Alcohols, Phenols and Ethers

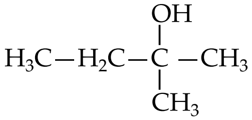
CHAPTER 11

NCERT FOCUS ANSWERS

TOPIC 1

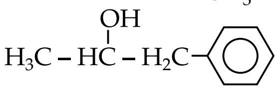
1. (i) 2,2,4-Trimethylpentan-3-ol
(ii) 5-Ethylheptan-2,4-diol
(iii) Butane-2,3-diol
(iv) Propane-1,2,3-triol

2. (i)

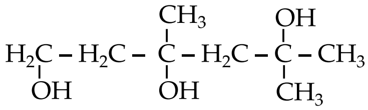


$H_3C-H_2C-\overset{\overset{\Large OH}{|}}{\underset{\underset{\Large CH_3}{|}}{C}}-CH_3$

(ii)

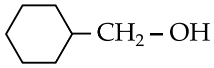


(iii)



$H_2\underset{\underset{\Large OH}{|}}{C}-H_2C-\overset{\overset{\Large CH_3}{|}}{\underset{\underset{\Large OH}{|}}{C}}-H_2C-\overset{\overset{\Large OH}{|}}{\underset{\underset{\Large CH_3}{|}}{C}}-CH_3$

(iv)



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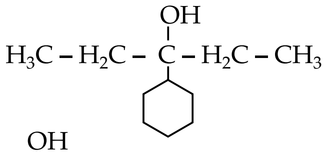

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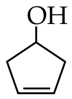

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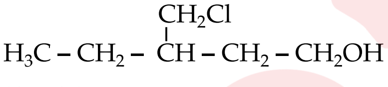
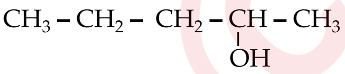


$H_3C-CH_2-\overset{\overset{\Large CH_2Cl}{|}}{CH}-CH_2-CH_2OH$

3. (i) (a) $CH_3-CH_2-CH_2-CH_2-CH_2-OH$

Pentanol (1°)

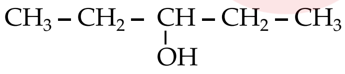
(b)



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

Pentan-2-ol (2°)

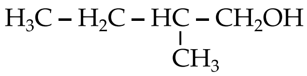
(c)



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

Pentan-3-ol (2°)

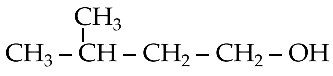
(d)



$H_3C-H_2C-\underset{\underset{\Large CH_3}{|}}{HC}-CH_2OH$

2-Methylbutan-1-ol (1°)

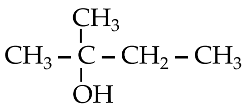
(e)



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

3-Methylbutan-1-ol (1°)

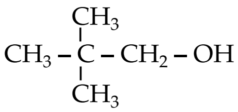
(f)



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

2-Methylbutan-2-ol (3°)

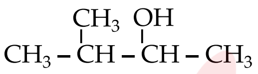
(g)



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

2,2-Dimethylpropan-1-ol (1°)

(h)



$CH_3-\overset{\overset{\Large CH_3}{|}}{CH}-\overset{\overset{\Large OH}{|}}{CH}-CH_3$

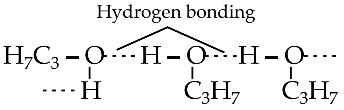
3-Methylbutan-2-ol (2°)

(ii) Isomers (a), (d), (e) and (g) are primary alcohols.
Isomers (b), (c) and (h) are secondary alcohols.
Isomer (f) is a tertiary alcohol.

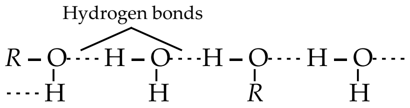
4. The boiling point of any compound depends on the strength of inter-molecular forces. Stronger is the inter-molecular attraction, higher is the boiling point.

In butane, the molecules interact with each other through weak van der Waals' forces. These weak forces can be easily overcome by supplying small amount of heat energy. Thus, they have low boiling point.

In propanol, the molecules are held together by strong hydrogen bonding. These attractive forces operating between molecules are more difficult to break and therefore higher amount of heat needs to be supplied, therefore, it has higher boiling point.



5. Organic compounds are soluble in water if they are able to form hydrogen bonds with it. Alcohols are able to establish this interaction by the virtue of their OH group and are therefore soluble in water. On the other hand, other hydrocarbons of comparable mass do not dissolve in water since they cannot form hydrogen bonds.



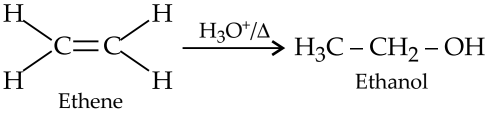
6. Hydroboration-oxidation is a method of preparation of alcohols from alkenes. The main advantage of this method is the high yield of alcohol obtained. During hydroboration, diborane $(BH_3)_2$ is made to react with an alkene to form an addition product. This product is then treated with hydrogen peroxide in the presence of sodium hydroxide to give alcohol.

For example,

$$\underset{\text{Propene}}{H_3C-CH=CH_2}+BH_3 \longrightarrow H_3C-CH_2-CH_2-BH_2 \xrightarrow{CH_3CH=CH_2} (H_3C-CH_2-CH_2)_2BH \xrightarrow{CH_3CH=CH_2} \underset{\text{Addition product}}{(H_3C-CH_2-CH_2)_3B}$$

$$\underset{\text{Propanol}}{3CH_3-CH_2-CH_2-OH} \xleftarrow{H_2O_2/H_2O/\bar{O}H} \underset{\text{Addition product}}{(H_3C-CH_2-CH_2)_3B}$$

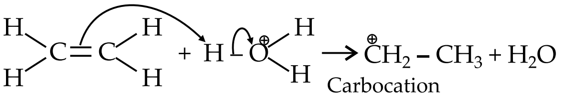
7. The acid catalysed hydration of ethene may be represented as :



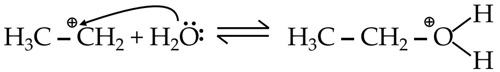
The mechanism followed by the above reaction may be depicted as

Step 1 : Generation of carbocation : Protonation of ethene yields a carbocation as

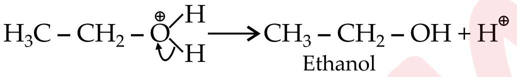
$$H_2\ddot{O}: + H^{\oplus} \longrightarrow H_3O^+$$



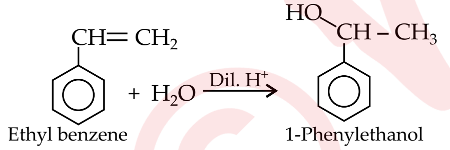
Step 2 : Nucleophilic attack of water on carbocation :
The carbocation polarizes the lone pair electrons of O of water and hydration takes place.



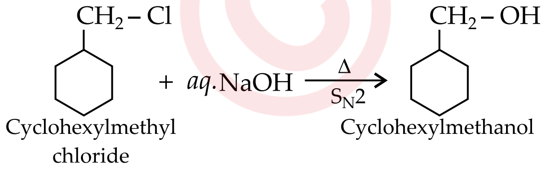
Step 3 : Formation of product,
Regeneration of the proton :



8. (i)



(ii)



(iii) $$\underset{\text{1-Chloropentane}}{CH_3-(CH_2)_3-CH_2-Cl} + aq.NaOH \xrightarrow[\Delta]{S_N2,\ hydrolysis} \underset{\text{Pentan-1-ol}}{CH_3-(CH_2)_3-CH_2-OH}$$

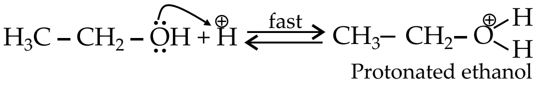
9. $$\underset{\text{Propan-1-ol}}{CH_3-CH_2-CH_2OH} \xrightarrow{alk.\ KMnO_4} \underset{\text{Propanoic acid}}{CH_3CH_2COOH} + H_2O$$

10. In the presence of conc. acids such as H_3PO_4 and H_2SO_4, alcohols undergo dehydration to yield alkenes.

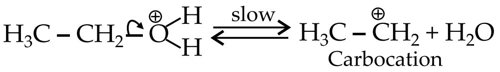
$$\underset{\text{Ethanol}}{H_3C-CH_2-OH} \xrightarrow{conc.\ H^+/\Delta} \underset{\text{Ethene}}{CH_2=CH_2} + H_2O$$

The mechanism for this reaction is :

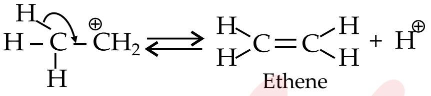
Step 1 : Protonation of ethanol



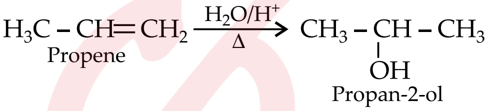
Step 2 : Formation of carbocation



Step 3 : Formation of ethene and regeneration of proton

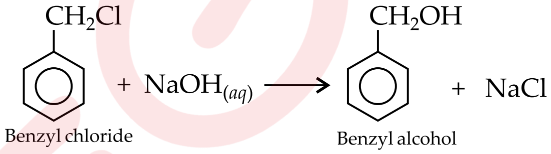


11. (i)

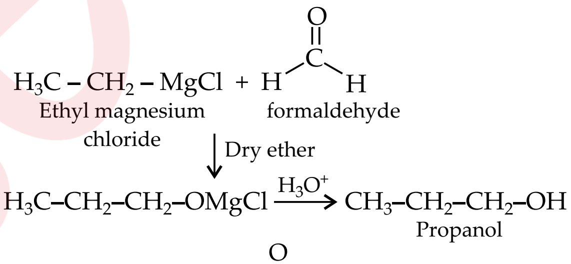


$$\underset{\text{Propene}}{H_3C-CH=CH_2} \xrightarrow[\Delta]{H_2O/H^+} \underset{\text{Propan-2-ol}}{CH_3-\underset{OH}{CH}-CH_3}$$

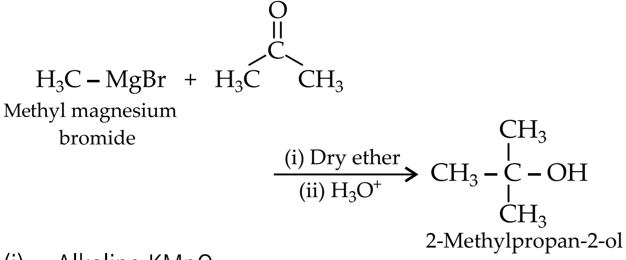
(ii)



(iii)

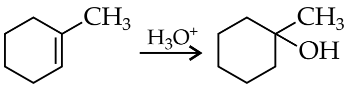


(iv)



12. (i) Alkaline $KMnO_4$
(ii) Pyridinium chlorochromate in chloromethane (CH_2Cl_2)
(iii) Alkaline $KMnO_4$
(iv) Conc. H_2SO_4 or H_3PO_4 at 433-443 K
(v) H_2/Ni or $NaBH_4$ or $LiAlH_4$

13. (i)



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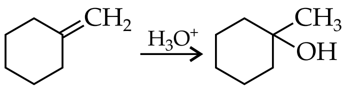
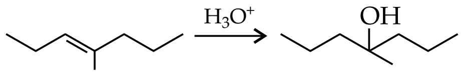


(ii)



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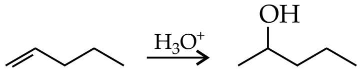
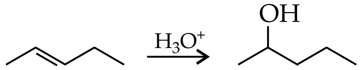
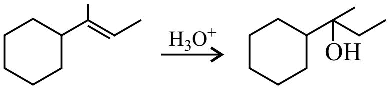


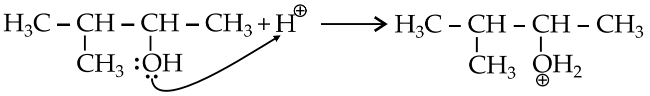
or 

(iv) 

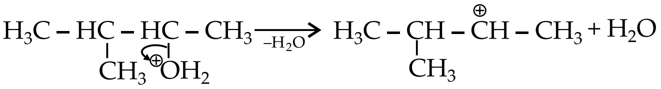
14. The given reaction is an example of carbocation rearrangement which takes place by hydride shift. The mechanism for it is :

Step 1 : Formation of carbocation : Protonation of alcohol.

$HBr \longrightarrow H^+ + Br^{\ominus}$



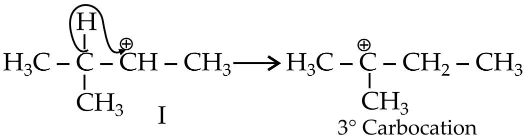
$$H_3C-\underset{CH_3}{\underset{|}{CH}}-\underset{:\ddot{O}H}{\underset{|}{CH}}-CH_3+H^{\oplus} \longrightarrow H_3C-\underset{CH_3}{\underset{|}{CH}}-\underset{\overset{\oplus}{O}H_2}{\underset{|}{CH}}-CH_3$$



$$H_3C-\underset{CH_3}{\underset{|}{HC}}-\underset{\overset{\oplus}{O}H_2}{\underset{|}{HC}}-CH_3 \xrightarrow{-H_2O} H_3C-\underset{CH_3}{\underset{|}{CH}}-\overset{\oplus}{C}H-CH_3+H_2O$$

2° Carbocation

Step 2 : 1,2-hydride shift : Formation of a more stable, 3° carbocation.



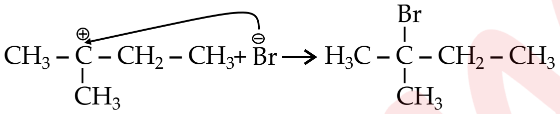
$$H_3C-\underset{CH_3}{\underset{|}{\overset{H}{\overset{|}{C}}}}-\overset{\oplus}{C}H-CH_3 \longrightarrow H_3C-\underset{CH_3}{\underset{|}{\overset{\oplus}{C}}}-CH_2-CH_3$$

I

3° Carbocation
II

Initially, a 2° carbocation (I) was formed. But, due to the higher stability of its 3° counter part, the 1, 2-hydride shift takes place and the more stable carbocation (II) is formed.

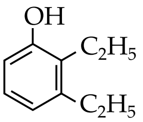
Step 3 : Attack of nucleophile : Generation of product



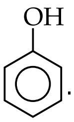
$$CH_3-\underset{CH_3}{\underset{|}{\overset{\oplus}{C}}}-CH_2-CH_3+\overset{\ominus}{Br}\longrightarrow H_3C-\underset{CH_3}{\underset{|}{\overset{Br}{\overset{|}{C}}}}-CH_2-CH_3$$

TOPIC 2

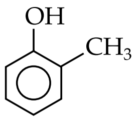
1. (i) 2-Methylphenol
(ii) 4-Methylphenol
(iii) 2,5-Dimethylphenol
(iv) 2,6-Dimethylphenol

2. 

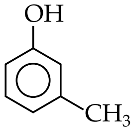
3. Given molecular formula : C_7H_8O

Since, it is given that it is a phenol the basic skeleton will be .

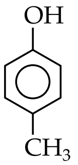
This structure accounts for C_6H_6O. Remaining CH_2 when added to the phenol gives following structures :



2-Methylphenol
(*o*-cresol)

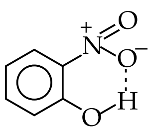


3-Methylphenol
(*m*-cresol)

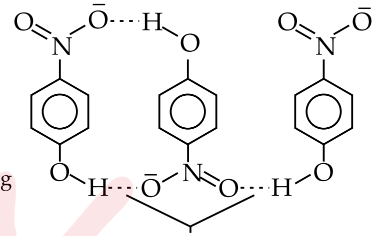


4-Methylphenol
(*p*-cresol)

4. During steam distillation, it is the lower boiling compound which distills out first. Between *ortho*- and *para*-nitrophenol it is the *ortho*-isomer which will be steam volatile since it has a lower boiling point. The difference in boiling point between the two isomers can be understood based on the structural difference. In *ortho*-isomer intramolecular hydrogen bonding takes place while in the *para*-isomer, intermolecular hydrogen bonding takes place.

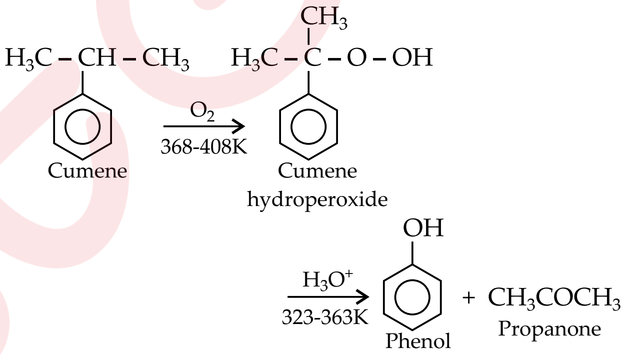


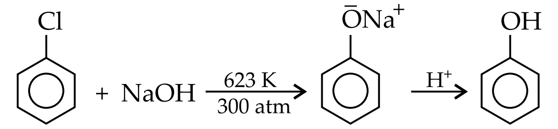
Intramolecular H-bonding
o-Nitrophenol



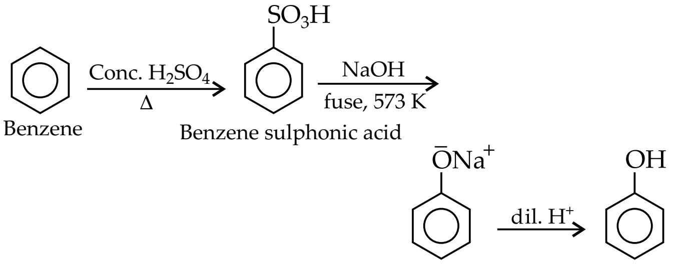
Intermolecular H-bonding
p-Nitrophenol

As a result of the strong forces operating between the molecules of *p*-isomer, the boiling point is higher and it is not steam volatile.

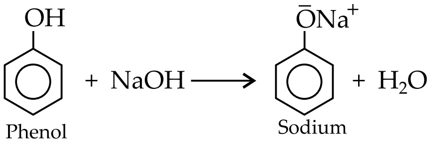
5. 

6. 

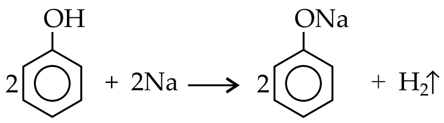
7. Using the given reagents, phenol may be prepared as :



8. (a) Acids react with base and so does phenol.



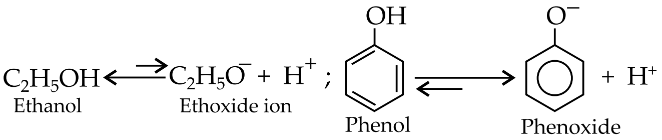
(b) Upon reaction with active metals such as Na, phenol liberates H_2.

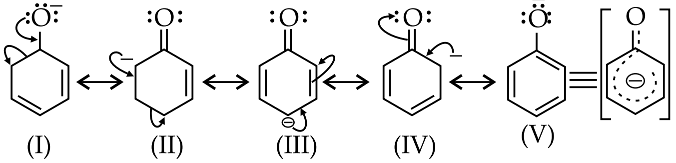


These two reactions demonstrate the acidic nature of phenol.

As compared to ethanol, phenols are more acidic. They lose their H atom as H^+ more readily than alcohols.

The reason for such a behaviour of phenol may be attributed to the resonance stabilisation that arises from the contributing structures of corresponding phenoxide ion.



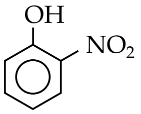


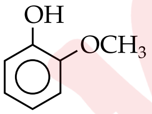
Charge dispersal by resonance

The resonance stabilization provided by the contributing structures (I)-(V) more than compensates for the bond breakage energy of O – H bond and thus causes phenol to be acidic in nature.

No such resonance structures are possible for ethoxide ion and therefore the conversion of ethanol to ethoxide is not favoured under normal conditions. Therefore, ethanol is less acidic than phenol.

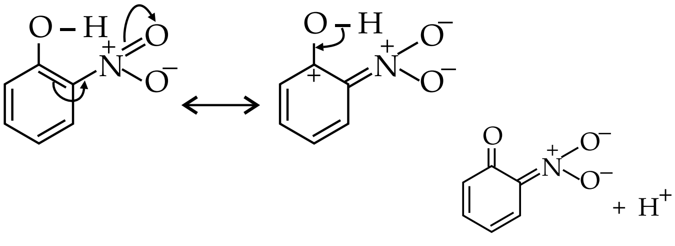
9.


o-Nitrophenol
(I)


o-Methoxyphenol
(II)

The acidity of phenol arises from the loss of H of O – H group as H^+. This loss is facilitated if the polarity of the O – H bond increases and H carries substantial δ+ charge.

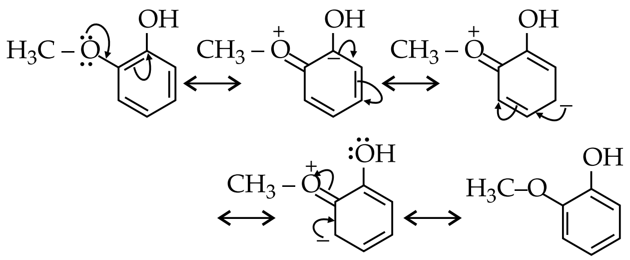
In (I), the presence of the highly electron withdrawing NO_2 group at the *ortho* position increases the polarity of the O – H bond.



Resonance structure of *o*-nitrophenol

This helps in release of H^+ and increases acidity.

(II) is less acidic because $-OCH_3$ is an electron releasing group and increases the e^- density on O of OH and H^+ release is suppressed. This can be understood from the resonance structures of II which are

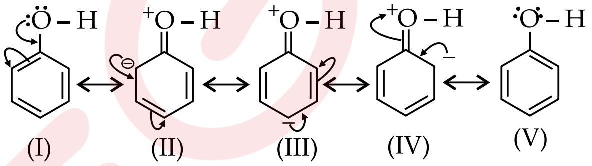


Resonance structure of *o*-methoxyphenol

10. In an electrophilic substitution reaction, an electron deficient species attacks the benzene ring which is electron rich.

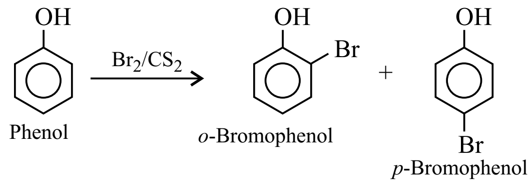
When an –OH group is attached to the benzene ring, by the virtue of its electron releasing nature increases the electron density of the ring and thus activates it, *i.e.*, makes it a welcome site for electrophiles.

The increase in electron density can be visualised as :

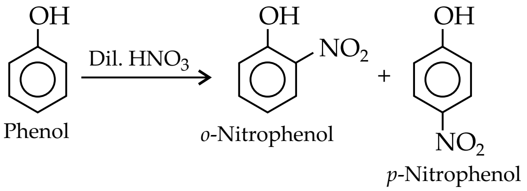


From structures (I) - (V), we find that the attachment of hydroxyl group to benzene has increased the electron density (–ve charge) on the ring carbon atoms (especially C-2, C-4 and C-6). It is therefore said to have activated the ring towards electrophiles which are attracted to the increased electron density.

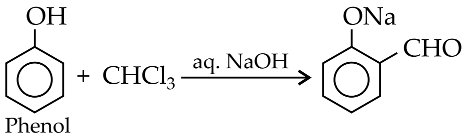
11. (i)



(ii)

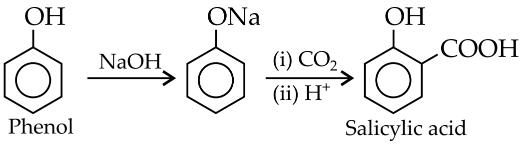


(iii)



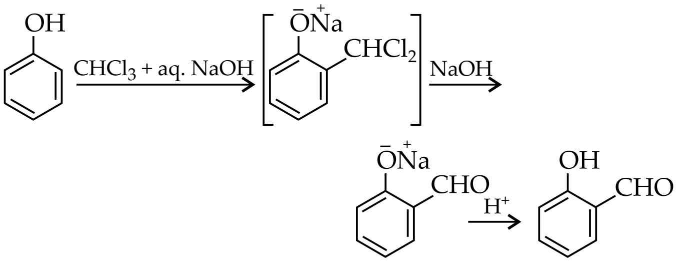
12. (i) Kolbe's reaction :

The fact that phenoxide ion is even more reactive than phenol towards incoming electrophiles is made use of in this reaction. Sodium phenoxide is reacted with CO_2 followed by acid treatment to yield *o*-hydroxybenzoic acid as the major product.



(ii) Reimer-Tiemann reaction :

Treatment of phenol with chloroform in the presence of aqueous alkali introduces a CHO group at the ortho position. Acidification yields salicylaldehyde.



Salicylaldehyde

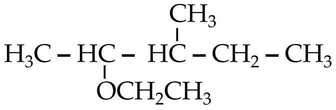
13. Br_2/H_2O

TOPIC 3

1. (i) 1-Methoxy-2-methylpropane
 (ii) Ethoxybenzene
 (iii) 1-Phenoxyheptane
 (iv) 2-Ethoxybutane

2. (i) $H_3C—CH_2—O—CH_2—CH_2—CH_3$

(ii)



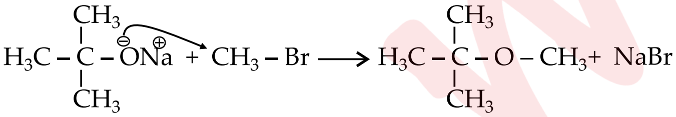
$$H_3C-\underset{\underset{OCH_2CH_3}{|}}{HC}-\overset{\overset{CH_3}{|}}{HC}-CH_2-CH_3$$

3. (i) Williamson synthesis :

In this method, an alkyl halides is reacted with sodium alkoxide.

$$R-X+R'-ONa \longrightarrow R-O-R'+NaX$$

The reaction involves S_N2 attack of an alkoxide ion on 1°*RX*.



$$H_3C-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-\overset{\ominus}{O}\overset{\oplus}{Na} + CH_3-Br \longrightarrow H_3C-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-O-CH_3+ NaBr$$

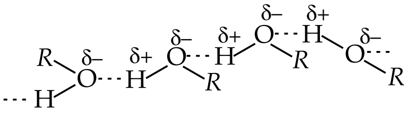
Better results are obtained when *RX* is primary.

(ii) Unsymmetrical ethers :

Unsymmetrical ethers are organic compounds where the ethereal oxygen atom is attached to two different alkyl or aryl groups. *e.g.*, $C_2H_5-O-CH_3$, $C_6H_5-O-C_2H_5$, etc.

4. The higher boiling point of ethanol may be attributed to the presence of intermolecular hydrogen bonding in it.

Due to such extensive bonding, more energy needs to be supplied to ethanol to break these bonds and move it into the vapour phase.



H-bonding in alcohol

$\boxed{R = C_2H_5}$

Methoxymethane, an ether, lacks such hydrogen bonding and is therefore a low boiling liquid.

5. (i) 1-Ethoxy-2-methylpropane

(ii) 2-Chloro-1-methoxyethane

(iii) 4-Nitroanisole

(iv) 1-Methoxypropane

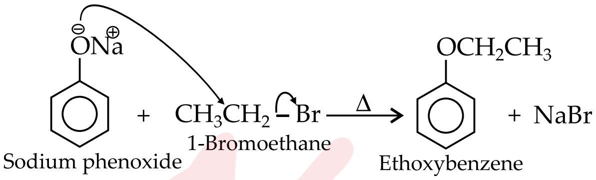
(v) 1-Ethoxy-4, 4-dimethylcyclohexane

(vi) Ethoxybenzene

6. (i)

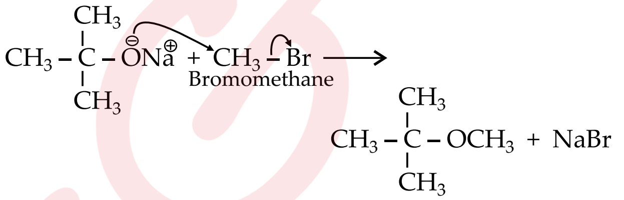
$$\underset{\text{Sodium propoxide}}{CH_3CH_2CH_2\overset{\ominus}{O}\overset{\oplus}{Na}} + \underset{\text{1-Bromopropane}}{CH_3CH_2CH_2-Br} \xrightarrow{\text{Heat}}$$
$$\underset{\text{1-Propoxypropane}}{CH_3CH_2CH_2-O-CH_2CH_2CH_3} + NaBr$$

(ii)



Sodium phenoxide 1-Bromoethane Ethoxybenzene

(iii)



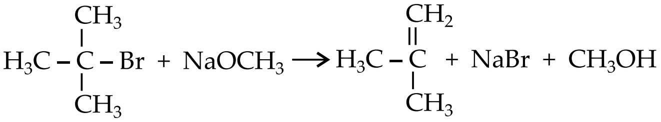
$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-\overset{\ominus}{O}\overset{\oplus}{Na} + \underset{\text{Bromomethane}}{CH_3-Br} \longrightarrow$$
$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-OCH_3 + NaBr$$

2-Methyl-2-methoxypropane

(iv)

$$\underset{\text{Sodium ethoxide}}{CH_3CH_2\overset{\ominus}{O}\overset{\oplus}{Na}} + \underset{\text{Bromomethane}}{CH_3-Br} \xrightarrow{\text{Heat}}$$
$$\underset{\text{1-Methoxyethane}}{CH_3CH_2-O-CH_3} + NaBr$$

7. The main limitation of Williamson's ether synthesis lies in its unemployability for preparation of unsymmetrical ethers where the compound contains secondary or tertiary alkyl groups. *e.g.*, reaction between tert-butyl bromide and sodium methoxide yields an alkene.



$$H_3C-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-Br + NaOCH_3 \longrightarrow H_3C-\overset{\overset{CH_2}{||}}{\underset{\underset{CH_3}{|}}{C}} + NaBr + CH_3OH$$

tert-Butylbromide 2-Methylpropene

This is because the competing elimination reaction predominates over S_N2 and alkene is formed.

8.

$$\underset{\text{Propanol}}{CH_3CH_2CH_2OH} \longrightarrow \underset{\text{Propoxypropane}}{(CH_3CH_2CH_2)_2O}$$

This reaction can be brought about as :

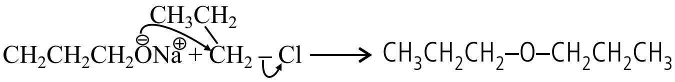
$$\underset{\text{Propanol}}{CH_3CH_2CH_2OH} + SOCl_2 \longrightarrow CH_3CH_2CH_2Cl + SO_2 + HCl$$

$$2CH_3CH_2CH_2OH + \underset{\text{metal}}{2Na} \longrightarrow CH_3CH_2CH_2\overset{\ominus}{O}\overset{\oplus}{Na} + H_2$$

$$\underset{\text{1-Chloropropane}}{CH_3CH_2CH_2Cl} + \underset{\text{Sodium propoxide}}{CH_3CH_2CH_2\overset{\ominus}{O}\overset{\oplus}{Na}} \longrightarrow \underset{\text{Propoxypropane}}{(CH_3CH_2CH_2)_2O}$$

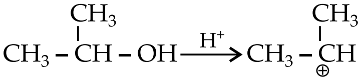
Mechanism :

S_N2 attack of propoxide on the halide



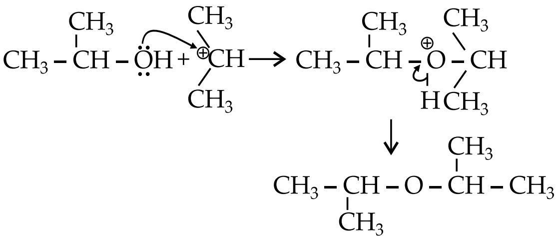
$$CH_2CH_2CH_2\overset{\ominus}{O}\overset{\oplus}{Na} + \overset{CH_3CH_2}{CH_2}-Cl \longrightarrow CH_3CH_2CH_2-O-CH_2CH_2CH_3$$

9. Consider the reaction between propan-2-ol molecules in the presence of acid.



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

If an ether is to be formed, another alcohol molecule must carry out a nucleophilic attack on the carbocation as



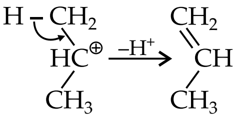
$$CH_3-\overset{CH_3}{\overset{|}{C}H}-\ddot{O}H+\overset{\oplus}{C}H(CH_3)_2 \longrightarrow CH_3-\overset{CH_3}{\overset{|}{C}H}-\underset{H}{\overset{\oplus}{O}}-CH(CH_3)_2 \longrightarrow CH_3-\underset{CH_3}{\underset{|}{C}H}-O-\overset{CH_3}{\overset{|}{C}H}-CH_3$$

However, this does not happen because of

(a) the steric hindrance around the carbocation, and

(b) bulky size of the nucleophile which would further cause crowding.

As a result, the carbocation prefers to lose a proton and forms an alkene.

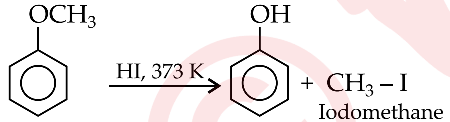


$$H-CH_2-\overset{\oplus}{C}H-CH_3 \xrightarrow{-H^+} CH_2=CH-CH_3$$

For the same reason 3° alcohols in the presence of acid do not form ethers since 3° alcohols are even more sterically hindered than 2° alcohols.

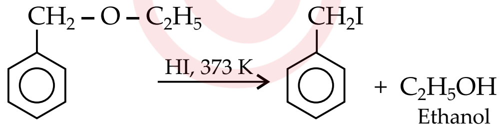
10. (i) $$\underset{\text{1-Propoxypropane}}{CH_3CH_2CH_2-O-CH_2CH_2CH_3} \xrightarrow[373\,K]{HI} \underset{\text{Propan-1-ol}}{CH_3CH_2CH_2-OH} + \underset{\text{Iodopropane}}{CH_3CH_2CH_2-I}$$

(ii)



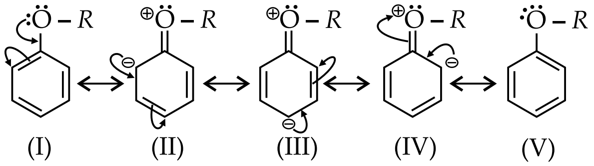
Methoxybenzene Phenol Iodomethane

(iii)



Benzyl ethyl ether Benzyl iodide Ethanol

11. Consider the following resonance structures of aryl alkyl ethers :



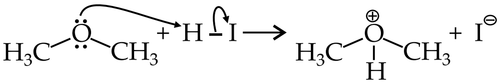
(i) From the above structures we find that the presence of the *OR* group has increased the electron density on the benzene ring and therefore the ring is said to have been activated towards incoming electrophiles.

(ii) From structures (II), (III) and (IV) we find that electron density has increased on C-2, C-4 and C-6, *i.e.*, at the *ortho* and *para* positions. As a result the electrophile ($E^{\oplus}$) attaches itself to these e^- rich sites and the $-OR$ group is said to have directed the $E^{\oplus}$ to *ortho* and *para* positions.

12. The reaction between methoxymethane and HI is :

$$CH_3-O-CH_3+HI \longrightarrow CH_3I+CH_3OH$$

Step I : Generation of oxonium ion : Protonation of ether molecule

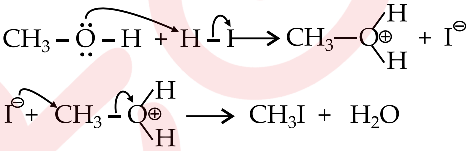


$$H_3C-\ddot{O}-CH_3 + H-I \longrightarrow H_3C-\underset{H}{\overset{\oplus}{O}}-CH_3 + I^{\ominus}$$

Step II : Nucleophilic attack on oxonium ion :

$$CH_3-\underset{H}{\overset{\oplus}{O}}-CH_3+I^{\ominus} \xrightarrow{S_N2} \underset{\text{Methanol}}{CH_3-O-H} + \underset{\text{Methyl iodide}}{ICH_3}$$

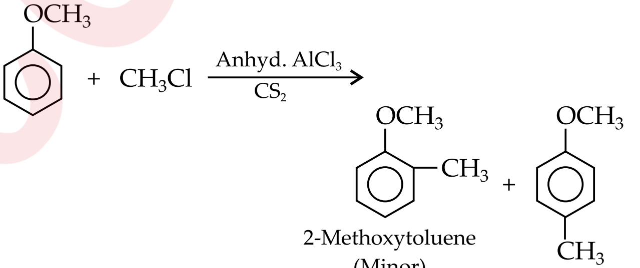
If excess HI is used, methanol formed above reacts with HI to form methyl iodide.



$$CH_3-\ddot{O}-H + H-I \longrightarrow CH_3-\overset{\oplus}{O}H_2 + I^{\ominus}$$

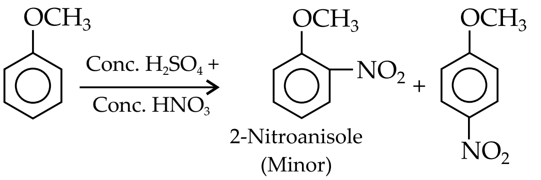
$$I^{\ominus} + CH_3-\overset{\oplus}{O}H_2 \longrightarrow CH_3I + H_2O$$

13. (i) Friedel-Crafts reaction (Alkylation) :



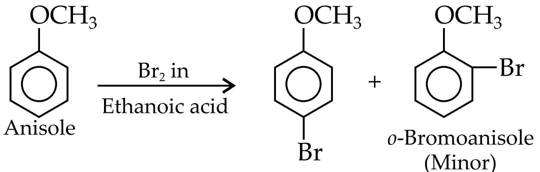
2-Methoxytoluene (Minor) 4-Methoxytoluene (Major)

(ii) Nitration of anisole : Anisole reacts with a mixture of concentrated sulphuric acid and nitric acid to yield a mixture of *ortho* and *para* nitroanisole.



2-Nitroanisole (Minor) 4-Nitroanisole (Major)

(iii) Bromination



Anisole *p*-Bromoanisole (Major) *o*-Bromoanisole (Minor)

(iv) Friedel-Crafts' acetylation of anisole.