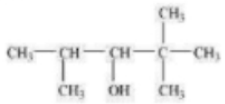
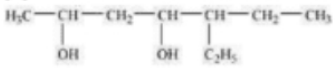
Q 11.1 :

Write IUPAC names of the following compounds:

(i)



(ii)



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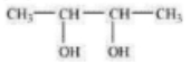

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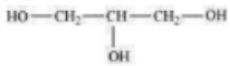

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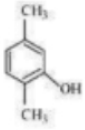
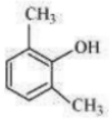
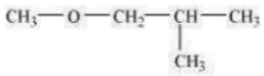


(viii)



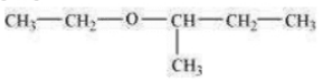
(ix)



(x) $C_6H_5-O-C_2H_5$

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

(xii)



Solution :

(i) 2, 2, 4 -Trimethylpentan – 3 – ol

(ii) 5 – Ethylheptane – 2, 4 – diol

(iii) Butane – 2, 3 – diol

(iv) Propane – 1, 2, 3 – triol

(v) 2-Methylphenol

(vi) 4 – Methyl phenol

(vii) 2, 5 – Dimethylphenol

(viii) 2, 6 – Dimethylphenol

(ix) 1 – Methoxy – 2 – methyl propane

(x) Ethoxy benzene

(xi) 1 – Phenoxyheptane

(xii) 2 – Ethoxybutane

Q 11.2 :

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

(i) 2 – Methylbutan – 2 – ol

(ii) 1 – Phenylpropan – 2 – ol

(iii) 3 , 5 – Dimethylhexane – 1 , 3 , 5 – triol

(iv) 2, 3 – Diethylphenol

(v) 1 – Ethoxypropane

(vi) 2 – Ethoxy – 3 – methylpentane

(vii) Cyclohexylmethanol

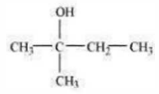
(viii) 3 – Cyclohexylpentan – 3 – ol

(ix) Cyclopent – 3 – en – 1 – ol

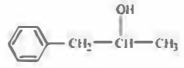
(x) 4-Chloro-3-ethylbutan-1-ol.

Solution :

(i)



(ii)



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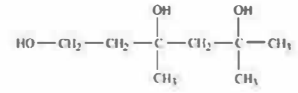

(iv)

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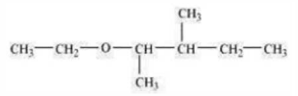
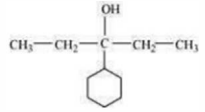


(vii)

(viii)



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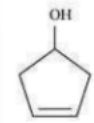
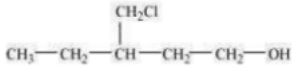


(x)



Q 11.3 :

(i) Draw the structures of all isomeric alcohols of molecular formula C5H12O and give their IUPAC names.

(ii) Classify the isomers of alcohols in question

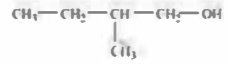
Solution :

(i) The structures & IUPAC names of all isomeric alcohols with a molecular formula of $C_5H_{12}O$ are shown below:

(a) CH_3-CH_2-CH_2-CH_2-CH_2-OH

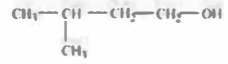
Pentan – 1 – ol (1 °)

(b)



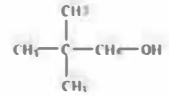
2-Methylbutan-1-ol (1°)

(c)



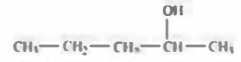
3-Methylbutan-1-ol (1°)

(d)



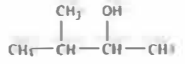
2, 2-Dimethylpropan-1-ol (1°)

(e)



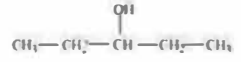
Pentan-2-ol (2°)

(f)



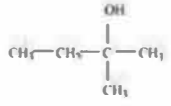
3-Methylbutan-2-ol (2°)

(g)



Pentan-3-ol (2°)

(h)



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

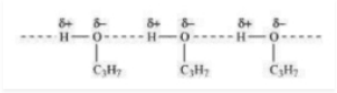
Tertiary alcohol : 2 – methylbutan – 2 – ol

Q 11.4:

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

Solution:

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.

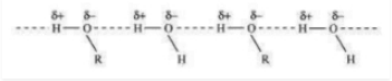
This is the reason why hydrocarbon butane has a lower boiling point than propanol.

Q 11.5:

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

Solution :

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



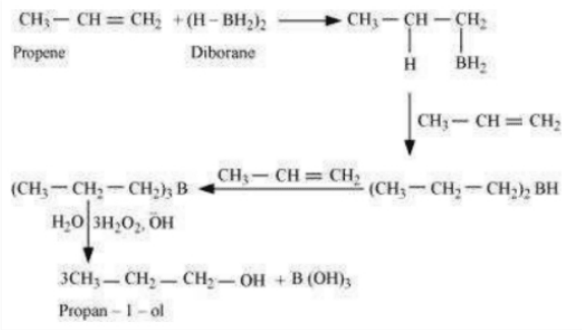
As a result, alcohols are comparatively more soluble in water than hydrocarbons of comparable molecular masses.

Q 11.6:

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

Solution :

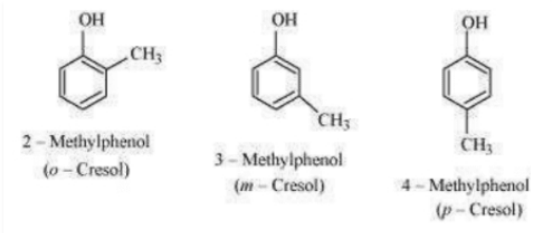
The hydroboration – oxidation reaction is the reaction borane is added in order for the oxidation to take place. For example, propan – 1 – ol is formed by making propene undergo the hydroboration – oxidation reaction. In the above reaction, the reaction between propene and diborane (BH_3)$_2$ takes place 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.



Q 11.7:

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

Solution :



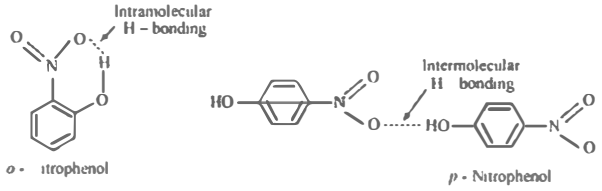
Q 11.8:

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

Solution :

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

therefore, o – nitrophenol is steam volatile.

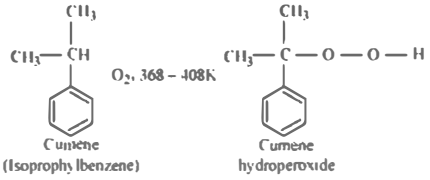


Q 11.9:

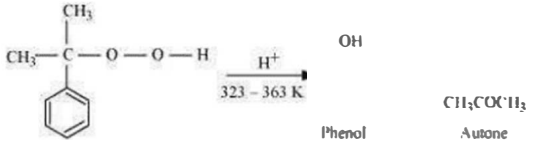
Give the equations of reactions for the preparation of phenol from cumene.

Solution :

To synthesize phenol, cumene is initially oxidized in the presence of air of cumene hydro peroxide.



Followed by, treating cumene hydroxide with dilute acid to prepare phenol & acetone as byproducts.



Q 11.10:

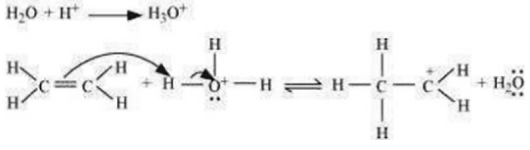
Write the mechanism of hydration of ethene to yield ethanol.

Solution :

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

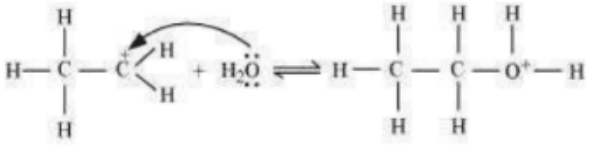
Step 1 :

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



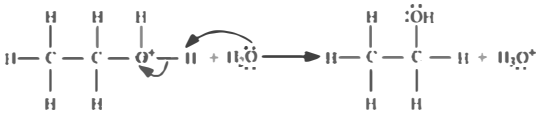
Step 2:

Nucleophilic attack of water on carbocation :



Step 3:

Deprotonation to form ethanol

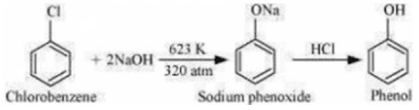


Q 11.11:

Write chemical reaction for the preparation of phenol from chlorobenzene.

Solution :

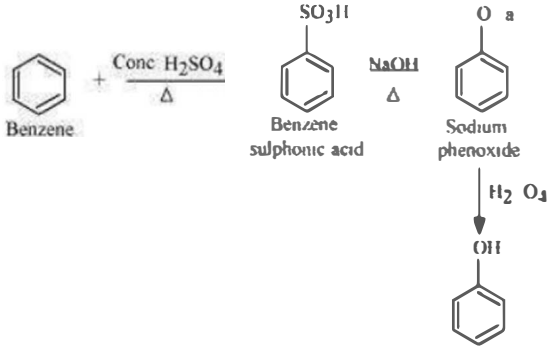
Chlorobenzene is combined with NaOH (at 623 K & 320 atm pressure) to prepare sodium phenoxide, resulting in phenol on acidification.



Q 11.12:

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

Solution :

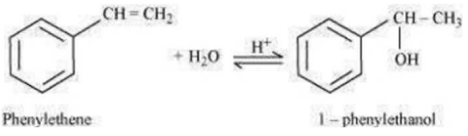


Q 11.13:

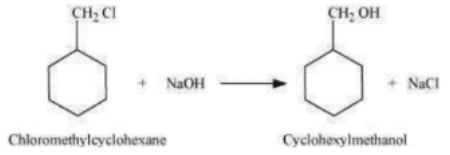
Show how will you synthesise:
(i) 1-phenylethanol from a suitable alkene.
(ii) cyclohexylmethanol using an alkyl halide by an SN2 reaction.
(iii) pentan-1-ol using a suitable alkyl halide?

Solution :

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



(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.

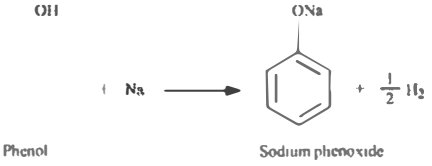
Q 11.14:

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

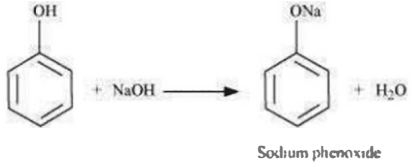
Solution :

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

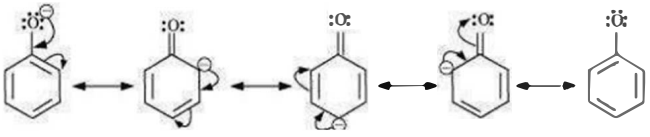
(i) Phenol reacts with sodium to give sodium phenoxide, liberating H_2.



(ii)Phenol reacts with sodium hydroxide to give sodium phenoxide & 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 & gets stabilized whereas ethoxide ion does not.



Q 11.15:

Explain why is ortho nitrophenol more acidic than ortho methoxyphenol ?

Solution :

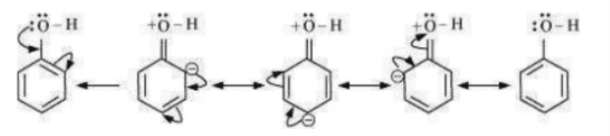
The nitro – group is an electron-withdrawing group. The existence of this group in the ortho position decreases the electron density in the O – H bond. Consequently, it is easier to give away a proton. Furthermore, the o -nitrophenoxide ion formed after the loss of protons is stabilized by resonance. Therefore, ortho nitrophenol is a stronger acid. In contrast, methoxy group is an electron – releasing group. Hence, it increases the electron density in the O – H bond & thus, losing proton is not possible easily. Therefore, ortho – nitrophenol is more acidic than ortho – methoxyphenol.

Q 11.16:

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

Solution :

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



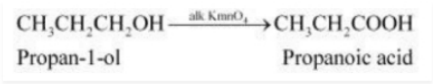
As a result, the benzene ring is activated towards electrophilic substitution.

Q 11.17:

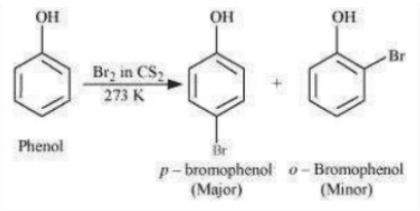
Give equations of the following reactions:
(i) Oxidation of propan-1-ol with alkaline KMnO4 solution.
(ii) Bromine in CS2 with phenol.
(iii) Dilute HNO3 with phenol.
(iv) Treating phenol with chloroform in presence of aqueous NaOH.

Solution :

(i)



(ii)



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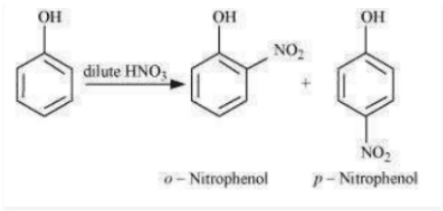

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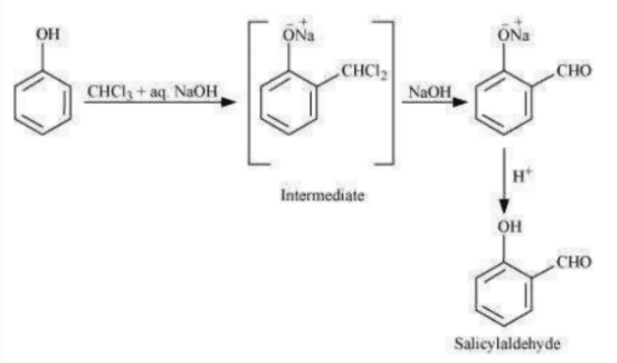


Q 11.18:

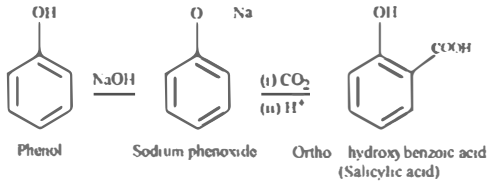
Explain the following with an example.
(i) Kolbe's reaction.
(ii) Reimer-Tiemann reaction.

(iii) Williamson ether synthesis.
(iv) Unsymmetrical ether.

Solution :

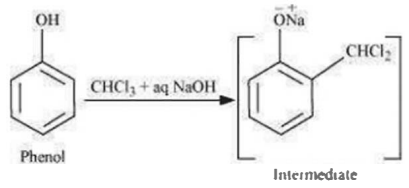
(i) Kolbe's reaction:

Sodium phenoxide is 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.



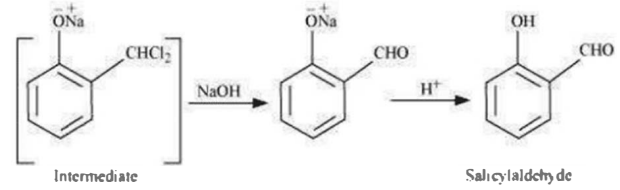
(ii) Reimer – Tiemann reaction:

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



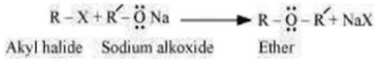
This reaction is known as the Reimer – Tiemann reaction.

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



(iii) Williamson ether synthesis:

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



The above reaction includes Sn_2 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 two of its side, it is called **Unsymmetrical ether**. (i.e., the number of carbon atoms is unequal). For eg: ethyl methyl ether ($CH_3 – O – CH_2 CH_3$).

Q 11.19:

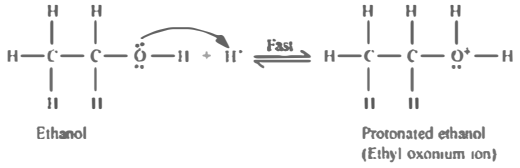
Write the mechanism of acid dehydration of ethanol to yield ethene.

Solution :

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

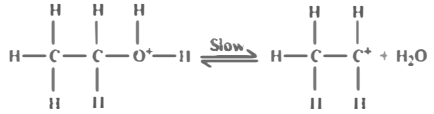
Step 1

Formation of ethyl oxonium by protonation of ethanol :



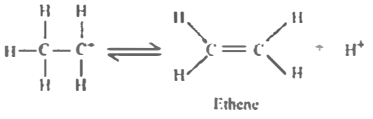
Step 2 :

Carbocation is formed (rate determining step) :



Step 3 :

Ethane is formed by elimination of proton:



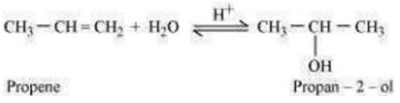
The acid is released in **Step 3** which was being consumed in **Step 1**. It is removed to shift the equilibrium in a forward direction, after ethene is formed.

Q 11.20:

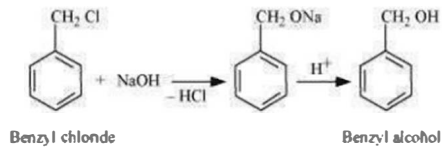
How are the following conversions carried out?
(i) Propene --→ Propan-2-ol.
(ii) Benzyl chloride --→ Benzyl alcohol.
(iii) Ethyl magnesium chloride --→ Propan-1-ol.
(iv) Methyl magnesium bromide --→ 2-Methylpropan-2-ol.

Solution :

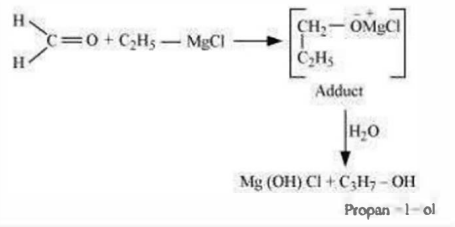
(i) when propene is reacted with water in the presence of an acid as a catalyst , as a result we obtain propan – 2 – ol.



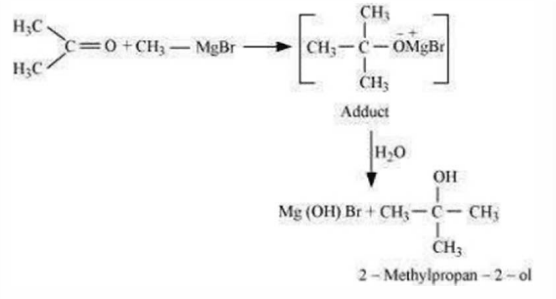
(ii) If then benzyl alcohol is obtained when benzyl chloride is reacted with NaOH which is then followed by acidification



(iii) An adduct is the obtained when ethyl magnesium chloride is reacted with methanal , as a result propan – 1 – ol on hydrolysis is obtained.



(iv) On treating methyl magnesium bromide with propane, an adduct is obtained which results in 2 – methylpropane – 2 – ol on hydrolysis.



Q 11.21:

Name the reagents used in the following reactions:
(i) Oxidation of a primary alcohol to carboxylic acid.
(ii) Oxidation of a primary alcohol to aldehyde.
(iii) Bromination of phenol to 2,4,6-tribromophenol.
(iv) Benzyl alcohol to benzoic acid.
(v) Dehydration of propan-2-ol to propene.
(vi) Butan-2-one to butan-2-ol.

Solution :

(i) $NaBH_4$ or $LiAlH_4$

(ii) 85 % phosphoric acid

(iii) Acidified potassium permanganate

(iv) Bromine water

(v) Pyridinium chlorochromate (PCC)

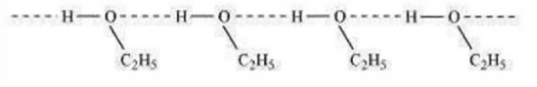
(vi) Acidified potassium permanganate

Q 11.22:

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

Solution :

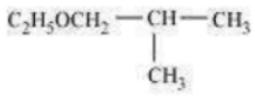
Ethanol experiences intermolecular H – bonding because of the presence of – OH group, which results in association of molecules. additional energy is necessary to break these hydrogen bonds. Conversely, methoxymethane does not experience H – bonding. Therefore, ethanol has a higher boiling point when compared to methoxymethane



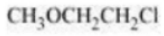
Q 11.23:

Give IUPAC names of the following ethers:

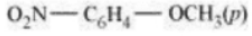
(i)



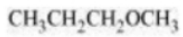
(ii)



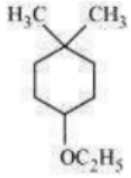
(iii)



(iv)



(v)



(vi)

Solution :

(i) 1 – Ethoxy – 2 – methylpropane

(ii) 2 – Chloro – 1 – methoxyethane

(iii) 4 – Nitroanisole

(iv) 1 – Methoxypropane

(v) 1 – Ethoxy – 4 , 4 – dimethylcyclohexane

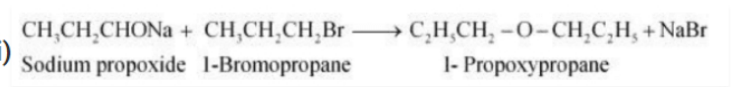
(vi) Ethoxybenzene

Q 11.24 :

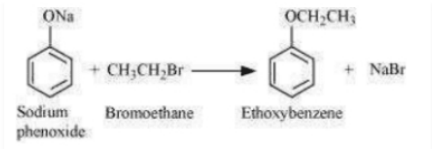
Write the names of reagents and equations for the preparation of the following ethers by Williamson's synthesis:
(i) 1-Propoxypropane (ii) Ethoxybenzene
(iii) 2-Methoxy-2-methylpropane (iv) 1-Methoxyethane

Solution :

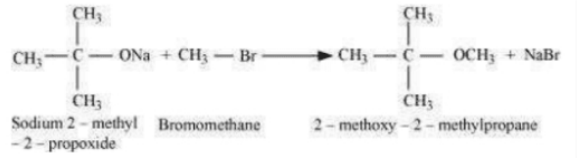
(i)



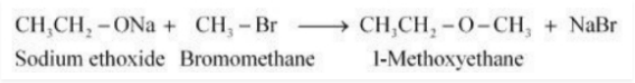
(ii)



(iii)



(iv)

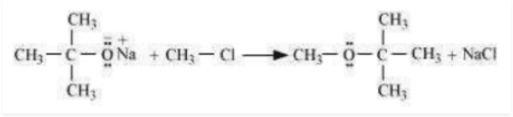


Q 11.25 :

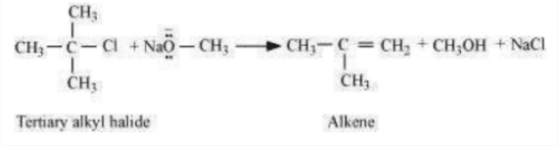
Illustrate with examples the limitations of Williamson synthesis for the preparation of certain types of ethers

Solution :

The reaction of Williamson synthesis includes SN_2 attack of an alkoxide ion on a primary alkyl halide.



while, tertiary alkyl halides or secondary alkyl halides were to be substituted in place of primary alkyl halides, in that case elimination would contend over substitution. This results in formation of alkenes. This happens because alkoxides are nucleophiles as well as strong bases. Therefore, they react with alkyl halides, which results in an elimination reaction.



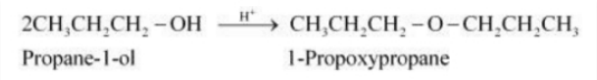
Q 11.26 :

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

Solution :

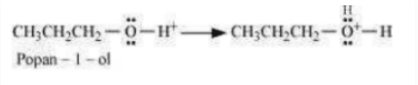
1 – propoxypropane can be synthesized from propan – 1 – ol by dehydration.

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

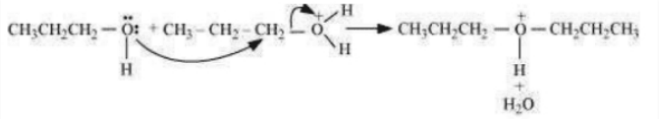


The mechanism of this reaction involves the following three steps :

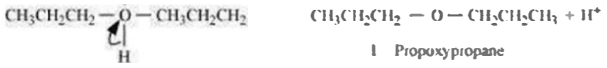
Step 1 : Protonation



Step 2 : Nucleophilic attack



Step 3 : Deprotonation



Q 11.27:

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

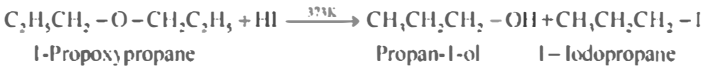
Solution :

The synthesis of ethers with dehydration of alcohol is a bimolecular reaction (SN_2) which involves 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.

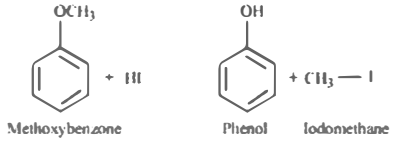
Q 11.28:

Write the equation of the reaction of hydrogen iodide with:
(i) 1-propoxypropane (ii) methoxybenzene and (iii) benzyl ethyl ether

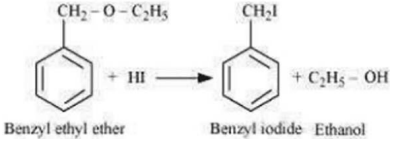
Solution :

(i) 

(ii)



(iii)



Q 11.29:

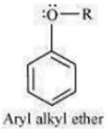
Explain the fact that in aryl alkyl ethers

(i) the alkoxy group activates thebenzene ring towards electrophilic substitution and

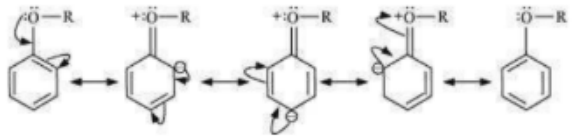
(ii) it directs theincoming substituents to ortho and para positions in benzene ring.

Solution :

(i)



The electron density in the benzene ring boosts up because of the existence of + R effect of the alkoxy group In aryl alkyl ethers which is given in the resonance configuration below :



Therefore, ***benzene ring is activated by the alkoxy group towards electrophilic substitution.***

(ii) The above resonance configuration , we infer that the electron density is higher at the para & ortho positions compared to meta position. consequently, the substituent which is incoming is directed to the para & ortho positions in the benzene ring.

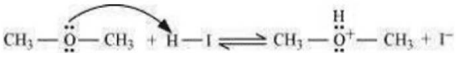
Q 11.30:

Write the mechanism of the reaction of HI with methoxymethane.

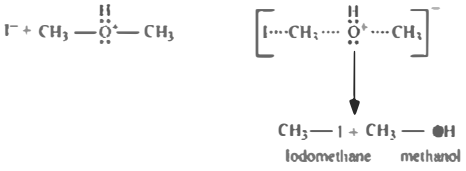
Solution :

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

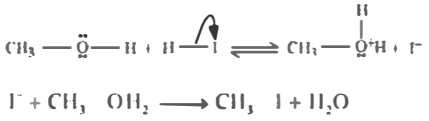
Step 1 : Protonation of methoxymethane :



Step 2 : Nucleophilic attack of I^- :



Step 3 : The methanol synthesized in the above step is made to react with another HI molecule which then converts to methyl iodide. This is done at a high temperature & HI is present in excess.

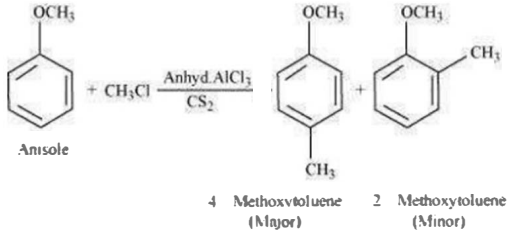


Q 11.31:

Write equations of the following reactions:
(i) Friedel-Crafts reaction – alkylation of anisole.
(ii) Nitration of anisole.
(iii) Bromination of anisole in ethanoic acid medium.
(iv) Friedel-Craft's acetylation of anisole.

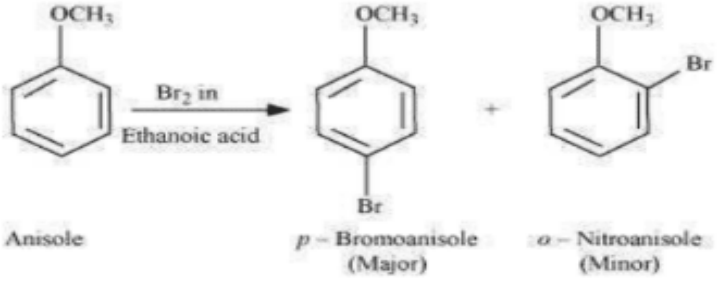
Solution :

(i)

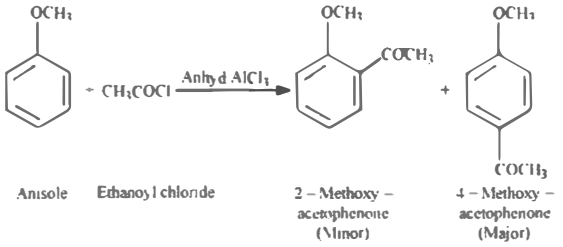


(ii)

(iii)



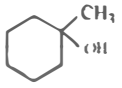
(iv)



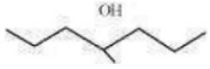
Q11.32:

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

(i)

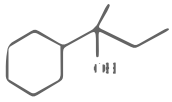


(ii)



(iii)

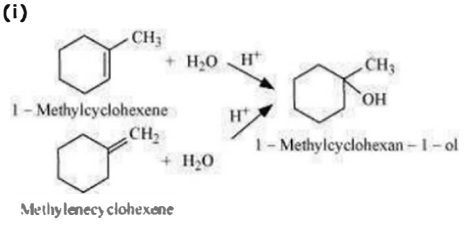
(iv)



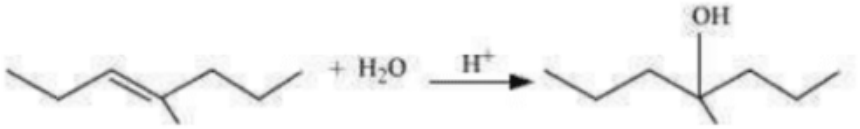
Solution :

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

(i)

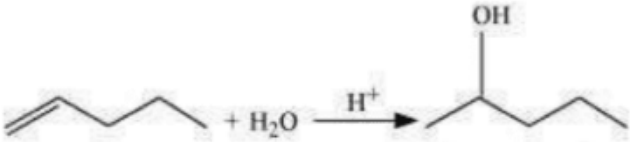


(ii)



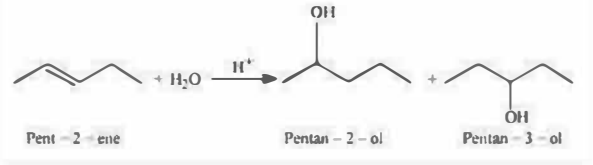
4 – Methylhept – 3 – ene 4 – Methylheptan – 4 – ol

(iii)



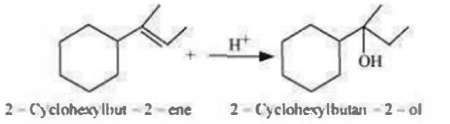
Pent – 1 – ene Pentan – 2 – ol

Acid-catalyzed hydration of pent-2-ene also produces pentan-2-ol but along with pentan3-ol.



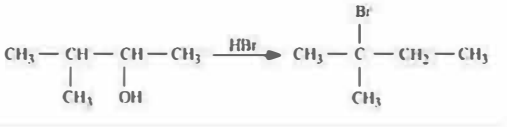
Thus, the first reaction is preferred over the second one to get pentan-2-ol.

(iv)



Q 11.33:

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

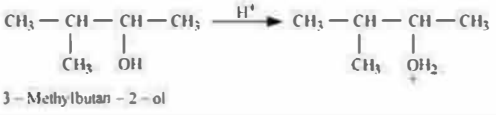


Give a mechanism for this reaction.
(Hint : The secondary carbocation formed in step II rearranges to a more stable tertiary carbocation by a hydride ion shift from 3rd carbon atom.

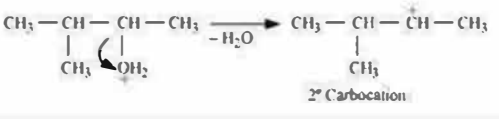
Solution :

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

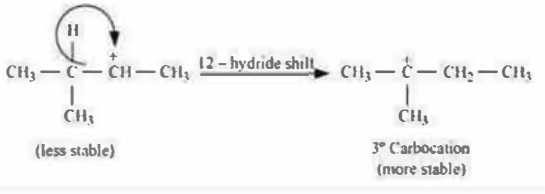
Step 1 : Protonation



Step 2 : Forming 2 ° carbonation by eliminating the water molecule



Step 3 : Re – arranging by the shifting hydride – ion



Step 4 : Nucleophilic attack