Chapter 11

Alcohols Phenols and Ethers

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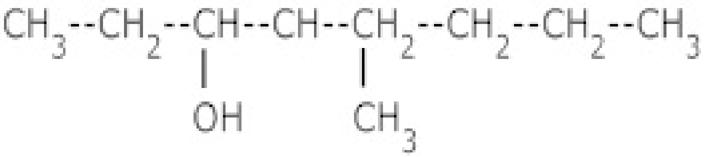
1 Mark Questions

1. Write IUPAC names of :-

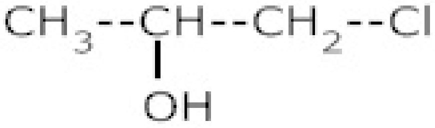
i.



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

Ans. 5 – Methyloctan-3-ol

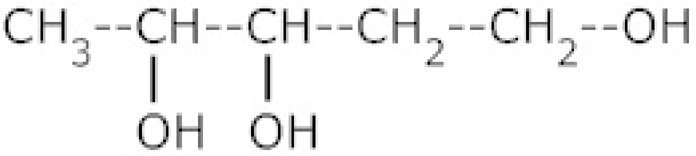
ii.



$CH_3--\underset{\overset{|}{OH}}{CH}--CH_2--Cl$

Ans. 1-Chloro propan-2-ol

iii.



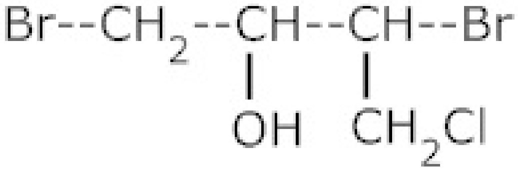
$CH_3--\underset{\overset{|}{OH}}{CH}--\underset{\overset{|}{OH}}{CH}--CH_2--CH_2--OH$

Ans. Pentan – 1,3,4 – triol

iv. $(CH_3)_3COH$

Ans. 2 – Methylpropan -2-ol

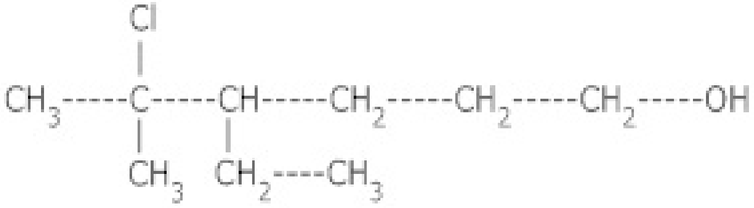
v.



$Br--CH_2--\underset{\overset{|}{OH}}{CH}--\underset{\overset{|}{CH_2Cl}}{CH}--Br$

Ans. 1,3 – Dibromo – 4- chloro – 2- butanol

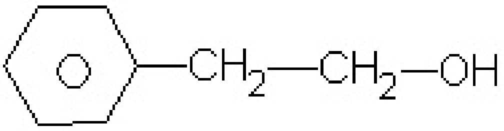
vi.



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

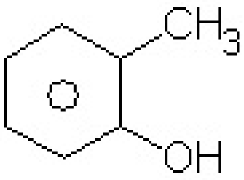
Ans. 5 – Chloro – 4 – ethyl – 5- methyl hexanol.

vii.



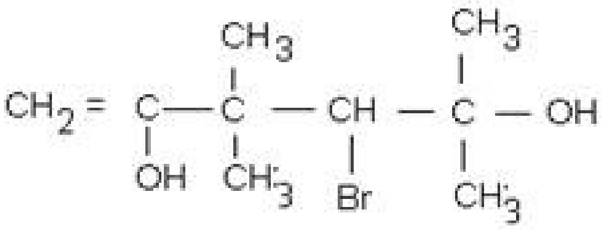
Ans. 2 – Phenyl ethanol

viii.



Ans. 2- Methyl phenol.

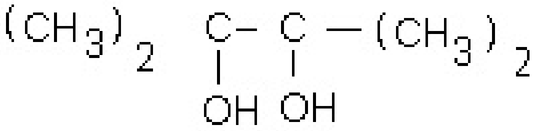
ix.



$CH_2=\underset{OH}{C}-\overset{CH_3}{\underset{CH_3}{C}}-\underset{Br}{CH}-\overset{CH_3}{\underset{CH_3}{C}}-OH$

Ans. 4- Bromo -3, 3,5 – trimethyl – hex -1-ene- 2,5- diol

x.

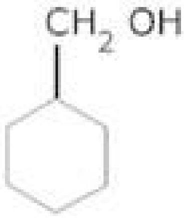


$(CH_3)_2\underset{OH}{C}-\underset{OH}{C}-(CH_3)_2$

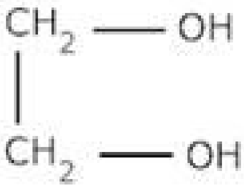
Ans. 2,3 – Dimethylbutan – 2,3 –diol

2. Write structural formula and give IUPAC names :-

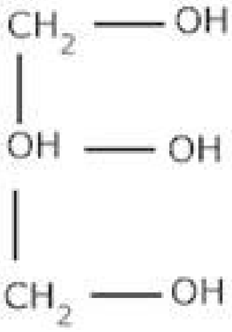
i. Benzyl Alcohol

Ans.  1- Phenyl methanol

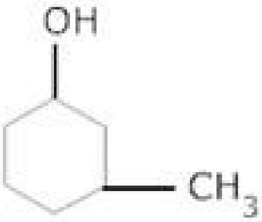
ii. Ethylene Glycol

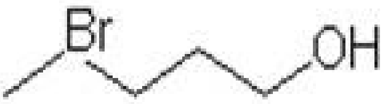
Ans.  Ethane - 1,2 - diol

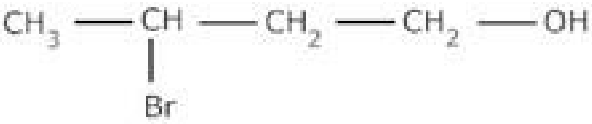
iii. Glycerol

Ans.  Propane - 1,2,3 - triol

iv. m- cresol

Ans.  3- Methyl phenol

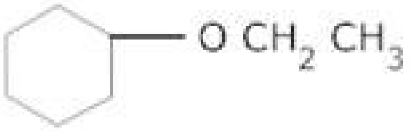
v. 

Ans. 

$CH_3 - \underset{\displaystyle Br}{\underset{|}{CH}} - CH_2 - CH_2 - OH$

3 - Bromobutanol

vi. Ethylphenylether

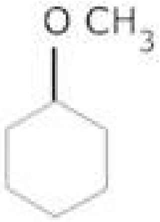
Ans. 

Ethoxybenzene

vii. Methylpropylether

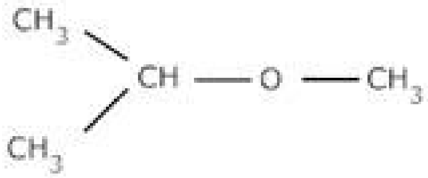
Ans. $CH_3-CH_2-CH_2-O-CH_3$ Methoxypropane

viii. Anisole

Ans. 

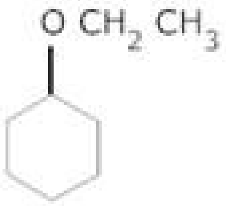
Methoxybenzene

ix. Isopropyl methylether

Ans. 

2 - Methoxy propane

x. Phenetole

Ans. 

Ethoxybenzene

3. What is denatured alcohol?

Ans. Industrial alcohol (ethyl alcohol) is made unfit for drinking purpose by addition of a small quantity of poisonous substance, methanol. This is called denatured alcohol. For denaturation, copper sulphate or pyridine can also be added.

4. Mention two important uses of methanol.

Ans. Uses of methanol:-

(i) It is used for denaturing alcohol.

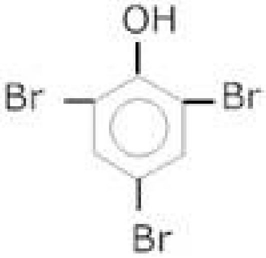
(ii) It is used as a solvent for paints & varnishes.

5. Arrange C_6H_5OH, C_2H_5OH & H_2O in the increasing order of acid strength.

Ans. The order is $C_2H_5OH < H_2O < C_6H_5OH$.

6. Give the structure of main product of action of excess of Br_2 on phenol.

Ans. The main product will be 2,4,6-tribromophenol.



7. What is wood sprit? Why is it so called?

Ans. Wood spirit is methanol. It is so called because earlier it was obtained from destructive distillation of wood only.

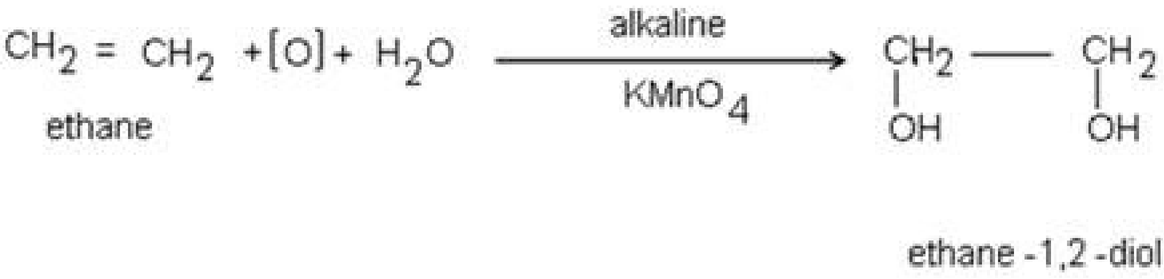
8. Identify allylic alcohols in the above examples.

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

2 Mark Questions

1. Ethene to 1,2 -ethanediol

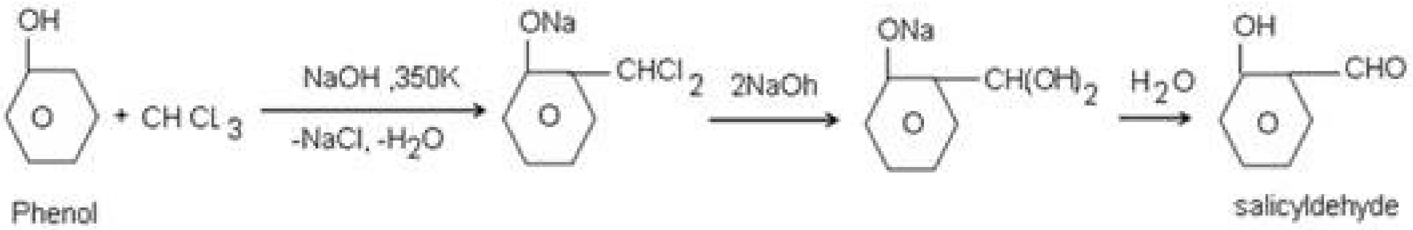
Ans.



$$\underset{\text{ethane}}{CH_2 = CH_2} + [O] + H_2O \xrightarrow[KMnO_4]{\text{alkaline}} \underset{\text{ethane -1,2 -diol}}{\underset{OH}{CH_2} - \underset{OH}{CH_2}}$$

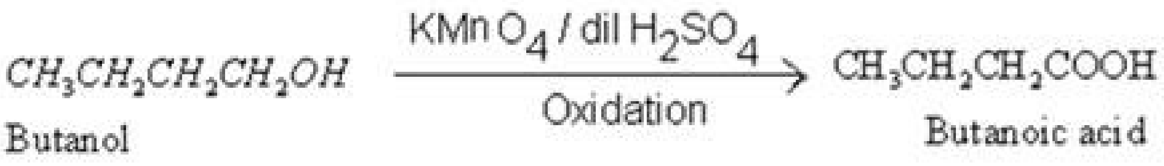
2. Phenol to Salicyldehyde

Ans.



3. Butanol to Butanoic acid

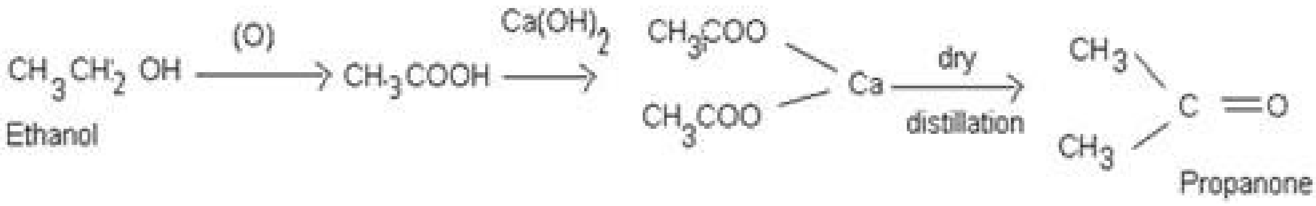
Ans.



$$\underset{\text{Butanol}}{CH_3CH_2CH_2CH_2OH} \xrightarrow[\text{Oxidation}]{KMnO_4 / \text{dil } H_2SO_4} \underset{\text{Butanoic acid}}{CH_3CH_2CH_2COOH}$$

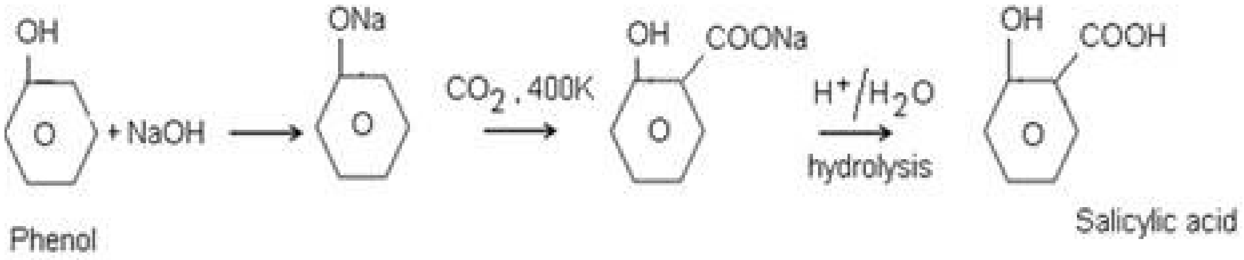
4. Ethanol to propanone

Ans.



5. Phenol to salicylic acid

Ans.



6. Methanol to Ethanol

Ans.

$$\underset{\text{Methanol}}{CH_3OH} \xrightarrow[\text{NaBr} \ + H_2SO_4]{\text{HBr}} CH_3Br \xrightarrow{\text{KCN}} CH_3CN \xrightarrow{LiAlH_4} CH_3CH_2NH_2 \xrightarrow{HNO_2} \underset{\text{Ethanol}}{CH_3CH_2OH}$$

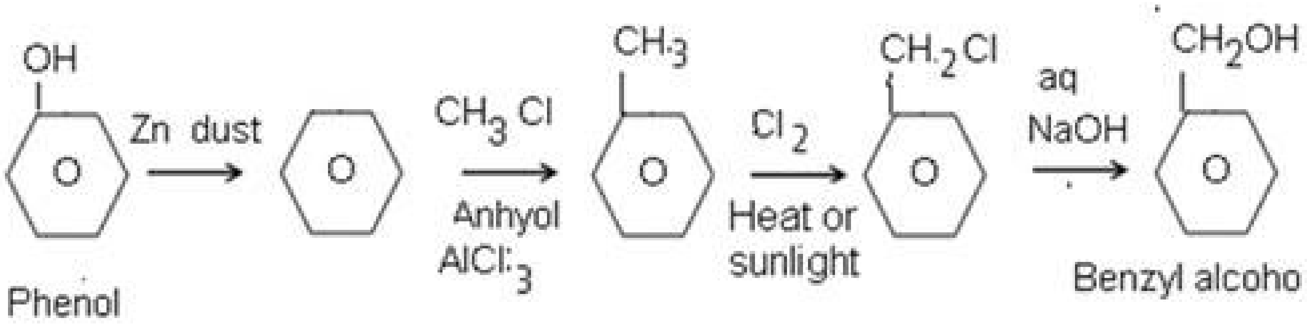
7. Ethanol to propanol

Ans.

$$\underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow[\text{NaBr}+ H_2SO_4]{\text{HBr}} CH_3CH_2Br \xrightarrow{\text{KCN}} CH_3CH_2CN \xrightarrow[\text{Reduction}]{[H]} CH_3CH_2CH_2NH_2 \xrightarrow{HNO_2} \underset{\text{Propanol}}{CH_3CH_2CH_2OH}$$

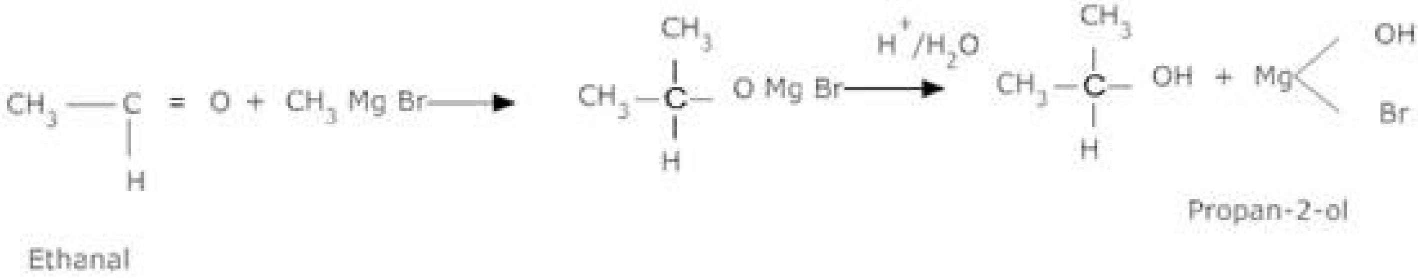
8. Phenol to Benzyl Alcohol

Ans.



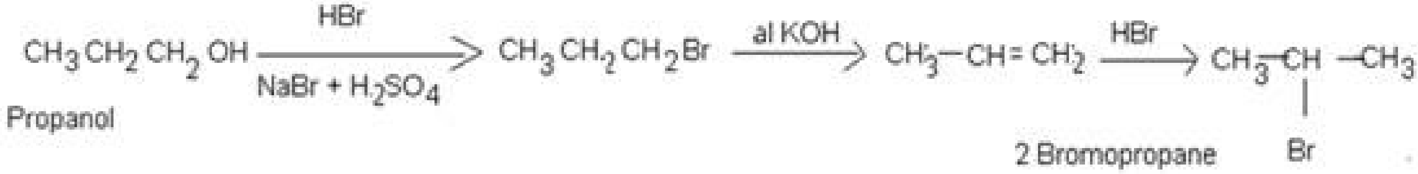
9. Ethanal to propan -2- ol

Ans.



10. l – propanol to 2 – bromo propane

Ans.



11. How is the presence of peroxides in ethers detected? How are peroxides removed from Ethers?

Ans. Presence of peroxides in ethers is detected by addition of freshly prepared $FeSO_4$ and KCNS. Appearance of blood red colour confirms the presence of peroxide. They can be removed by shaking ethers well with $FeSO_4$ solution.

12. Explain a chemical test to distinguish between primary, secondary and tertiary alcohols.

Ans. Primary tertiary and secondary alcohols can be distinguished by oxidation reaction.

Primary alcohols give aldehyde with CrO_3

$$RCH_2OH \xrightarrow{CrO_3} \mathrm{RCHO}$$

Secondary alcohols give ketone with CrO_3.

$$R_2CHOH \xrightarrow{CrO_3} \mathrm{R_2CO}$$

Tertiary alcohol do not get oxidized with CrO_3

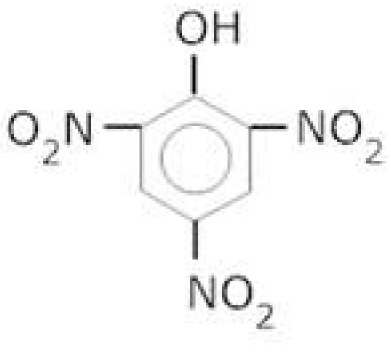
$$R_3COH \xrightarrow{CrO_3} \text{No reaction}$$

13. What is Lucas test?

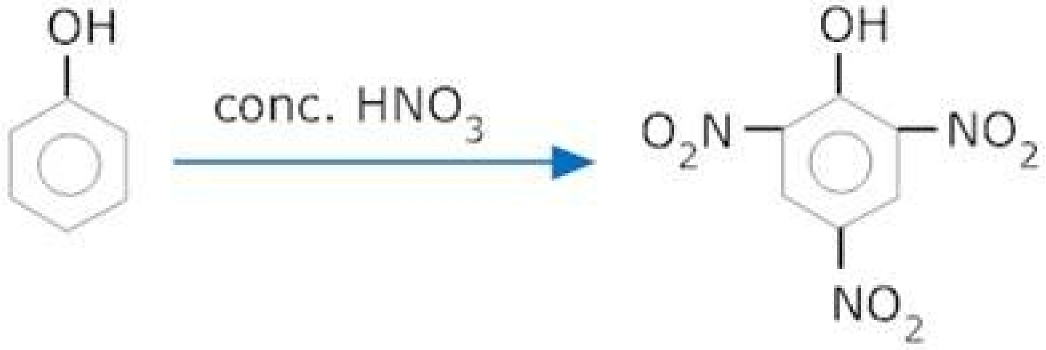
Ans. Lucas test is used for distinguishing between primary secondary and tertiary alcohols. When a tertiary alcohol is dissolved in Lucas reagent $(Conc.\, HCl + ZnCl_2)$ it produces turbidity immediately where as secondary alcohols produce turbidity after some time and primary alcohols do not react at all and no turbidity is product.

14. What is Picric acid? How is it prepared from phenol?

Ans. Picric acid is 2,4,6 – trinitrophenol



It is prepared from phenol by nitration with conc. HNO_3.



15. Give equations for preparation of ethanol by fermentation.

Ans. Ethanol can be prepared by fermentation of sugar –

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow[\text{enzymes}]{\text{Invertase}} C_6H_{12}O_6 + C_6H_{12}O_6$$

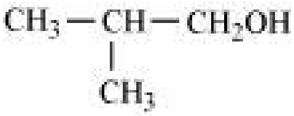
Sugar Glucose fructose

$$C_6H_{12}O_6 \xrightarrow[\text{enzymes}]{\text{Zymase}} 2C_2H_5OH + 2CO_2$$

Ehanol

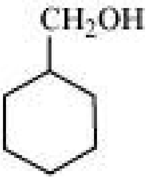
16. Show how are the following alcohols prepared by the reaction of a suitable Grignard reagent on methanal?

(i)

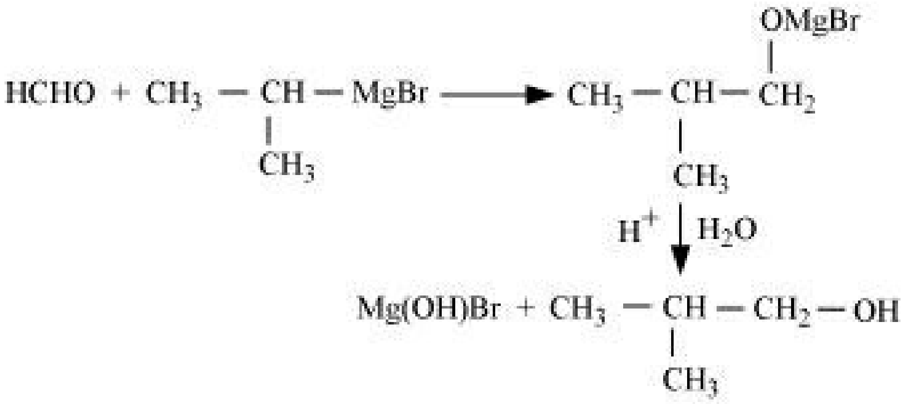


$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2OH$

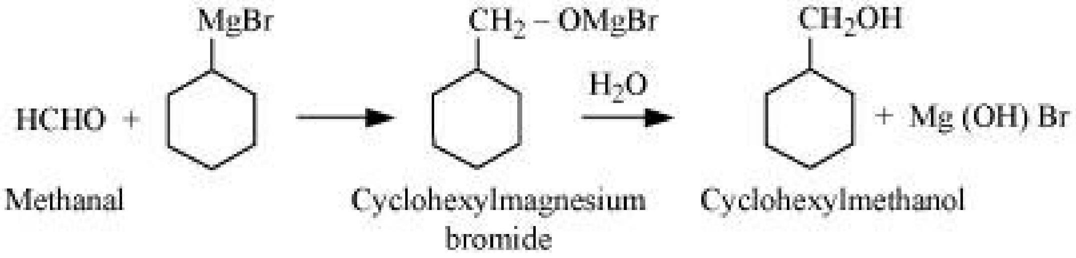
(ii)



Ans. (i)



(ii)

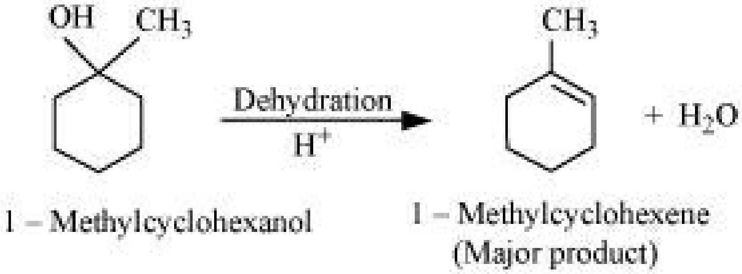


17. Predict the major product of acid catalysed dehydration of

(i) 1-Methylcyclohexanol and

(ii) Butan-1-ol

Ans. (i)



(ii)

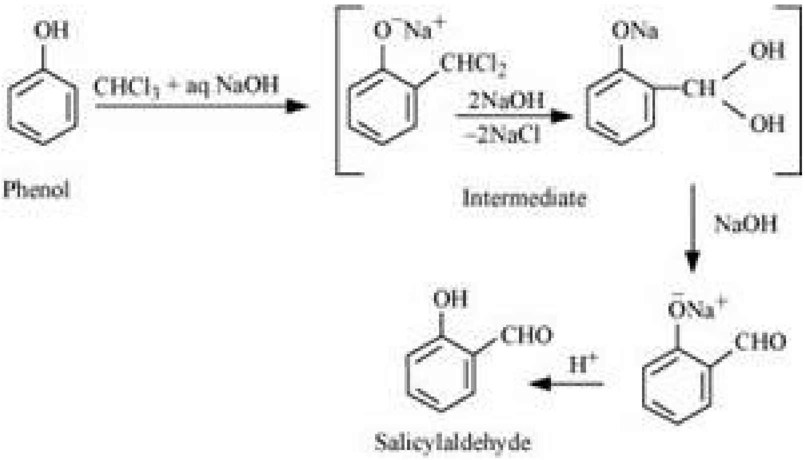
$$\underset{\text{Butan-1-ol}}{CH_3CH_2CH_2CH_2OH} \xrightarrow[H^+]{\text{Dehydration}} \underset{\substack{\text{But-2-ene}\\\text{(Major product)}}}{CH_3CH=CHCH_3} + H_2O$$

18. Write the equations involved in the following reactions:

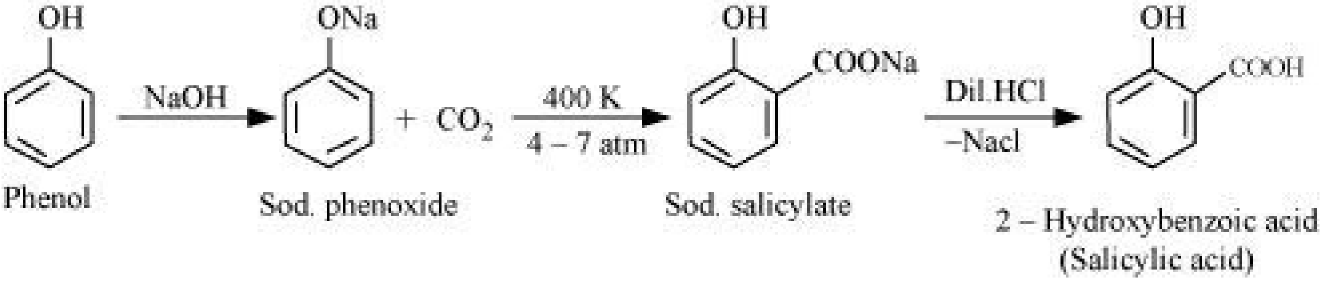
(i) Reimer-Tiemann reaction

(ii) Kolbe's reaction

Ans. (i) Reimer-Tiemann reaction

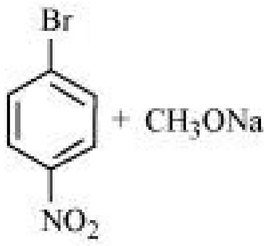


(ii) Kolbe's reaction

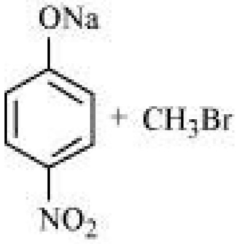


19. Which of the following is an appropriate set of reactants for the preparation of 1-methoxy-4-nitrobenzene and why?

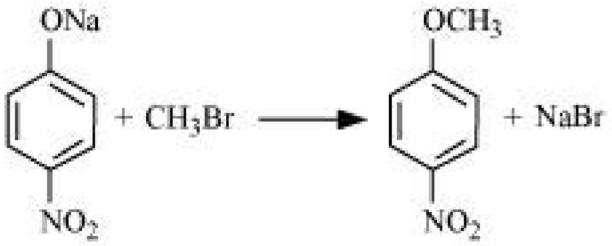
(i)



(ii)



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

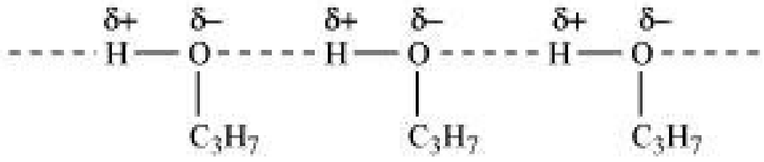


1 – Methoxy – 4 – nitrobenzene

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

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

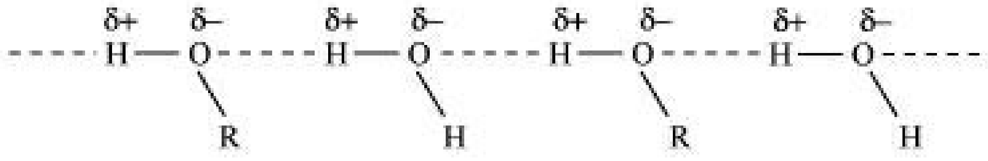
Ans. Propanol undergoes intermolecular H-bonding because of the presence of -OH group. On the other hand, butane does not



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

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

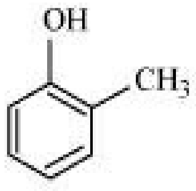
Ans. Alcohols form H-bonds with water due to the presence of -OH group. However, hydrocarbons cannot form H-bonds with water.



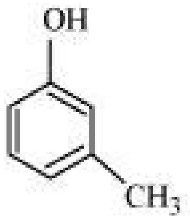
As a result, alcohols are comparatively more soluble in water than hydrocarbons of comparable molecular masses.

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

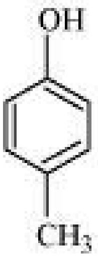
Ans.



2 – Methylphenol
(*o* – Cresol)



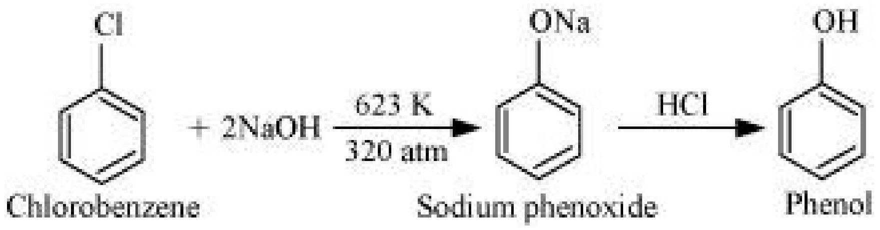
3 – Methylphenol
(*m* – Cresol)



4 – Methylphenol
(*p* – Cresol)

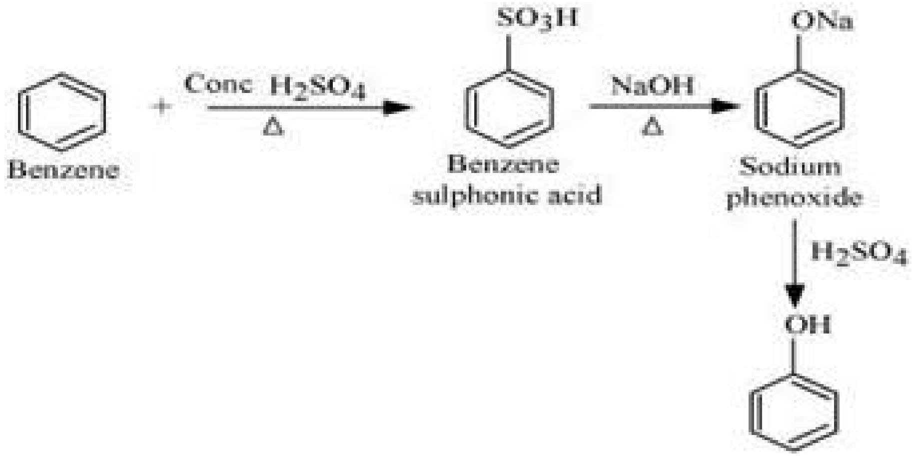
23. Write chemical reaction for the preparation of phenol from chlorobenzene.

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



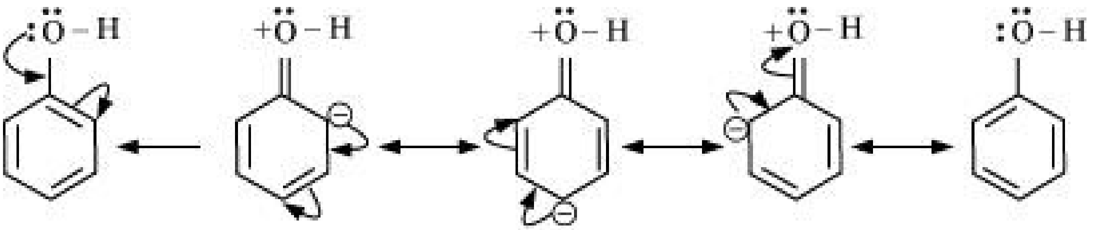
24. You are given benzene, conc. H_2SO_4 and NaOH. Write the equations for the preparation of phenol using these reagents.

Ans.



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

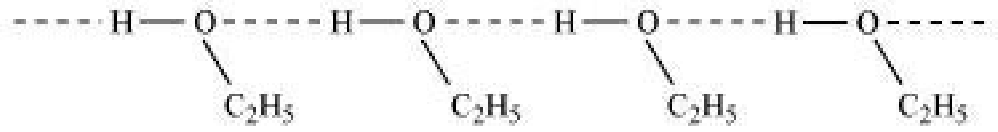
Ans. The -OH group is an electron-donating group. Thus, it increases the electron density in the benzene ring as shown in the given resonance structure of phenol.



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

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

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



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

Ans. The formation of ethers by dehydration of alcohol is a bimolecular reaction (S_N^2) involving the attack of an alcohol molecule on a protonated alcohol molecule. In the method, the alkyl group should be unhindered. In case of secondary or tertiary alcohols, the alkyl group is hindered. As a result, elimination dominates substitution. Hence, in place of ethers, alkenes are formed.

28. Explain the fact that in aryl alkyl ethers

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

(ii) It directs the incoming substituents to ortho and para positions in benzene ring.

Ans. (i) In aryl alkyl ethers, due to the +R effect of the alkoxy group, the electron density in the benzene ring increases as shown in the following resonance structure.

Thus, benzene is activated towards electrophilic substitution by the alkoxy group.

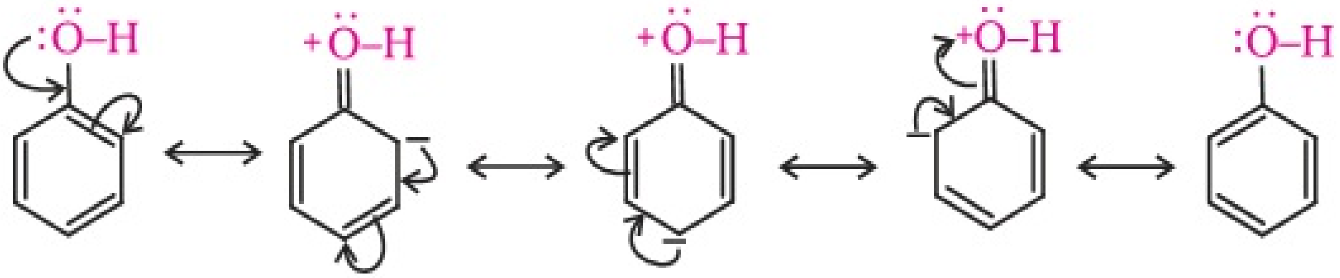
(ii) It can also be observed from the resonance structures that the electron density increases more at the ortho and para positions than at the meta position. As a result, the incoming substituents are directed to the ortho and para positions in the benzene ring.

3 Mark Questions

1. Phenol is acidic in nature.

Ans. Phenol is acidic in nature because

(a) phenol, due to resonance, the positive charge rests on oxygen making the shared pair of electrons more towards oxygen and hydrogen as H^+



(b) The carbon attached to OH is SP^2 hybridize and is more electronegative, this decreases the electron density on oxygen, increasing the polarity of O-H bond and ionization of phenol.

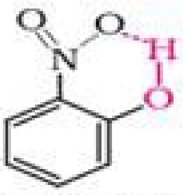
The phenoxide ion formed by loss of H^+ is more resonance stabilized than phenol itself.

2. Phenol has a smaller dipole moment than methanol.

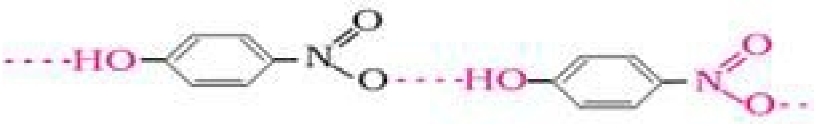
Ans. In phenol due to electron rich benzene ring the C-O bond is less polar whereas in methanol the C-O bond is highly polar. Therefore the dipole moment of methanol is higher than phenol.

3. o- nitrophenol has lower boiling point (is more volatile) than p – nitrophenol.

Ans. P- nitrophenol has intermolecular hydrogen bonding which increases the boiling point while in o- nitro phenol due to presence of intra molecular hydrogen bonding, there is a decrease in boiling point and increase in volatility.



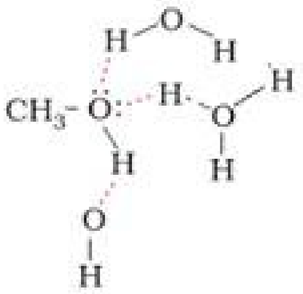
o-Nitrophenol
(Intramolecular
H-bonding)



p-Nitrophenol
(Intermolecular
H-bonding)

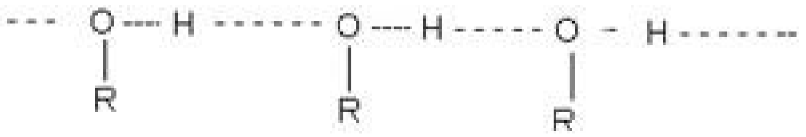
4. Methanol is miscible with water while iodomethane is not.

Ans. Methanol can form intermolecular hydrogen bonding with water but there is no hydrogen bonding in iodomethane and water. Therefore methanol in miscible in water.



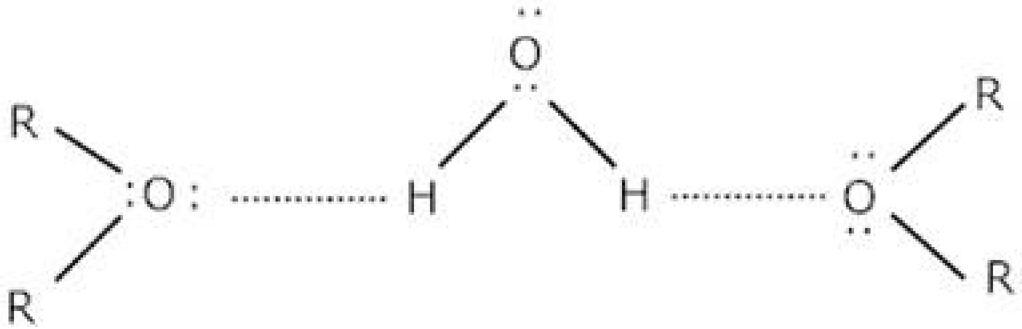
5. Alcohols have higher boiling points than isomeric ethers.

Ans. Alcohols can form intermolecular hydrogen bonds due to their high polarity whereas, ether cannot. Therefore alcohols have higher boiling points than isomeric ethers.



6. Ethers are soluble in water alkanes are not.

Ans. Ethers can form H- bonding with water molecule whereas alkenes cannot. Therefore ethers are soluble in water and alkanes are not.



7. The order of acidic strength in alcohols is R $CH_2OH > R_2CHOH > R_3COH$

Ans. In alcohols, the acidic strength is due to polar nature of O-H bond. An electron releasing group e.g., alkyl groups, increases electron density on oxygen tending to decrease the polarity of O-H bond. This decreases the acid strength. Therefore the order of acid strength is .

8. During preparation of ester from alcohol and acid, water has to be removed as soon as it is formed.

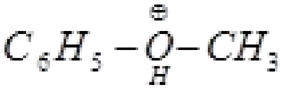
Ans. The reaction between alcohol and carboxylic acid is reversible and goes in backward direction if water is not removed as soon as it is formed.

$$ROH + RCOOH \xrightleftharpoons{H^+} \mathrm{RCOOR'} + \mathrm{H_2O}$$

9. Ethers can not be prepared by dehydration of secondary or tertiary alcohols.

Ans. For secondary and tertiary alcohols, elimination competes over substitution and alkenes are formed on acidic dehydration as the reaction follows Sn1 mechanism. Therefore the acidic dehydration of secondary or tertiary alcohols does not give ethers.

10. Reaction of anisole with HI gives methyl iodide and phenol.

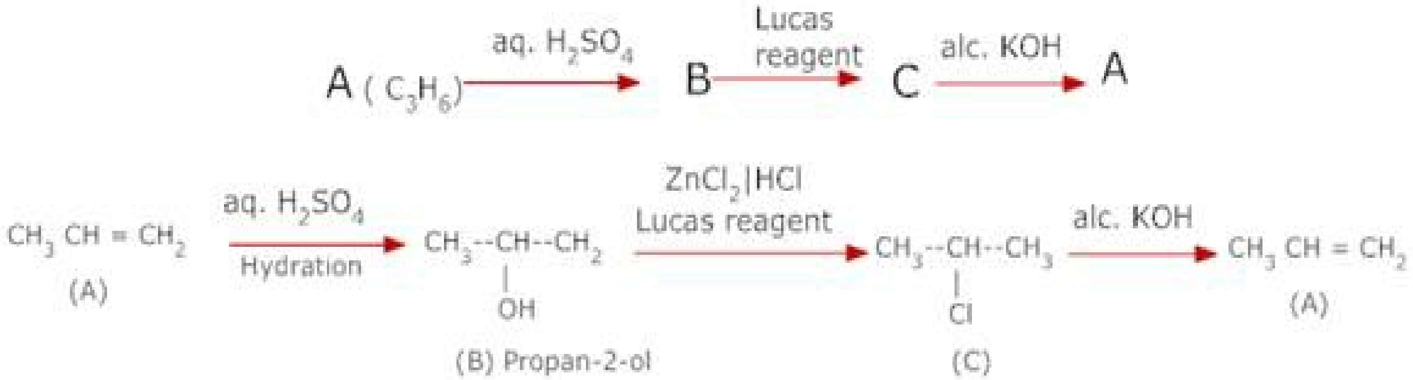
Ans. In case of anisole, methyl phenyl oxonium ion,  $C_6H_5-\underset{H}{\overset{\ominus}{O}}-CH_3$ is formed by

protonation of ethers during reaction with HI. The bond between O- CH_3 is weaker than the bond between $O-C_6H_5$ because carbon of phenyl group is SP^2 hybridised and there is a partial double bond character. Therefore the attack by I^- ion breaks $O-CH_3$ bond to form CH_3I.

$C_6H_5\ \ OCH_3 + HI \rightarrow C_6H_5OH + CH_3I$

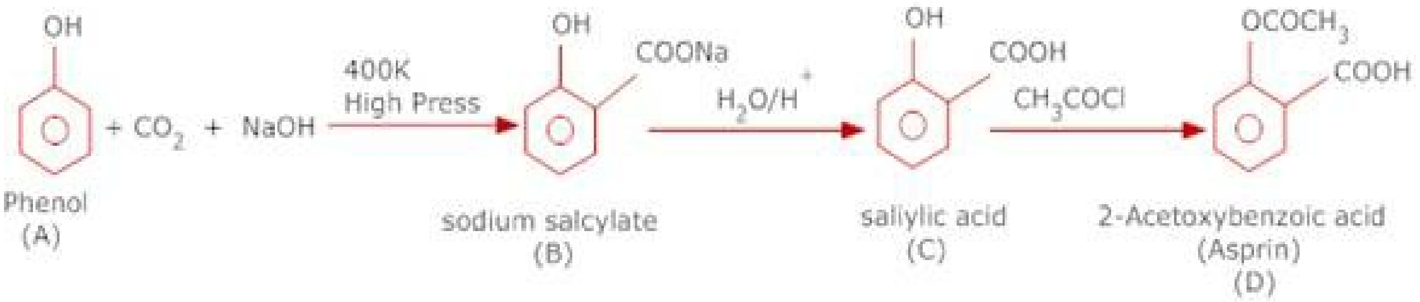
11. An organic compound ‘ A ‘ having molecular formula C_3H_6 on treatment with aq. H_2SO_4 give ‘B’ which on treatment with Lucas reagent gives ‘C’. The compound ‘C’ on treatment with ethanolic KOH gives back ‘A’ .Identify A, B, C .

Ans.



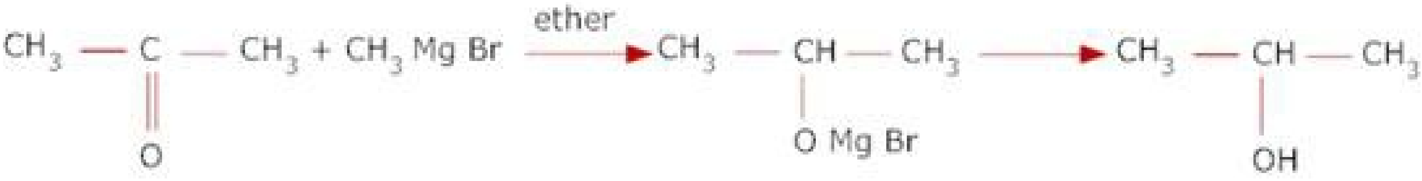
12. An organic compound $A(C_6H_6O)$ gives a characteristic colour with aq. $FeCl_3$ solution. (A) On reacting with CO_2 and NaOH at 400k under pressure gives (B) which on acidification gives a compound (C) .The compound (C) reacts with acetyl chloride to give (D) which is a popular pain killer. Deduce the structure of A,B,C & D.

Ans.



13. An organic compound (X) when dissolved in ether and treated with magnesium metal forms a compound Y. The compound, Y, on treatment with acetaldehyde and the product on acid hydrolysis gives isopropyl alcohol. Identify the compound X. What is the general name of the compounds of the type Y.

Ans. The compound X is CH_3Br and Y is CH_3MgBr The compounds of the type 'Y' are called Grignard reagent.



Isopropyl alcohol

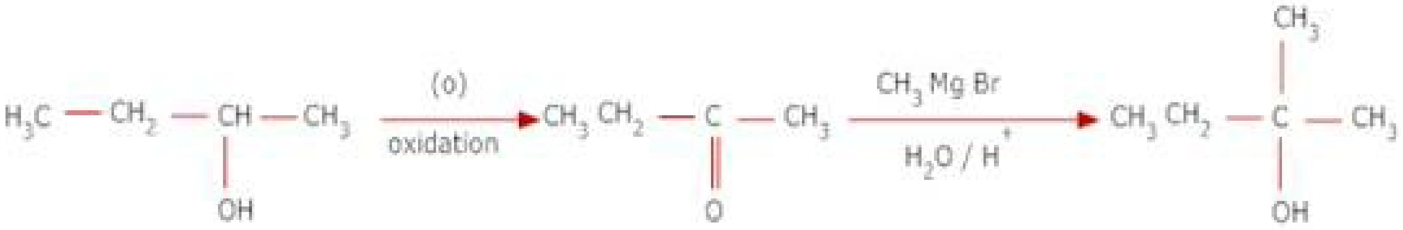
14. A compound 'A' with molecular formula $C_4H_{10}O$ on oxidation forms compound 'B' gives positive iodoform test and on reaction with CH_3MgBr followed by hydrolysis gives (c). Identify A, B & C.

Ans. The compound 'B' is obtained by oxidation of $C_4H_{10}O$ and gives positive iodoform test and also reacts with CH_3MgBr , it must be methyl Ketone , it must be methyl ketone having four carbon atoms i.e, $CH_3COCH_2CH_3$.

This can be obtained by oxidation of 2 – butanol i.e ,

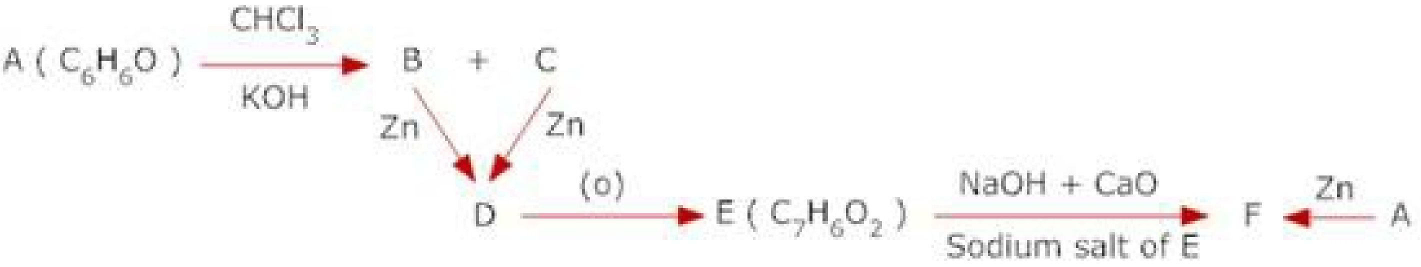
$\underset{HO}{CH_3\,CH}\;CH_2CH_3$

Therefore , the reactions are.



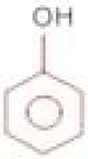
15. An aromatic compound (A) having molecular formula C_6H_6O on treatment with $CHCl_3$ and KOH gives a mixture two isomers 'B' and 'C' both of 'B' & 'C' give same product 'D' when distilled with Zn dust. Oxidation of 'D' gives 'E' of formula $C_7H_6O_2$. The sodium salt of 'E' on heating with soda lime gives 'F' which may also be obtained by distilling 'A' with zinc dust. Identify compounds 'A' to 'F' giving sequence of reactions.

Ans.

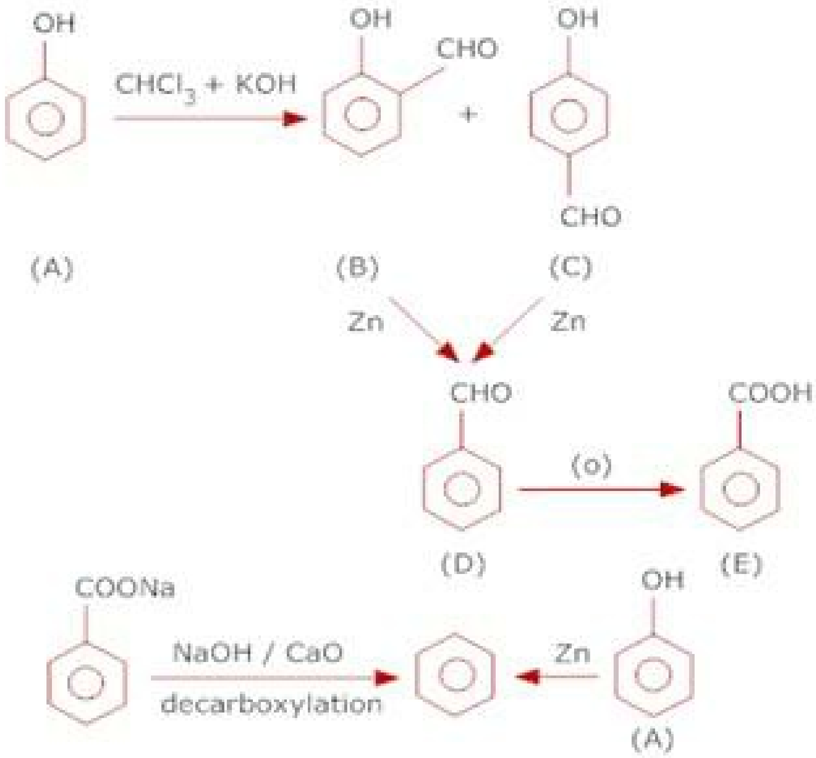


The aromatic compound having molecular formula C_6H_6O and which gives a mixture of two isomers on reacting with $CHCl_3$ and KOH is phenol i.e.

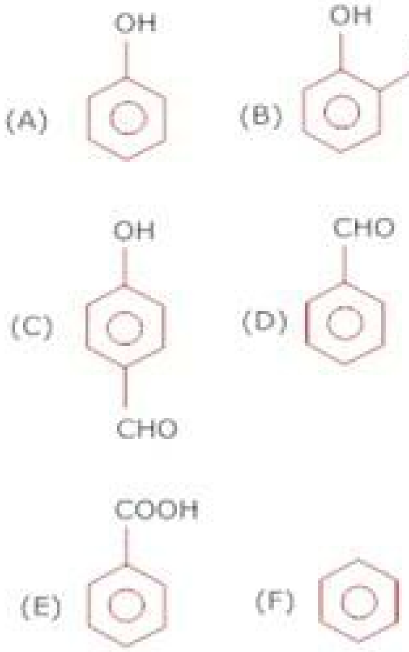
(A) =



The reactions are



Therefore



16. Compound 'A' of molecular formula $C_5H_{11}Br$ gives a compound 'B' of molecular formula $C_5H_{12}O$ when treated with aq. NaOH. On oxidation the compound yields a mixture of acetic acid & propionic acid. Deduce the structure of A, B & C.

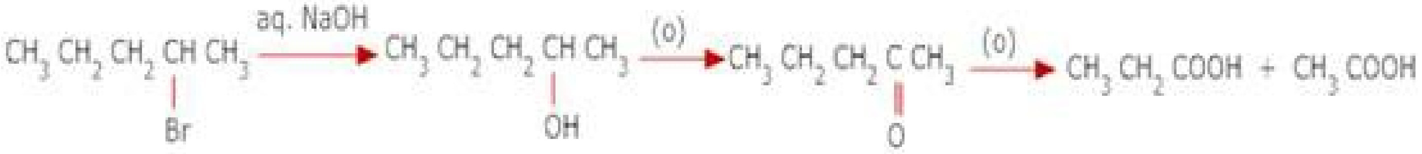
Ans.

$$\underset{(A)}{C_5H_{11}Br} \xrightarrow{\text{aq. NaOH}} \underset{(B)}{C_5H_{12}O} \xrightarrow{(o)} \underset{(C)}{\text{Ketone}} \xrightarrow[(o)]{KMnO_4} CH_3\,CH_2\,COOH + CH_3\,COOH$$

Since acetic acid & propionic acid are the products of oxidation of C which is a ketone, C is $CH_3CH_2CH_2CO\ CH_3$. Since it is the oxidation product of B, therefore

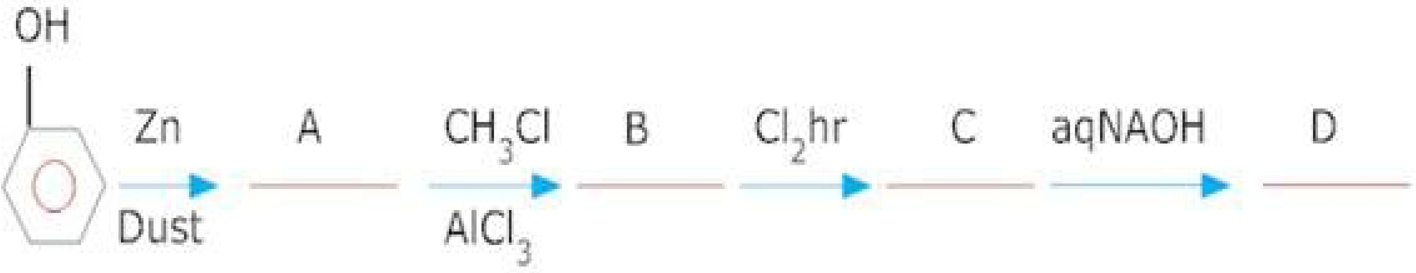
$$\text{A is } CH_3\,CH_2\,CH_2\,\underset{\overset{|}{Br}}{CH}\,CH_3 \quad \text{and} \quad \text{B is } CH_3\,CH_2\,CH_2\,\underset{\overset{|}{OH}}{CH}\,CH_3$$

The reactions are

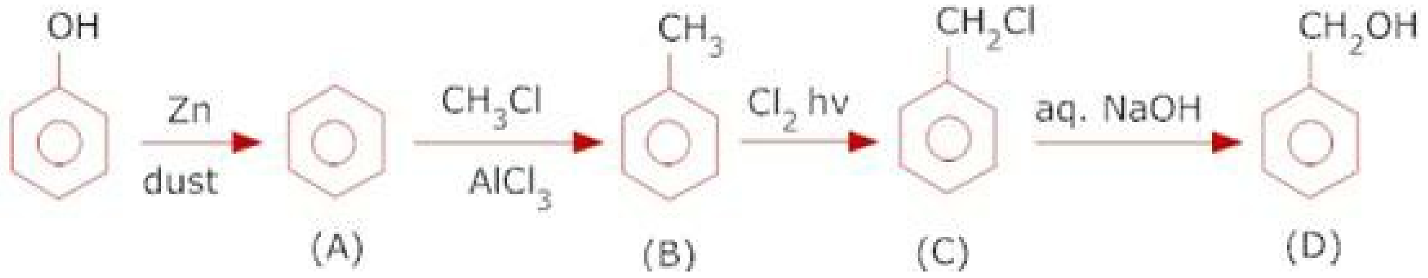


$$CH_3\,CH_2\,CH_2\,\underset{\overset{|}{Br}}{CH}\,CH_3 \xrightarrow{\text{aq. NaOH}} CH_3\,CH_2\,CH_2\,\underset{\overset{|}{OH}}{CH}\,CH_3 \xrightarrow{(o)} CH_3\,CH_2\,CH_2\,\underset{\overset{\|}{O}}{C}\,CH_3 \xrightarrow{(o)} CH_3\,CH_2\,COOH + CH_3\,COOH$$

17.



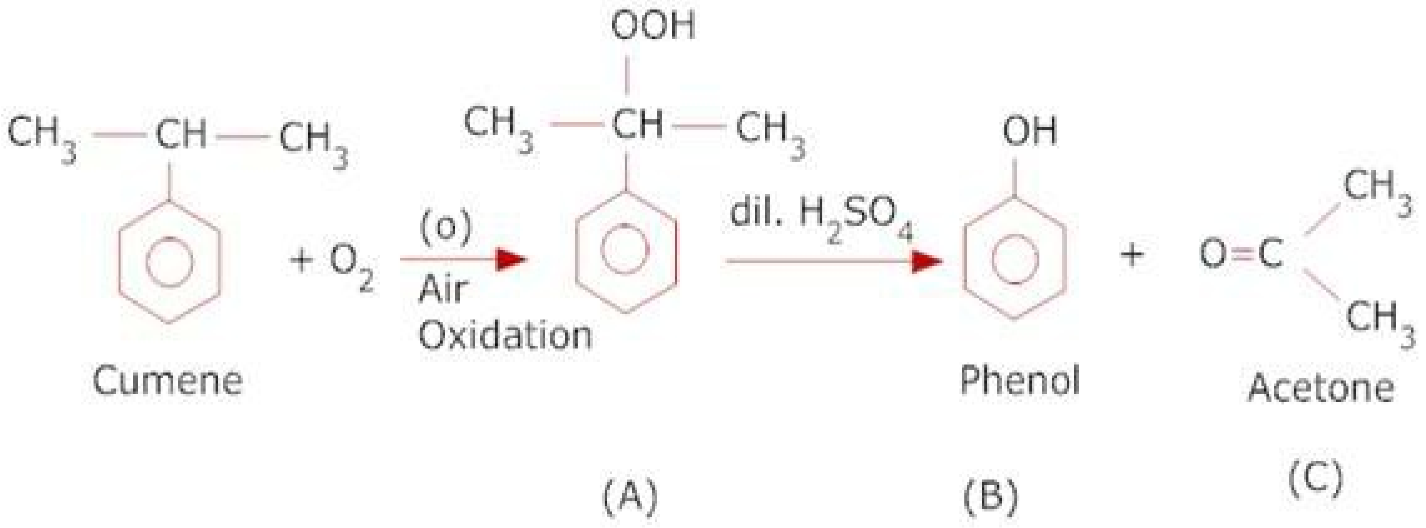
Ans.


OH
Zn
dust
CH3Cl
AlCl3
CH3
Cl2 hv
CH2Cl
aq. NaOH
CH2OH
(A)
(B)
(C)
(D)

18.


CH3-CH-CH3
+ O2
[0]
A
dil H2SO4
B
+
C

Ans.

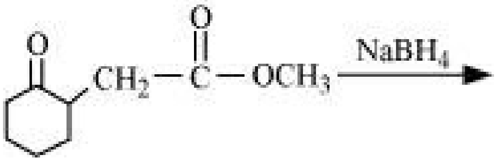

CH3
CH
CH3
+ O2
(o)
Air
Oxidation
OOH
CH3
CH
CH3
dil. H2SO4
OH
+
O=C
CH3
CH3
Cumene
Phenol
Acetone
(A)
(B)
(C)

19. **Write structures of the products of the following reactions:**

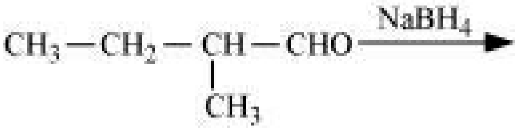
(i)

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

(ii)

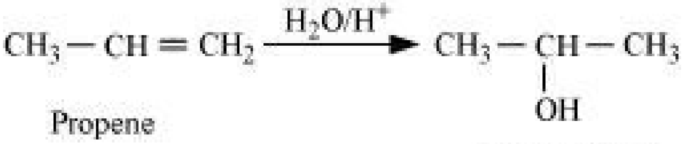


(iii)



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

Ans. (i)



$$\underset{\text{Propene}}{CH_3-CH=CH_2} \xrightarrow{H_2O/H^+} CH_3-\underset{\substack{|\\OH}}{CH}-CH_3$$

Propene

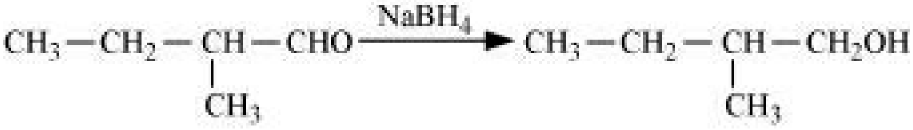
Propene–2–ol

(ii)

Methyl (2 – oxocyclohexyl) ethanoate

Methyl (2 – hydroxycyclohexyl) ethanoate

(iii)



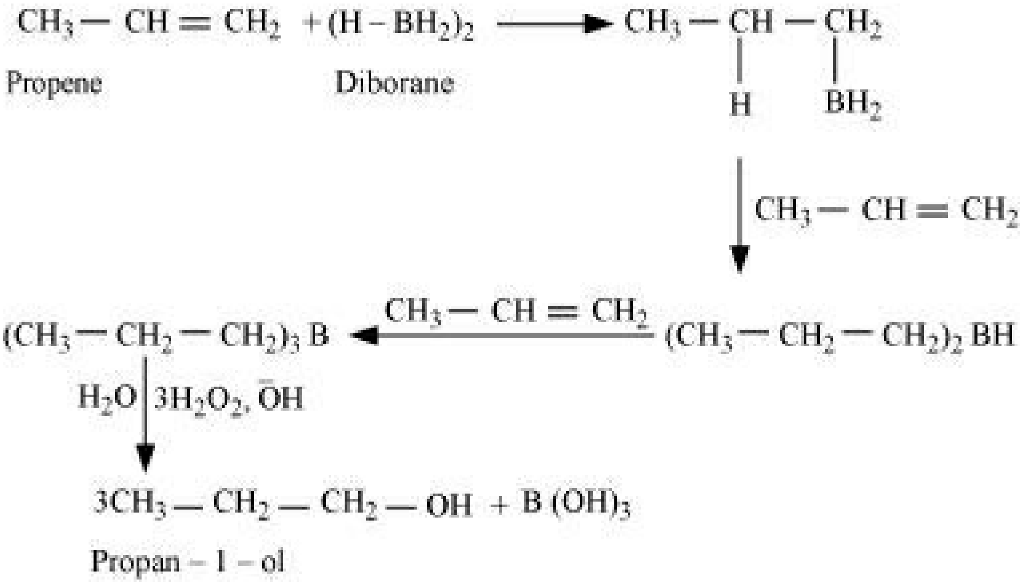
$$CH_3-CH_2-\underset{\substack{|\\CH_3}}{CH}-CHO \xrightarrow{NaBH_4} CH_3-CH_2-\underset{\substack{|\\CH_3}}{CH}-CH_2OH$$

2 – Methylbutanal

2 – Methylbutan – 1 – ol

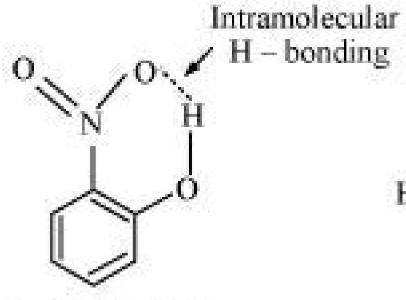
20. **What is meant by hydroboration-oxidation reaction? Illustrate it with an example.**

Ans. The addition of borane followed by oxidation is known as the hydroboration-oxidation reaction. For example, propan-1-ol is produced by the hydroboration-oxidation reaction of propene. In this reaction, propene reacts with diborane $(BH_3)^2$ to form trialkyl borane as an addition product. This addition product is oxidized to alcohol by hydrogen peroxide in the presence of aqueous sodium hydroxide.

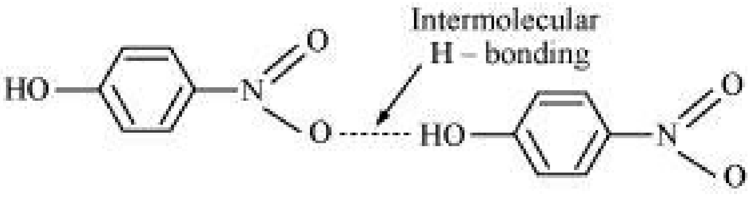


21. **While separating a mixture of *ortho* and *para* nitrophenols by steam distillation, name the isomer which will be steam volatile. Give reason.**

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



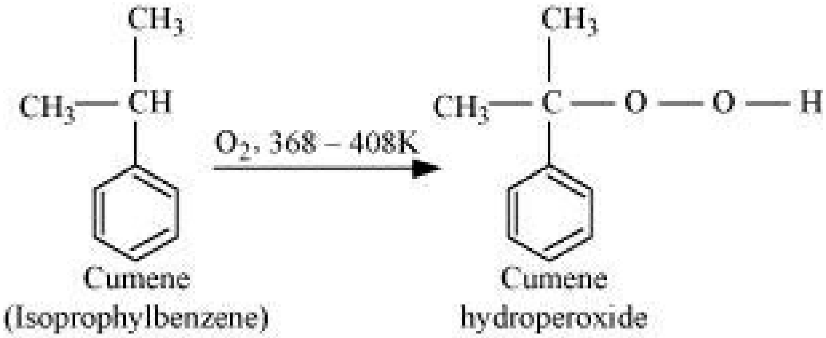
o - Nitrophenol



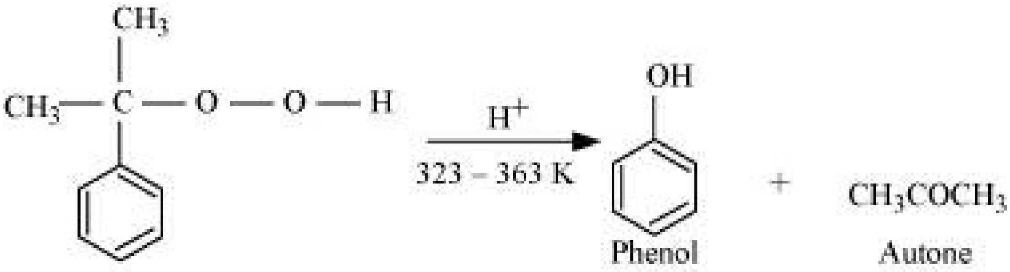
p - Nitrophenol

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

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

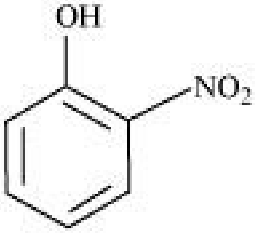


Then, cumene hydroxide is treated with dilute acid to prepare phenol and acetone as by-products.

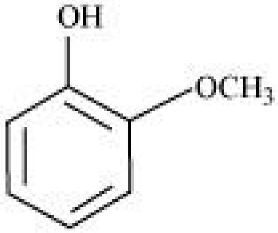


23. **Explain why is *ortho* nitrophenol more acidic than *ortho* methoxyphenol?**

Ans.



o – Nitrophenol



o – Methoxyphenol

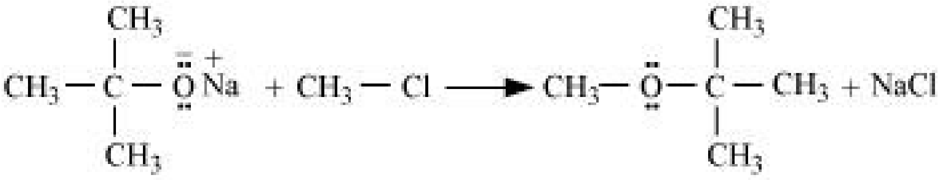
The nitro-group is an electron-withdrawing group. The presence of this group in the ortho position decreases the electron density in the O-H bond. As a result, it is easier to lose a proton. Also, the *o*-nitrophenoxide ion formed after the loss of protons is stabilized by resonance. Hence, *ortho* nitrophenol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

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

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

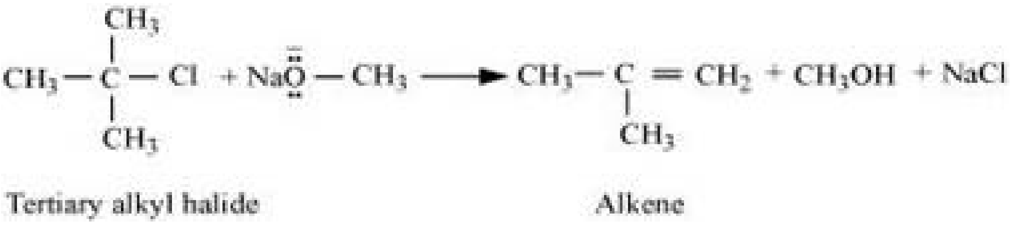
24. **Illustrate with examples the limitations of Williamson synthesis for the preparation of certain types of ethers.**

Ans. The reaction of Williamson synthesis involves S_N^2 attack of an alkoxide ion on a primary alkyl halide.



$$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-\overset{-}{\ddot{\underset{..}{O}}}\overset{+}{Na} + CH_3-Cl \longrightarrow CH_3-\ddot{\underset{..}{O}}-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-CH_3 + NaCl$$

But if secondary or tertiary alkyl halides are taken in place of primary alkyl halides, then elimination would compete over substitution. As a result, alkenes would be produced. This is because alkoxides are nucleophiles as well as strong bases. Hence, they react with alkyl halides, which results in an elimination reaction.



$$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-Cl + Na\overset{-}{\ddot{\underset{..}{O}}}-CH_3 \longrightarrow CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}}=CH_2 + CH_3OH + NaCl$$

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

(i) 1-propoxypropane

(ii) Methoxybenzene and

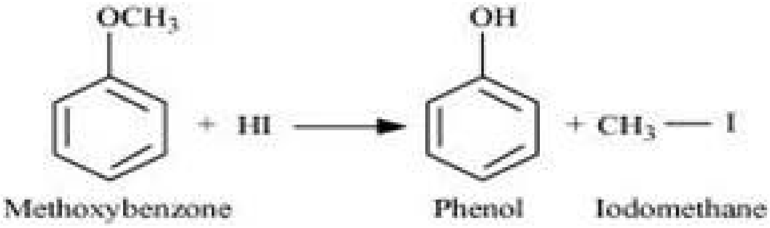
(iii) Benzyl ethyl ether

Ans. (i)

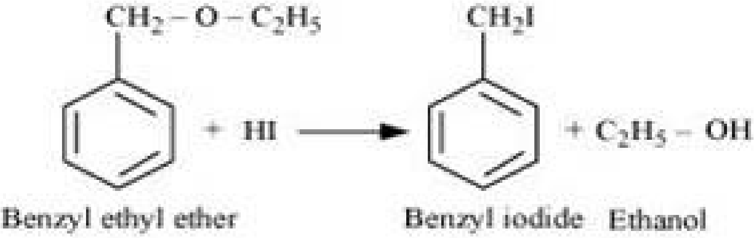
$$C_2H_5CH_2-O-CH_2C_2H_5 + HI \xrightarrow{373K} CH_3CH_2CH_2-OH + CH_3CH_2CH_2-I$$

1-Propoxypropane Propan-1-ol 1 – Iodopropane

(ii)



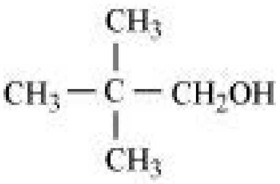
(iii)



5 Mark Questions

1. Classify the following as primary, secondary and tertiary alcohols:

(i)

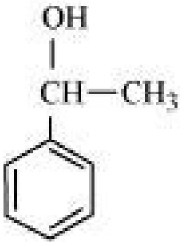


$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2OH$$

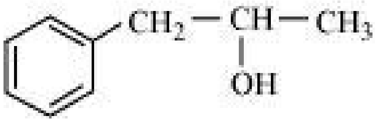
(ii) $H_2C=CH-CH_2OH$

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

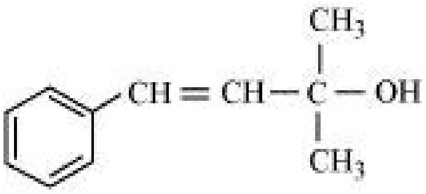
(iv)



(v)



(vi)



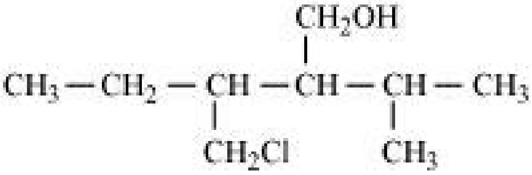
Ans. Primary alcohol → (i), (ii), (iii)

Secondary alcohol → (iv), (v)

Tertiary alcohol → (vi)

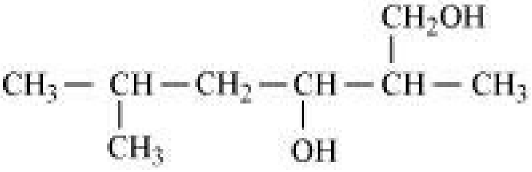
2. Name the following compounds according to IUPAC system.

(i)



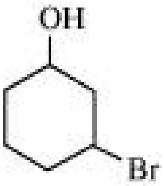
$$CH_3-CH_2-\underset{\displaystyle CH_2Cl}{\underset{|}{CH}}-\overset{\displaystyle CH_2OH}{\overset{|}{CH}}-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3$$

(ii)

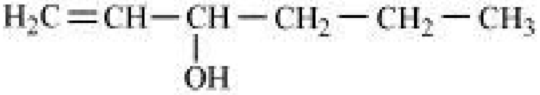


$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-\underset{\displaystyle OH}{\underset{|}{CH}}-\overset{\displaystyle CH_2OH}{\overset{|}{CH}}-CH_3$$

(iii)

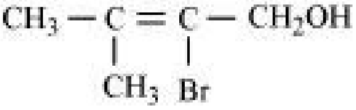


(iv)



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

(v)



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

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

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

(iii) 3-Bromocyclohexanol

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

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

3. 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

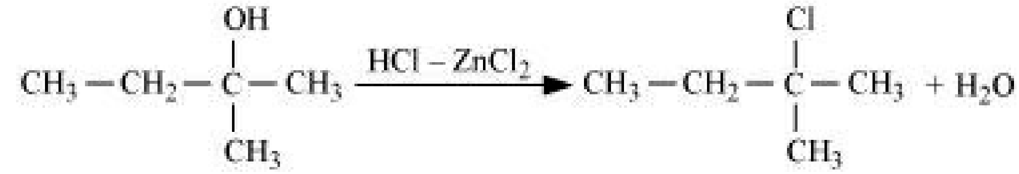
(ii) 2-Methylbutan-2-ol

Ans. (a)(i)

$$\underset{\text{Butan}-1-\text{ol}}{CH_3-CH_2-CH_2-CH_2-OH} \xrightarrow{HCl-ZnCl_2} \text{No reaction}$$

Primary alcohols do not react appreciably with Lucas' reagent (HCl-ZnCl2) at room temperature.

(ii)



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

2 – Methylbutan – 2 – ol (3°)

2 – Chloro – 2 – Methylbutane
(White turbidity)

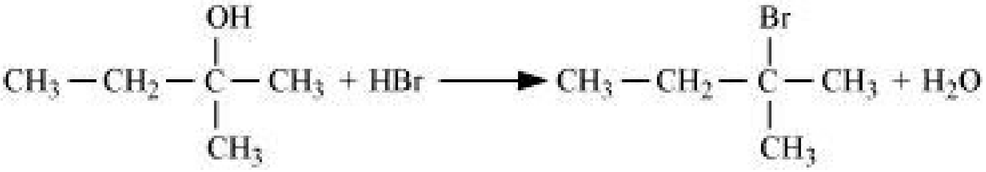
Tertiary alcohols react immediately with Lucas' reagent.

(b)

(i)

$$\underset{\text{Butan}-1-\text{ol}}{CH_3CH_2CH_2CH_2OH} + HBr \xrightarrow[-H_2O]{} \underset{\text{1-Bromobutane}}{CH_3CH_2CH_2CH_2Br}$$

(ii)



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

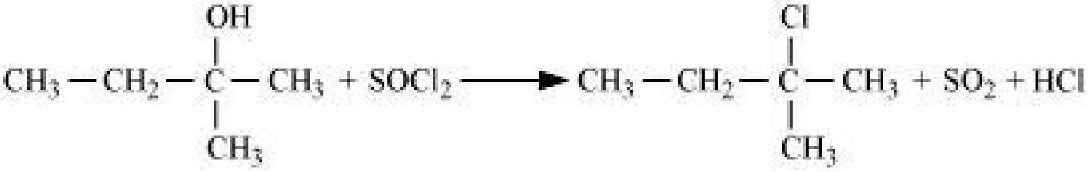
2 – Methylbutan – 2 – ol (3°) 2 – Bromo – 2 – Methylbutane

(c)

(i)

$$\underset{\text{Butan-1-ol}}{CH_3CH_2CH_2CH_2OH} + SOCl_2 \longrightarrow \underset{\text{1-chlorobutane}}{CH_3CH_2CH_2CH_2Cl} + SO_2 + HCl$$

(ii)

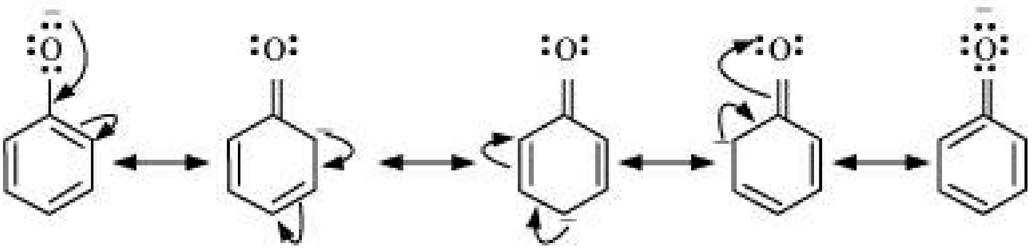


$$CH_3-CH_2-\overset{\displaystyle OH}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-CH_3 + SOCl_2 \longrightarrow CH_3-CH_2-\overset{\displaystyle Cl}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-CH_3 + SO_2 + HCl$$

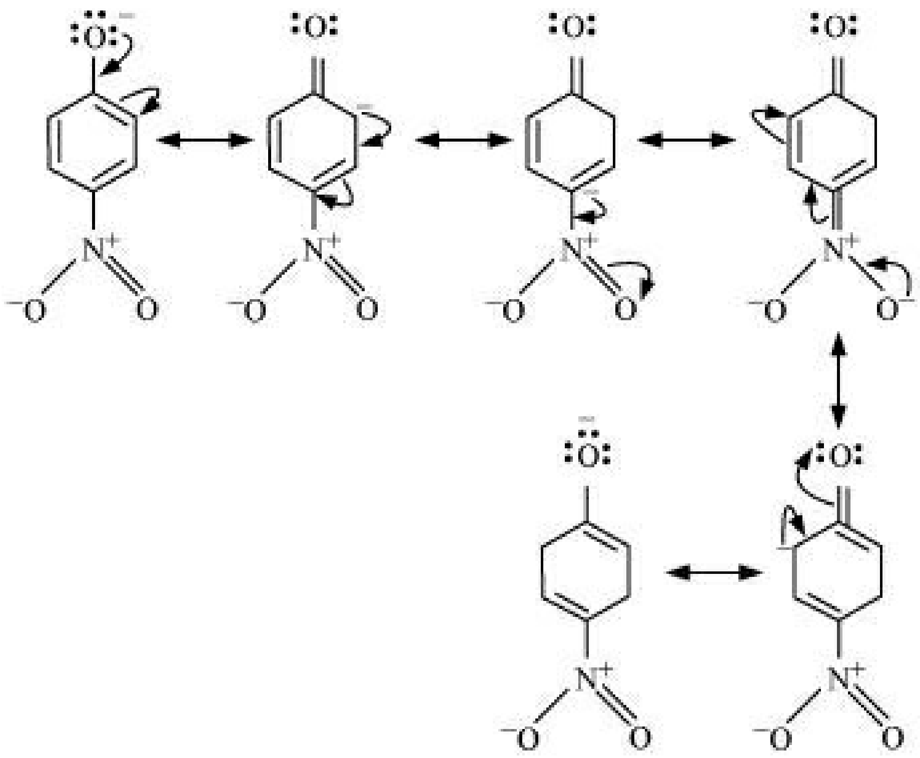
2 – Methylbutan – 2 – ol 2 – Chloro – 2 – Methylbutane

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

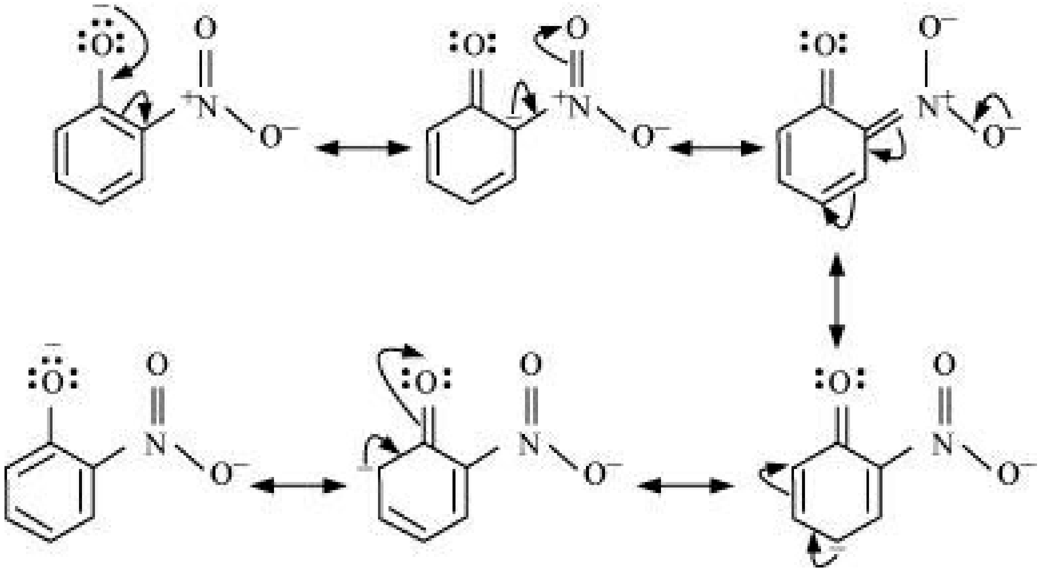
Ans.



Resonance structure of the phenoxide ion



Resonance structures of *p*-nitrophenoxide ion



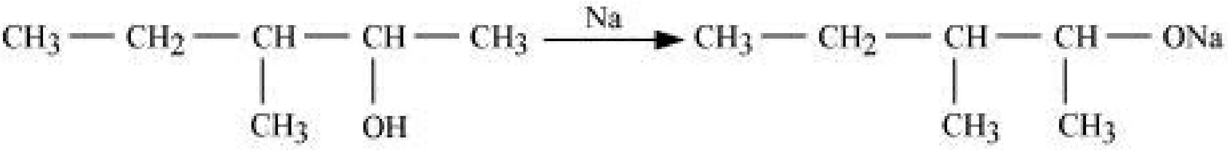
Resonance structures of *o*-nitrophenoxide ion

It can be observed that the presence of nitro groups increases the stability of phenoxide ion.

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

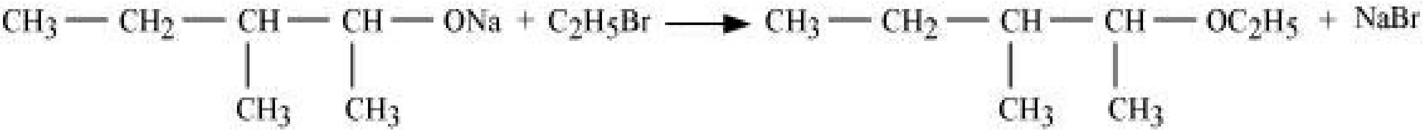
Ans. In Williamson synthesis, an alkyl halide reacts with an alkoxide ion. Also, it is an S_N^2 reaction. In the reaction, alkyl halides should be primary having the least steric hindrance. Hence, an alkyl halide is obtained from ethanol and alkoxide ion from 3-methylpentan-2-ol.

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



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

3 – Methylpentan – 2 – ol   Sodium 3 – Methylpentan – 2 – oxide



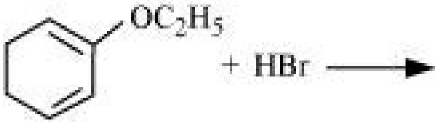
$$CH_3-CH_2-\underset{CH_3}{\underset{|}{CH}}-\underset{CH_3}{\underset{|}{CH}}-ONa + C_2H_5Br \longrightarrow CH_3-CH_2-\underset{CH_3}{\underset{|}{CH}}-\underset{CH_3}{\underset{|}{CH}}-OC_2H_5 + NaBr$$

2 – Ethoxy – 3 – methylpentane

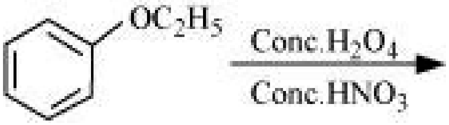
6. Predict the products of the following reactions:

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

(ii)



(iii)



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

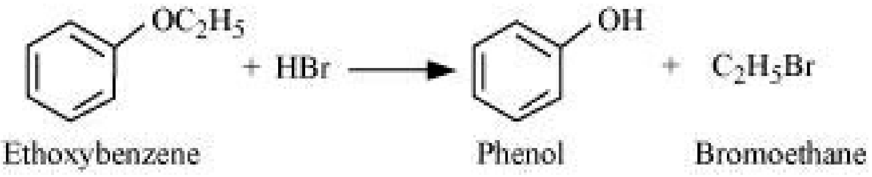
Ans. (i)

$$CH_3-CH_2-CH_2-O-CH_3 + HBr \longrightarrow CH_3-CH_2-CH_2-OH + CH_3-Br$$

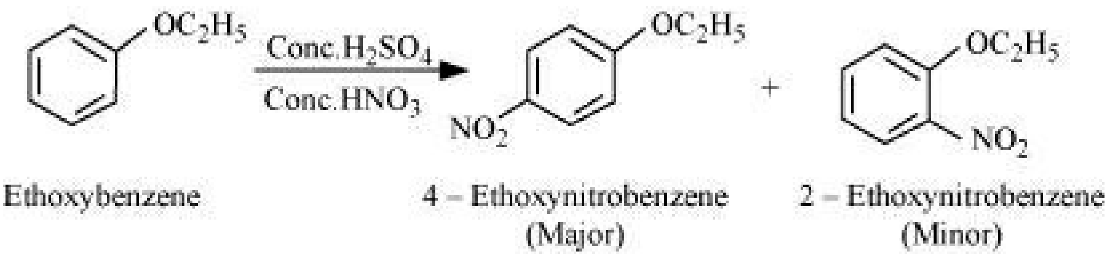
n-propylmethyl ether

Propanol Bromomethane

(ii)



(iii)



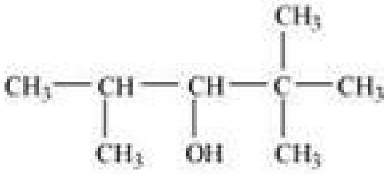
(iv)

$$(CH_3)_3C-OC_2H_5 \xrightarrow{HI} (CH_3)_3C-I + C_2H_5OH$$

tert-Butyl ethyl ether *tert*-Butyliodide Ethanol

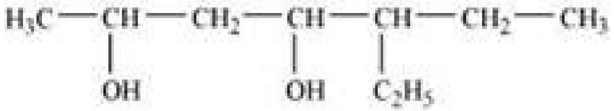
7. **Write IUPAC names of the following compounds:**

(i)



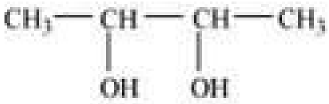
$$CH_3-\underset{CH_3}{\underset{|}{CH}}-\underset{OH}{\underset{|}{CH}}-\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CH_3$$

(ii)



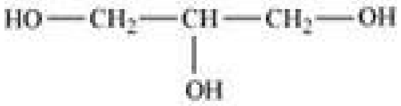
$$H_3C-\underset{OH}{\underset{|}{CH}}-CH_2-\underset{OH}{\underset{|}{CH}}-\underset{C_2H_5}{\underset{|}{CH}}-CH_2-CH_3$$

(iii)



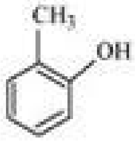
$CH_3-\underset{\underset{OH}{|}}{CH}-\underset{\underset{OH}{|}}{CH}-CH_3$

(iv)

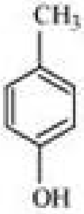


$HO-CH_2-\underset{\underset{OH}{|}}{CH}-CH_2-OH$

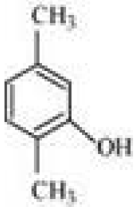
(v)



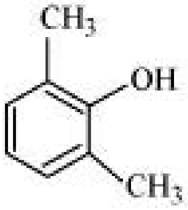
(vi)



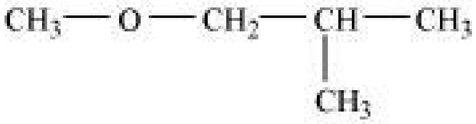
(vii)



(viii)



(ix)

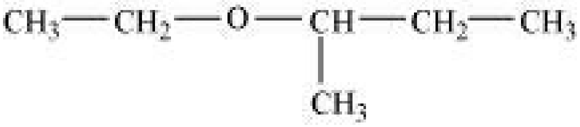


$CH_3-O-CH_2-\underset{\underset{CH_3}{|}}{CH}-CH_3$

(x) $C_6H_5-O-C_2H_5$

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

(xii)



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

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

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

(i) 2-Methylbutan-2-ol

(ii) 1-Phenylpropan-2-ol

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

(iv) 2,3 - Diethylphenol

(v) 1 - Ethoxypropane

(vi) 2-Ethoxy-3-methylpentane

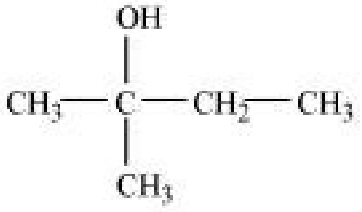
(vii) Cyclohexylmethanol

(viii) 3-Cyclohexylpentan-3-ol

(ix) Cyclopent-3-en-1-ol

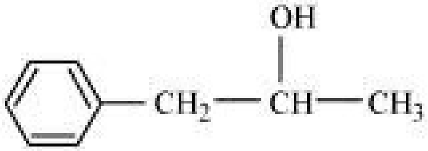
(x) 3-Chloromethylpentan-1-ol.

Ans. (i)

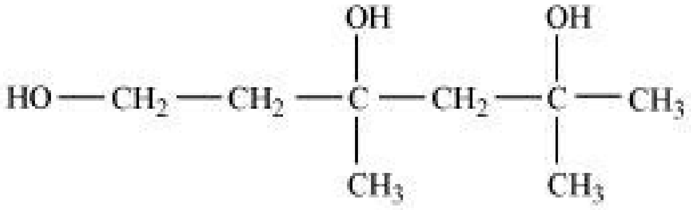


$$CH_3-\overset{OH}{\underset{CH_3}{C}}-CH_2-CH_3$$

(ii)

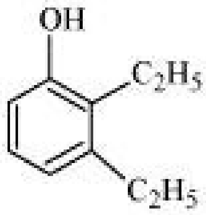


(iii)



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

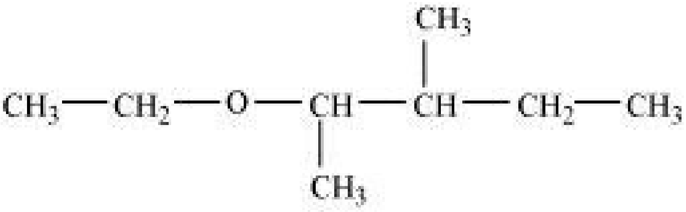
(iv)



(v)

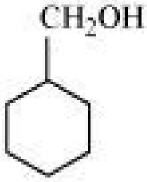
$CH_3-CH_2-O-CH_2-CH_2-CH_3$

(vi)

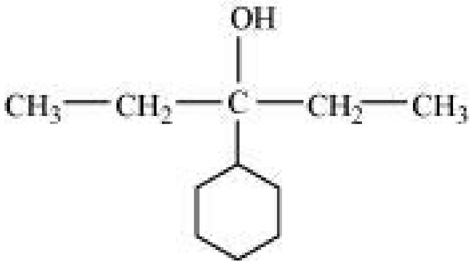


$CH_3-CH_2-O-\underset{\displaystyle CH_3}{CH}-\overset{\displaystyle CH_3}{CH}-CH_2-CH_3$

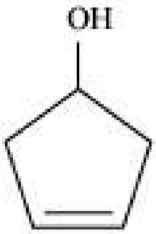
(vii)



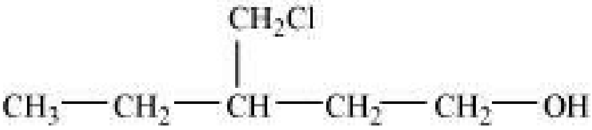
(viii)



(ix)



(x)



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

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

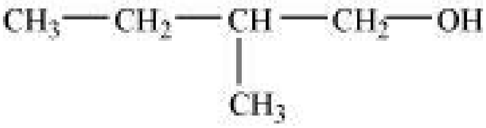
(ii) Classify the isomers of alcohols in question 11.3 (i) as primary, secondary and tertiary alcohols.

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

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

Pentan-1-ol $(1°)$

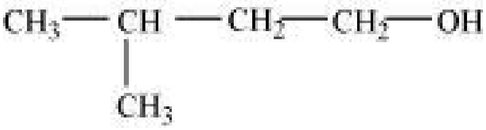
(b)



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

2-Methylbutan-1-ol $(1°)$

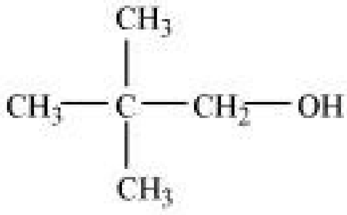
(c)



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

3-Methylbutan-1-ol $(1°)$

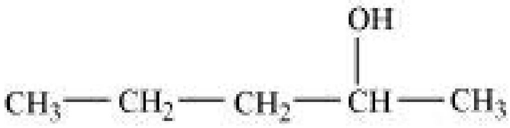
(d)



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

2, 2-Dimethylpropan-1-ol (1°)

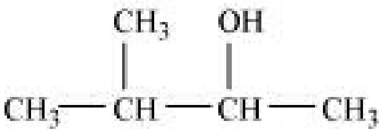
(e)



$CH_3-CH_2-CH_2-\overset{\displaystyle OH}{CH}-CH_3$

Pentan-2-ol (2°)

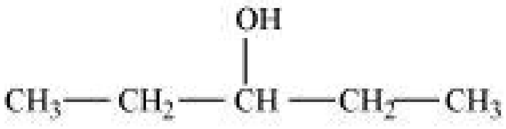
(f)



$CH_3-\overset{\displaystyle CH_3}{CH}-\overset{\displaystyle OH}{CH}-CH_3$

3-Methylbutan-2-ol (2°)

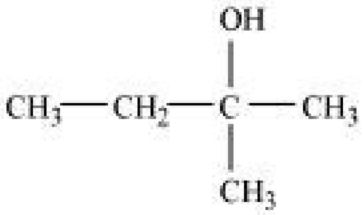
(g)



$CH_3-CH_2-\overset{\displaystyle OH}{CH}-CH_2-CH_3$

Pentan-3-ol (2°)

(h)



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

2-Methylbutan-2-ol (3°)

(ii) Primary alcohol: Pentan-1-ol; 2-Methylbutan-1-ol;

3-Methylbutan-1-ol; 2, 2 - Dimethylpropan-1-ol

Secondary alcohol: Pentan-2-ol; 3-Methylbutan-2-ol;

Pentan-3-ol

Tertiary alcohol: 2-methylbutan-2-ol

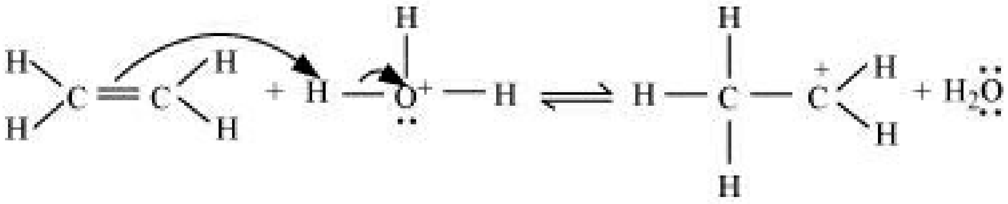
10. Write the mechanism of hydration of ethene to yield ethanol.

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

Step 1:

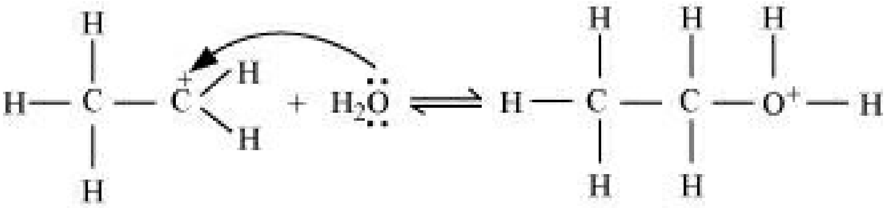
Protonation of ethene to form carbocation by electrophilic attack of H_3O+:

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



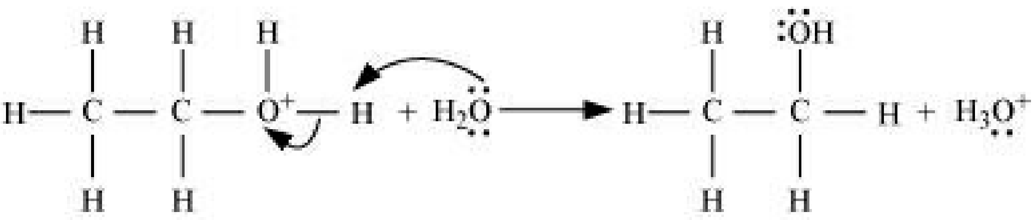
Step 2:

Nucleophilic attack of water on carbocation:



Step 3:

Deprotonation to form ethanol:



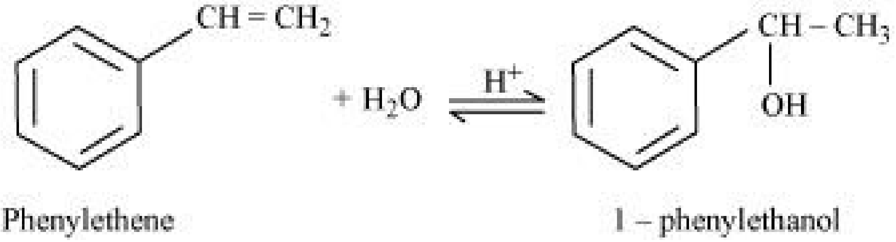
11. Show how will you synthesize:

(i) 1-phenylethanol from a suitable alkene.

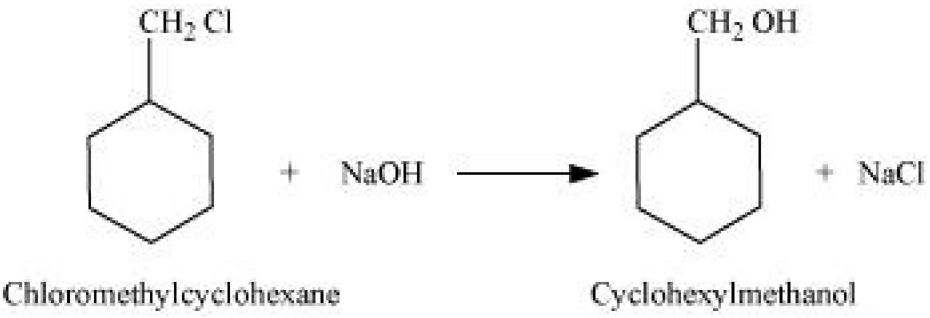
(ii) cyclohexylmethanol using an alkyl halide by an S_N^2 reaction.

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

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



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



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

$$CH_3CH_2CH_2CH_2CH_2Cl + NaOH \longrightarrow CH_3CH_2CH_2CH_2CH_2OH + NaCl$$

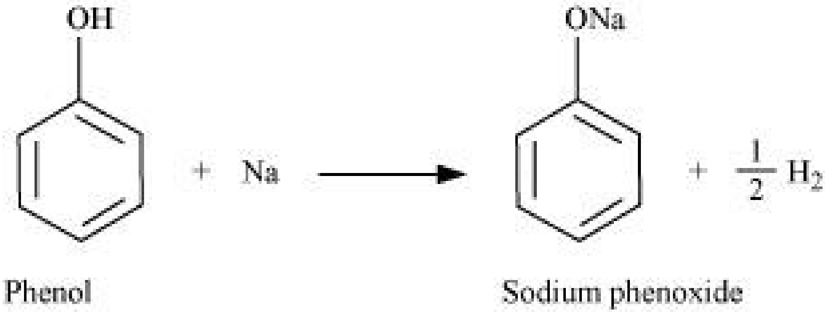
1-Chloropentane

Pantan-1-ol

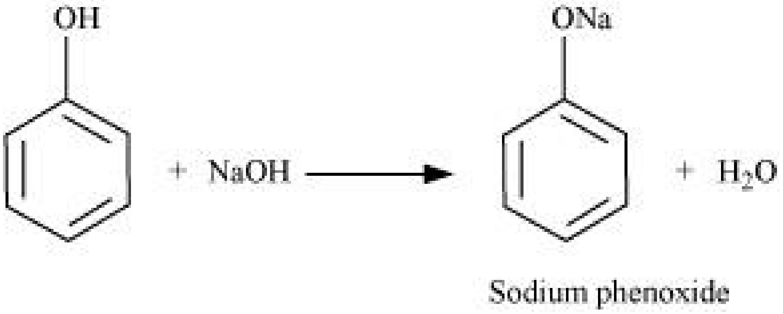
12. Give two reactions that show the acidic nature of phenol. Compare acidity of phenol with that of ethanol.

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

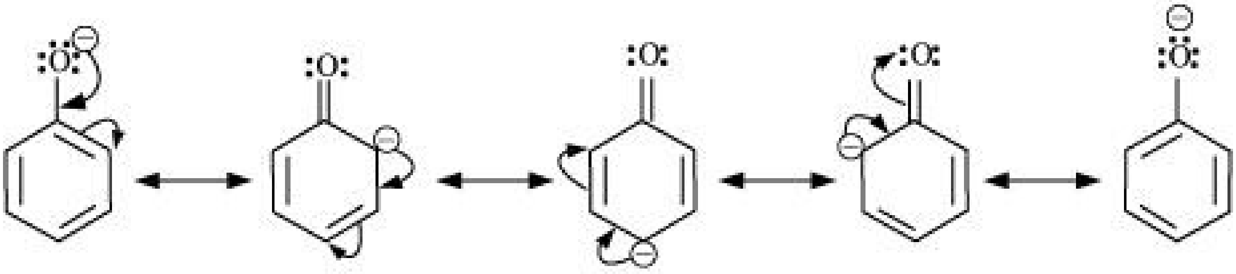
(i) Phenol reacts with sodium to give sodium phenoxide, liberating H_2.



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



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



12. **Give equations of the following reactions:**

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

(ii) Bromine in CS_2 with phenol.

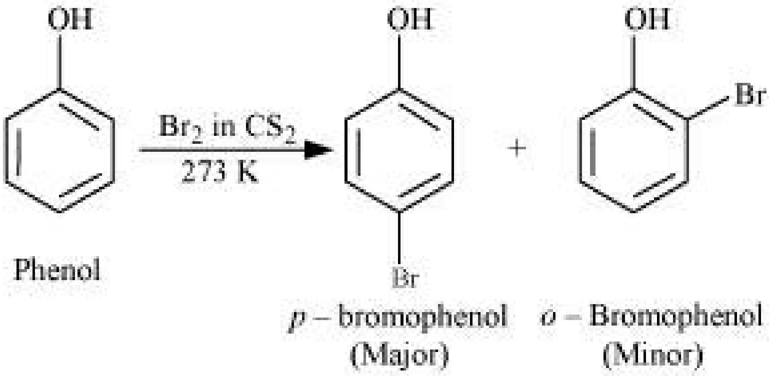
(iii) Dilute HNO_3 with phenol.

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

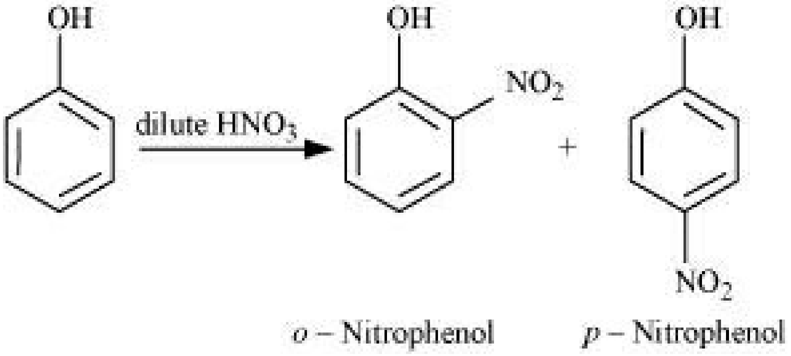
Ans. (i) $CH_3CH_2CH_2OH \xrightarrow{\text{alk KmnO}_4} CH_3CH_2COOH$

Propan-1-ol Propanoic acid

(ii)



(iii)



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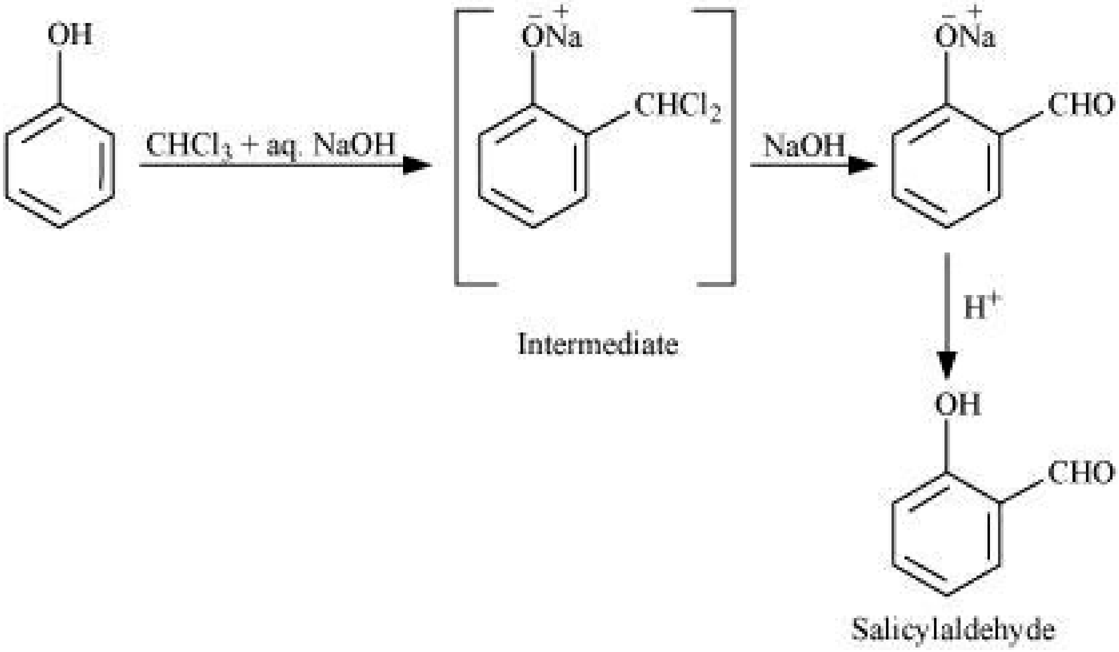


13. Explain the following with an example.

(i) Kolbe's reaction.

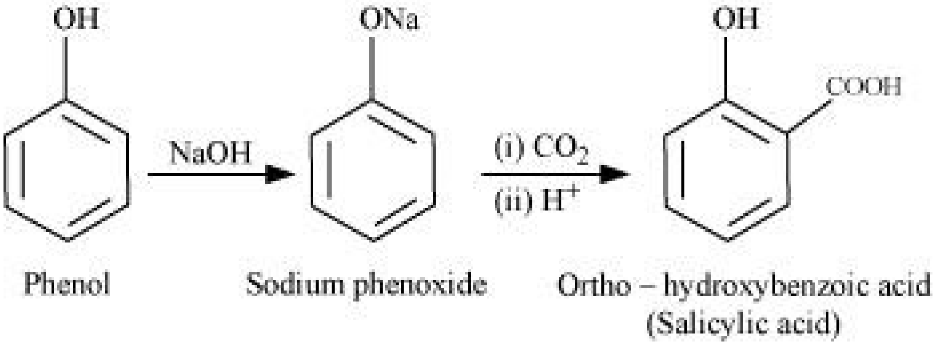
(ii) Reimer-Tiemann reaction.

(iii) Williamson ether synthesis.

(iv) Unsymmetrical ether.

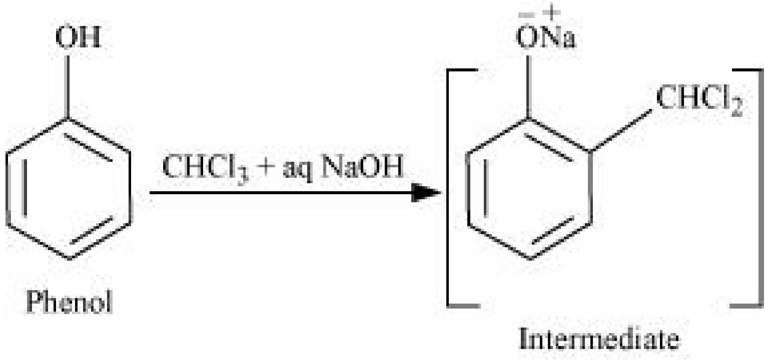
Ans. (i)Kolbe's reaction:

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



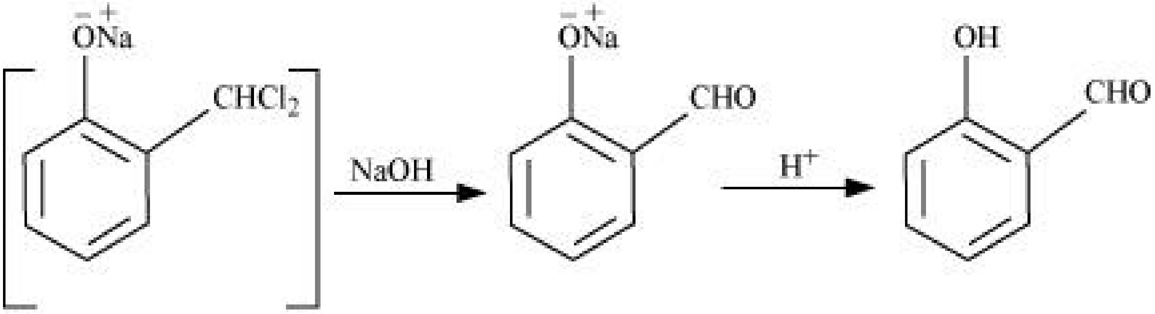
(ii)Reimer-Tiemann reaction:

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



This reaction is known as the Reimer-Tiemann reaction.

The intermediate is hydrolyzed in the presence of alkalis to produce salicyclaldehyde.



Intermediate Salicylaldehyde

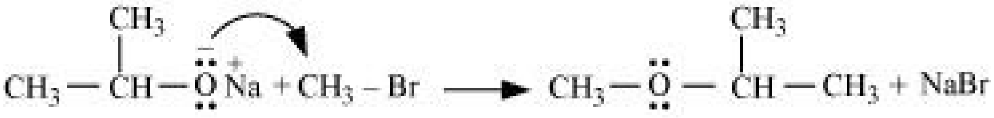
(iii)Williamson ether synthesis:

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

$$R-X+R'-\ddot{\underset{\cdot\cdot}{O}}\,Na \longrightarrow R-\ddot{\underset{\cdot\cdot}{O}}-R'+NaX$$

Akyl halide Sodium alkoxide Ether

This reaction involves S_N^2 attack of the alkoxide ion on the alkyl halide. Better results are obtained in case of primary alkyl halides.



$$CH_3-\overset{CH_3}{\overset{|}{CH}}-\overset{-}{\ddot{\underset{\cdot\cdot}{O}}}\overset{+}{Na}+CH_3-Br \longrightarrow CH_3-\ddot{\underset{\cdot\cdot}{O}}-\overset{CH_3}{\overset{|}{CH}}-CH_3+NaBr$$

If the alkyl halide is secondary or tertiary, then elimination competes over substitution.

(iv)Unsymmetrical ether:

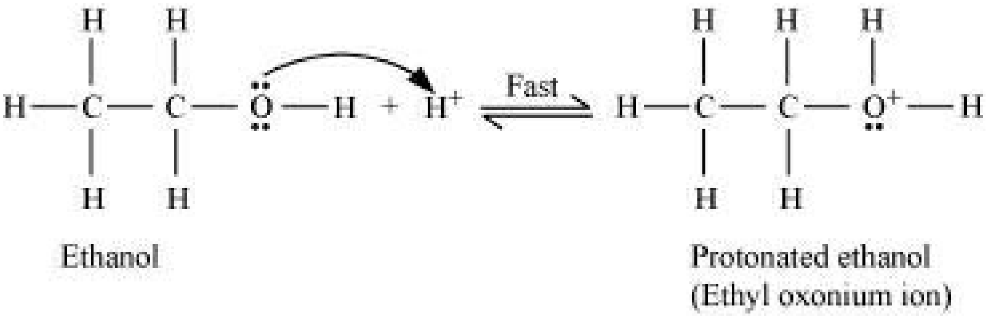
An unsymmetrical ether is an ether where two groups on the two sides of an oxygen atom differ (i.e., have an unequal number of carbon atoms). For example: ethyl methyl ether $(CH_3-O-CH_2CH_3)$.

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

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

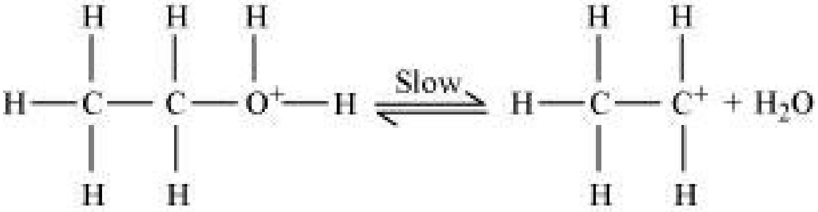
Step 1:

Protonation of ethanol to form ethyl oxonium ion:



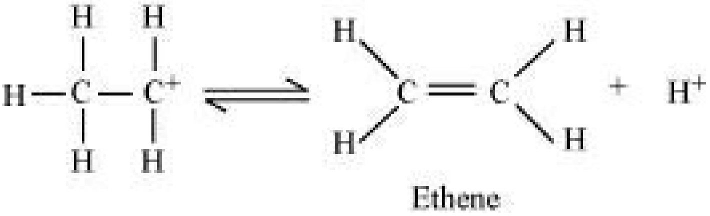
Step 2:

Formation of carbocation (rate determining step):



Step 3:

Elimination of a proton to form ethene:



The acid consumed in step 1 is released in Step 3. After the formation of ethene, it is removed to shift the equilibrium in a forward direction.

15. How are the following conversions carried out?

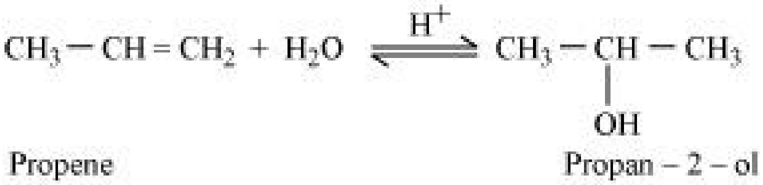
(i) Propene → Propan-2-ol

(ii) Benzyl chloride → Benzyl alcohol

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

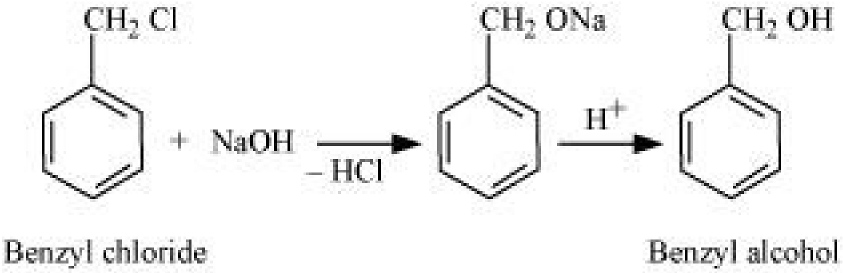
(iv) Methyl magnesium bromide → 2-Methylpropan-2-ol.

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

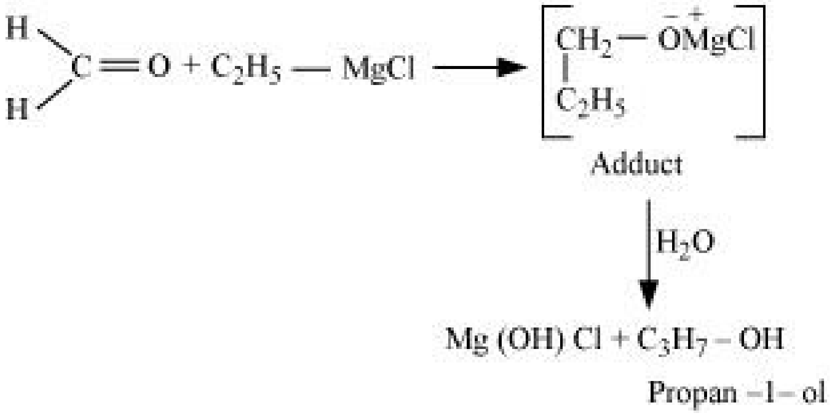


$$CH_3-CH=CH_2 + H_2O \overset{H^+}{\rightleftharpoons} CH_3-\underset{OH}{\underset{|}{CH}}-CH_3$$

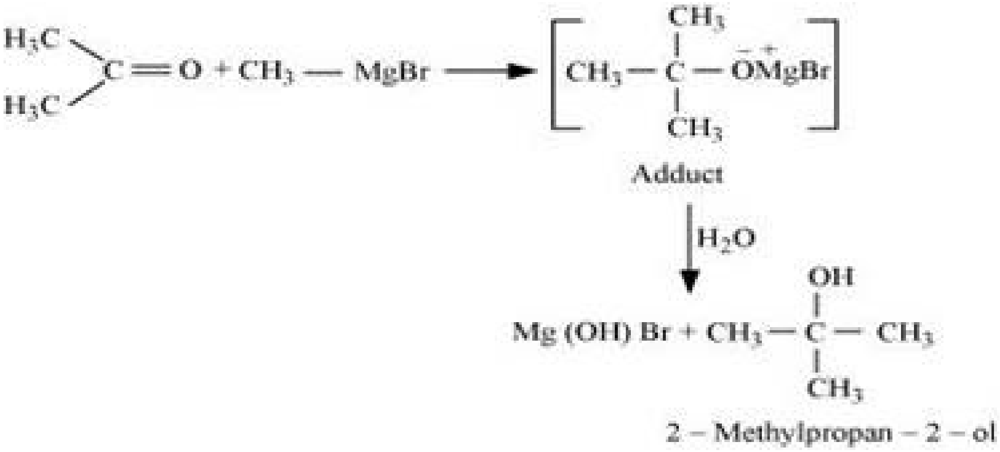
(ii) If benzyl chloride is treated with NaOH (followed by acidification) then benzyl alcohol is produced.



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



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



16. 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

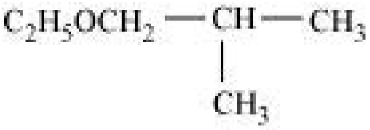
(iv) Acidified potassium permanganate

(v) 85% phosphoric acid

(vi) $NaBH_4$ or $LiAlH_4$

18. Give IUPAC names of the following ethers:

(i)



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

(ii)

$CH_3OCH_2CH_2Cl$

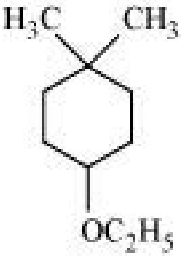
(iii)

$O_2N-C_6H_4-OCH_3(p)$

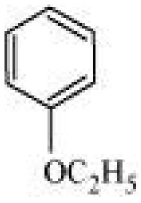
(iv)

$CH_3CH_2CH_2OCH_3$

(v)



(vi)



Ans. **(i)** 1-Ethoxy-2-methylpropane

(ii) 2-Chloro-1-methoxyethane

(iii) 4-Nitroanisole

(iv) 1-Methoxypropane

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

(vi) Ethoxybenzene

19. 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

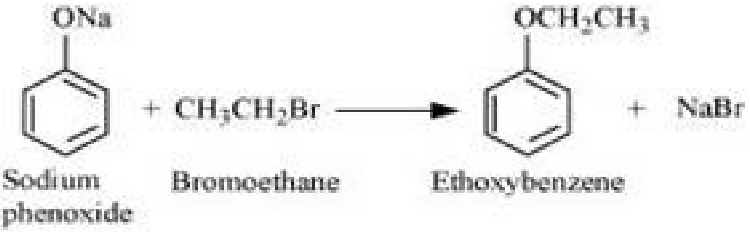
(iv) 1-Methoxyethane

Ans.

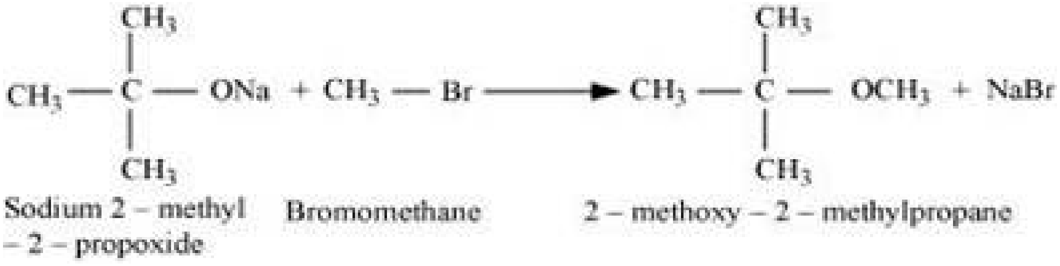
(i)

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

(ii)



(iii)



$$\underset{\text{Sodium 2 – methyl – 2 – propoxide}}{CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-ONa} + \underset{\text{Bromomethane}}{CH_3-Br} \longrightarrow \underset{\text{2 – methoxy – 2 – methylpropane}}{CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-OCH_3} + NaBr$$

(iv)

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

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

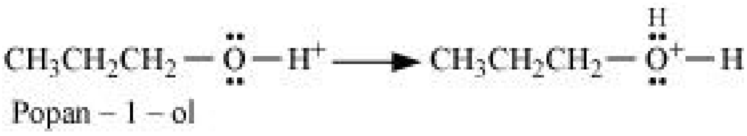
Ans. 1-propoxypropane can be synthesized from propan-1-ol by dehydration.

Propan-1-ol undergoes dehydration in the presence of protic acids (such as H2SO4, H3PO4) to give 1-propoxypropane.

$$\underset{\text{Propane-1-ol}}{2CH_3CH_2CH_2-OH} \xrightarrow{H^+} \underset{\text{1-Propoxypropane}}{CH_3CH_2CH_2-O-CH_2CH_2CH_3}$$

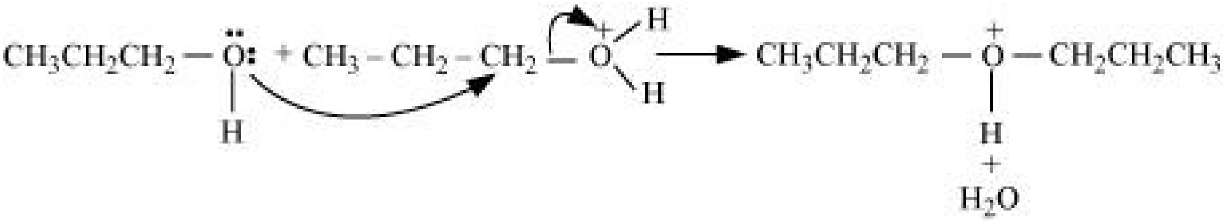
The mechanism of this reaction involves the following three steps:

Step 1: Protonation



$$\underset{\text{Popan}-1-\text{ol}}{CH_3CH_2CH_2-\ddot{\underset{..}{O}}-H^+} \longrightarrow CH_3CH_2CH_2-\overset{H}{\ddot{\underset{..}{O}}{}^+}-H$$

Step 2: Nucleophilic attack



$$CH_3CH_2CH_2-\underset{H}{\ddot{O}}: + CH_3-CH_2-CH_2-\overset{+}{O}\begin{smallmatrix}H\\H\end{smallmatrix} \longrightarrow CH_3CH_2CH_2-\underset{\underset{\underset{H_2O}{+}}{H}}{\overset{+}{O}}-CH_2CH_2CH_3$$

Step 3: Deprotonation

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

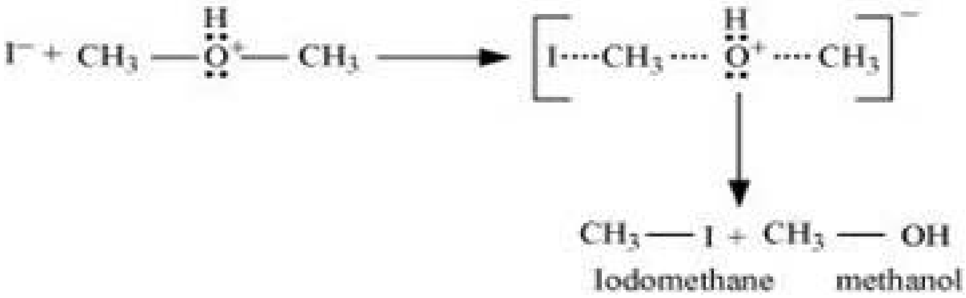
21. **Write the mechanism of the reaction of HI with methoxymethane.**

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

Step1: Protonation of methoxymethane:

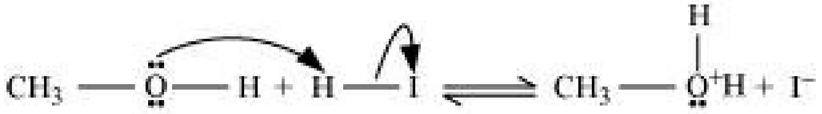
$$CH_3-\ddot{O}-CH_3 + H-I \rightleftharpoons CH_3-\overset{H}{\overset{|}{O^+}}-CH_3 + I^-$$

Step2: Nucleophilic attack of I - :



$$I^- + CH_3-\overset{H}{\overset{|}{O^+}}-CH_3 \longrightarrow \left[I\cdots CH_3\cdots\overset{H}{\overset{|}{O^+}}\cdots CH_3\right]^- \longrightarrow CH_3-I + CH_3-OH$$

Step3: When HI is in excess and the reaction is carried out at a high temperature, the methanol formed in the second step reacts with another HI molecule and gets converted to methyl iodide



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

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

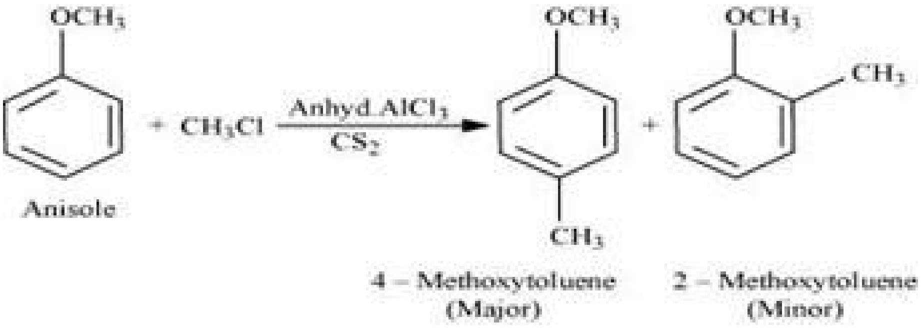
22. **Write equations of the following reactions:**

(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)



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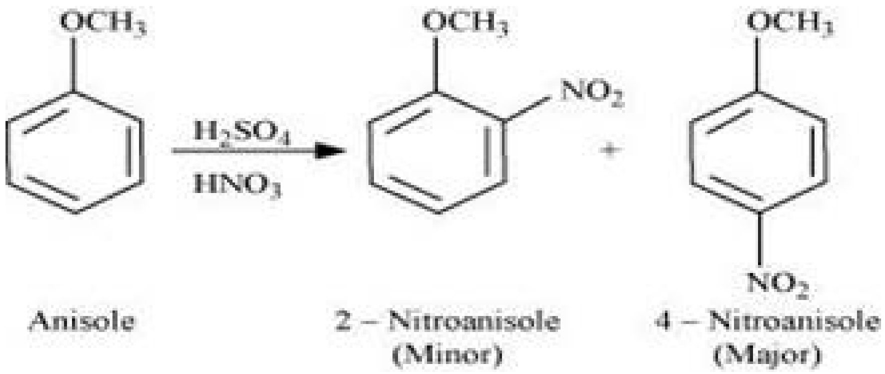

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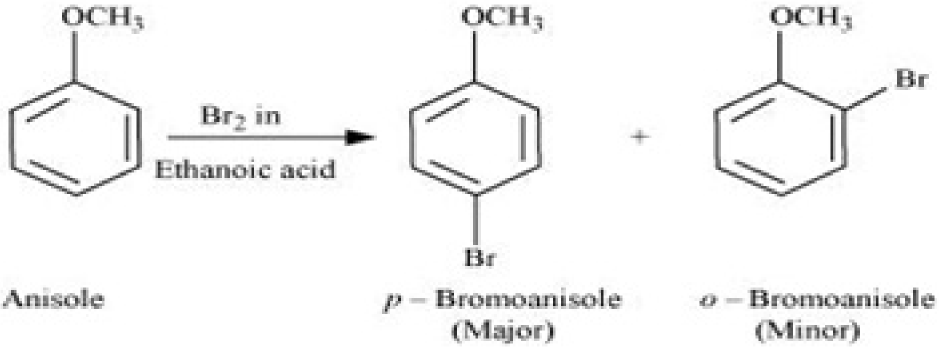

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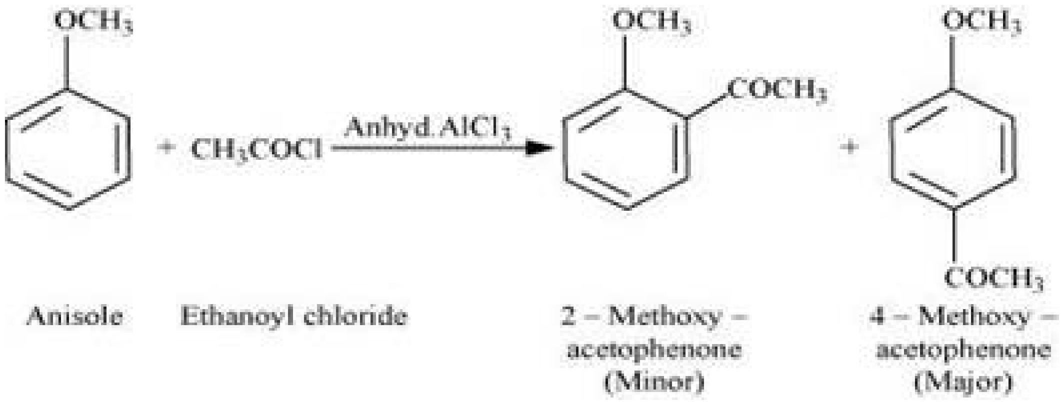
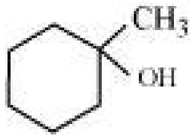
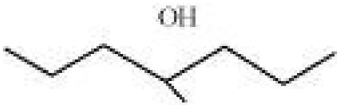


23. Show how would you synthesise the following alcohols from appropriate alkenes?

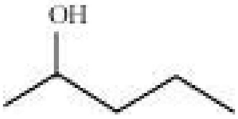
(i)



(ii)



(iii)



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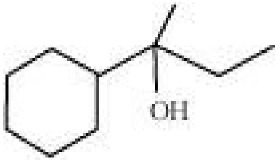
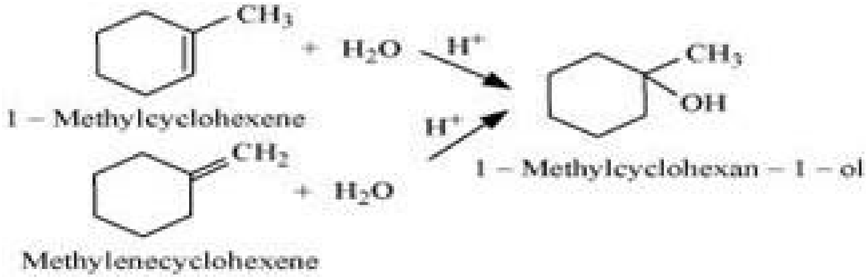
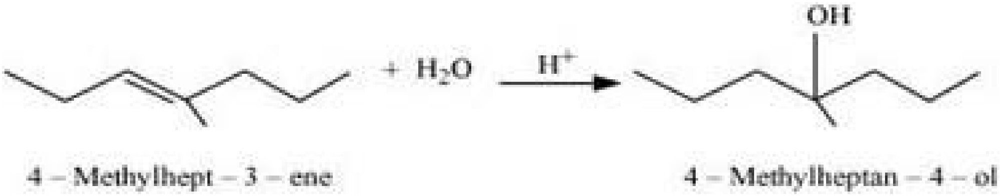


Ans. The given alcohols can be synthesized by applying Markovnikov's rule of acid-catalyzed hydration of appropriate alkenes.

(i)



(ii)



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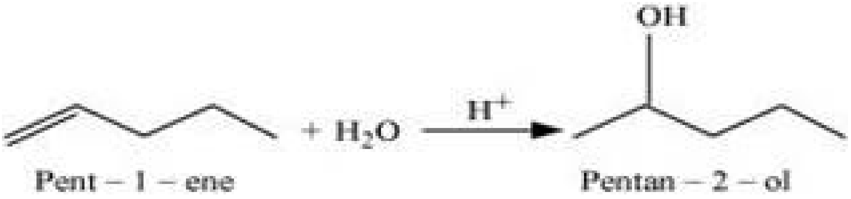
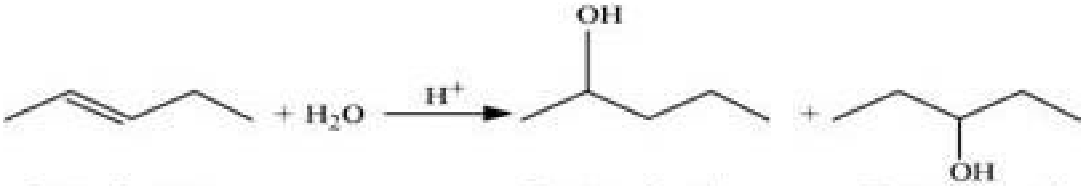


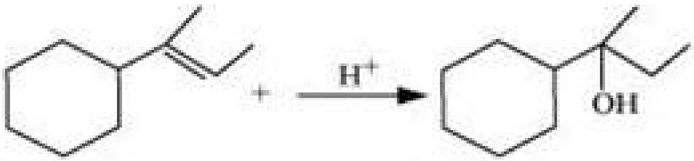
Acid-catalyzed hydration of pent-2-ene also produces pentan-2-ol but along with pentan-3-ol.



Pent – 2 – ene   Pentan – 2 – ol   Pentan – 3 – ol

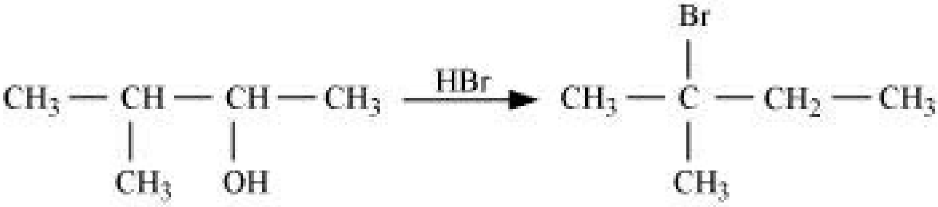
Thus, the first reaction is preferred over the second one to get pentan-2-ol.

(iv)



2 – Cyclohexylbut – 2 – ene   2 – Cyclohexylbutan – 2 – ol

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

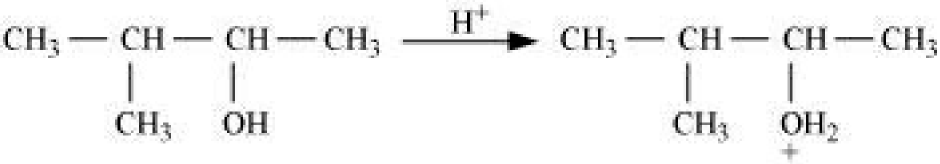


$$CH_3-\underset{\underset{CH_3}{|}}{CH}-\underset{\underset{OH}{|}}{CH}-CH_3 \xrightarrow{HBr} CH_3-\overset{\overset{Br}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2-CH_3$$

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 mechanism of the given reaction involves the following steps:

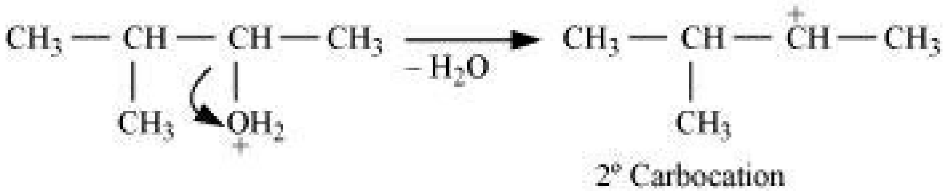
Step 1: Protonation



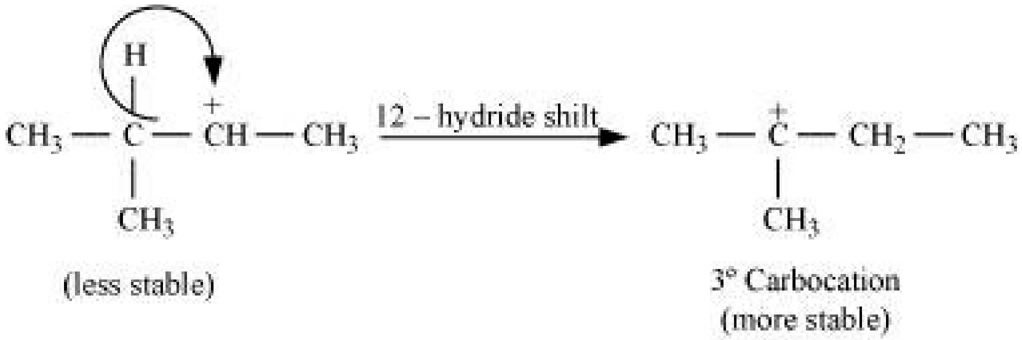
$$CH_3-\underset{\underset{CH_3}{|}}{CH}-\underset{\underset{OH}{|}}{CH}-CH_3 \xrightarrow{H^+} CH_3-\underset{\underset{CH_3}{|}}{CH}-\underset{\underset{\underset{+}{OH_2}}{|}}{CH}-CH_3$$

3 – Methylbutan – 2 – ol

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



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



Step 4: Nucleophilic attack