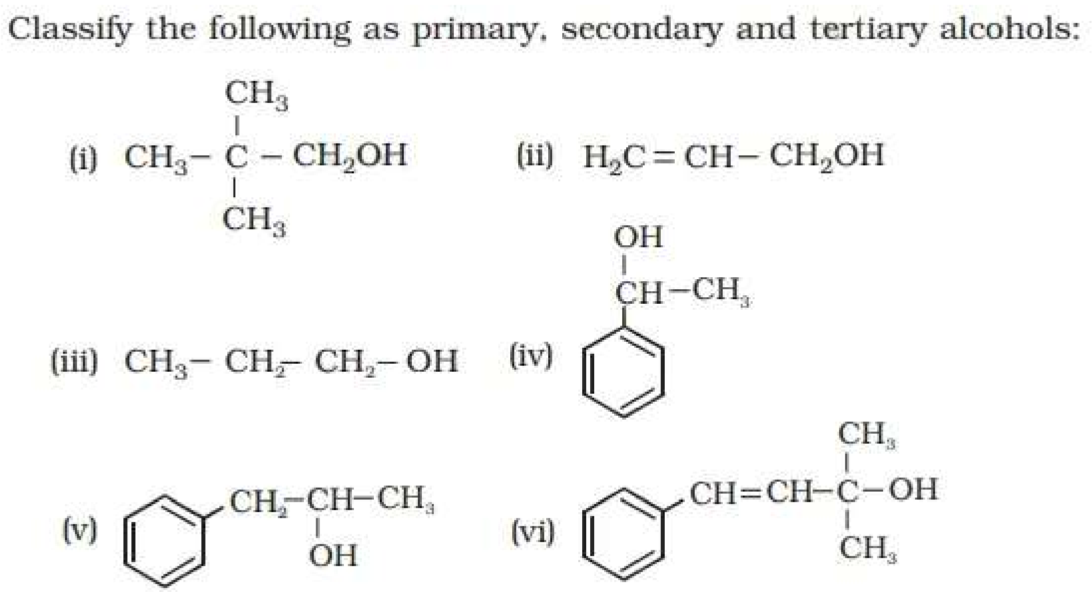
NCERT Solutions for Class 12 Chemistry

Chapter 7 – Alcohols, Phenols, and Ethers

Intext Questions with Solutions of Class 12 Chemistry Chapter 7 – Alcohols, Phenols, and Ethers

7.1



Classify the following as primary, secondary and tertiary alcohols:

(i) $CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-CH_2OH$

(ii) $H_2C=CH-CH_2OH$

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

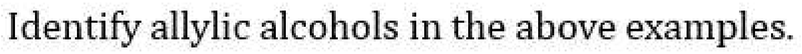
(iv)

(v)

(vi)

Ans – Primary alcohols will be (i), (ii), (iii)
Secondary alcohols will be (iv), (v)
Tertiary alcohols will be (vi)

7.2



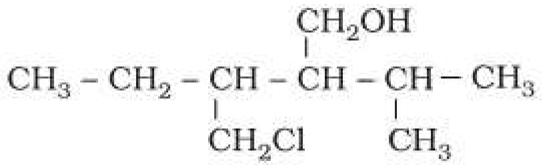
Identify allylic alcohols in the above examples.

Ans – From the above examples (ii) and (iv) are aliylic alcohols.

7.3

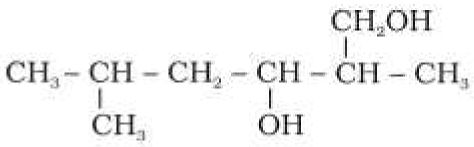
Name the following compounds according to IUPAC system.

(i)



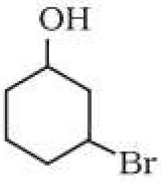
$CH_3-CH_2-\underset{CH_2Cl}{CH}-\overset{CH_2OH}{CH}-\underset{CH_3}{CH}-CH_3$

(ii)

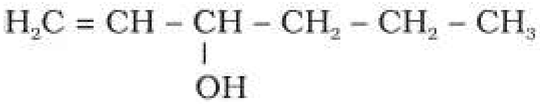


$CH_3-\underset{CH_3}{CH}-CH_2-\underset{OH}{CH}-\overset{CH_2OH}{CH}-CH_3$

(iii)

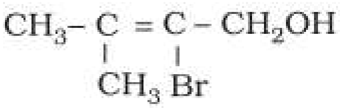


(iv)



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

(v)



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

Ans – (i) 3-Chloromethyl-2-isopropyl pentan- 1-ol

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

(iii) 3-Bromocyclohexanol

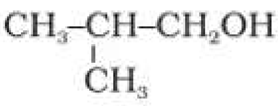
(iv) Hex-1-en-3-ol

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

7.4

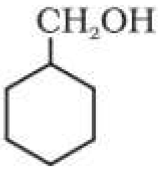
Show how are the following alcohols prepared by the reaction of a suitable Grignard reagent on methanal?

(i)



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

(ii)



📌 ***Key Points to Note from Question***

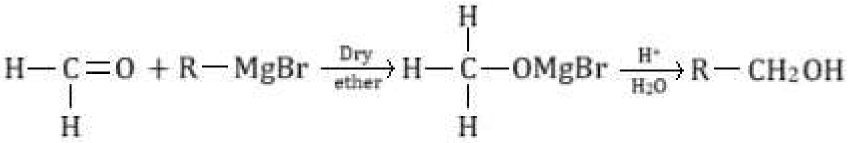
Given Data:

- Preparation of alcohols using Grignard reagent and methanal

Key Concept:

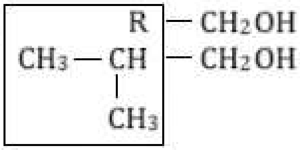
- Methanal + Grignard reagent (R-MgX) → Primary alcohol after hydrolysis.

Ans – The reaction will be as below:



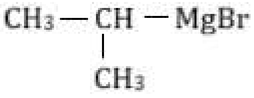
$H-\underset{H}{C}=O + R-MgBr \xrightarrow[\text{ether}]{\text{Dry}} H-\overset{H}{\underset{H}{C}}-OMgBr \xrightarrow[H_2O]{H^+} R-CH_2OH$

From this we need to find R for each question in order to find grignard reagent.

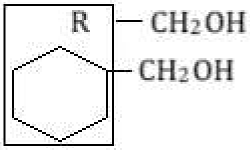
(i) 

$$\boxed{\underset{\displaystyle CH_3}{CH_3-\overset{R}{CH}}}\!\!\begin{array}{l}-CH_2OH\\-CH_2OH\end{array}$$

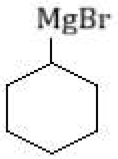
⇒ Grignard reagent used will be



$$CH_3-\underset{\displaystyle CH_3}{CH}-MgBr$$

(ii) 

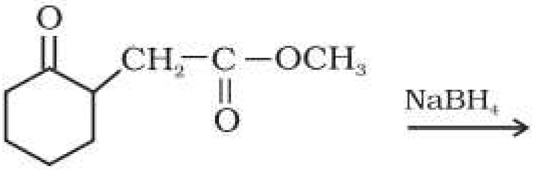
⇒ Grignard reagent used will be

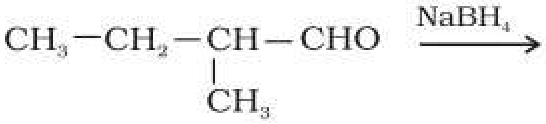


7.5

Write structures of the products of the following reactions:

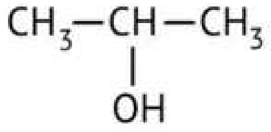
(i) $CH_3-CH=CH_2 \xrightarrow{H_2O/H^+}$

(ii) 

(iii) 

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

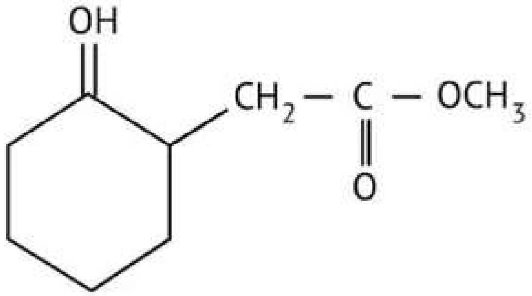
Ans - (i)



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

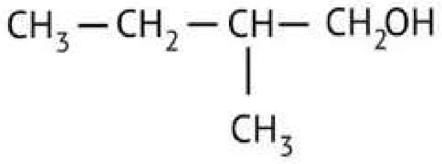
Propan-2-ol

(ii)



Methyl (2-hydroxycyclohexyl)
ethanoate

(iii)



$$CH_3-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2OH$$

2 - Methylbutan - 1 -ol

7.6

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

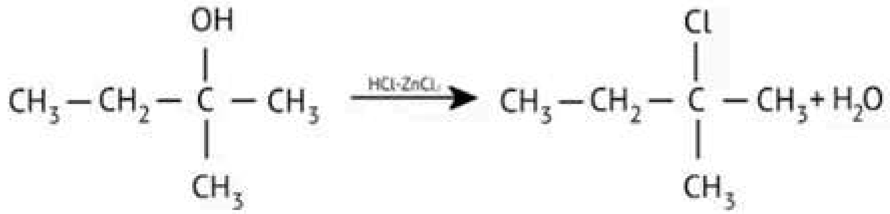
(i) Butan-1-ol **(ii) 2-Methylbutan-2-ol**

Ans – (i) $CH_3CH_2CH_2CH_2OH + HCl - ZnCl_2 \rightarrow$ No Reaction

$CH_3CH_2CH_2CH_2OH + HBr \rightarrow CH_3CH_2CH_2CH_2Br$

$CH_3CH_2CH_2CH_2OH + SOCl_2 \rightarrow CH_3CH_2CH_2CH_2Cl + HCl$

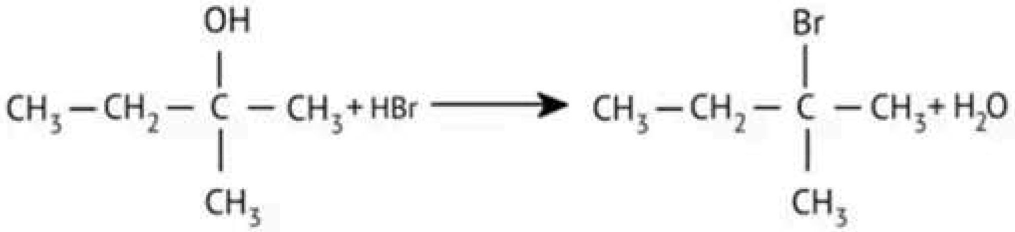
(ii)



$$CH_3-CH_2-\underset{CH_3}{\overset{OH}{C}}-CH_3 \xrightarrow{HCl\text{-}ZnCl_2} CH_3-CH_2-\underset{CH_3}{\overset{Cl}{C}}-CH_3+H_2O$$

2 - Methylbutan - 2- ol (3°)

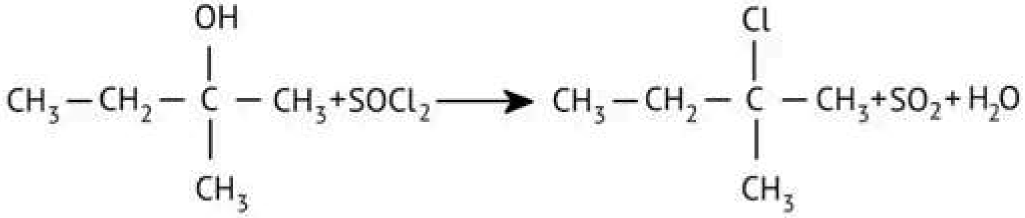
2- chloro - 2 - Methylbutane
(white turbidity)



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

2 - Methylbutan - 2- ol (3°)

2- Bromo - 2 - Methylbutane



$$CH_3-CH_2-\underset{CH_3}{\overset{OH}{C}}-CH_3+SOCl_2 \longrightarrow CH_3-CH_2-\underset{CH_3}{\overset{Cl}{C}}-CH_3+SO_2+H_2O$$

2 - Methylbutan - 2- ol

2- Chloro - 2 - Methylbutane

7.7

Predict the major product of acid catalysed dehydration of

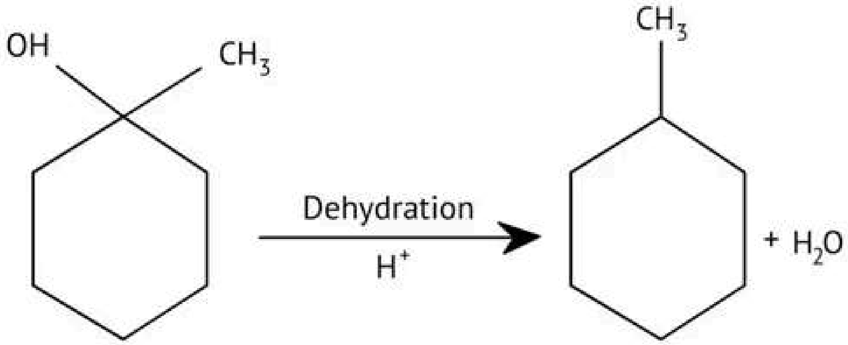
(i) 1-methylcyclohexanol and (ii) butan-1-ol

📌 ***Key Points to Note from Question***

Key Concept:

- **Follows E1 mechanism for secondary/tertiary alcohols** (carbocation formation, rearrangement possible).
- **Follows E2 for primary alcohols** (no carbocation).
- **Zaitsev's rule**: More **substituted alkene** is the major product.

Ans - (i)



1 - Methylcyclohexanol

1 - Methylcyclohexanol
(Major product)

(ii)

$$CH_3CH_2CH_2CH_2OH \xrightarrow[H^+]{dehydration} CH_3CH = CHCH_3 + H_2O$$

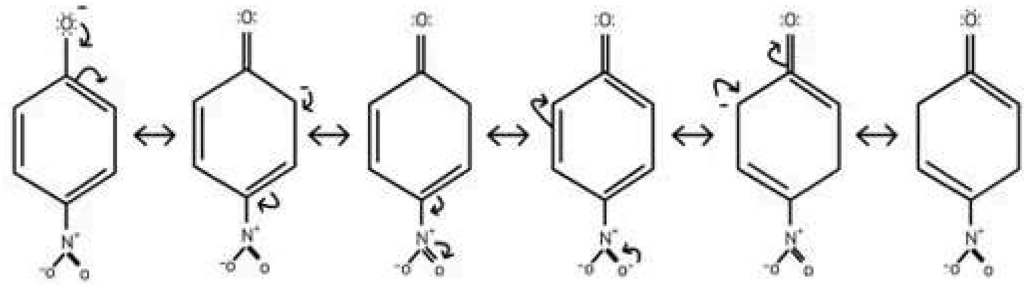
Butanol

But - 2 - ene

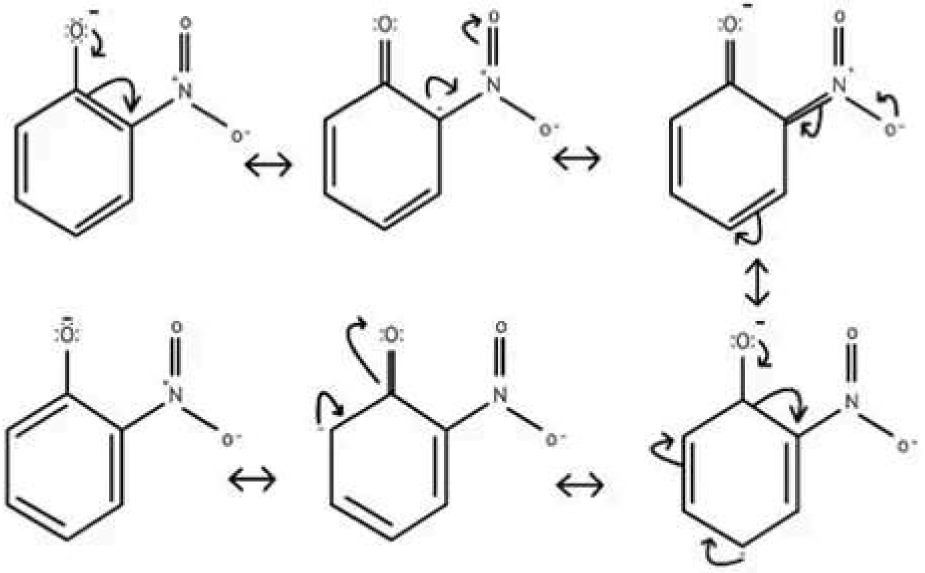
7.8

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

Ans - (i)



(ii)

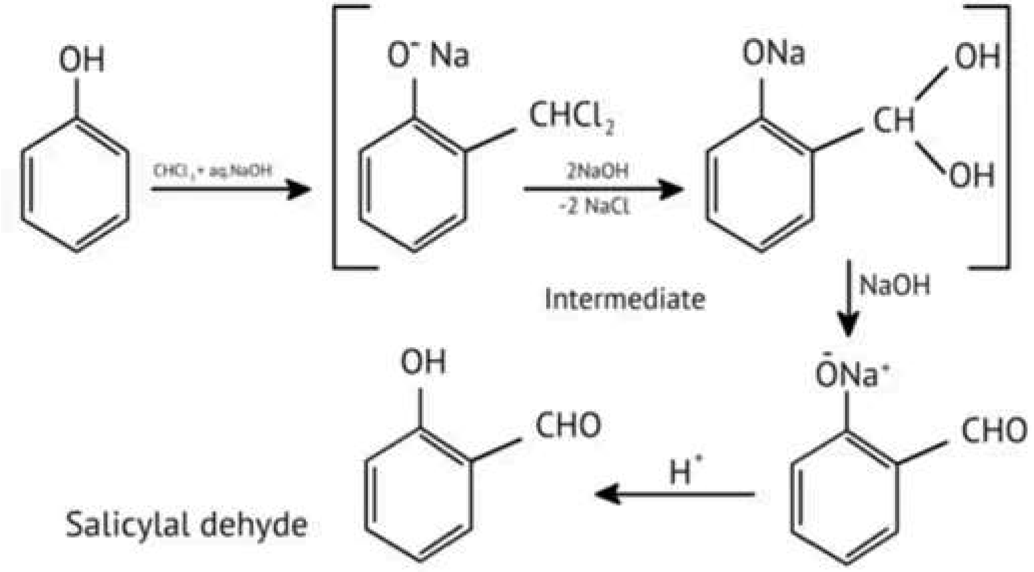


7.9

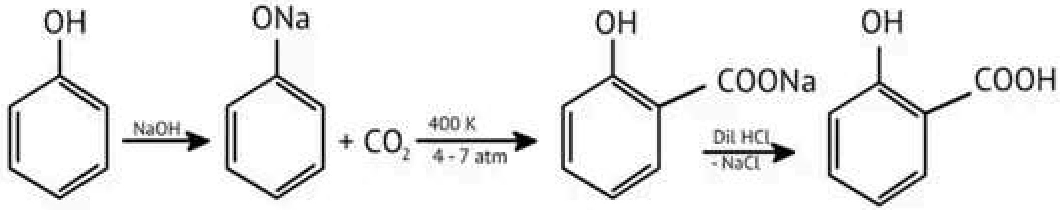
Write the equations involved in the following reactions:

(i) Reimer - Tiemann reaction (ii) Kolbe's reaction

Ans - (i)



(ii)



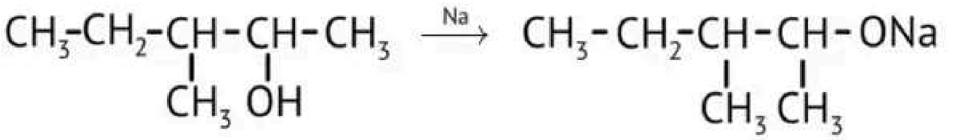
phenol Sod phenoxide Sod Salleylate 2 - Hydroxy benzoic (Salicylic acid)

7.10

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

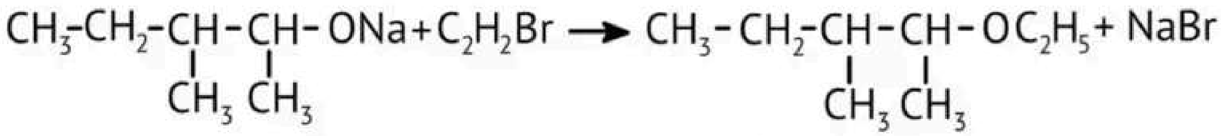
Ans –

$$\underset{\text{ethanol}}{C_2H_5OH} \xrightarrow{HBr} \underset{\text{Bromoethane}}{C_2H_5Br}$$



$$CH_3\text{-}CH_2\text{-}\underset{CH_3}{\underset{|}{CH}}\text{-}\underset{OH}{\underset{|}{CH}}\text{-}CH_3 \xrightarrow{Na} CH_3\text{-}CH_2\text{-}\underset{CH_3}{\underset{|}{CH}}\text{-}\underset{CH_3}{\underset{|}{CH}}\text{-}ONa$$

3-Methylpentan-2-ol Sodium 3- methylpentan-2-oxide



$$CH_3\text{-}CH_2\text{-}\underset{CH_3}{\underset{|}{CH}}\text{-}\underset{CH_3}{\underset{|}{CH}}\text{-}ONa + C_2H_2Br \longrightarrow CH_3\text{-}CH_2\text{-}\underset{CH_3}{\underset{|}{CH}}\text{-}\underset{CH_3}{\underset{|}{CH}}\text{-}OC_2H_5 + NaBr$$

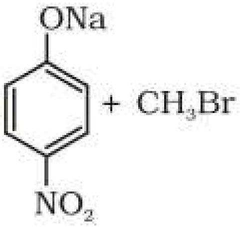
2- Ethoxy-3-methylpentane

7.11

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

(i)

(ii)



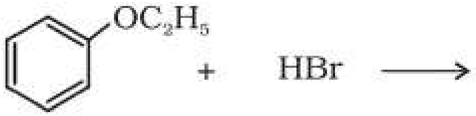
Ans – Set (ii) of reactants is appropriate for the preparation of 1-methoxy-4-nitrobenzene. Sodium methoxide serves as strong nucleophile and a strong base in set (i). Hence, the elimination reaction occurs over the substitution reaction.

7.12

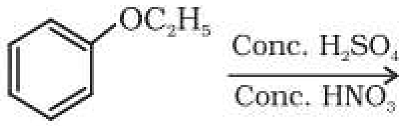
Predict the products of the following reactions:

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

(ii)



(iii)

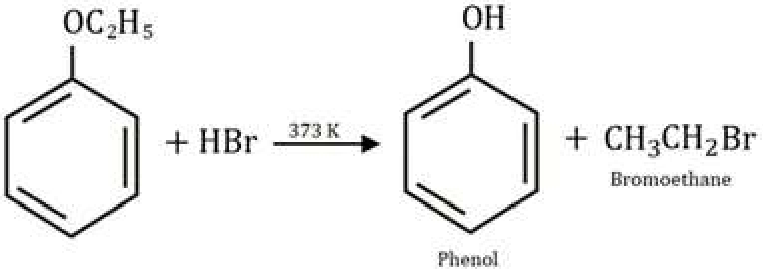


(iv) $(CH_3)_3C-OC_2H_5 \xrightarrow{HI}$

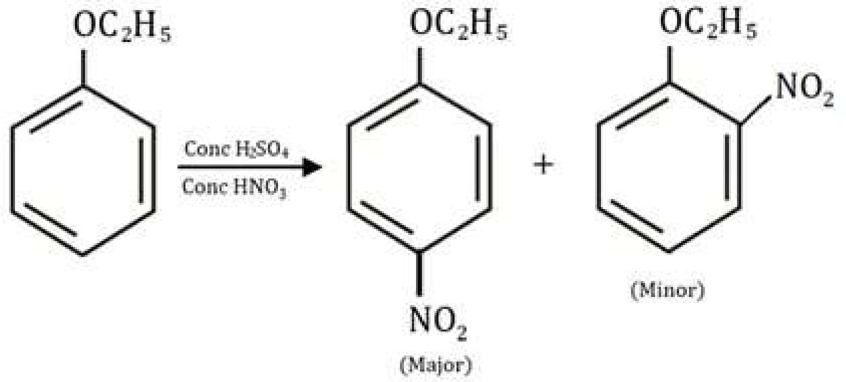
Ans – (i) The strong acids HBr cut alkyl ethers via nucleophilic substitution, similar to that of alcohols. The ethereal oxygen protonation generates an appropriate leaving group, a neutral alcohol molecule.

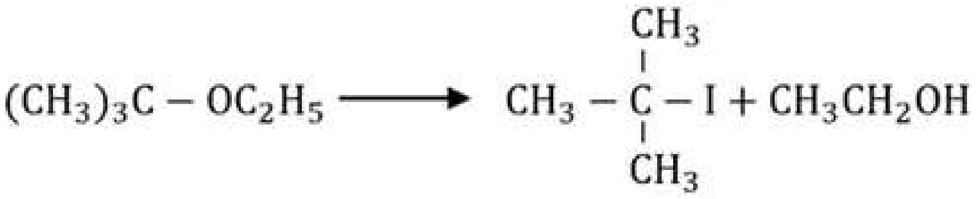
$CH_3-CH_2-CH_2-O-CH_3$ + HBr → $CH_3-CH_2-CH_2-OH$ + CHBr

(ii)



(iii) A nitration reaction will take place. -OC_2H_5 is a meta-directing group. Thus, meta-substituted compounds are produced.



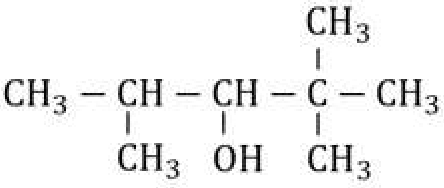
(iv) 

$$(CH_3)_3C-OC_2H_5 \longrightarrow CH_3-\overset{CH_3}{\underset{CH_3}{C}}-I+CH_3CH_2OH$$

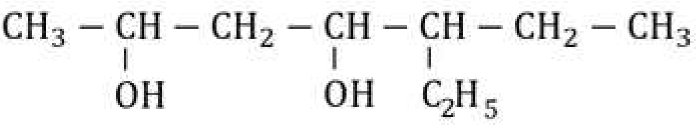
Exercise Questions with Solutions of Class 12 Chemistry Chapter 7 – Alcohols, Phenols, and Ethers

7.1

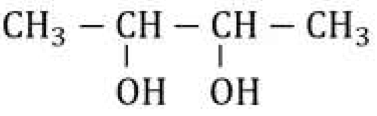
Write IUPAC names of the following compounds:

(i) 

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

(ii) 

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

(iii) 

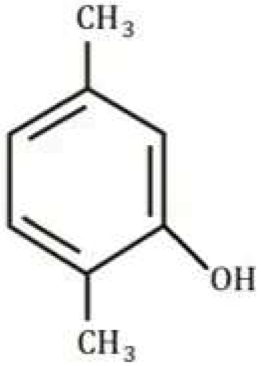
$$CH_3-\underset{OH}{CH}-\underset{OH}{CH}-CH_3$$

(iv) $HOCH_2-CHOH-CH_2OH$

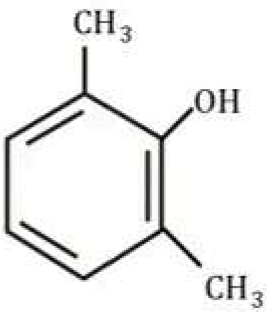
(v)

(vi)

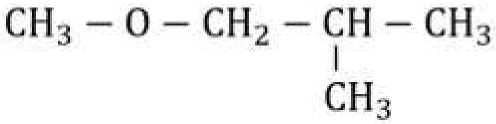
(vii)



(viii)



(ix)

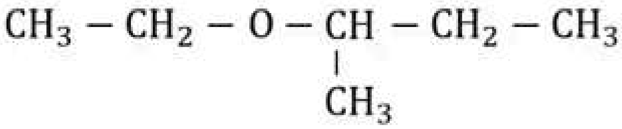


$CH_3-O-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3$

(x) $C_6H_5-O-C_2H_5$

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

(xii)



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

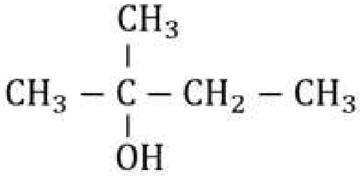
Ans – (i) 2,2,4-Trimethylpentan-3-ol
(ii) 5-Ethylheptane-2,4-diol
(iii) Butane-2,3-diol
(iv) Propane-1,2,3-triol
(v) 2-Methylphenol
(vi) 4-Methylphenol
(vii) 2,5-Dimethylphenol
(viii) 2,6-Dimethylphenol
(ix) 1-Methoxy-2-methylpropane
(x) Ethoxybenzene
(xi) 1-Phenoxyheptane
(xii) 2-Ethoxybutane

7.2

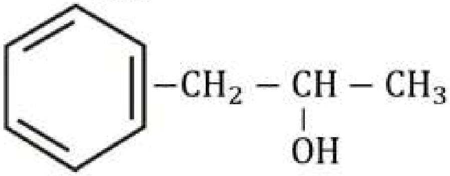
Write structures of the compounds whose IUPAC names are as follows:

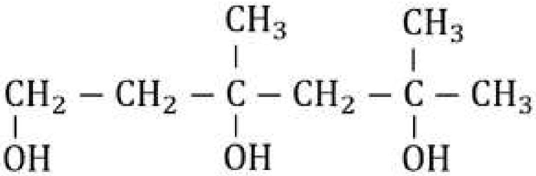
(i) 2-Methylbutan-2-ol **(ii) 1-Phenylpropan-2-ol**
(iii) 3,5-Dimethylhexane –1, 3, 5-triol **(iv) 2,3 – Diethylphenol**
(v) 1 – Ethoxypropane **(vi) 2-Ethoxy-3-methylpentane**
(vii) Cyclohexylmethanol **(viii) 3-Cyclohexylpentan-3-ol**
(ix) Cyclopent-3-en-1-ol **(x) 4-Chloro-3-ethylbutan-1-ol.**

Ans -

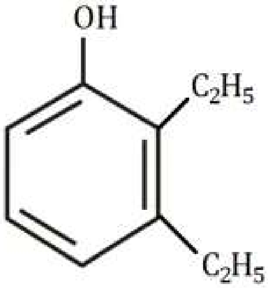
(i)


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

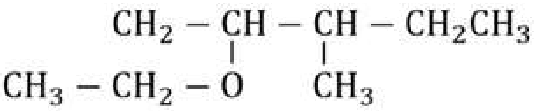
(ii)


(iii)


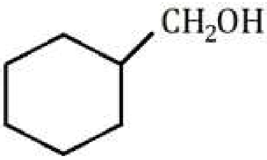
$$\underset{OH}{\underset{|}{CH_2}}-CH_2-\underset{OH}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CH_2-\underset{OH}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CH_3$$

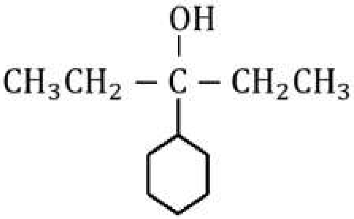
(iv)


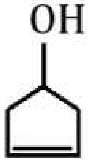
(v) $CH_3CH_2-O-CH_2CH_2CH_3$

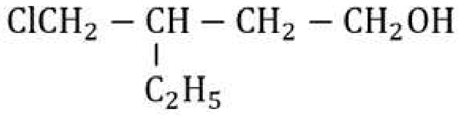
(vi)


$$\begin{array}{l} \qquad\qquad\quad CH_2-\underset{|}{CH}-\underset{|}{CH}-CH_2CH_3 \\ CH_3-CH_2-O \qquad CH_3 \end{array}$$

(vii)


(viii) 

(ix) 

(x) 

$$\mathrm{ClCH_2 - \underset{\substack{|\\ C_2H_5}}{CH} - CH_2 - CH_2OH}$$

7.3

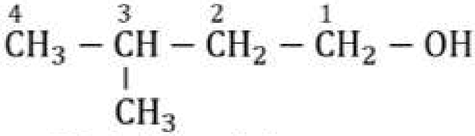
(i) Draw the structures of all isomeric alcohols of molecular formula $C_5H_{12}O$ and give their IUPAC names.

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

Ans – (i)

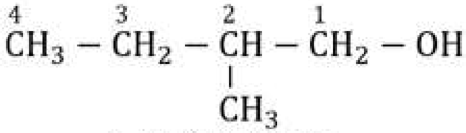
(i) $\mathrm{\overset{5}{C}H_3 - \overset{4}{C}H_2 - \overset{3}{C}H_2 - \overset{2}{C}H_2 - \overset{1}{C}H_2 - OH}$

Pentan-l-ol

(ii) 

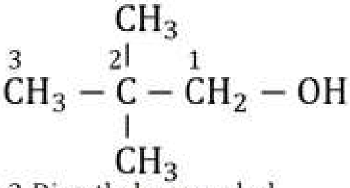
$$\mathrm{\overset{4}{C}H_3 - \underset{\substack{|\\ CH_3}}{\overset{3}{C}H} - \overset{2}{C}H_2 - \overset{1}{C}H_2 - OH}$$

3-Methylbutane-l-ol

(iii) 

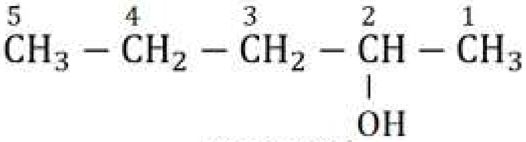
$$\mathrm{\overset{4}{C}H_3 - \overset{3}{C}H_2 - \underset{\substack{|\\ CH_3}}{\overset{2}{C}H} - \overset{1}{C}H_2 - OH}$$

2- Methylbutan-l-ol

(iv) 

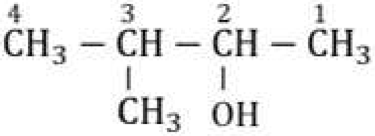
$$\mathrm{\overset{3}{C}H_3 - \underset{\substack{|\\ CH_3}}{\overset{\substack{CH_3\\ 2|}}{C}} - \overset{1}{C}H_2 - OH}$$

2, 2-Dimethylpropan-l-ol

(v) 

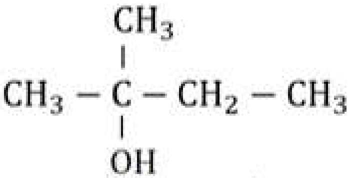
$$\overset{5}{\mathrm{CH_3}} - \overset{4}{\mathrm{CH_2}} - \overset{3}{\mathrm{CH_2}} - \underset{\mathrm{OH}}{\overset{2}{\mathrm{CH}}} - \overset{1}{\mathrm{CH_3}}$$

Pentan-2-ol

(vi) 

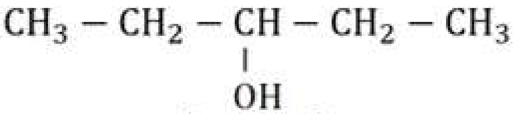
$$\overset{4}{\mathrm{CH_3}} - \underset{\mathrm{CH_3}}{\overset{3}{\mathrm{CH}}} - \underset{\mathrm{OH}}{\overset{2}{\mathrm{CH}}} - \overset{1}{\mathrm{CH_3}}$$

3-Methylbutane-2-ol

(vii) 

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

2-Methylbutan-2-ol

(viii) 

$$\mathrm{CH_3} - \mathrm{CH_2} - \underset{\mathrm{OH}}{\mathrm{CH}} - \mathrm{CH_2} - \mathrm{CH_3}$$

Pentan-3-ol

(ii) Primary alcohols are (i), (ii), (iii), (iv)
Secondary alcohols are (v), (vi), (viii)
Tertiary alcohols are (vii)

7.4

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

📌 ***Key Points to Note from Question***

Key Concept:

- **Hydrogen Bonding:** Propanol has an -OH group, enabling strong intermolecular hydrogen bonding, increasing its boiling point.
- **Van der Waals Forces:** Butane, a hydrocarbon, experiences only weak van der Waals forces, leading to a lower boiling point.
- **Polarity:** Propanol is polar, while butane is non-polar, affecting intermolecular interactions.

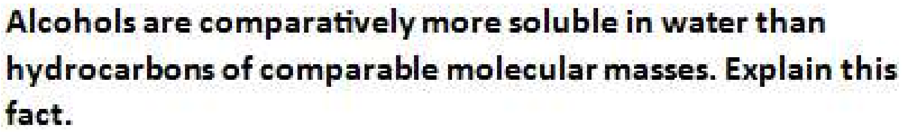
Ans – The solvent propane really comes with a significantly greater boiling temperature compared to butane, though. The existence of intermolecular bonds made of hydrogen is the root cause of the phenomenon.

A standalone hydrogen atom is joined to the electronegative nature of the oxygen atom present in the hydroxyl category in propanol. Meanwhile, the petroleum product propane develops intermolecular communication bonding between hydrogen as a result. Molecular interaction results are based on this approach. A tremendous amount of energy is required to disrupt this molecular bond. Propanol's degree of boiling rises is referred to as a result.

Bonds made of hydrogen have no existence across butane. The substance butane is known to have a more modest boiling point according to a result. Propanol therefore possesses a greater boiling point compared to butane.

The petroleum product propane experiences intermolecular H-bonding due to the presence of OH elements in its structure. On the other hand, butane cannot. As a result, breaking the bonds between hydrogen requires greater amounts of energy. Hydrocarbons such as butane have resulted in a lower temperature at boiling compared to propanol.

7.5



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

📌 ***Key Points to Note from Question***

Key Concept:

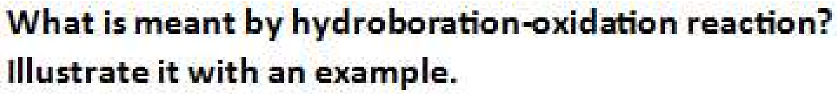
- **Hydrogen Bonding:** Alcohols have an -OH group, which forms hydrogen bonds with water molecules, increasing solubility.
- **Polarity:** Alcohols are polar, making them more compatible with water, while hydrocarbons are non-polar and cannot form hydrogen bonds.
- **Hydrocarbons' Insolubility:** Since hydrocarbons only have weak van der Waals forces, they do not interact well with polar water molecules.

Ans – The two atoms of hydrogen & oxygen elements that make up water molecules are arranged polarly; each atom of hydrogen has a positive electrical charge on one region, while the opposite side of the oxygen atom possesses an electrical charge that is negative. Alcoholic substances are able to create hydrogen bonds when combined with water because they have the group -OH in their structure, whereas hydrocarbons are unable to do so since that group is insufficient.

Meanwhile, as a result, alcoholic compounds dissolve in water much more readily than molecules of hydrocarbons with similar molecular weights. Given that the contact exists among two distinct atoms—a solute along with a solvent, such as alcohol and water—intramolecular bonding using hydrogen appears at the forefront in this instance.

By fragmenting the bonds made of hydrogen that currently have developed amongst the molecules of water, alcoholic substances may construct new ones together with water. As a result, they ought to dissolve in water molecules. However, molecules of hydrocarbons are insoluble in water because they are unable to create hydrogen associations with it.

7.6



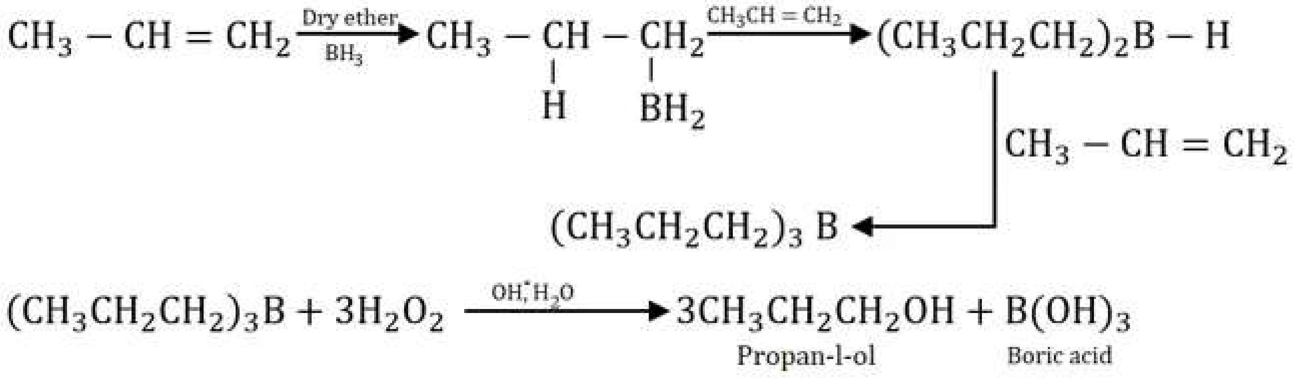
What is meant by hydroboration-oxidation reaction?
Illustrate it with an example.

Ans – The alkaline compound can be changed into a neutral entity alcoholic substance using a naturally occurring chemical process called hydroboration oxidation. This kind of event represents an oxidation reaction. Another two-stage procedure comprising an oxidation phase and a hydroboration procedure is used to achieve the following. A supplementary addition of water (across the whole double bonds) is used to achieve this result.

One way to conceptualize the underlying structure of the hydroboration oxidation process is referred to as the anti-Markovnikov reaction. In contrast to the idea that Markovnikov's principle seems to indicate, an anti-Markovnikov reaction occurs when an alternate element (such as a halogen) makes an area to the weaker substituted carbon-atom structure that makes up an unsymmetrical alkene.
Since carbocations, that are frequently created while on alkene or alkyne responses, are inclined to favour more extensively substituted the element carbon, this mechanism is relatively rare. The event typically happens via a free radical formation procedure, which frequently necessitates the existence of a peroxide catalyst to start the radical generation process.

In contrast, a compound called hydroxyl binds onto a carbon which has been considerably fewer substituted than the other two carbons in the process that follow. The mentioned hydroboration oxidation process was first identified in the later part of the mid-1950s based on the United States scientist Herbert Charles Brown, who was raised in New York in 1927 and is of English descent. Despite his work in this area, he was later awarded the Nobel Prize in 1979 for Chemistry.

Hydroboration-oxidation is a method of adding diborane towards alkenes to generate trialkyl boranes, which are then oxidized along with alkaline hydrogen peroxide for the generation of alcohol-based compounds. The anti-Markonikov introduction of water within an unsymmetrical alkene is what hydroboration oxidation is. For instance,



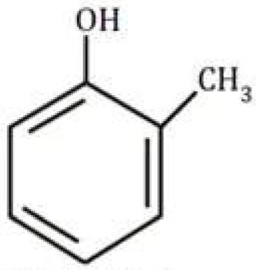
$$CH_3-CH=CH_2 \xrightarrow[BH_3]{\text{Dry ether}} CH_3-\underset{H}{CH}-\underset{BH_2}{CH_2} \xrightarrow{CH_3CH=CH_2} (CH_3CH_2CH_2)_2B-H \xrightarrow{CH_3-CH=CH_2} (CH_3CH_2CH_2)_3\,B$$

$$(CH_3CH_2CH_2)_3B + 3H_2O_2 \xrightarrow{OH^-, H_2O} \underset{\text{Propan-l-ol}}{3CH_3CH_2CH_2OH} + \underset{\text{Boric acid}}{B(OH)_3}$$

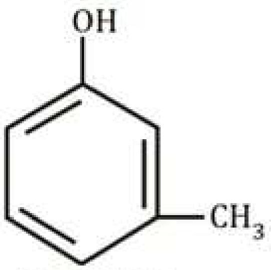
7.7

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

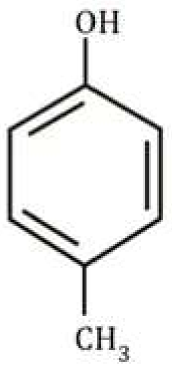
Ans –



2-methylphenol
o-Cresol



3-methylphenol
m-Cresol



4-methylpehnol
p-Cresol

7.8

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

📌 ***Key Points to Note from Question***

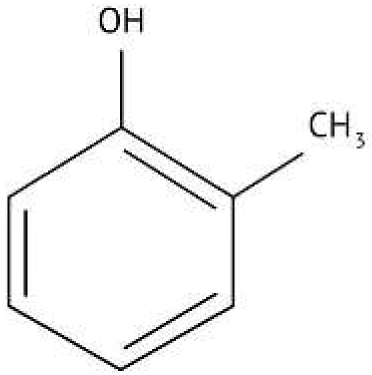
Key Concept:

- **Steam Volatility:** A compound is steam volatile if it has intermolecular hydrogen bonding rather than intramolecular hydrogen bonding.
- **Intramolecular vs. Intermolecular H-Bonding:**
    - **Ortho-nitrophenol** has intramolecular hydrogen bonding, reducing intermolecular interactions, making it steam volatile.
    - **Para-nitrophenol** has strong intermolecular hydrogen bonding, leading to higher boiling points and lower volatility.

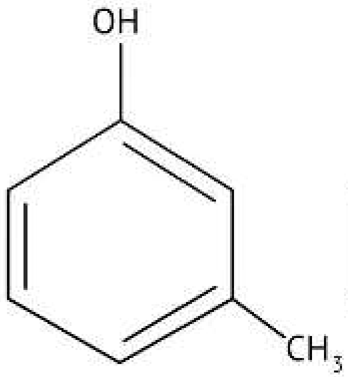
Ans – As we all know, the two o-nitrophenol & p-nitrophenol compounds exhibit intramolecular H-bonding. Due to the phenomenon of intramolecular bonding through hydrogen, resulting in decreased boiling level of the compound, ortho-nitrophenol becomes the volatile isomer. This in turn occurs when a combination of ortho along with para-nitrophenols is separated via steam distillation. In contrast, para-nitrophenol undergoes intermolecular bonds of hydrogen, which causes the components to be firmly bound in tandem.

Ortho-nitrophenol intramolecular hydrogen bonding: Inside ortho-nitrophenol, the hydroxyl group (OH) may establish an intramolecular hydrogen bond with the nitro group (NO2) on the subsequent location. This keeps the molecular structure in a loop that is closed and lowers the boiling point of the compound.

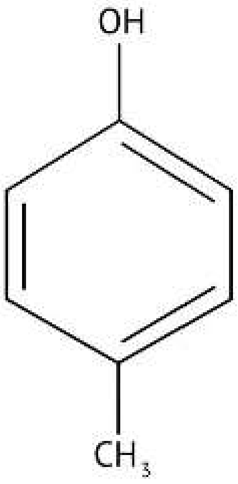
Para-nitrophenol intermolecular hydrogen bonding: The hydroxyl group that exists in para-nitrophenol is limited to creating hydrogen bonds with molecules that are nearby, leading to intermolecular hydrogen bonding, thus further solidifying molecular connections. As a result, this structure experiences an exceeding boiling level.
Below is the structure,



2-Methylphenol
(o-Cresol)



3-Methylphenol
(*m*-Cresol)



4-Methylphenol
(*p*-Cresol)

7.9

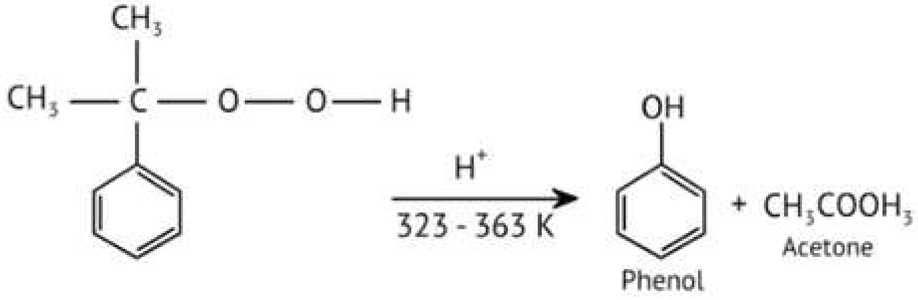
Give the equations of reactions for the preparation of phenol from cumene.

Ans – The group of hydroxyl gets attached together with a benzene ring to form the organic molecule known as phenol. They are also defined as weak acidic substances. Phenols typically lose a single positive hydrogen ion (H^+) from the group known as hydroxyl to generate phenoxide ions from their surroundings Back in the day, this substance was mostly made from coal tar-based products. However, as technology has advanced, a number of innovative techniques for making phenols have already been developed. The main source of phenol produced in labs involves benzene derivatives.

Friedel-Crafts alkylation process of benzene using propylene yields cumene, a naturally occurring molecule. Cumene hydroperoxide is produced when cumene (isopropylbenzene) is oxidized under the influence of the atmosphere. Phenols are produced when cumene hydroperoxide is subsequently treated with acid in a diluted form.

Large amounts of solvent acetone are also created as a consequence of this process. Therefore, purification procedures are required for phenols made using these production techniques. There are two additional techniques to prepare phenol from cumene:

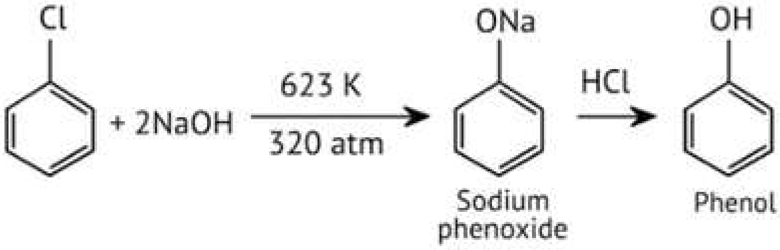
a. Cumene hydroperoxide is produced whenever an alkaline solution containing cumene (isopropyl benzene or 2-phenylpropane) in the form of sodium carbonate gets oxidized by flowing either oxygen or air around 423 K with cobalt naphthenate acting as a catalyst for the process.
b. During the auto-oxidation process, the hydroperoxide cumene breaks down into phenol and acetone when heated with diluted H_2SO_4. The solvent acetone is a significant residue of this process that can be extracted using the process of distillation.



7.10

Write chemical reaction for the preparation of phenol from chlorobenzene.

Ans – Chlorobenzene reacts with NaOH to produce sodium phenoxide, which, upon acidification, generates phenol. (at 623 K and 320 atm pressure)

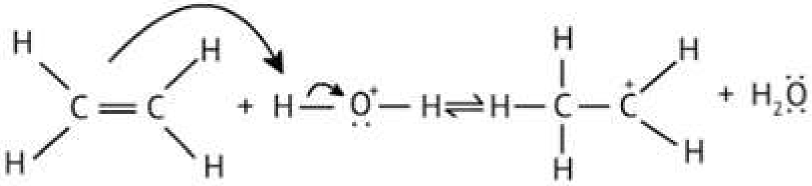


7.11

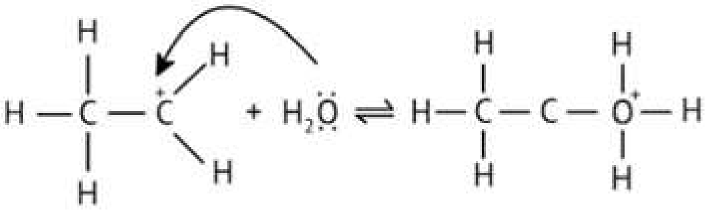
Write the mechanism of hydration of ethene to yield ethanol.

Ans – There are three steps involved in the hydration of ethene to produce ethanol.
Step 1: Carbocation is formed through an electrophilic reaction between hydronium ions and protonated ethene.

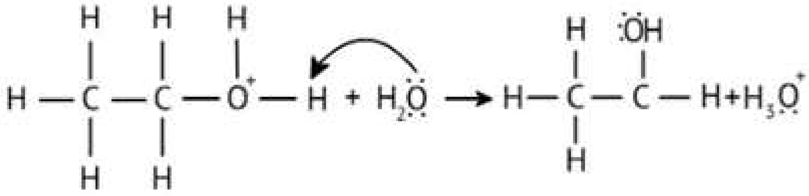
$H_2O + H^+ \rightarrow H_3O^+$



Step 2: The nucleophilic action of water on the carbocation.



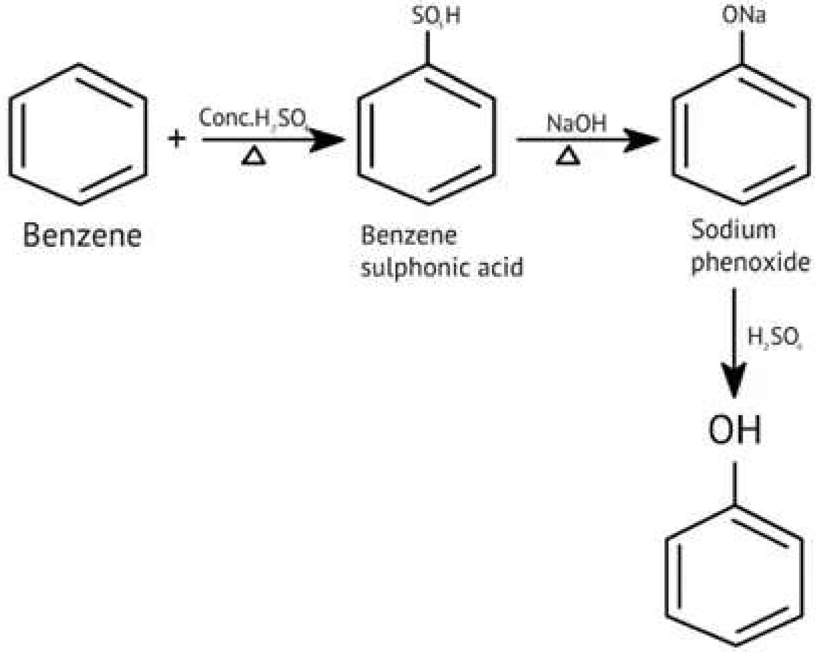
Step 3: Formation of ethanol by deprotonation



7.12

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

Ans –



7.13

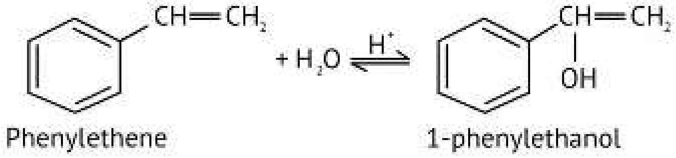
Show how will you synthesise:

(i) 1-phenylethanol from a suitable alkene.

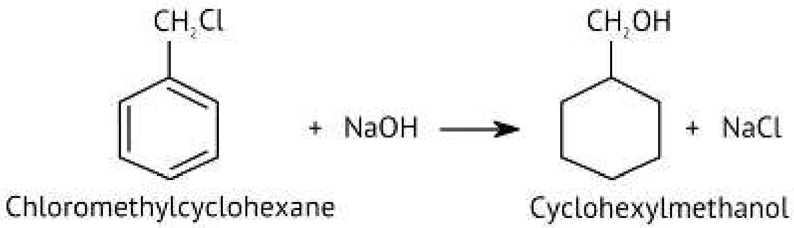
(ii) cyclohexylmethanol using an alkyl halide by an S_N2 reaction.

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

Ans – (i) 1-phenylethanol can be synthesised through the acid-catalyzed hydration of ethylbenzene (styrene).



(ii) Cyclohexylmethanol can be synthesised through the reaction of chloromethylcyclohexane with sodium hydroxide.



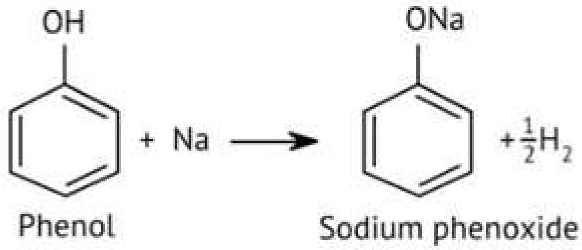
(iii) Pentan-1-ol is produced through the reaction of 1-chloropentane with sodium hydroxide.

$$\underset{\text{1 -chloropentane}}{CH_3CH_2CH_2CH_2CH_2Cl} + NaoH \rightarrow \underset{\text{pentan - 1 - ol}}{CH_3CH_2CH_2CH_2CH_2OH} + NaCl$$

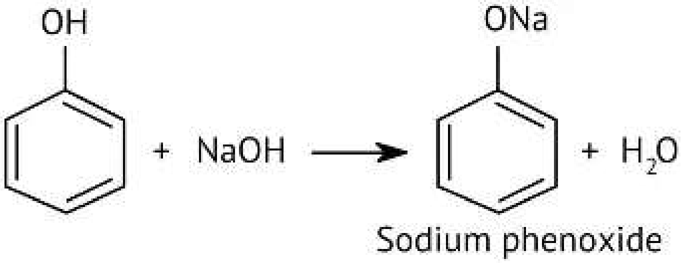
7.14

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

Ans – (a) When phenol reacts with sodium, sodium phenoxide is produced, releasing H_2.



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



Phenol has stronger acidity than ethanol. This is because the phenoxide ion resonates and remains stable after losing a proton, whereas the ethoxide ion does not.

7.15

Explain why is ortho nitrophenol more acidic than ortho methoxyphenol ?

📌 ***Key Points to Note from Question***

Electron-Withdrawing vs. Electron-Donating Groups:

- **-NO_2 (Nitro Group)** is an **electron-withdrawing group (-I and -M effect)**, stabilizing the phenoxide ion via **resonance and inductive effects**, increasing acidity.
- **-OCH_3 (Methoxy Group)** is an **electron-donating group (+I and +M effect)**, destabilizing the phenoxide ion and reducing acidity.

Ans – An electron-withdrawing compound belongs to the nitro group. The electron density present in the O-H bond becomes lower when the corresponding group is present in the ortho configuration. The process is therefore simpler to give up a proton. Additionally, resonance stabilizes the o-nitrophenoxide ion that is produced following proton depletion. Orthonitrophenol is consequently a more potent acidic solution.

The methoxy category, on the other hand, releases electrons. As a result, the proton is unable to escape readily because it raises the percentage of electrons across the bonds of O-H. Additionally, the $-CH_3$ compound releases electrons, thereby diminishing the acidic nature of the compound. Meanwhile, the nitro group raises its acidic feature.

At this point, resonance energy causes the o-methoxy phenoxide ions that are left over shortly after the element proton is lost to become unstable. O-nitrophenol happens to be more acidic compared to o-methoxyphenol because both of their charges that are negative oppose one another and cause the o-methoxyphenoxide ion to become unstable.

7.16

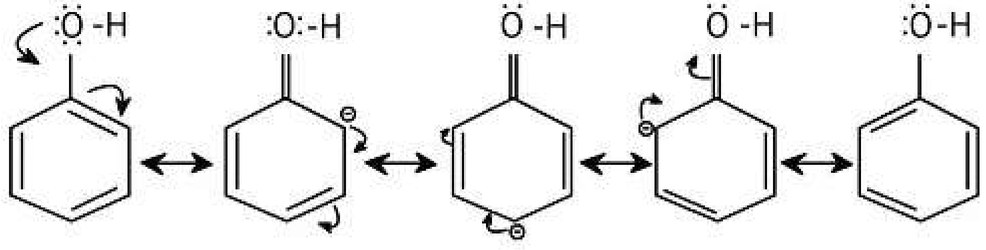
Explain how does the –OH group attached to a carbon of benzene ring activate it towards electrophilic substitution?

📌 ***Key Points to Note from Question***

Key Concept:

- **Resonance Effect:** The **–OH group** has a **+M (mesomeric) effect**, donating electron density to the benzene ring via resonance.
- **Increased Electron Density:** This donation activates the ring, making it more reactive towards electrophiles, particularly at the ortho and para positions.
- **Stabilization of the Intermediate:** The resonance forms stabilize the **carbocation intermediate**, lowering the activation energy for substitution.

Ans – The -OH group undergoes +R action contributing to the electron density within the benzene ring becoming higher. Thus, making it easier for electrophiles to cause damage to the ring as mentioned in the phenol resonance formation. Stated differently, the benzene ring is activated for electrophilic replacements by the existence of the -OH group connected to the element carbon.
Furthermore, both of the o and p positions along with a single p-position have a comparatively larger electron density. This makes it extremely susceptible towards electrophilic substitution, which mostly takes place around the o & p locations.



7.17

Give equations of the following reactions:

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

(ii)Bromine in CS_2 with phenol.

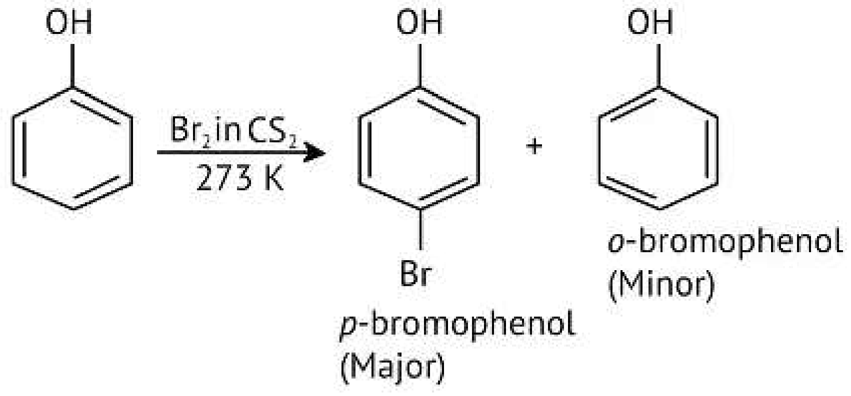
(iii)Dilute HNO_3 with phenol.

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

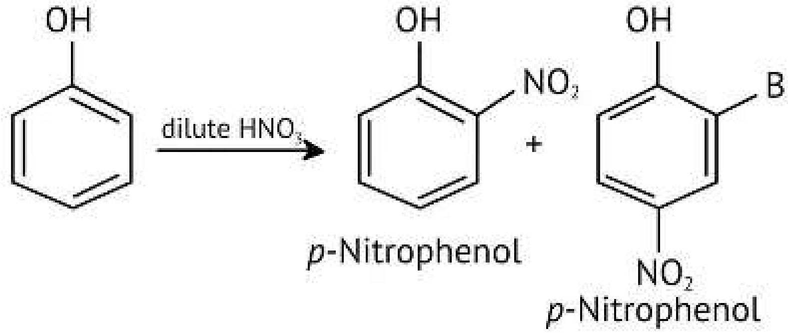
Ans – (i) KMnO4 efficiently oxidises primary alcohols to carboxylic acids under controlled conditions. Thus, propanol is converted into propanoic acid.

$$CH_3CH_2CH_2OH \xrightarrow{\text{alk.}KMnO_4} CH_3CH_2COOH$$

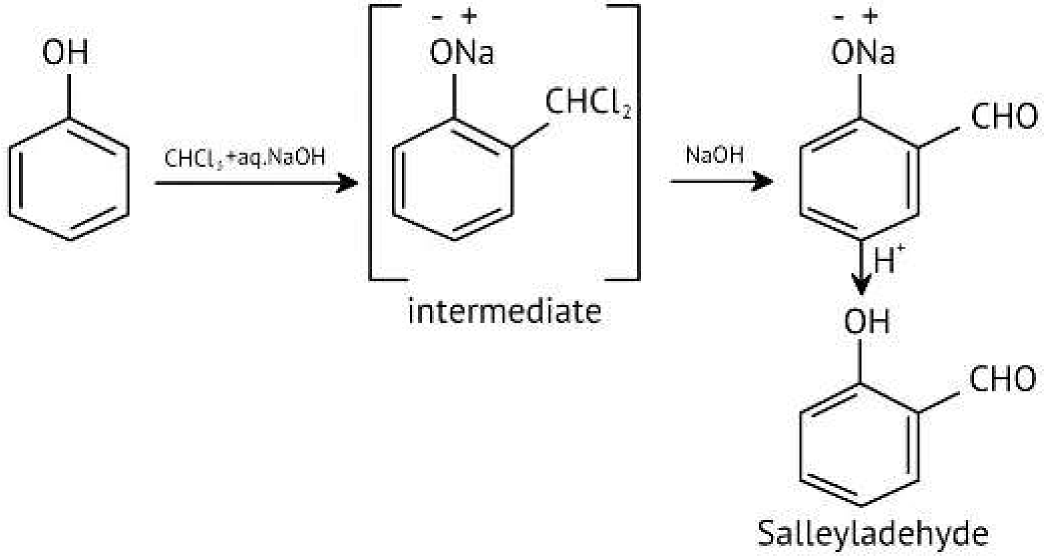
(ii) The reaction of phenol with bromine in carbon disulphide results in the formation of brominated derivatives. The -OH group functions as an ortho/para directing entity. The resulting compounds are p-bromophenol and o-bromophenol.



(iii) The nitration process will occur with dilute HNO_3.



(iv) Riemer-Tiemann reaction takes place.



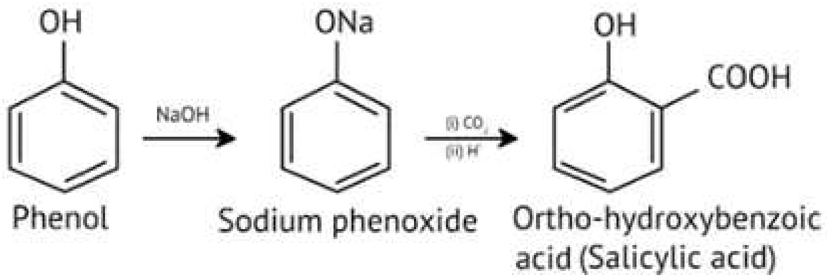
7.18

Explain the following with an example.

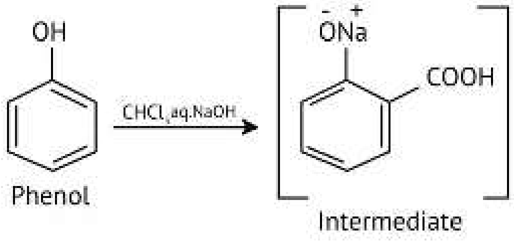
- **(i)** **Kolbe's reaction.**
- **(ii)** **Reimer-Tiemann reaction.**
- **(iii)** **Williamson ether synthesis.**
- **(iv)** **Unsymmetrical ether.**

Ans – (i) In regards to the process, the Kolbe reaction is similar to the Grignard reagents involving the carbon dioxide effect. Once sodium hydroxide gets added to phenol, a phenoxide ion is produced, which initiates Kolbe's reaction. In electrophilic aromatic replacement processes, this ion has become more susceptible to reaction compared to phenol. The salicylate is produced as the consequence of the nucleophilic bonding of phenoxide from carbon dioxide during Kolbe's process.

As an outcome, it interacts alongside carbon dioxide, which is an inadequate electrophile, and its primary compound is ortho-hydroxybenzoic acid, also known as salicylic acid. Salicylic acid's composition is the result of the reaction between the acidic substance and the compound salicylate. During this procedure, sodium phenoxide along with carbon dioxide is heated to 125 °C together with 100 atm pressure to initiate a carboxylation event.

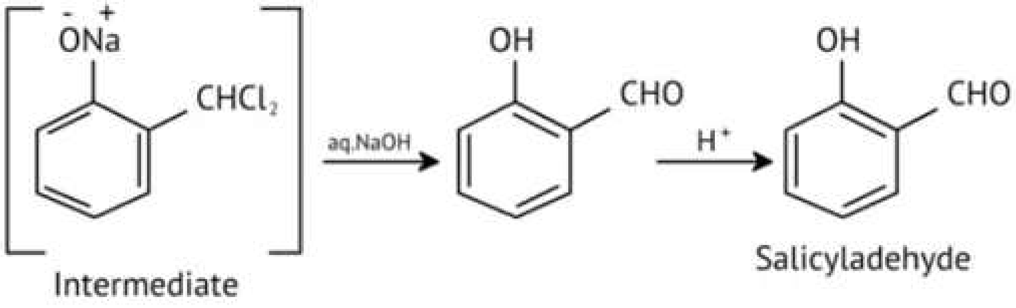


(ii) Chloroform, a neutralizing agent, and sequential acid exposure are used in the Reimer-Tiemann reaction, a type of chemical reaction mechanism that turns phenols into ortho-hydroxy benzaldehydes. It bears the names of the chemists who created the technique, Karl Reimer and Ferdinand Tiemann.

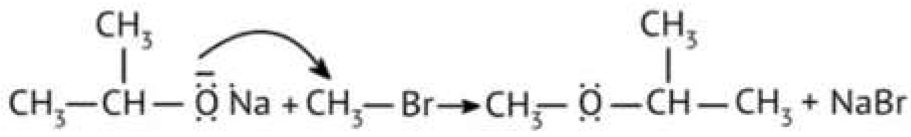


A CHO band is introduced at the ortho activity of the benzene ring whenever phenol is treated with chloroform within the general availability of NaOH called the Reimer-Tiemann reaction. Salicylaldehyde involves the end result of hydrolysing the intermediate technique, which is altered by benzyl chloride, in an environment full of alkali. Although the chemical process is utilized to ortho-formylate phenols, it is likewise known as the Reimer-Tiemann reaction.

Whenever phenol undergoes a reaction with chloroform within an environment of sodium hydroxide, the -CHO group is added at the opposite side of the benzene ring. In an atmosphere of alkalis, the intermediate product is hydrolysed to generate salicylaldehyde.



(iii) By allowing alkyl group halides to be responsive to sodium alkoxides in working environments, the Williamson ether synthesis technique produces both symmetrical and unsymmetrical ethers. During the process known as S_N2, the alkoxide particle that is harmful to the organic material is included in the reaction itself. Better results are achieved in the instance of primary alkyl group halides. When the organic molecule is secondary or tertiary, replacement prevails above removal.



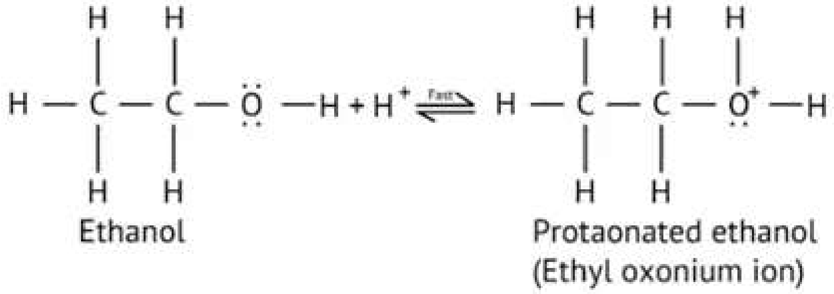
$CH_3-CH(CH_3)-\bar{\ddot{O}}\dot{N}a + CH_3-Br \rightarrow CH_3-\ddot{O}-CH(CH_3)-CH_3 + NaBr$

(iv) Ethyl methyl ether ($CH_3-O-CH_2CH_3$) is an example of a naturally occurring unsymmetrical ether, which has two distinct groups on opposing sides of an oxygen atom which differ (i.e., having an uneven amount of carbon atoms).

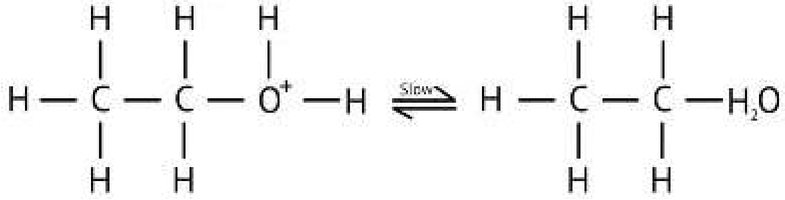
7.19

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

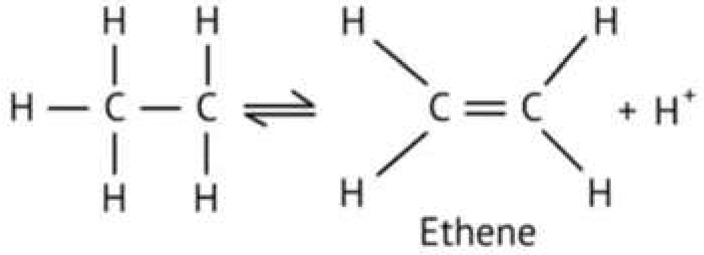
Ans – There are three steps involved in the acid dehydration of ethanol to yield ethene
Step 1: Protonation of ethanol to produce the ethyl oxonium ion



Step 2: Formation of carbocation (rate-determining step)



Step 3: Creating ethene by eliminating a proton



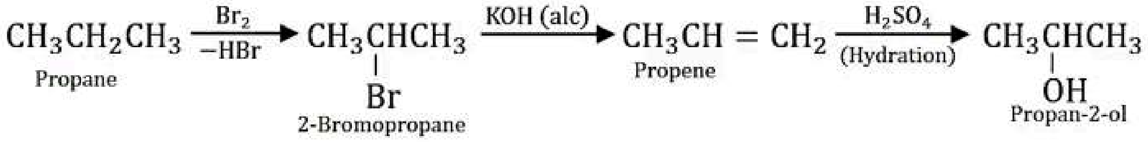
The acid consumed in Step 1 is released in Step 3. It is removed following the creation of ethene to forward the equilibrium.

7.20

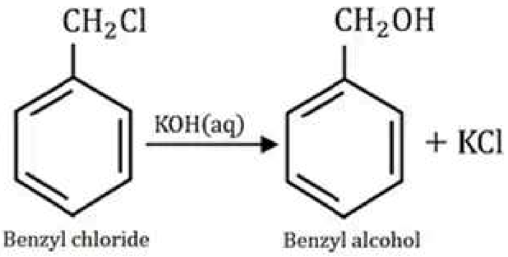
How are the following conversions carried out?

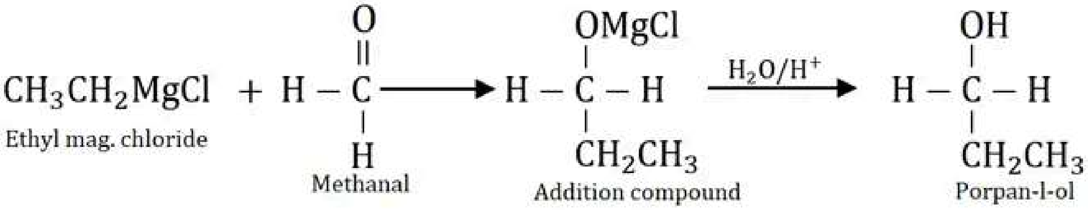
- **(i)** **Propene → Propan-2-ol.**
- **(ii)** **Benzyl chloride → Benzyl alcohol.**
- **(iii)** **Ethyl magnesium chloride → Propan-1-ol.**
- **(iv)** **Methyl magnesium bromide → 2-Methylpropan-2-ol.**

Ans -

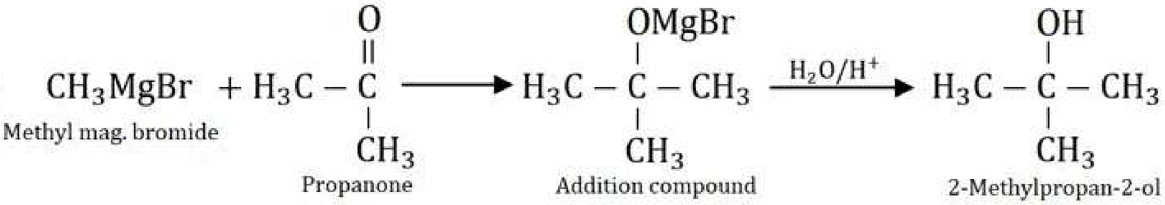
(i)


$$\underset{\text{Propane}}{CH_3CH_2CH_3} \xrightarrow[-HBr]{Br_2} \underset{\text{2-Bromopropane}}{CH_3\underset{\underset{Br}{|}}{C}HCH_3} \xrightarrow{KOH\ (alc)} \underset{\text{Propene}}{CH_3CH=CH_2} \xrightarrow[(Hydration)]{H_2SO_4} \underset{\text{Propan-2-ol}}{CH_3\underset{\underset{OH}{|}}{C}HCH_3}$$

(ii)


(iii)


$$\underset{\text{Ethyl mag. chloride}}{CH_3CH_2MgCl} + \underset{\text{Methanal}}{H-\overset{\overset{O}{\|}}{\underset{\underset{H}{|}}{C}}} \longrightarrow \underset{\text{Addition compound}}{H-\overset{\overset{OMgCl}{|}}{\underset{\underset{CH_2CH_3}{|}}{C}}-H} \xrightarrow{H_2O/H^+} \underset{\text{Porpan-l-ol}}{H-\overset{\overset{OH}{|}}{\underset{\underset{CH_2CH_3}{|}}{C}}-H}$$

(iv)


$$\underset{\text{Methyl mag. bromide}}{CH_3MgBr} + \underset{\text{Propanone}}{H_3C-\overset{\overset{O}{\|}}{\underset{\underset{CH_3}{|}}{C}}} \longrightarrow \underset{\text{Addition compound}}{H_3C-\overset{\overset{OMgBr}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3} \xrightarrow{H_2O/H^+} \underset{\text{2-Methylpropan-2-ol}}{H_3C-\overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3}$$

7.21

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.**

Ans – (i) Acidified potassium permanganate

(ii) Pyridinium chlorochromate (PCC)

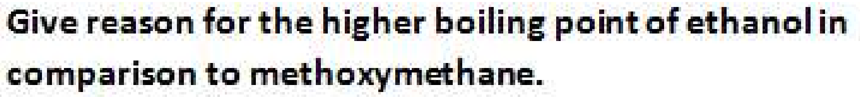
(iii) Bromine water

(iv) Acidified potassium permanganate

(v) 85% H_2S0_4 at 440 K

(vi) $NaBH_4$ or $LiAlH_4$

7.22



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

📌 ***Key Points to Note from Question***

Key Concept:

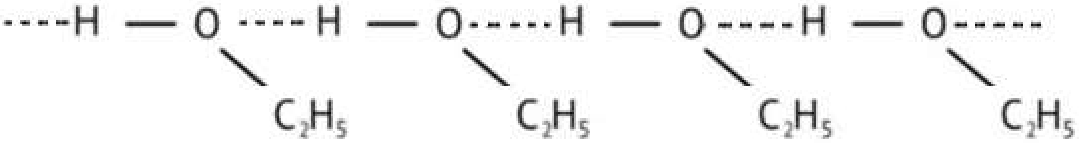
- **Hydrogen Bonding:** Ethanol forms strong intermolecular hydrogen bonds due to the -OH group, increasing its boiling point.
- **Dipole Interactions:** Methoxymethane has dipole-dipole interactions but lacks hydrogen bonding, leading to a lower boiling point.

Ans – The alcohol group -OH in a substance of ethanol allows it to establish bonds composed of hydrogen. Meanwhile, significant intermolecular interactions can be produced when the hydrogen atom that is bonded around the oxygen interacts with the oxygen within a different ethanol molecular structure. Grain alcohol is another name for ethanol, which has a molecular composition called C_2H_5OH.

However, methoxy methane has an ether bond (R-O-R) that differs from alcohol in its characteristics. Since the atoms of hydrogen are joined to form carbon atoms. It also has a lower electronegative element compared to oxygen. Hence, these atoms are unable to make hydrogen bonds efficiently. Consequently, there aren’t any substantial forces between molecules.

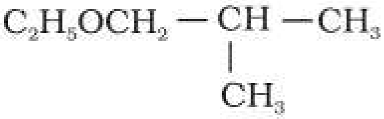
In the course of the phase transition between liquid to gas, additional energy (in the way of steam) is needed to dissolve more potent intermolecular interactions, such as bonds made up of hydrogen. Given its powerful hydrogen bonding, ethanol currently has an elevated boiling point which means that it takes a greater temperature for it to break down these bonds. Methoxy methane exhibits an inferior boiling point because it lacks strong hydrogen bonds, which weaken intermolecular interactions.

The main reason ethanol comes with higher boiling temperatures, as opposed to methoxy methane, is because it contains hydrogen bonds, which tend to be far more challenging to break compared with the weakened pull found in methoxy methane.



7.23

Give IUPAC names of the following ethers:

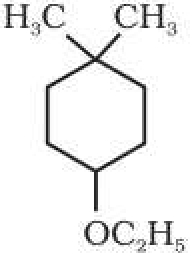
(i) 

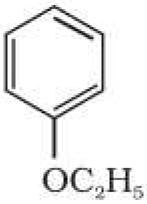
$C_2H_5OCH_2-\underset{|\atop CH_3}{CH}-CH_3$

(ii) $CH_3OCH_2CH_2Cl$

(iii) $O_2N-C_6H_4-OCH_3(p)$

(iv) $CH_3CH_2CH_2OCH_3$

(v) 

(vi) 

Ans – (i) 1-Ethoxy-2-methylpropane

(ii) 2-Chlorlo-l-methoxy ethane

(iii) 4-Nitroanisole

(iv) 1-Methoxypropane

(v) 1 -Ethoxy-4 -4 – dimethyl cyclohexane

(vi) Ethoxybenzene

7.24

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

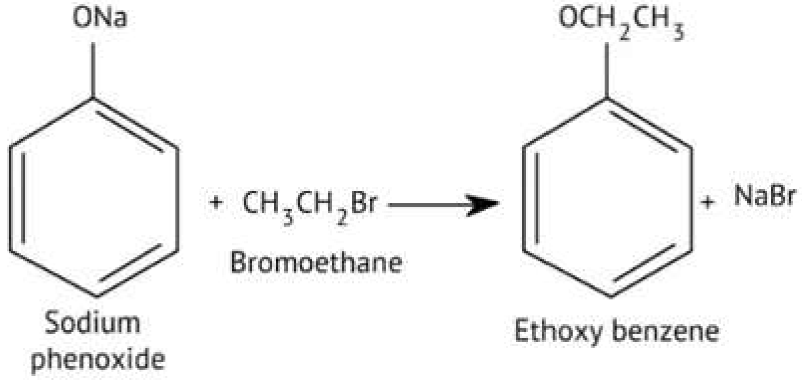
(i) 1-Propoxypropane **(ii) Ethoxybenzene**

(iii) 2-Methoxy-2-methylpropane **(iv) 1-Methoxyethane**

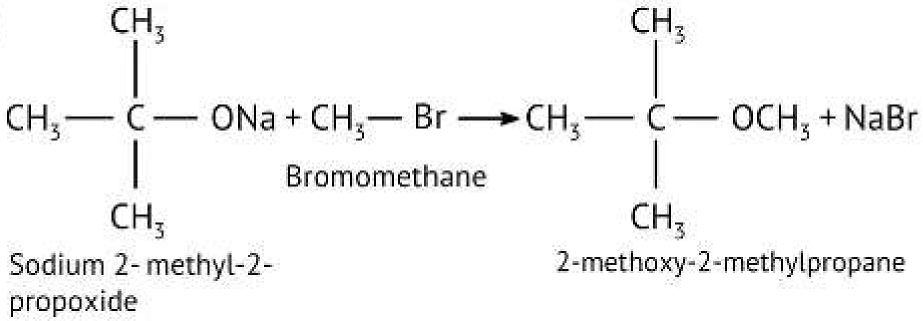
Ans –

$$\text{(i) }\underset{\text{Sodium propxoxide}}{CH_3CH_2CHONa} + \underset{\text{1 - bromopropane}}{CH_3CH_2CH_2Br} \rightarrow \underset{\text{1 - propoxypropane}}{C_2H_5CH_2 - O - CH_2C_2H_5} + NaBr$$

(ii)



(iii)



$$CH_3-C(CH_3)_2-ONa + CH_3-Br \rightarrow CH_3-C(CH_3)_2-OCH_3 + NaBr$$

(iv) $CH_3CH_2ONa + CH_3Br \rightarrow CH_3CH_2-O-CH_3 + NaBr$

Sodium ethoxide bromoethane 1 - methoxyethane

7.25

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

Ans – According to the context of Williamson synthesis, a compound containing an alkoxide ion can target a fundamental alkyl halide via S_N2. When the alkyl halides are basic compounds, superior results can be achieved. When it comes to secondary and tertiary alkyl halides, substitution is trumped by elimination. Ultimately, alkenes rather than ethers would end up being produced.

This is especially difficult when utilizing effectively hindered primary or secondary alkyl halides or while attempting to synthesize ethers comprising bulky alkyl chains. Alkoxides combine with alkyl halides, causing a mechanism of elimination since these substances are extremely powerful bases and nucleophiles. Some of the illustrative examples include,

i. An alkene becomes the main product if the alkyl halide reaction is tertiary, and the alkoxide functions as an intense base rather than a nucleophile.
ii. Because the C—Cl link is an incomplete double-bonded structure, chlorobenzene is not generated by Williamson's reaction. Therefore, sodium phenoxide is used to make fragrant ether compounds.

Because of the steric barrier and tendency for elimination, the main reaction that occurs when tert-butyl bromide along with sodium tert-butoxide are combined is the creation of an isobutene/alkaline compound.

7.26

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

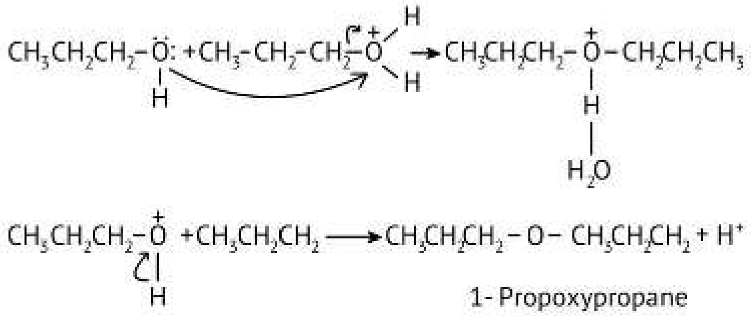
📌 ***Key Points to Note from Question***

Key Concept:

- **Williamson Ether Synthesis:** Alcohol is converted to an alkoxide (by reaction with a strong base) and then reacts with an alkyl halide.
- **Acid-Catalyzed Dehydration:** In the presence of acid (H_2SO_4), two alcohol molecules undergo dehydration to form an ether.

Ans – A substance named Propan-1-ol is converted to 1-propoxypropane via dehydration. Therefore, Propan-1-ol gets dehydrated to generate 1-propoxypropane whenever protic acids are present.
The following three phases comprise this reaction's technique:

1. Protonation is the initial stage. Here, the oxygen atom that exists within Propan-1-ol is protonated in this phase.
2. The subsequent stage, known to be the nucleophile assault, occurs when the oxygen atom concerning the second Propan-1-ol molecule breaches the protonated state of the compound, forming protonated 1-propoxypropane along with water.
3. Deprotonation is the final stage, whereas protonated 1-propoxypropane has emerged as deprotonated.



7.27

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

📌 ***Key Points to Note from Question***

Key Concept:

- **Carbocation Formation:** Secondary and tertiary alcohols form stable carbocations under acidic conditions.
- **Competing Reactions:** Instead of ether formation, these carbocations favor elimination (E1) leading to alkene formation.

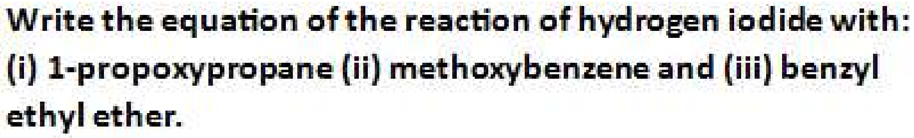
Ans – Due to the fact that secondary or tertiary alcoholic substances typically go through elimination processes, like E1 or E2 reactions, instead of creating ethers, the acid-based dehydration technique of ether synthesis does not constitute a viable approach. Ethers, a bimolecular mechanism (S_N2) that occurs when a molecule of alcohol targets a protonated alcohol molecule, are produced when alcohol is dehydrated. During the process, the alkyl group that is formed ought to be released.

Instead of interacting to generate an ether throughout an acid-catalyzed dehydration process, the alcohol molecules might eliminate a molecule of water and generate a compound called an alkene. Because of the longstanding stability underlying the resultant alkene, secondary and tertiary alcohols are particularly susceptible to elimination processes.

Conversely to this situation, 2° alongside 3° alcoholic substances produce alkenes as opposed to ethers because of steric hindrance, which prevents the alcohol molecular structure from attacking the protonated alcohol molecular structure nucleophilically. On the contrary, protonated 2° and 3° alcohols decrease in their water molecules in order to generate solid 2° and 3° carbocations.

To identify the production of ethers, the situation is often more suitable to use a different procedure, like the Williamson ether synthesis, known to be more dependable and effective for ether getting ready by involving the interaction of an alkyl halide paired with sodium alkoxide (RONa).

7.28



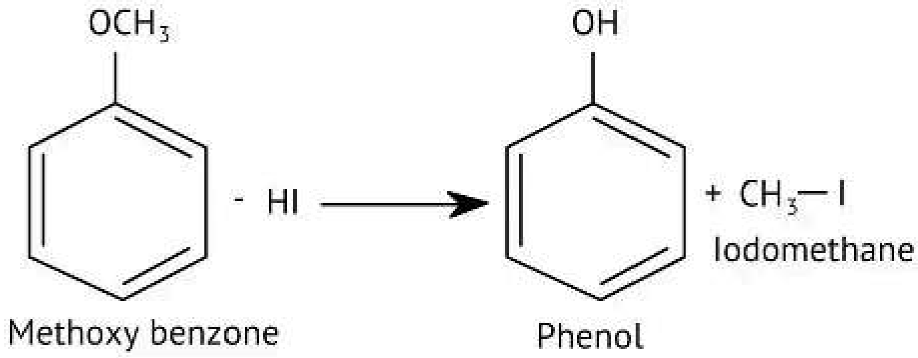
Write the equation of the reaction of hydrogen iodide with:
(i) 1-propoxypropane (ii) methoxybenzene and (iii) benzyl ethyl ether.

Ans –

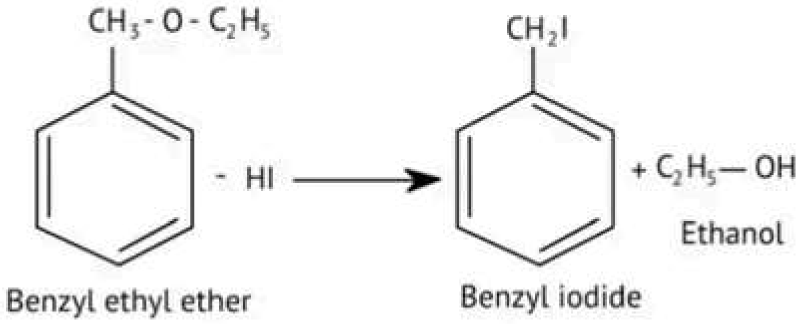
(i) $C_2H_5CH_2-O-CH_2C_2H_5 + HI \overset{373K}{------>} CH_3CH_2CH_2-OH + CH_3CH_2CH_2-I$

1 - propoxypropane propan - 1 - ol 1 - iodopropane

(ii)



(iii)



7.29

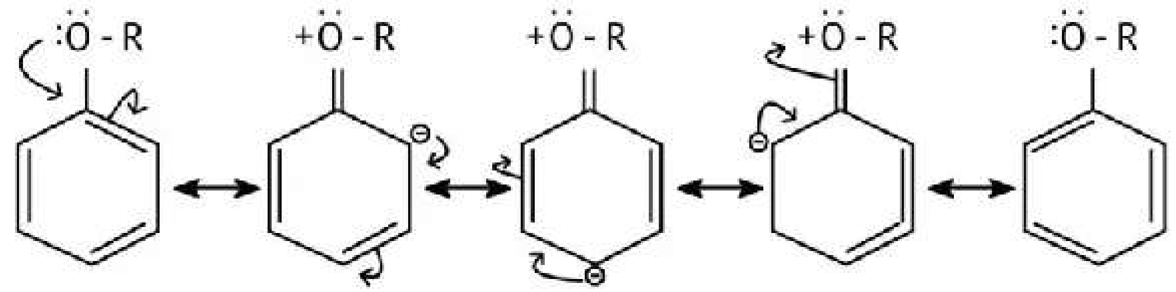
Explain the fact that in aryl alkyl ethers (i) the alkoxy group activates the benzene ring towards electrophilic substitution and (ii) it directs the incoming substituents to ortho and para positions in benzene ring.

📌 ***Key Points to Note from Question***

Key Concept:

- **+M Effect of -OR Group:** The alkoxy (-OR) group donates electron density to the benzene ring via resonance, increasing reactivity toward electrophiles.
- **Ortho-Para Directing:** The resonance effect creates high electron density at the ortho and para positions, making them more favorable for substitution.

Ans – (i) As seen within the resonance pattern listed below, the influence generated by the alkoxy position causes the number of electrons in the benzene ring to rise in aryl alkyl ethers.



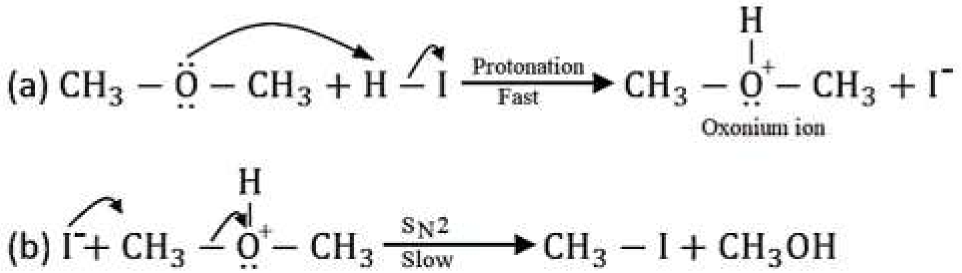
Consequently, benzene is activated onto an electrophilic substitution by the alkoxy unit.

(ii) The resonance configurations show that the electron concentration increases at the para and ortho postures compared to the meta region. Consequently, the ortho and para positions of the benzene ring receive the incoming substituted elements.

7.30

Write the mechanism of the reaction of HI with methoxymethane.

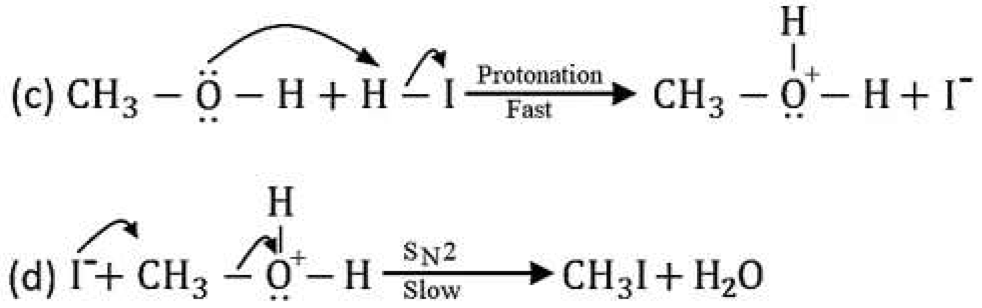
Ans – Upon the reaction of equimolar quantities of HI and methoxy methane, a mixture of methyl alcohol and methyl iodide is produced through the following mechanism:



$$\text{(a) } \mathrm{CH_3-\ddot{\underset{\cdot\cdot}{O}}-CH_3 + H-I} \xrightarrow[\text{Fast}]{\text{Protonation}} \underset{\text{Oxonium ion}}{\mathrm{CH_3-\overset{\displaystyle H}{\overset{|}{\underset{\cdot\cdot}{O}^+}}-CH_3}} + \mathrm{I^-}$$

$$\text{(b) } \mathrm{I^- + CH_3-\overset{\displaystyle H}{\overset{|}{\underset{\cdot\cdot}{O}^+}}-CH_3} \xrightarrow[\text{Slow}]{\mathrm{S_N2}} \mathrm{CH_3-I + CH_3OH}$$

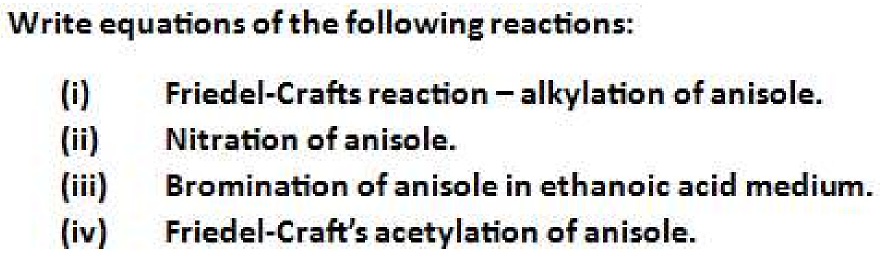
However, if an excess of HI is used, the methyl alcohol produced in step (b) is also converted into methyl iodide through the following mechanism.



$$\text{(c) } \mathrm{CH_3-\ddot{\underset{\cdot\cdot}{O}}-H + H-I} \xrightarrow[\text{Fast}]{\text{Protonation}} \mathrm{CH_3-\overset{\displaystyle H}{\overset{|}{\underset{\cdot\cdot}{O}^+}}-H + I^-}$$

$$\text{(d) } \mathrm{I^- + CH_3-\overset{\displaystyle H}{\overset{|}{\underset{\cdot\cdot}{O}^+}}-H} \xrightarrow[\text{Slow}]{\mathrm{S_N2}} \mathrm{CH_3I + H_2O}$$

7.31

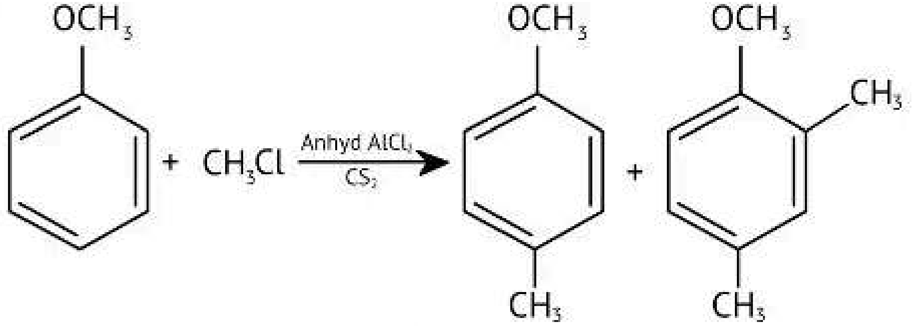


Write equations of the following reactions:

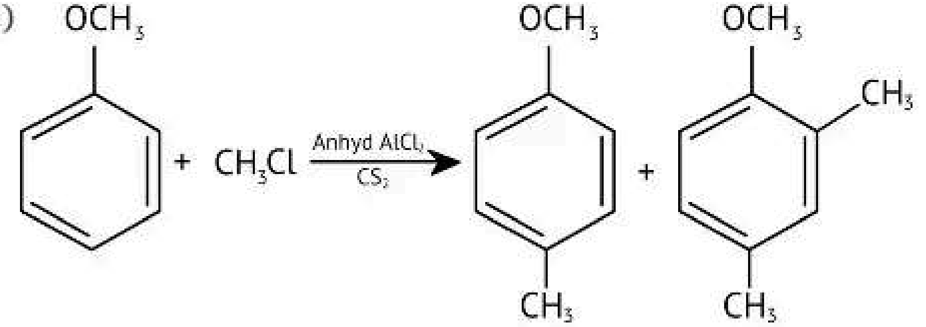
- (i) Friedel-Crafts reaction – alkylation of anisole.
- (ii) Nitration of anisole.
- (iii) Bromination of anisole in ethanoic acid medium.
- (iv) Friedel-Craft's acetylation of anisole.

Ans –

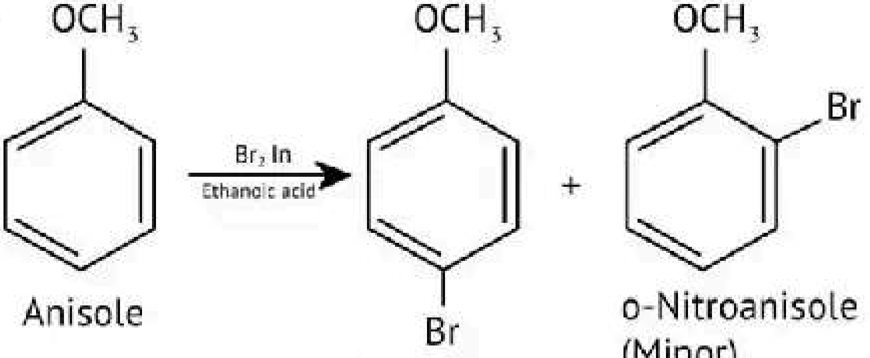
(i)


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

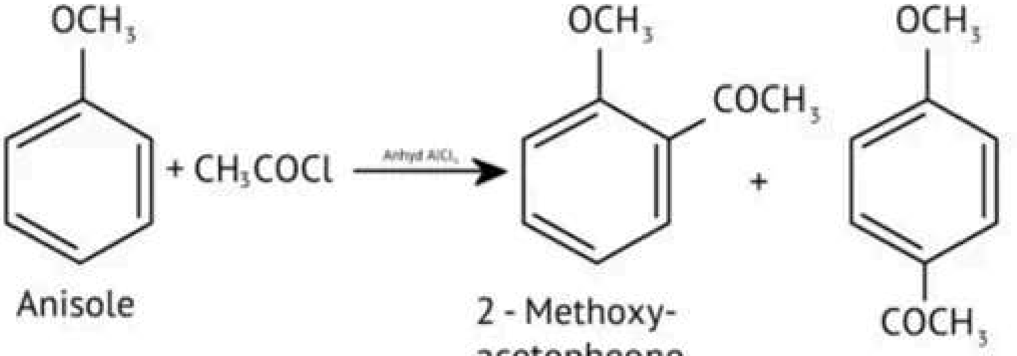
(ii)


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

(iii)

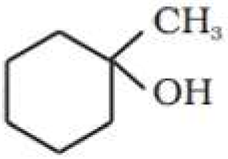

OCH3
Anisole
Br2 In
Ethanoic acid
OCH3
Br
OCH3
Br
p -Bromoanisole
(Major)
o-Nitroanisole
(Minor)

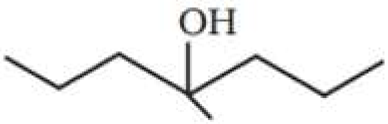
(iv)

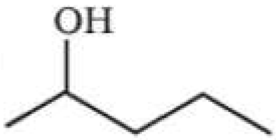

OCH3
Anisole
CH3COCl
Anhyd AlCl3
OCH3
COCH3
OCH3
COCH3
2 - Methoxy-
acetopheone
(Minor)
4 - Methoxy-
acetopheone
(Major)

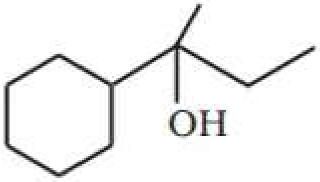
7.32

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

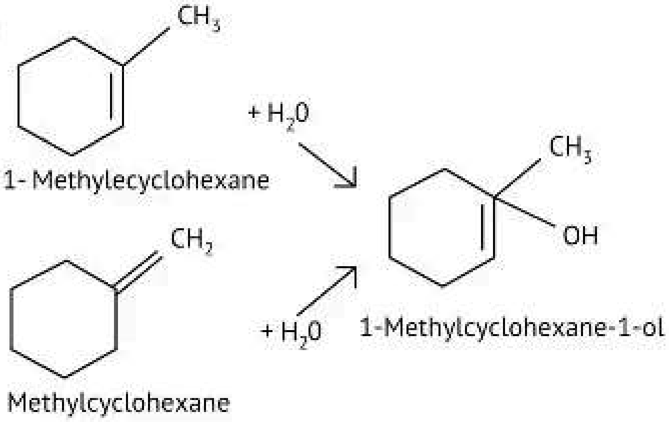
(i)


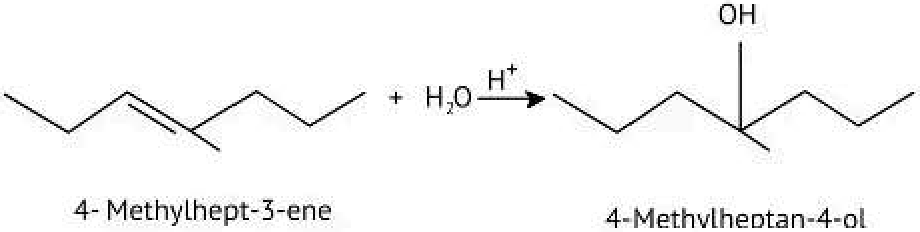
(ii)


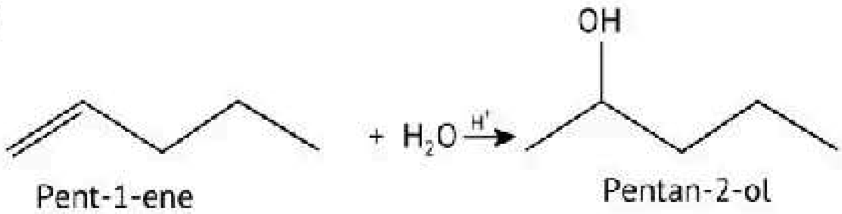
(iii)


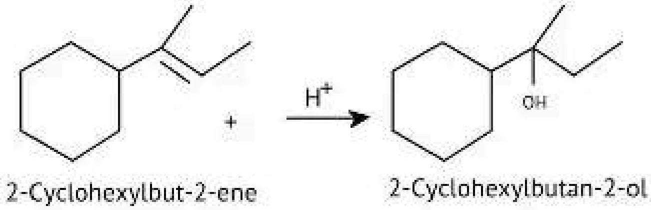
(iv)


Ans – The application of Markovnikov's rule in the acid-catalyzed hydration of suitable alkenes facilitates the synthesis of the specified alcohols.

(i)


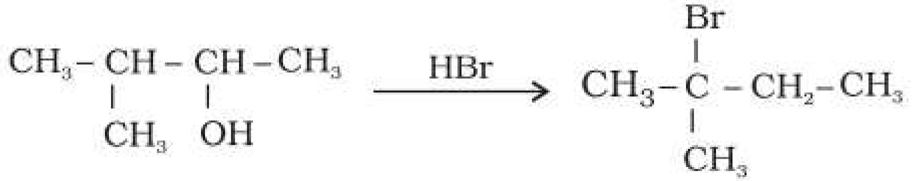
(ii)


(iii)


(iv)


7.33

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



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

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.

Ans – The protonation of the specified alcohol, followed by the elimination of water, results in the formation of a secondary carbocation (I), which, due to its instability, undergoes a 1,2-hydride shift to yield a more stable tertiary carbocation (II). The nucleophilic attack by the bromide ion on this carbocation (II) yields the end product.