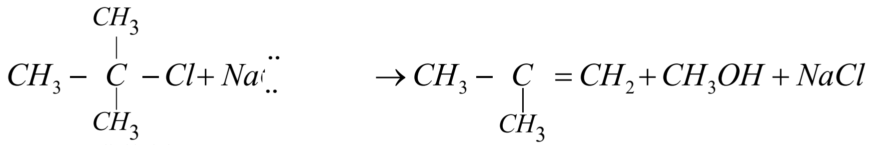
Illustrate with examples the limitations of Williamson synthesis for the preparation of certain types of ethers.

Solution 25:

The reaction of Williamson synthesis involves S_N2 attack of an alkoxide ion on a primary alkyl halide.

$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}- \qquad\qquad CH_3 \qquad +NaCl$$

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.



$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-Cl+Na \rightarrow CH_3-\underset{CH_3}{C}=CH_2+CH_3OH+NaCl$$

Teritary alkyl halide; Alkene

Question 26:

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

Solution 26:

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.

$$2CH_3CH_2CH_2-OH\xrightarrow{H^+}CH_3CH_2CH_2-O-CH_2CH_2CH_3$$

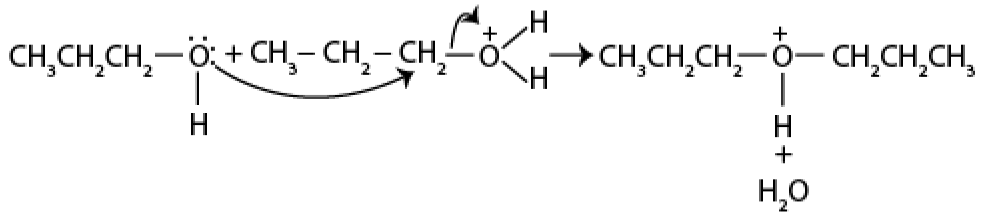
Propan-1-ol 1-propoxypropane

The mechanism of this reaction involves the following three steps:

Step 1: Protonation

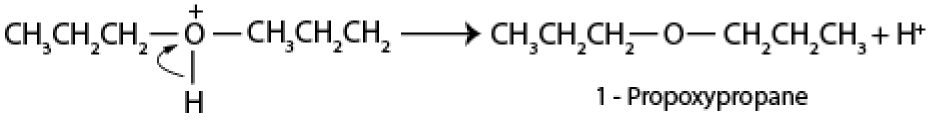
$\underset{\text{popan−1−ol}}{CH_3CH_2CH_2-}$

Step 2: Nucleophilic attack



$$CH_3CH_2CH_2-\underset{H}{\underset{|}{\ddot{O}}}: + CH_3-CH_2-CH_2-\overset{+}{O}H_2 \rightarrow CH_3CH_2CH_2-\underset{H}{\underset{|}{\overset{+}{O}}}-CH_2CH_2CH_3 + H_2O$$

Step 3:Deprotonation



$$CH_3CH_2CH_2-\underset{H}{\underset{|}{\overset{+}{O}}}-CH_2CH_2CH_3 \longrightarrow \underset{\text{1 - Propoxypropane}}{CH_3CH_2CH_2-O-CH_2CH_2CH_3} + H^+$$

Question 27:

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

Solution 27:

The formation of ethers by dehydration of alcohol is a bimolecular reaction (S_N2) 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 28:

Write the equation of the reaction of hydrogen iodide with:

(i) 1-propoxypropane

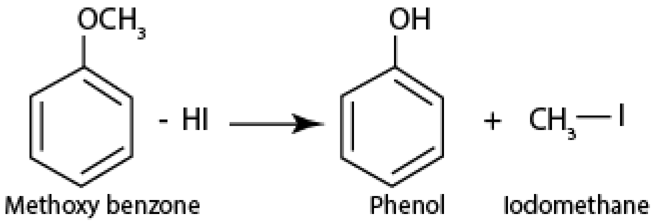
(ii) Methoxybenzene and

(iii) Benzylethylether

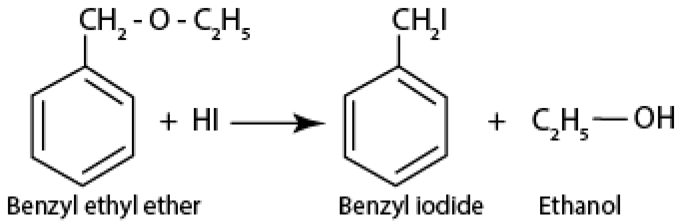
Solution 28:

(i) $\underset{\text{1−Propoxypropane}}{C_2H_5CH_2-O-CH_2C_2H_5} + HI \xrightarrow{373K} \underset{\text{Propan−1−ol}}{CH_3CH_2CH_2-OH} + \underset{\text{1−Iodopropane}}{CH_3CH_2CH_3-I}$

(ii)



(iii)



Question 29:

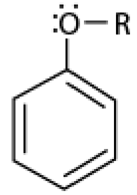
Explain the fact that in aryl alkyl ethers.

(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.

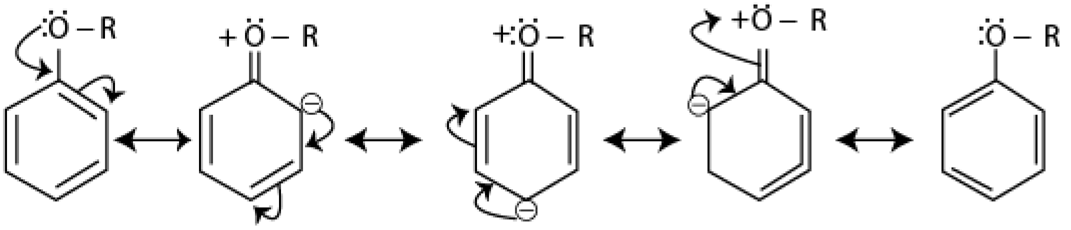
Solution 29:

(i)



Aryl alkyl ether

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 30:

Write the mechanism of the reaction of HI with methoxymethane.

Solution 30:

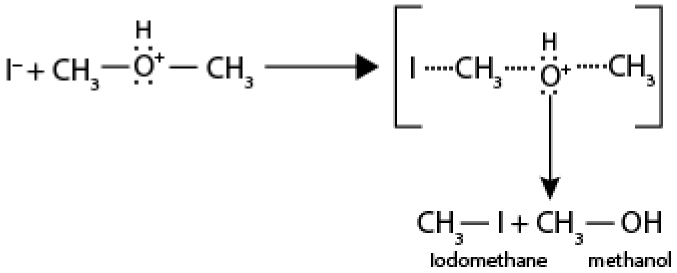
The mechanism of the reaction of HI with methoxymethane involves the following steps:

Step 1: Protonation of methoxymethane:

$$CH_3-\ddot{O}-CH_3+H-I \rightleftharpoons CH_3-\overset{H}{\ddot{O}^+}-CH_3+I^-$$

Step2: Nucleophilic attack of I^{-}:

(Iodide ion is a good nucleophile. It attacks the least substituted carbon of the oxonium ion formed in step 1 and displaces an alcohol molecule by S_N2 reaction)



$$I^-+CH_3-\overset{H}{\ddot{O}^+}-CH_3 \longrightarrow \left[I\cdots CH_3\cdots\overset{H}{\ddot{O}^+}\cdots CH_3\right] \longrightarrow \underset{\text{Iodomethane}}{CH_3-I}+\underset{\text{methanol}}{CH_3-OH}$$

Step 3:

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

$$CH_3-\ddot{O}-H+H-I \rightleftharpoons CH_3-\overset{H}{\ddot{O}^+}H+I^-$$

$$I^- + CH_3 - \overset{+}{O}H_2 \longrightarrow CH_3 - I + H_2O$$

Question 31:

Write equations of the following reactions:

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

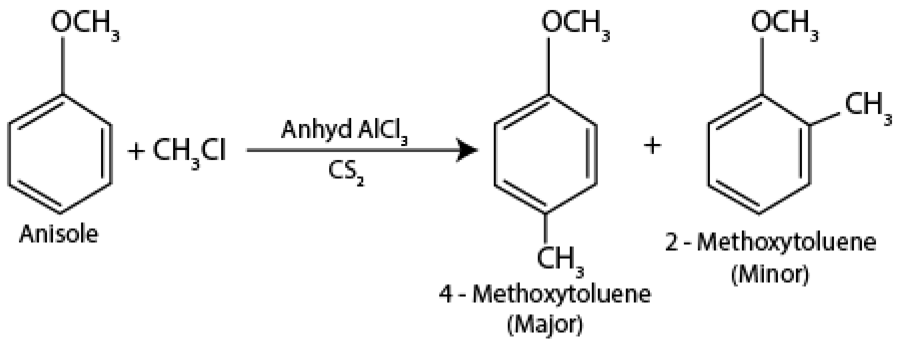
(ii) Nitration of anisole.

(iii) Bromination of anisole in ethanoic acid medium.

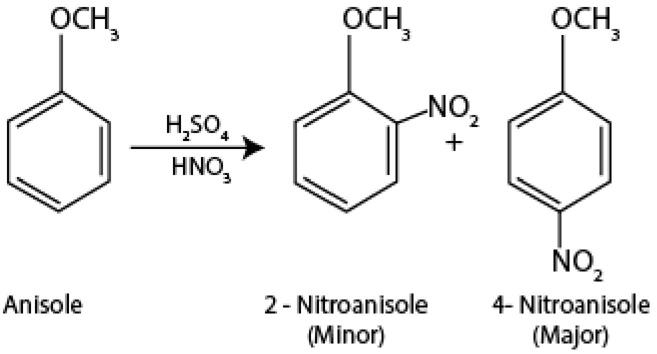
(iv) Friedel-Craft’s acetylation of anisole.

Solution 31:

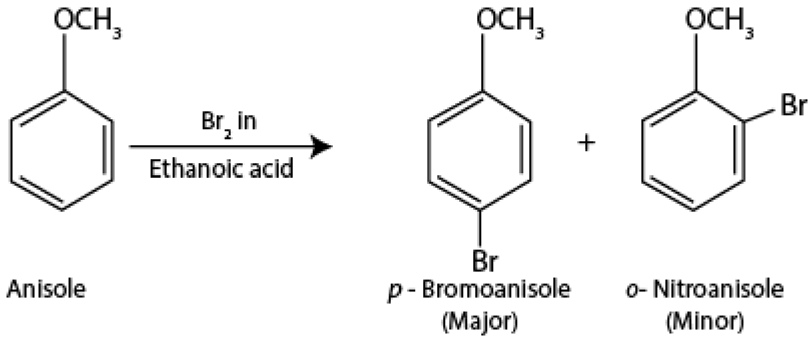
(i)


OCH3
Anisole
+ CH3Cl
Anhyd AlCl3
CS2
OCH3
CH3
4 - Methoxytoluene
(Major)
+
OCH3
CH3
2 - Methoxytoluene
(Minor)

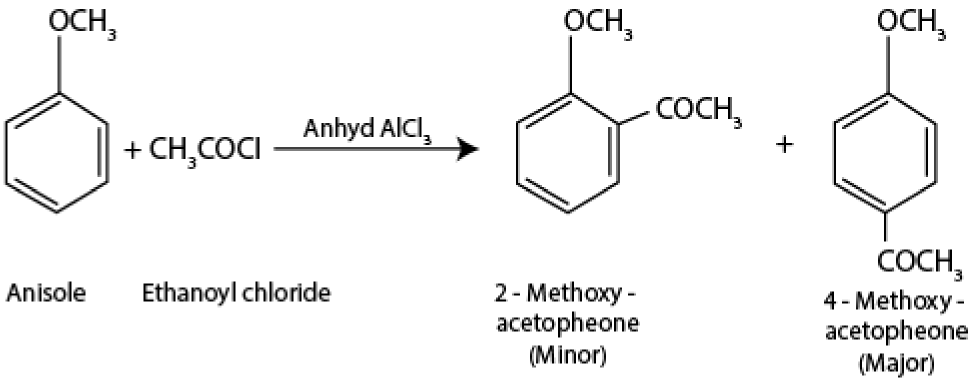
(ii)


OCH3
Anisole
H2SO4
HNO3
OCH3
NO2
2 - Nitroanisole
(Minor)
+
OCH3
NO2
4- Nitroanisole
(Major)

(iii)


OCH3
Anisole
Br2 in
Ethanoic acid
OCH3
Br
p - Bromoanisole
(Major)
+
OCH3
Br
o- Nitroanisole
(Minor)

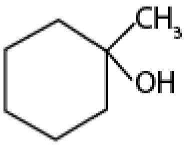
(iv)


OCH3
Anisole
+ CH3COCl
Ethanoyl chloride
Anhyd AlCl3
OCH3
COCH3
2 - Methoxy - acetopheone
(Minor)
+
OCH3
COCH3
4 - Methoxy - acetopheone
(Major)

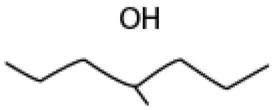
Question 32:

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

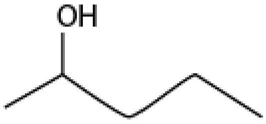
(i)



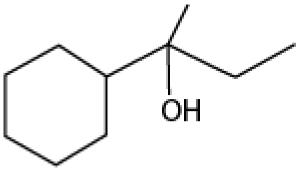
(ii)



(iii)



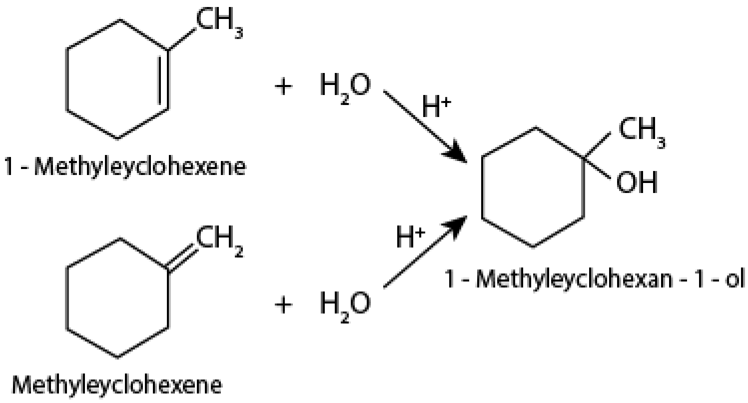
(iv)



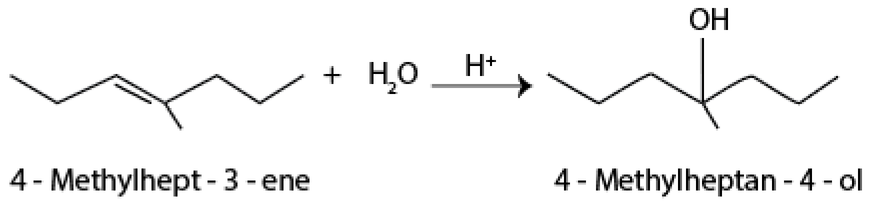
Solution 32:

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

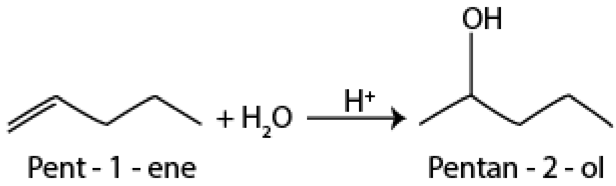
(i)



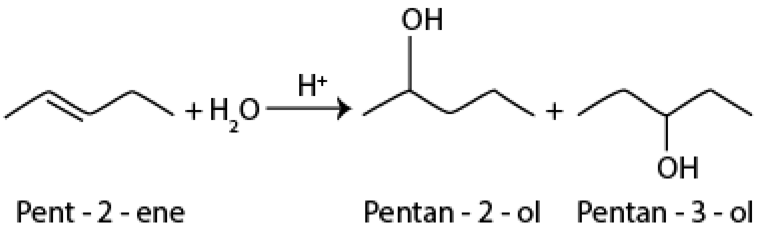
(ii)



(iii)

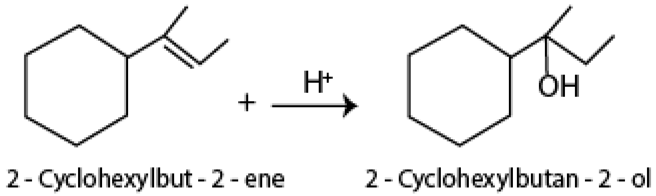


Acid-catalysed hydration of pent-2-ene also produces pentan-2-ol but along with pentan-3-ol.



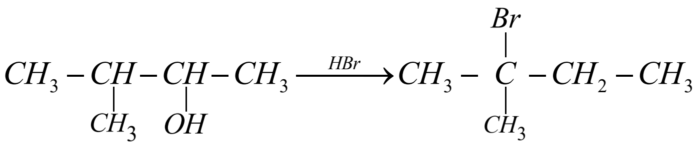
Thus, the first reaction is preferred over the second one to get pentan-2-ol.

(iv)



Question 33:

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



$$CH_3-\underset{CH_3}{\underset{|}{C}H}-\underset{OH}{\underset{|}{C}H}-CH_3 \xrightarrow{HBr} CH_3-\overset{Br}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-CH_2-CH_3$$

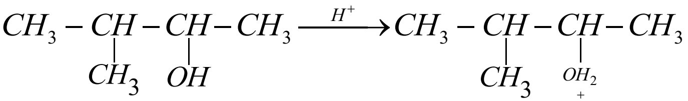
Give a mechanism for this reaction.

(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 33:

The mechanism of the given reaction involves the following steps:

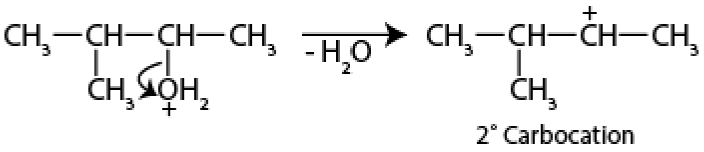
Step 1: Protonation



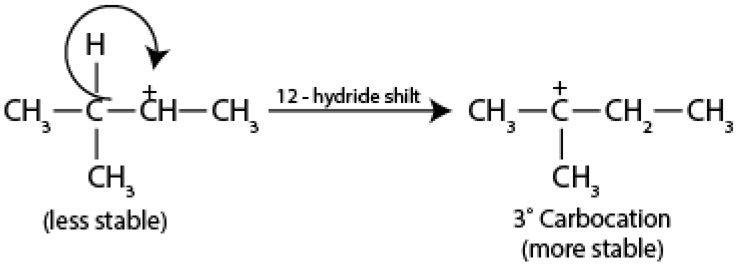
$$CH_3-\underset{CH_3}{\underset{|}{C}H}-\underset{OH}{\underset{|}{C}H}-CH_3 \xrightarrow{H^+} CH_3-\underset{CH_3}{\underset{|}{C}H}-\underset{\underset{+}{OH_2}}{\underset{|}{C}H}-CH_3$$

3-Methylbutan-2-ol

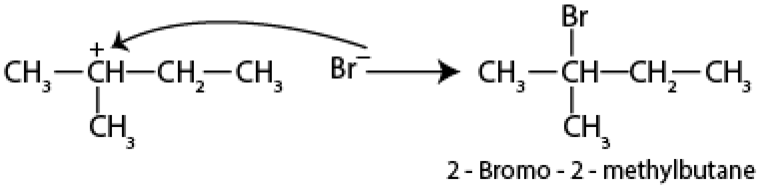
Step 2: Formation of 2° carbocation by the elimination of a water molecule



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



Step 4: Nucleophilic attack

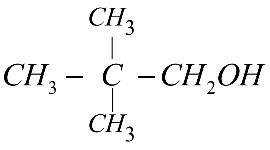


Text solution

Question 1:

Classify the following as primary, secondary and tertiary alcohols:

(i)

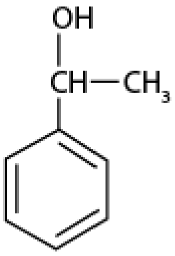


$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2OH$$

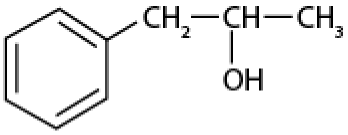
(ii) $H_2C=CH-CH_2OH$

(iii) $CH_3-CH_2-CH_2-OH$

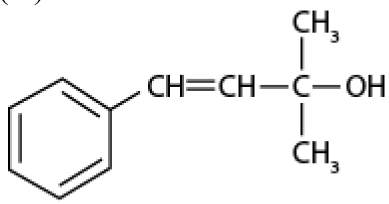
(iv)



(v)



(vi)



Solution 1:

Primary alcohol → (i), (ii), (iii)

Secondary alcohol → (iv), (v)

Tertiary alcohol →(vi)

Question 2:

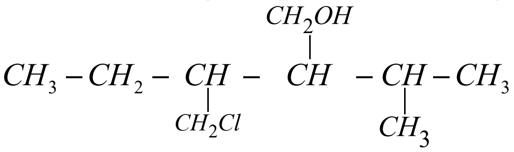
Identify allylic alcohols in the above examples.

Solution 2:

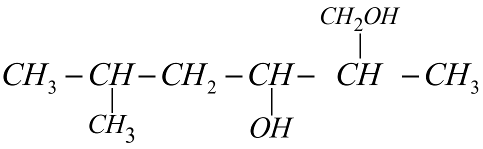
The alcohols given in (ii) and (vi) are allylic alcohols.

Question 3:

Name the following compounds according to IUPAC system.

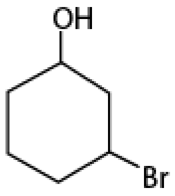
(i) 

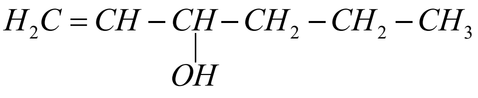
$$CH_3-CH_2-\underset{CH_2Cl}{CH}-\overset{CH_2OH}{CH}-\underset{CH_3}{CH}-CH_3$$

(ii) 

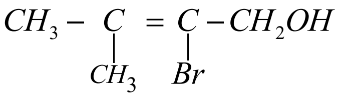
$$CH_3-\underset{CH_3}{CH}-CH_2-\underset{OH}{CH}-\overset{CH_2OH}{CH}-CH_3$$

(iii)



(iv)


$H_2C=CH-\underset{\underset{OH}{|}}{CH}-CH_2-CH_2-CH_3$

(v)


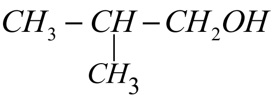
$CH_3-\underset{\underset{CH_3}{|}}{C}=\underset{\underset{Br}{|}}{C}-CH_2OH$

Solution 3:

(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

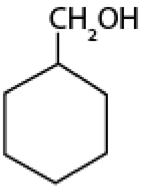
Question 4:

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

(i)


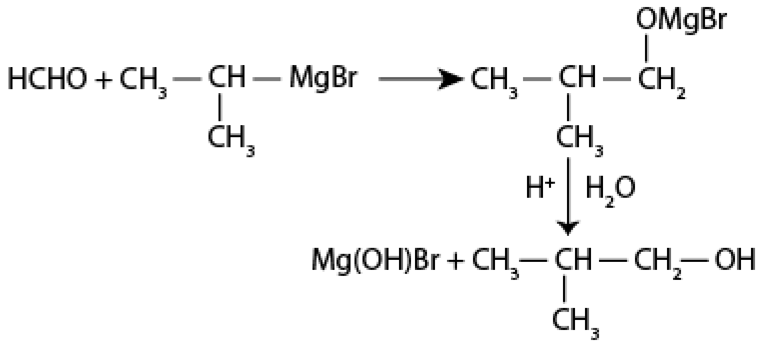
$CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2OH$

(ii)

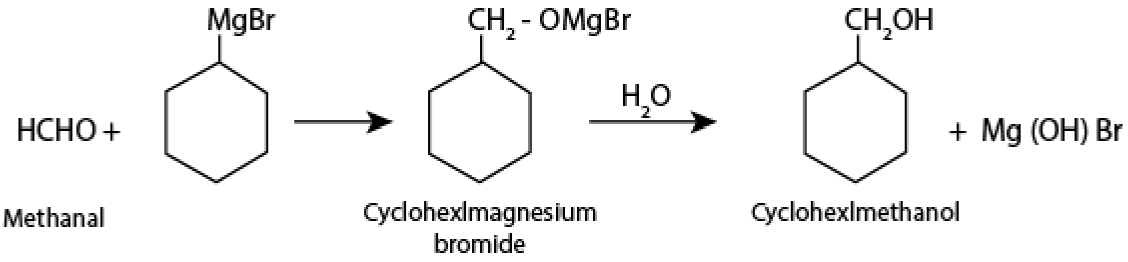


Solution 4:

(i)



(ii)



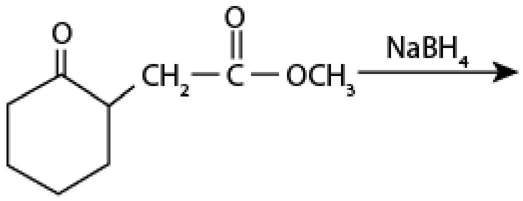
Question 5:

Write structures of the products of the following reactions:

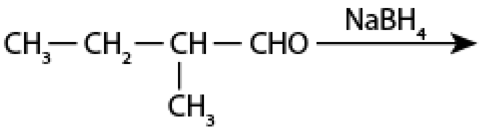
(i)

$$CH_3-CH=CH_2 \xrightarrow{H_2O/H^+}$$

(ii)



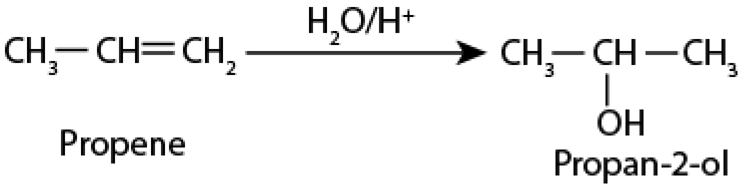
(iii)



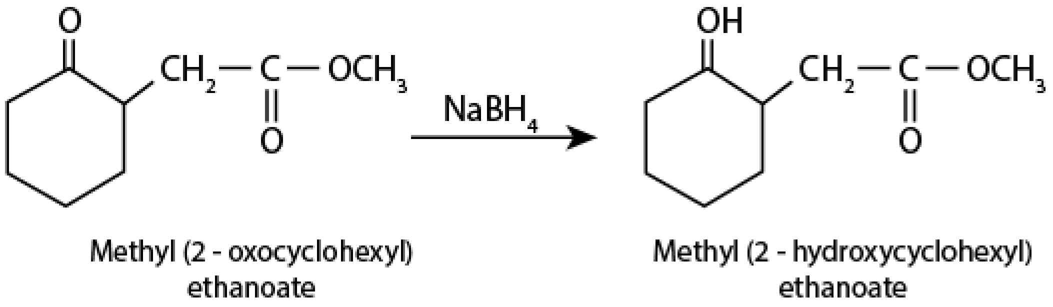
$$CH_3-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CHO \xrightarrow{NaBH_4}$$

Solution 5:

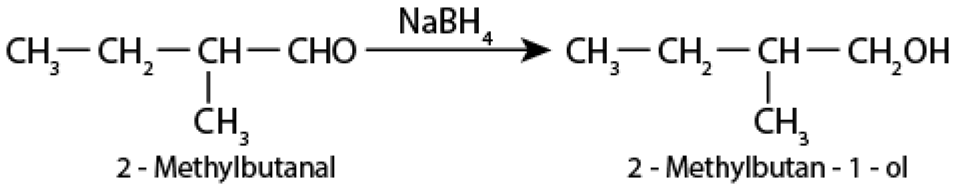
(i)



(ii)



(iii)



Question 6:

Give structures of the products you would expect when each of the following alcohol reacts with (a) $HCl-ZnCl_2$ (b) HBr and (c) $SOCl_2$.

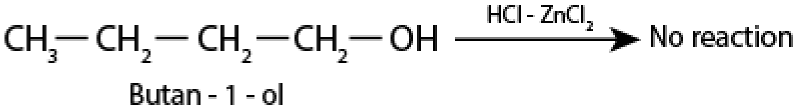
(i) Butan-1-ol

(ii) 2-Methylbutan-2-ol

Solution 6:

(a)

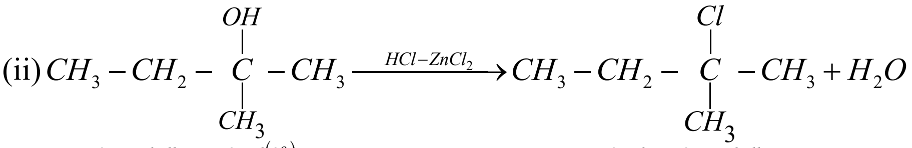
(i)



$$CH_3-CH_2-CH_2-CH_2-OH \xrightarrow{HCl-ZnCl_2} \text{No reaction}$$

Butan - 1 - ol

Primary alcohols do not react appreciably with Lucas’ reagent $(HCl-ZnCl_2)$ at room Temperature.



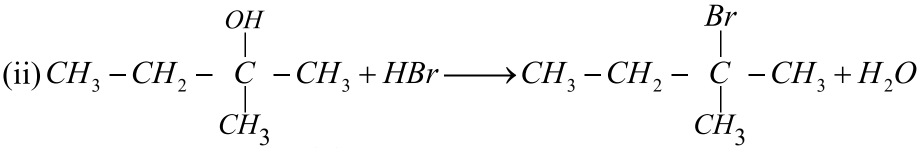
(ii) $$CH_3-CH_2-\overset{OH}{\underset{CH_3}{\overset{|}{\underset{|}{C}}}}-CH_3\xrightarrow{HCl-ZnCl_2}CH_3-CH_2-\overset{Cl}{\underset{CH_3}{\overset{|}{\underset{|}{C}}}}-CH_3+H_2O$$

$2-Methylbutan-2-ol(3^o)$ $2-cloro-2-Methylbutane$ $(White\ turbidity)$

Tertiary alcohols react immediately with Lucas' reagent.

(b)

(i) $$\underset{Butan-1-ol}{CH_3CH_2CH_2CH_2OH}+HBr\longrightarrow\underset{1-Bromobutane}{CH_3CH_2CH_2CH_2Br}$$



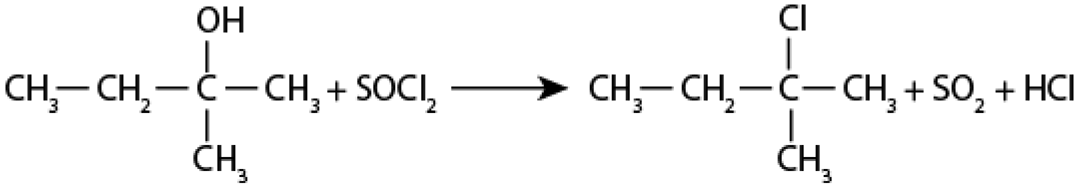
(ii) $$CH_3-CH_2-\overset{OH}{\underset{CH_3}{\overset{|}{\underset{|}{C}}}}-CH_3+HBr\longrightarrow CH_3-CH_2-\overset{Br}{\underset{CH_3}{\overset{|}{\underset{|}{C}}}}-CH_3+H_2O$$

$2-Methylbutan-2-ol(3^o)$ $2-Bromo-2-Methylbutane$

(c)

(i) $$\underset{Butan-1-ol}{CH_3CH_2CH_2CH_2OH}+SOCl_2\longrightarrow\underset{1-Chlorobutane}{CH_3CH_2CH_2CH_2Cl}+SO_2+HCl$$

(ii)



$$CH_3-CH_2-\overset{OH}{\underset{CH_3}{\overset{|}{\underset{|}{C}}}}-CH_3+SOCl_2\longrightarrow CH_3-CH_2-\overset{Cl}{\underset{CH_3}{\overset{|}{\underset{|}{C}}}}-CH_3+SO_2+HCl$$

2 - Methylbutan - 2 - ol 2 - Chloro - 2 - Methylbutane

Question 7:

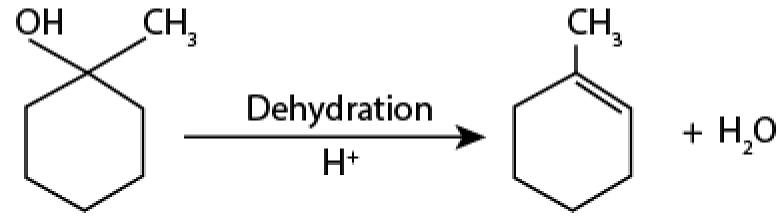
Predict the major product of acid catalyzed dehydration of

(i) 1-methylcyclohexanol and

(ii) butan-1-ol

Solution 7:

(i)



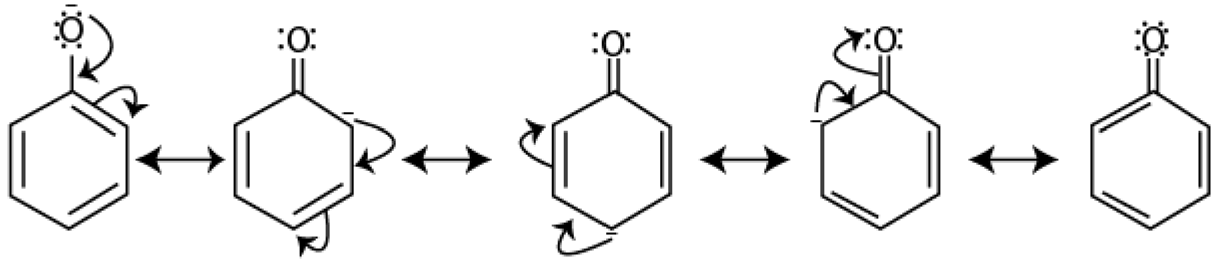
1 - Methylcyclohexanol 1 - Methylcyclohexene (Major product)

(ii) $\underset{Butan-1-ol}{CH_3CH_2CH_2CH_2OH} \xrightarrow[H^+]{Dehydration} \underset{\substack{But-2-ene \\ (Major\ product)}}{CH_3CH = CHCH_3} + H_2O$

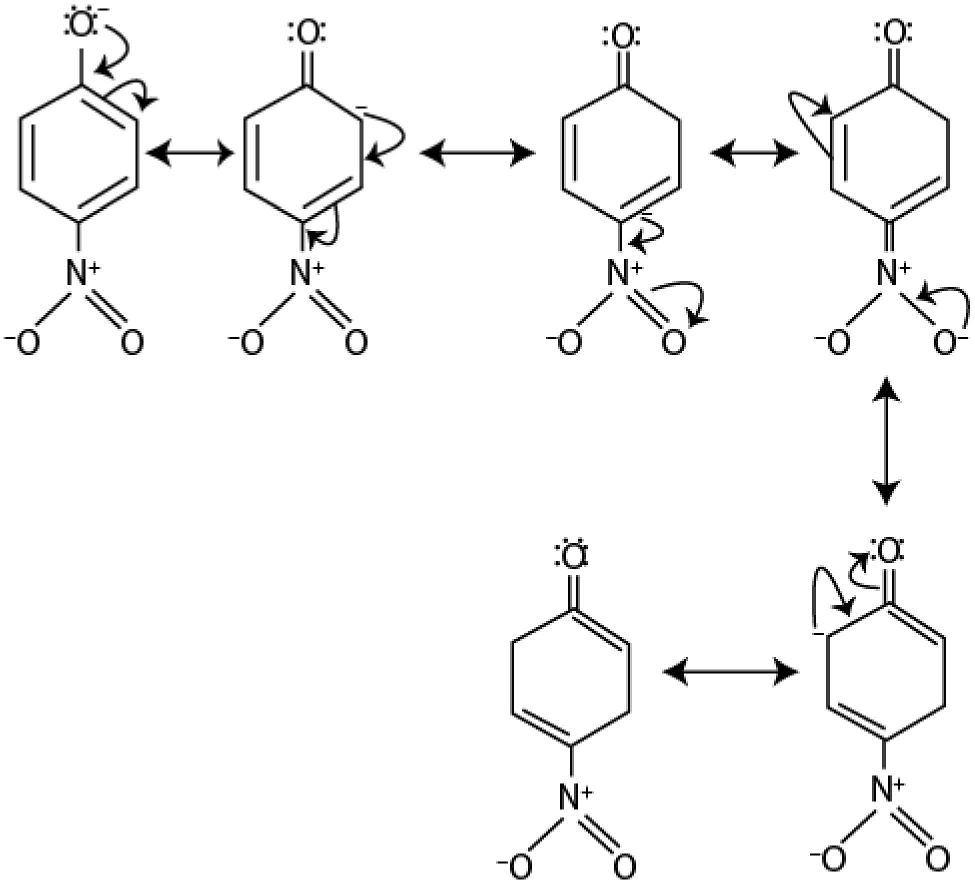
Question 8:

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

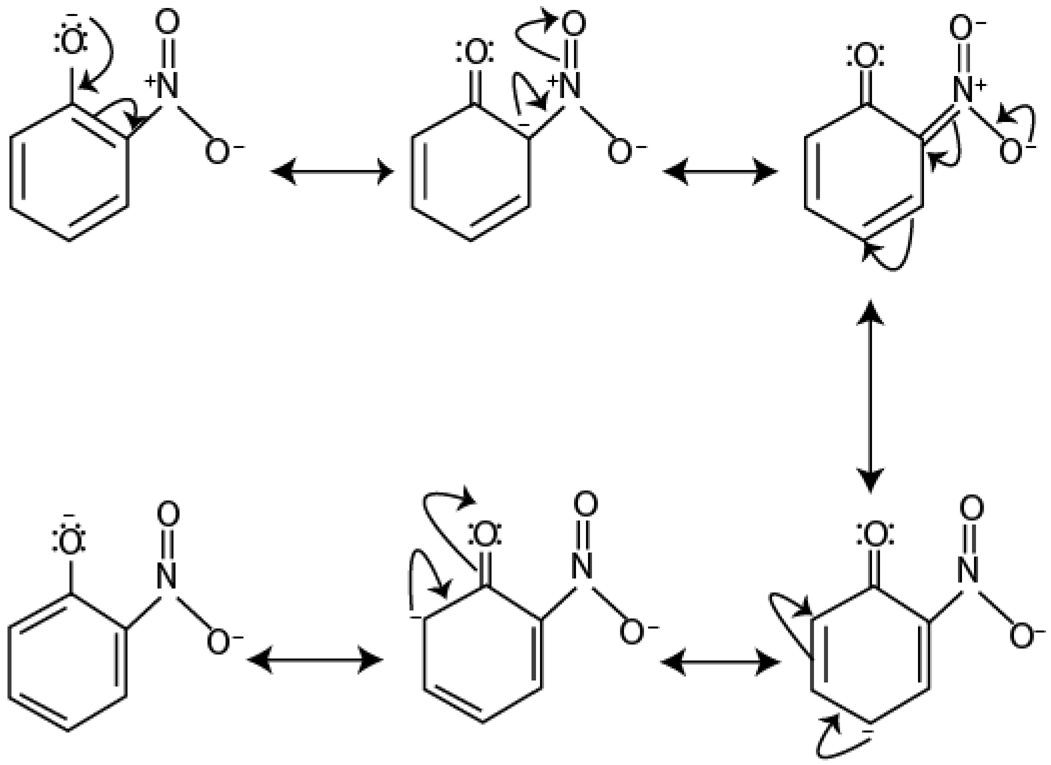
Solution 8:



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 phenoxideion.

Question 9:

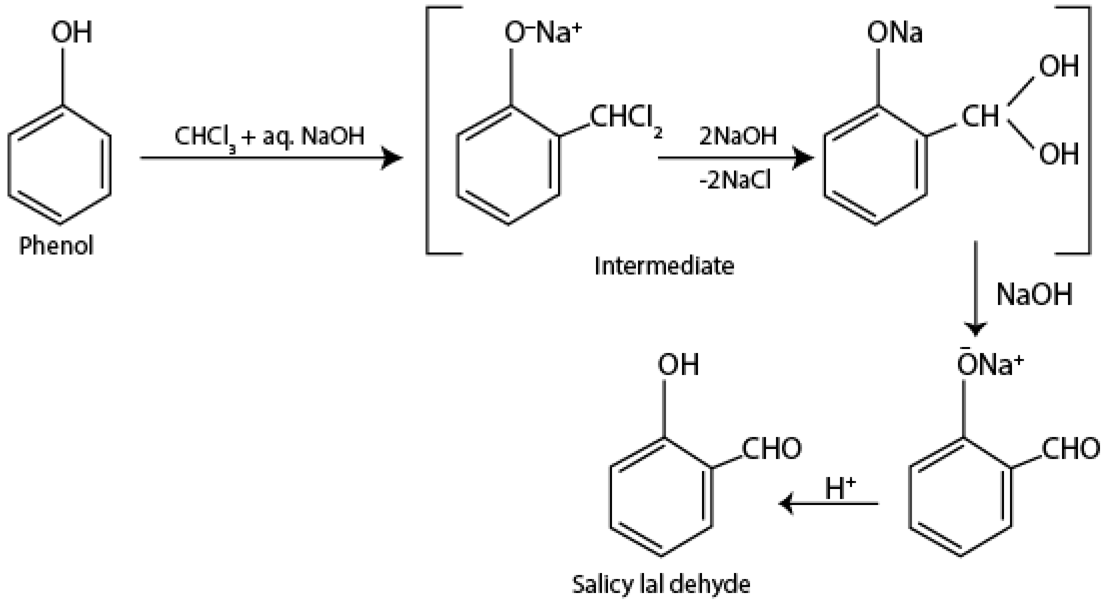
Write the equations involved in the following reactions:

(I) Reimer-Tiemann reaction

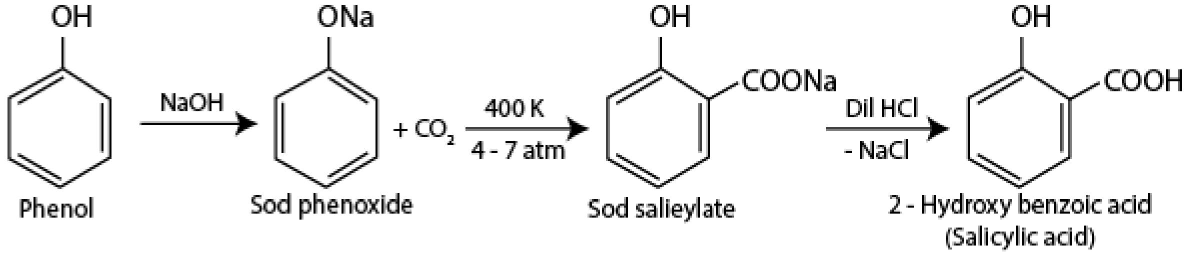
(ii) Kolbe's reaction

Solution 9:

i. Reimer-Tiemann reaction



ii. Kolbe's reaction



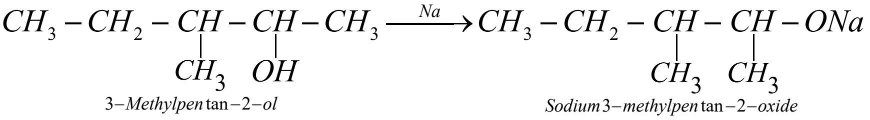
Question 10:

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

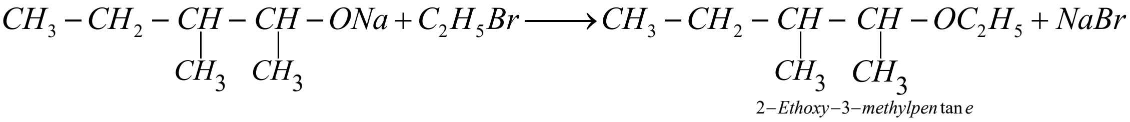
Solution 10:

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.

$$\underset{Ethanol}{C_2H_5OH} \xrightarrow{HBr} \underset{Bromoethane}{C_2H_5Br}$$



$$\underset{3-Methylpentan-2-ol}{CH_3-CH_2-\underset{\large CH_3}{\underset{|}{CH}}-\underset{\large OH}{\underset{|}{CH}}-CH_3} \xrightarrow{Na} \underset{Sodium\,3-methylpentan-2-oxide}{CH_3-CH_2-\underset{\large CH_3}{\underset{|}{CH}}-\underset{\large CH_3}{\underset{|}{CH}}-ONa}$$

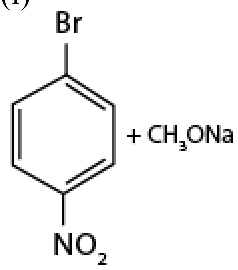


$$CH_3-CH_2-\underset{\large CH_3}{\underset{|}{CH}}-\underset{\large CH_3}{\underset{|}{CH}}-ONa+C_2H_5Br \longrightarrow \underset{2-Ethoxy-3-methylpentane}{CH_3-CH_2-\underset{\large CH_3}{\underset{|}{CH}}-\underset{\large CH_3}{\underset{|}{CH}}-OC_2H_5}+NaBr$$

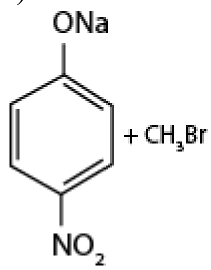
Question 11:

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

(i)

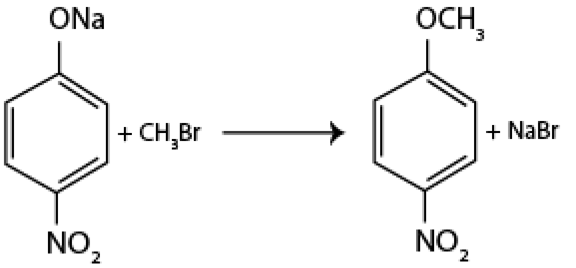


(ii)



Solution 11:

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



1 - Methoxy - 4 - nitrobenzene

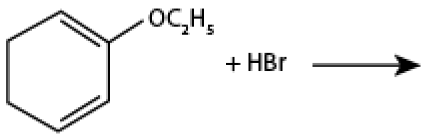
In set (i), sodium methoxide (CH_3ONa) is a strong nucleophile as well as a strong base. Hence, an elimination reaction predominates over a substitution reaction.

Question 12:

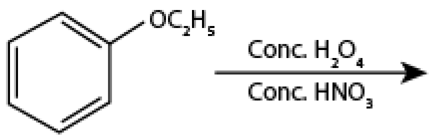
Predict the products of the following reactions:

(i) $CH_2 - CH_2 - CH_2 - O - CH_3 + HBr \rightarrow$

(ii)



(iii)

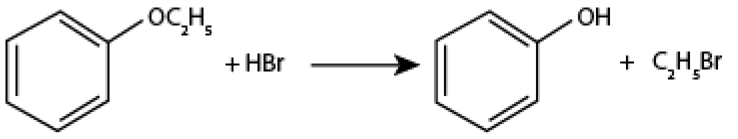


(iv) $(CH_3)_3C-OC_2H_2 \xrightarrow{HI}$

Solution 12:

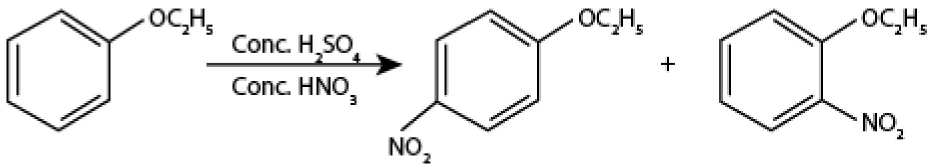
(i) $\underset{n-propylmethyl\,ether}{CH_3-CH_2-CH_2-O-CH_3}+HBr\longrightarrow \underset{Propanol}{CH_3-CH_2-CH_2-OH}+\underset{Bromomethane}{CH_3-Br}$

(ii)



Ethoxybenzene Phenol Bromoethane

(iii)



Ethoxybenzene 2 - Ethoxynitrobenzene (Major) 2 - Ethoxynitrobenzene (Minor)

(iv) $\underset{tert-Butyl\,ethyl\,ether}{(CH_3)_3C-OC_2H_5}\xrightarrow{HI}\underset{tert-Butyliodide}{(CH_3)_3C-I}+\underset{Ethanol}{C_2H_5OH}$