

## CHAPTER 2



# ALCOHOLS, PHENOLS AND ETHERS

- \* Alcohols
- \* Phenols
- \* Ethers

## ALCOHOLS

Alcohols are hydroxyl derivatives of hydrocarbons. They are formed by the displacement of a H atom, by a –OH group in hydrocarbons. Thus the functional group in alcohols is –OH group. Alcohols are regarded as mono-alkyl derivatives of water.

If –OH group is connected to  $sp^3$  carbon atom of an alkane, it is aliphatic saturated alcohol. eg :  $CH_3-CH_2-OH$  (ethyl alcohol).

If –OH group is connected to  $sp^3$  or  $sp^2$  carbon atom of an alkene or alkyne, it is unsaturated alcohol. eg :  $CH_2=CH-OH$  (vinyl alcohol);  $HO-CH_2-CH=CH_2$  (allyl alcohol).

If –OH group is connected to  $sp^2$  carbon atom of benzene ring, it is phenol,  $C_6H_5OH$ .

If –OH group is connected to  $sp^3$  carbon atom of side chain present in an aromatic compound, it is an aromatic alcohol behaves like an alcohol. eg :  $C_6H_5-CH_2-OH$  (benzyl alcohol).

### 2.1.1

#### Classification

**Monohydric**  
alcohols contain  
only one  
–OH group

Alcohols with only one –OH group are monohydric alcohols.

eg :  $CH_3-CH_2-OH$ ,  $CH_3-CH_2-CH_2-OH$ ,  $C_6H_5-CH_2-OH$ .

Alcohols with two –OH groups are dihydric alcohols.

eg : Ethylene glycol,  $CH_2OHCH_2OH$ .

Alcohols with three –OH groups are glycerols. eg :  $CH_2OHCHOHCH_2OH$ .

Polyhydric alcohols contain many –OH groups. Sorbitol and mannitol are hexahydric alcohols,  $CH_2OH(CHOH)_4CH_2OH$ .

Monohydric alcohols are sub-classified as primary, secondary and tertiary alcohols. They are listed in Table 2.1.

### 2.1.2

#### Nomenclature

**Common names :** The name of the alkyl group holding the –OH group is written first followed by the word alcohol. Methyl alcohol is the simplest alcohol and ethyl alcohol is the commonest alcohol.

**IUPAC System :** The longest continuous carbon chain with –OH group is selected as parent chain. The carbon atoms of this chain are allotted numbers so that the carbon holding –OH group gets least number. An appropriate root word and primary suffix are written.

Table 2.1 Types of alcohols

Type of alcohol	Symbol	General formula	Example	Description
Primary alcohol	1°	R-CH <sub>2</sub> -OH	C <sub>2</sub> H <sub>5</sub> OH, CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> OH	-OH attached carbon is linked with one more carbon atom
Secondary alcohol	2°	R-CH(OH)   R'	CH <sub>3</sub> CH(OH)CH <sub>3</sub>	-OH attached carbon is linked with two more carbon atoms
Tertiary alcohol	3°	OH   R-C-R'   R''	CH <sub>3</sub> OCH(CH <sub>3</sub> ) <sub>2</sub>	-OH attached carbon is linked with three more carbon atoms

*IUPAC name of saturated alcohol is alkanol*

The names of substituent alkyl groups with their positions are included before the root word in alphabetical order. Common and IUPAC names of some alcohols are listed in Table 2.2.

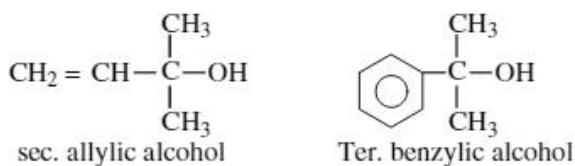


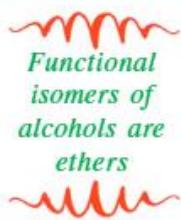
Table 2.2 Common and IUPAC names of some alcohols

Compound	Common name	IUPAC name
CH <sub>3</sub> OH	Methyl alcohol	Methanol
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> OH	n-Propyl alcohol	Propan-1-ol
CH <sub>3</sub> CH(OH)CH <sub>3</sub>	Isopropyl alcohol	Propan-2-ol
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> OH	n-Butyl alcohol	Butan-1-ol
CH <sub>3</sub> CH(OH)CH <sub>2</sub> CH <sub>3</sub>	sec-Butyl alcohol	Butan-2-ol
(CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub> OH	Isobutyl alcohol	2-Methylpropan-1-ol
(CH <sub>3</sub> ) <sub>3</sub> COH	tert-Butyl alcohol	2-Methylpropan-2-ol
(CH <sub>3</sub> ) <sub>2</sub> C(OH)CH <sub>2</sub> CH <sub>3</sub>	tert-Amyl alcohol	2-methylbutan-2-ol
$\begin{array}{c} \text{CH}_2-\text{CH}_2 \\   \quad   \\ \text{OH} \quad \text{OH} \end{array}$	Ethylene glycol	Ethan-1,2-diol
$\begin{array}{c} \text{CH}_2-\text{CH}-\text{CH}_2 \\   \quad   \quad   \\ \text{OH} \quad \text{OH} \quad \text{OH} \end{array}$	Glycerol	Propan-1,2,3-triol
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> OH	Benzyl alcohol	Phenylmethanol

### 2.1.3

#### Isomerism

Alcohols may exhibit chain, positional and functional isomerism. Functional isomers of alcohols are ethers.



$\text{CH}_3\text{---CH}_2\text{---CH}_2\text{---CH}_2$  and  $\begin{array}{c} \text{CH}_3\text{---CH---CH}_2 \\ | \\ \text{OH} \end{array}$  are chain isomers.

$\text{CH}_3\text{---CH}_2\text{---CH}_2\text{---CH}_2$  and  $\begin{array}{c} \text{CH}_3\text{---CH---CH}_2\text{---CH}_3 \\ | \\ \text{OH} \end{array}$  are position isomers.

$\text{CH}_3\text{---CH}_2\text{---OH}$  and  $\text{CH}_3\text{---O---CH}_3$  are functional isomers.

Unsaturated alcohols and carbonyl compounds are tautomers.

$\begin{array}{c} \text{CH}_3\text{---C=CH}_2 \\ | \\ \text{OH} \end{array}$  and  $\begin{array}{c} \text{CH}_3\text{---C---CH}_3 \\ || \\ \text{O} \end{array}$  are tautomers.

Alcohols containing chiral centres can exhibit optical isomerism. The simplest monohydric alcohol that can exhibit enantiomerism is butan-2-ol.



**P.2.1** How many amyl alcohol structures are possible?

**Solution** Amyl alcohol is a five carbon alcohol with the formula,  $\text{C}_5\text{H}_{11}\text{OH}$ .

Eight structural isomers are possible for  $\text{C}_5\text{H}_{11}\text{OH}$ .

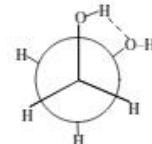
They are : Four primary, three secondary and one tertiary alcohols.



**P.2.2** Identify the most stable conformer of glycol.

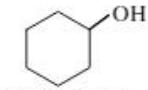
**Solution** Gauche form of glycol is most stable.

This is due to intramolecular hydrogen bonding.



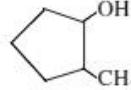
**P.2.3** Write two examples of cycloalkanols and their IUPAC names.

**Solution** eg. 1



Cyclohexanol

eg. 2



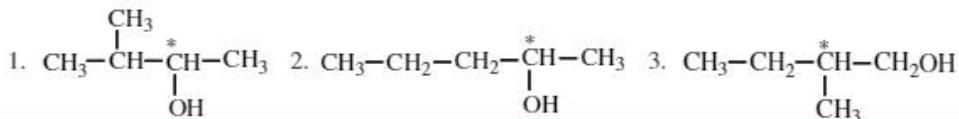
2-methylcyclopentanol



**P.2.4** Write the structures of the alcohols with the molecular formula,  $\text{C}_5\text{H}_{12}\text{O}$  which exhibit enantiomorphism.

**Solution** With formula  $\text{C}_5\text{H}_{12}\text{O}$ , eight alcohol and six ether constitutional isomers are possible.

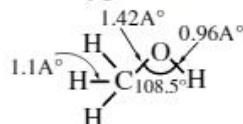
Among alcohols following three can exhibit enantiomerism.



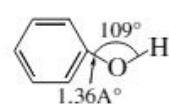
#### 2.1.4

##### Structures

In alcohols, the oxygen of the  $-\text{OH}$  group is attached to carbon by a sigma bond formed by the overlap of a  $\text{sp}^3$  hybridised orbital of carbon with a  $\text{sp}^3$  hybridised orbital of oxygen. Structures of methanol and phenol are given below.



Methanol  $\mu = 1.71\text{D}$



Phenol  $\mu = 1.54\text{D}$

The COH bond angle in alcohols is slightly less than the tetrahedral angle ( $109^{\circ}28'$ ). It is due to the repulsion between the unshared electron pairs of oxygen. In phenols, the  $-OH$  group is attached to  $sp^2$  hybridised carbon of benzene ring. The carbon-oxygen bond length ( $1.36\text{ \AA}$ ) in phenol is slightly less than that in methanol ( $1.42\text{ \AA}$ ). This is due to (i) partial double bond character on account of the conjugation of unshared electron pair of oxygen with the ring and (ii)  $sp^2$  hybridised state of carbon to which oxygen is attached.

## 2.1.5

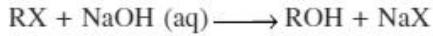
## Preparation

*Alkyl halides  
on base  
hydrolysis give  
alcohols*

*Aldehydes or carboxylic acids on reduction give 1° alcohols*

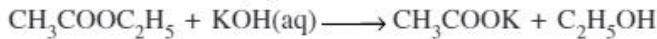
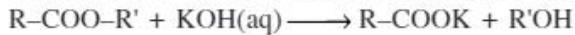
*Hydration of ethylene gives ethyl alcohol*

- i) **From alkyl halides :** Alcohols are prepared by the action of aqueous alkali or moist silver oxide ( $\text{AgOH}$ ) on alkyl halides. This is called base hydrolysis reaction.



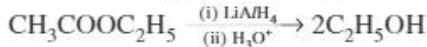
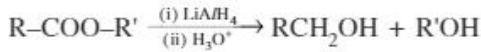
Hydrolysis of primary halides proceeds by  $S_{N2}$  mechanism while those of tertiary halides by  $S_{N1}$  mechanism. The hydrolysis of secondary alkyl halides may proceed by  $S_{N1}$  or  $S_{N2}$  reaction. Good yield of alcohols can be obtained from primary, alkene is obtained from tertiary and a mixture of alcohol and alkene can be obtained from secondary alkyl halide.

- ii) From esters : Alcohols are prepared by the hydrolysis of esters.

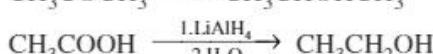
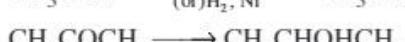
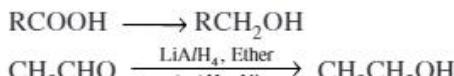
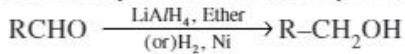


The hydrolysis of esters with alkali is called **saponification**.

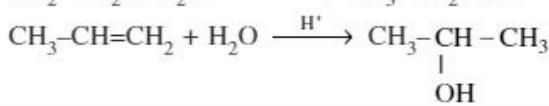
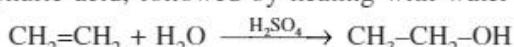
Alcohols are also obtained by the reduction of esters.



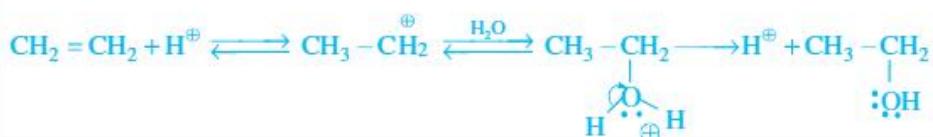
- iii) **From Carbonyls** : Aldehydes on reduction form primary alcohols and ketones give secondary alcohols. Carboxylic acids also give primary alcohols on reduction.



- iv) From alkenes :** Alkenes undergo hydration in presence of concentrated sulphuric acid, followed by heating with water form alcohols.

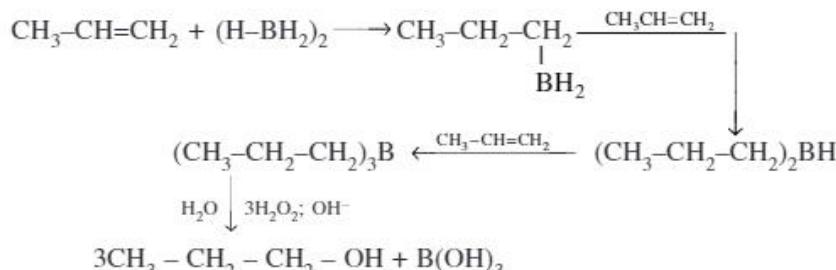


## Mechanism



In acid catalysed hydration of unsymmetrical alkenes, addition of water at carbon, carbon double bond takes place according to **Markovnikov's rule**.

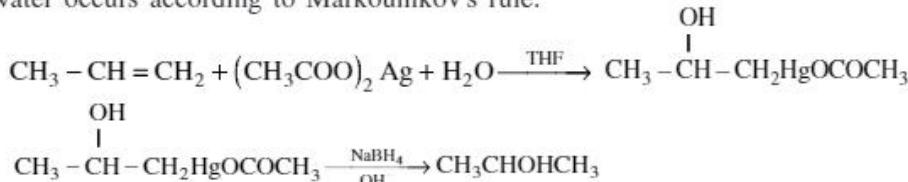
v) **By hydroboration–oxidation :** Diborane ( $B_2H_6$ ), the electrophile reacts with alkenes to give trialkyl borane as addition product. Hydrogen peroxide oxidises this to alcohol in presence of aqueous sodium hydroxide.



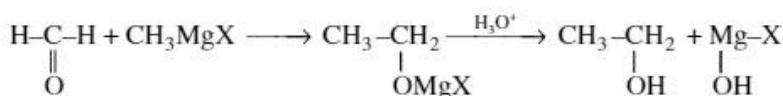
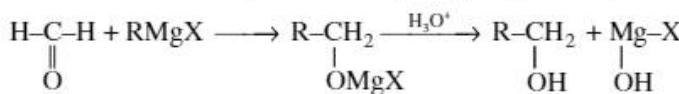
*Yield of alcohol obtained in the hydroboration is excellent*

In the above case, boron atom gets attached to the  $sp^2$  carbon carrying greater number of hydrogen atoms. The alcohol so formed looks as if it has been formed by the addition of water to the alkene in a way opposite to the Markovnikov's rule. In this reaction, alcohol is obtained in excellent yield.

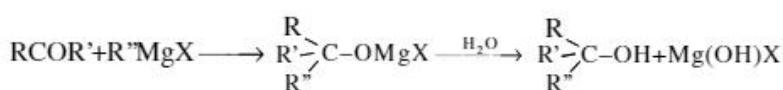
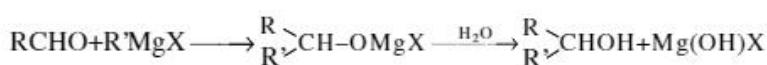
vi) **Oxymercuration-demercuration process** : Mercuric acetate in presence of water - tetrahydrofuran solution reacts with alkene to form an adduct, organomercury compound. This step is called oxymercuration. This is reduced with  $\text{NaBH}_4$  in basic medium when alcohol is formed. This second step is called demercuration. Addition of water occurs according to Markownikov's rule.



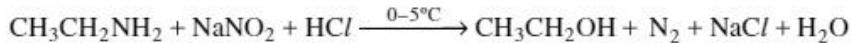
vii) **From Grignard reagent :** Formaldehyde undergoes addition with Grignard reagent and the addition product on hydrolysis gives a primary alcohol.



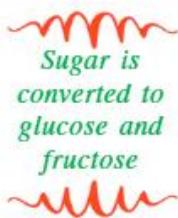
Aldehydes other than formaldehyde give secondary alcohols and ketones from tertiary alcohols.



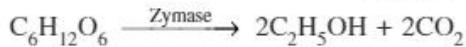
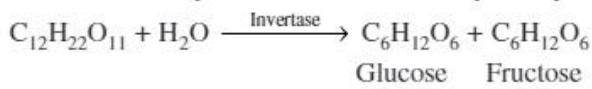
viii) **From primary amines** : Aliphatic primary amines react with nitrous acid at 0-5°C to form alcohols.



## **ALCOHOLS, PHENOLS AND ETHERS**



ix) **By Fermentation :** Decomposition of complex compounds into simple compounds by enzymes derived from microorganisms like yeast (one celled organism) is called fermentation. The sugar in molasses, sugar cane or fruits such as grapes is converted to glucose and fructose, (both of which have the formula  $C_6H_{12}O_6$ ), in the presence of an enzyme, invertase. Glucose and fructose undergo fermentation in the presence of another enzyme, zymase, which is found in yeast.

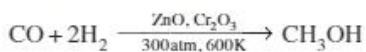


In wine making, grapes are the source of sugars and yeast. As grapes ripen, the quantity of sugar increases and yeast grows on the outer skin. When grapes are crushed, sugar and the enzyme come in contact and fermentation starts. Fermentation takes place in anaerobic conditions i.e., in absence of air. Carbon dioxide is released during fermentation. The action of zymase is inhibited once the alcohol formed exceeds 14 percent. In air gets into fermentation mixture, the oxygen of air oxidises ethanol to ethanoic acid which in turn destroys the taste of alcoholic drinks.



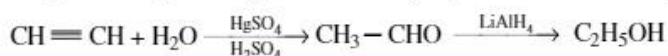
**P.2.5** How is methanol prepared, now-a-days, commercially ?

**Solution** Most of the methanol is now prepared by catalytic hydrogenation of carbon monoxide at high pressure and high temperature.



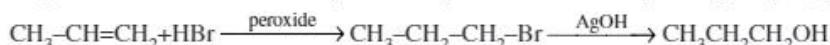
**P.2.6** How acetylene is converted to ethyl alcohol ?

**Solution** Acetylene on hydration gives acetaldehyde, which on reduction gives ethanol.



**P.2.7** How is propyl alcohol prepared from propene ?

**Solution** Propene on addition with HBr in presence of peroxide followed by base hydrolysis gives propanol.



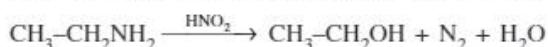
**P.2.8**  $CH_3 - \underset{CH_3}{\underset{|}{|}} - CH = CH_2 + H_2O \xrightarrow{H^+}$  X . What is X ?

**Solution** X is 2-methyl-2-butanol.



**P.2.9** Suggest a method for the conversion of  $CH_3 - CH_2 - NH_2$  into ethyl alcohol.

**Solution** Primary alcohol is prepared from a primary amine using nitrous acid.



**P.2.10** How is methyl alcohol converted to ethyl alcohol ?

**Solution** Ethanol can be obtained from methanol in the following sequence of steps.





**P.2.11** Write the order of reactivity of  $\text{CH}_3\text{OH}$ (I),  $\text{C}_2\text{H}_5\text{OH}$ (II),  $\text{CH}_3\text{CHCH}_3$ (III) towards metallic sodium.

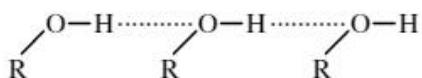
**Solution** The order of reactivity is : I > II > III

The reactivity with sodium depends on acidic nature of alcohols.

### 2.1.6

#### Physical properties

Alcohols have higher boiling points than hydrocarbons, ethers, aldehydes and ketones of comparable molecular masses. Alcohols have greater intermolecular attractions arising due to intermolecular hydrogen bonds.

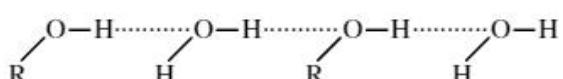


The boiling points of alcohols increase with an increase in molecular mass arising due to van der Waals forces. In case of alcohols with same alkyl group, boiling point decreases with increasing branching. Among isomeric alcohols the boiling order of

Order of boiling points : Methanol < Ethanol < Propanol < Butanol.

n-Butyl alcohol > iso butyl alcohol > Tert. butyl alcohol.

Alcohols are soluble in water due to hydrogen bonding between molecules of alcohol and water.



Solubility decreases with an increase in the size of non polar hydrophobic alkyl group, which resists dissolution. Among isomeric alcohols, solubility decreases with increase in surface area.

Order of solubility :  $\text{CH}_3\text{CH}_2\text{OH} > \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH} > \text{CH}_3(\text{CH}_2)_4\text{CH}_2\text{OH}$

Tertiary butyl alcohol > isobutyl alcohol > n-butyl alcohol.

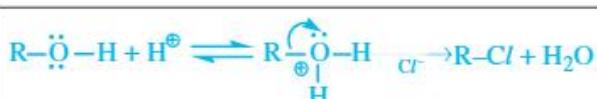
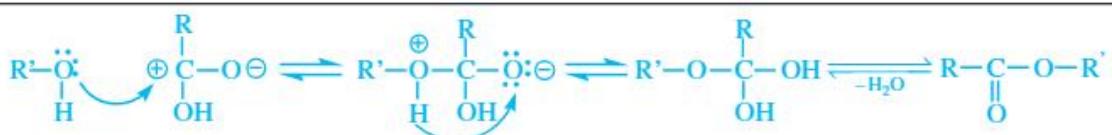
Methanol is called wood spirit and is prepared by destructive distillation of wood. It is highly poisonous in nature. Ingestion of even small quantities can cause blindness and large quantities causes even death.

Ethanol is a sweet smelling colourless liquid. It is soluble in water as well as organic solvents. Its boiling point is  $78.1^\circ\text{C}$ . It is called grain alcohol.

### 2.1.7

#### Chemical properties

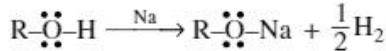
Alcohols can act as nucleophiles and protonated alcohols act as electrophiles.



Thus both O-H bond and C-O bonds can undergo cleavage in alcohols.

### Reactions involving fission of O–H bond

**Action of alkali metals :** Alcohols liberate hydrogen when they react with active metals like sodium and potassium giving metal alkoxide.



Alcohols behave like acids. Ethyl alcohol is less acidic than water, so ethoxide ion,  $\text{C}_2\text{H}_5\text{O}^-$  is a stronger base than hydroxide ion,  $\text{OH}^-$ .

Acidic nature of alcohols is in the order : primary > secondary > tertiary.

Reactivity of alcohols with active metal is in the order :



**Relative acidities :**  $\text{H}_2\text{O} > \text{R-OH} > \text{HC}\equiv\text{CH} > \text{NH}_3 > \text{RH}$

Relative basicities :  $\text{HO}^- < \text{RO}^- < \text{HC}\equiv\bar{\text{C}} < \text{NH}_2^- < \text{R}^-$

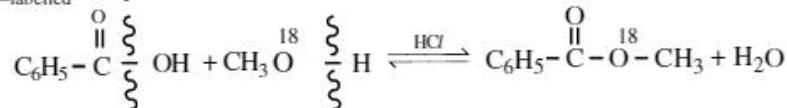
**Esterification :** Alcohols form esters with carboxylic acids in presence of conc. sulphuric acid. This reaction is called **Fischer's esterification**.



Alcohols give esters with acid halides, acid anhydrides and also with mineral acids. Inorganic esters are formed with mineral acids.



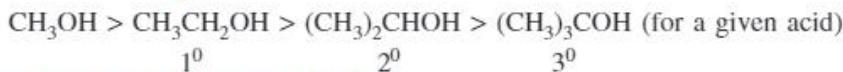
In esterification, it is proved that acyl-oxygen bond is cleaved by using  $^{18}\text{O}$ -labelled istope.



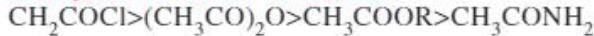
The increase in number of alkyl substituents at the  $\alpha$ -carbon of either carboxylic acid or alcohol decreases the rate of esterification.

Order of reactivity of acids :  $\text{HCOOH} > \text{CH}_3\text{COOH} > \text{CH}_3\text{CH}_2\text{COOH} > (\text{CH}_3)_2\text{CHCOOH} > (\text{CH}_3)_3\text{CCOOH}$  (for a given alcohol)

## Order of reactivity alcohols



### Reactivity order for esterification

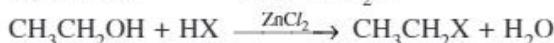
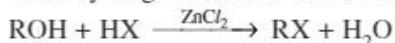


**Grignard reaction :** Alcohols give hydrocarbons with Grignard reagent.



### Reactions involving fission of C–O bond

With hydrogen halides, alcohols give alkyl halides.

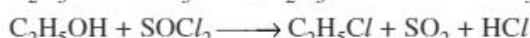
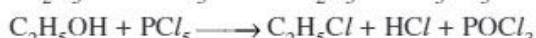


Reactivity order : HI > HBr > HCl > HF.

Tert. alcohol > sec. alcohol > primary alcohol.

Lucas reagent is a mixture of conc.  $HCl$  and anhydrous  $ZnCl_2$ . When alcohol reacts with Lucas reagent, alkyl chloride is formed. A turbidity develops as the product alkyl chloride is insoluble under experimental conditions.

Alcohols give alkyl halides with halogen carriers like  $PCl_5$ ,  $PCl_3$  and  $SOCl_2$ .

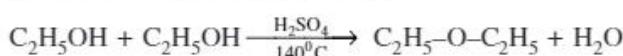


**Dehydration :** Ethyl alcohol undergoes dehydration on treating with sulphuric acid. The product formed depends upon temperature.

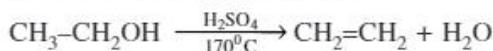
At  $100^\circ C$ , ethyl hydrogen sulphate is formed.



At  $140^\circ C$ , diethylether is formed.

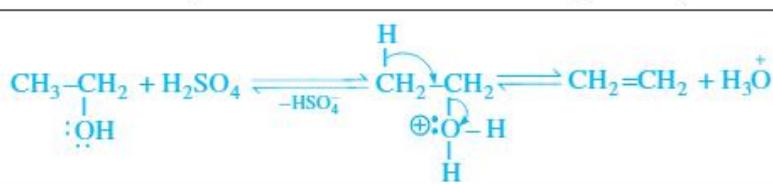


At  $170^\circ C$ , ethylene is formed.



Dehydration of alcohols catalysed by acids is an elimination reaction. Alkene is the product obtained in the dehydration.

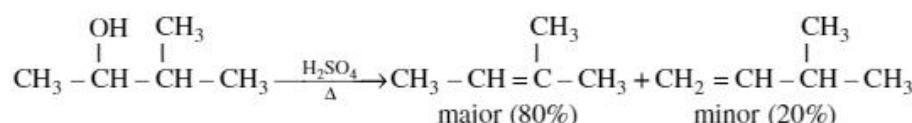
Alcohol is protonated and then molecule of  $H_2O$  and a  $\beta$  hydrogen as  $H^+$  are eliminated simultaneously. A  $\pi$  bond is formed between  $\alpha$ - and  $\beta$ - carbon atoms.



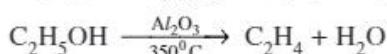
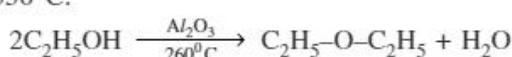
Primary alcohols undergo  $E_2$  reaction. Tertiary and secondary alcohols undergo  $E_1$  reaction.

Ease of dehydration of alcohols is in the order :  $3^\circ > 2^\circ > 1^\circ$ .

When two or more alkenes are possible during the elimination reaction from the same alcohol, according to Saytzeff's rule, the alkene with more number of alkyl groups is the major product. The adjacent carbon with less number of hydrogen atoms, contributes to the elimination.



Heating with alumina, ethyl alcohol gives diethyl ether at  $260^\circ C$  and ethylene at  $350^\circ C$ .



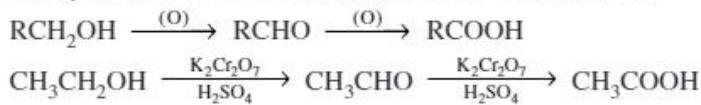
**Acid catalysed  
dehydration of  
alcohol is an  
elimination  
reaction**

**Alkene with more  
alkyl groups is  
formed during  
dehydration**

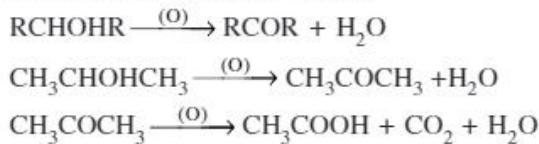
**Dehydration of  
ethyl alcohol  
with  $Al_2O_3$  at  
 $260^\circ C$  gives  
diethyl ether and  
at  $350^\circ C$  gives  
ethylene**

**Other reactions**

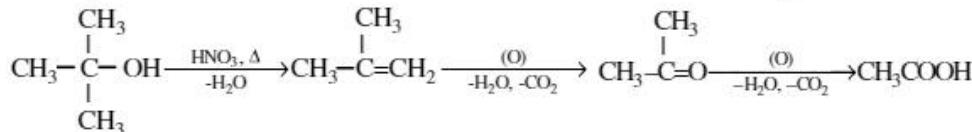
- i) **Oxidation :** Oxidation of primary alcohol with chromic acid gives aldehyde and finally an acid with the same number of carbon atoms.



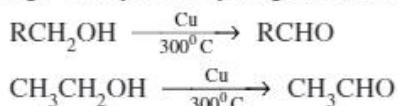
Secondary alcohol on oxidation gives ketone and finally a carboxylic acid with less number of carbon atoms.



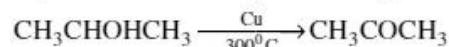
Tertiary alcohols are difficult to oxidise. However, when oxidation is carried out under drastic conditions, tertiary alcohols first undergo dehydration to form alkene. The alkene formed is then oxidised to ketone which is finally oxidised to carboxylic acid with less number of carbon atoms than the starting alcohol.



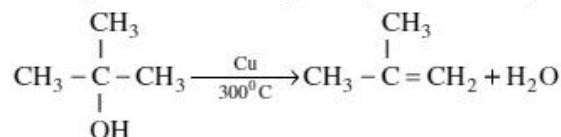
- ii) **Dehydrogenation :** When passed over copper at  $300^\circ\text{C}$ , primary alcohols undergo catalytic dehydrogenation and give aldehydes.



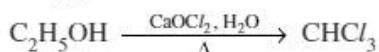
Vapours of secondary alcohols give ketones on catalytic dehydrogenation.



Tertiary alcohols undergo dehydration and give alkenes.



- iii) **Haloform reaction :** Ethyl alcohol gives chloroform on distillation with moist bleaching powder.



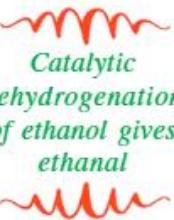
On reaction of ethyl alcohol with iodine followed by hydrolysis with potash, iodoform is formed.

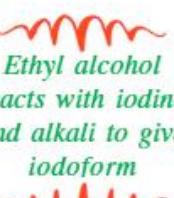


The overall reaction of ethyl alcohol with iodine and alkali to give iodoform is,

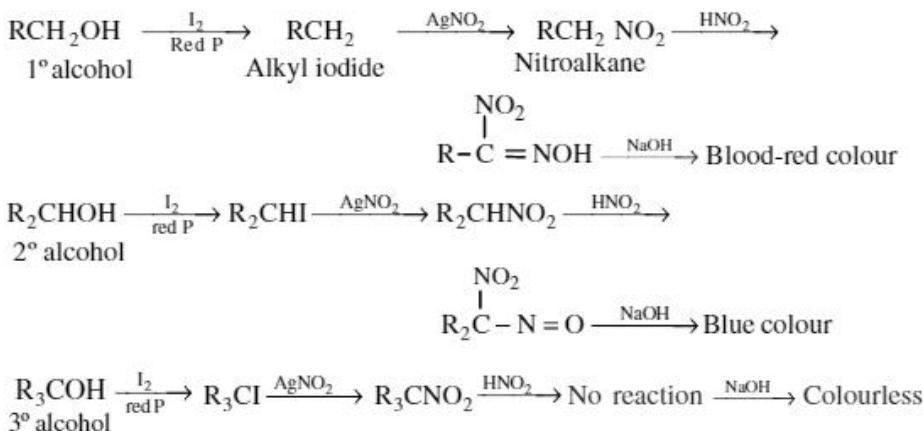


Alcohols with  $\text{CH}_3\text{CH}(\text{OH})-$ , carbonyl compounds with  $\text{CH}_3\text{CO}-$  groups can give yellow crystals of iodoform on reaction with mixture of iodine and alkali.

  
**Catalytic  
dehydrogenation  
of ethanol gives  
ethanal**

  
**Ethyl alcohol  
reacts with iodine  
and alkali to give  
iodoform**

**iv) Victor Meyer Test :** The given alcohol is first treated with iodine and red phosphorus followed by treating with silver nitrite to produce nitroalkane. This nitroalkane is treated with nitrous acid and the mixture is then made alkaline with excess of aqueous sodium hydroxide. If the resulting solution develops a blood-red colour, the alcohol is primary; if it develops a blue colour, the alcohol is secondary and if no colour is developed, the alcohol is tertiary.



Identification of 3 types of alcohols using suitable reagents is summarised in Table 2.3.

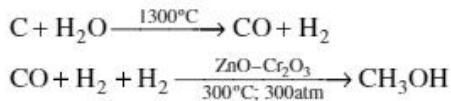
**Table 2.3 Identification of primary, secondary and tertiary alcohols**

Test	Primary alcohol	Secondary alcohol	Tertiary alcohol
<b>Lucas reagent</b> Testing with a mixture of conc. $\text{HCl}$ and anhyd. $\text{ZnCl}_2$	Does not form turbidity at room temperature (turbidity is obtained only upon heating)	Turbidity is formed in 5 to 10 minutes	Turbidity is formed immediately
<b>Catalytic dehydrogenation</b> (vapours of alcohol are passed over hot metal)	$\text{RCH}_2\text{OH} \xrightarrow[\text{300}^\circ\text{C}]{\text{Cu}}$  RCHO	$\text{RCHOHR} \xrightarrow[\text{300}^\circ\text{C}]{\text{Cu}}$  RCOR	$\begin{array}{c} \text{R} \\   \\ \text{R}-\text{C}-\text{CH}_3 \\   \\ \text{OH} \end{array} \xrightarrow[\text{300}^\circ\text{C}]{\text{Cu}} \begin{array}{c} \text{R} \\   \\ \text{R}-\text{C}=\text{CH}_2 \end{array}$  An alkene is obtained due to dehydration
<b>Oxidation</b> (with acidified permanganate or dichromate solution)	$\begin{array}{c} \text{RCH}_2\text{OH} \\ \downarrow \\ \text{RCHO} \\ \downarrow \\ \text{RCOOH} \end{array}$  (same number of carbon atoms in the three compounds)	$\begin{array}{c} \text{RCHOHR} \\ \downarrow \\ \text{RCOR} \\ \downarrow \\ \text{Two acids} \end{array}$  (with less number of carbon atoms)	$\begin{array}{c} \text{R}_3\text{C}-\text{OH} \\ \downarrow \\ \text{RCOR} \\ \downarrow \\ \text{Two acids} \end{array}$  (with less number of carbon atoms under drastic conditions)
<b>Victor Meyer Test</b> $\text{Alcohol} \xrightarrow[\text{red P}]{\text{I}_2} \xrightarrow{\text{AgNO}_2} \text{HNO}_2 \xrightarrow{\text{NaOH}}$	Blood-red colour	Blue colour	Colourless

  
**Methanol is obtained from water gas at high pressure**

### Preparation of methanol

**From water gas :** Water gas is formed by passing steam over coke at 1300°C. Water gas is mixed with half its volume of hydrogen under 300 atmosphere and then passed over a catalyst ( $\text{ZnO} + \text{Cr}_2\text{O}_3$ ) at 300°C. Methyl alcohol vapours are formed which are condensed.



**From methane :** A mixture of methane (obtained from natural gas) and oxygen (9:1 by volume) compressed to 110 atmospheres is passed over copper catalyst at 250°C. Methane is oxidised to methanol.

### Uses of methanol and ethanol

Methanol is used as solvent in making paints, varnishes, shellac, and as antifreeze. It is also used in preparing formaldehyde, methylated spirit, etc.

  
**Anaerobic fermentation of grape juice gives wine**

Ethanol is used to prepare alcoholic beverages, as solvent in perfumes, paints, varnishes, dyes and as preservative for biological specimens. Ethanol is used as antifreeze in car radiators and to prepare power alcohol.

**Preparation of wine :** Grapes are crushed under anaerobic conditions, fermentation of sugar in grapes takes place due to the presence of yeast on the outer skin of grapes.

Wine contains usually 10 to 25% of ethyl alcohol.



**P.2.12**

tert-Butyl alcohol is much more soluble in water than n-butyl alcohol. Explain.

**Solution** In tert-butyl alcohol, alkyl group is highly branched and hence approaches almost spherical shape. As a result, non-polar part of the molecule becomes less prominent and hence it can have stronger intermolecular hydrogen bonds with water molecules. On the other hand, n-butyl alcohol has predominantly non-polar character.



**P.2.13**

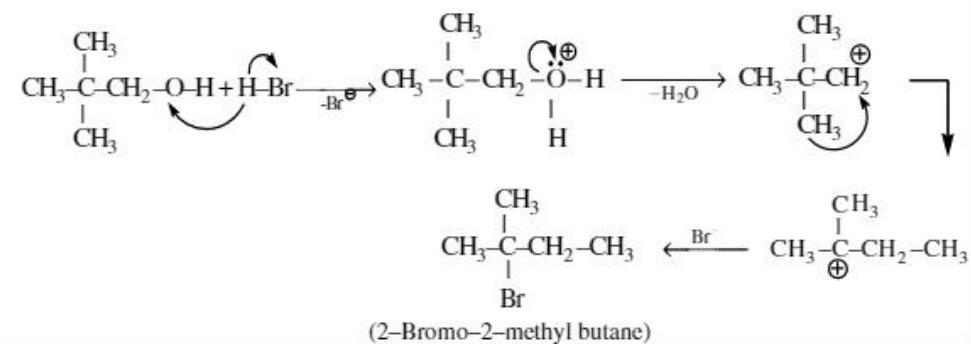
What happens when one drinks ethanol mixed with methanol? Why?

**Solution** If one drinks ethanol mixed with methanol, he may become blind or even sometimes it leads to death. In the body, methanol is oxidised to methanal first and then to methanoic acid which is a poison.



**P.2.14**

Write the structure of the product and mechanism of the following reaction:

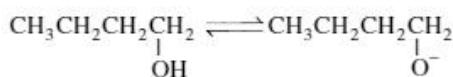




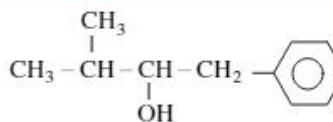
**P.2.15** Identify the stronger acid among the following :

Butanol-1, butan-2-ol, isobutyl alcohol and tert butyl alcohol. Give Reason.

**Solution** Butan-1-ol is stronger acid. The conjugate base of this alcohol is more stable.

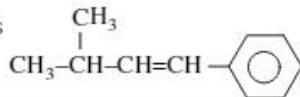


**P.2.16**



A is the major product. What is 'A' ?

**Solution** The major product is



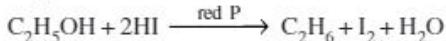
**P.2.17** How do you distinguish between methyl alcohol and ethyl alcohol ?

**Solution** Using iodine and alkali methyl alcohol and ethyl alcohol can be distinguished. Only ethyl alcohol gives yellow precipitate of iodoform. Methyl alcohol does not form iodoform.



**P.2.18** What happens when ethyl alcohol is treated with HI and red phosphorous ?

**Solution** Ethyl alcohol is reduced to ethane when treated with HI and red phosphorous.



**P.2.19** Give the structures and IUPAC names of the products expected from the following reactions.

a) Catalytic reduction of butanal

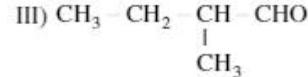
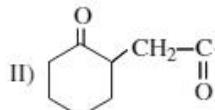
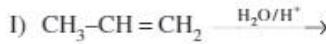
b) Reaction of propanone with methylmagnesium bromide followed by hydrolysis.

**Solution** a) Catalytic reduction of butanal give  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ . IUPAC name is Butanol-1

b) Reduction of propanone with methylmagnesium halide, followed by hydrolysis gives  $(\text{CH}_3)_3\text{COH}$ . IUPAC name is Methylpropanol-2

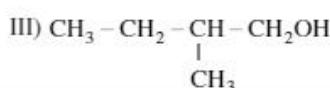
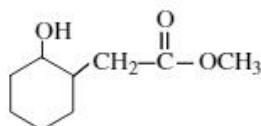


**P.2.20** Write structures of products of the following reactions :



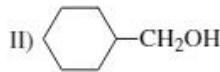
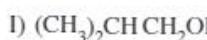
**Solution** I)  $\text{CH}_3-\text{CH}(\text{OH})-\text{CH}_3$

II)  $\text{NaBH}_4$  can reduce aldehydes and ketones to the corresponding alcohols but it has no effect on ester group. Hence the product is

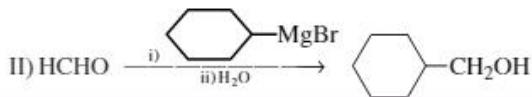
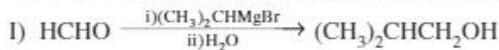




**P.2.21** Show how are the following alcohols are prepared by the reaction of a suitable Grignard reagent on methanal?



**Solution** The equations showing the preparation of alcohols from formaldehyde are :



**P.2.22** Arrange the following sets of compounds in order of their increasing boiling points.

- I) (a) Pentanol-1 ; (b) Butanol-1 ; (c) Butanol-2 ; (d) Ethanol ; (e) Propanol and (f) Methanol  
 II) (p) Pentanol-1 ; (q) n-Butane ; (r) Pentanoil and (s) ethoxyethane

**Solution** Boiling points of Set I compounds increase in the order : f < d < e < c, b < a

Increasing order of boiling points of Set II compound is : q < s < r < p

### EXERCISE - 2.1.1

- What are 2° and 3° alcohols? Give examples.
- Write any four methods of preparation of ethyl alcohol and four properties of ethyl alcohol.
- Describe the oldest fermentation process of preparing ethyl alcohol.
- Write the equations of the reactions of ethyl alcohol with the following reagents :  
 (a) conc.  $H_2SO_4$  at 170° C, (b) Thionyl chloride, (c) Bleaching powder, water and (d) Methyl magnesium bromide.
- What are dihydric and trihydric alcohols? Give examples.
- Write the products of dehydration of ethyl alcohol using conc.  $H_2SO_4$  at different temperatures.
- Discuss the action of  $Al_2O_3$  ethanol at 260 and 350°C.
- How does ethanol react with copper at 300°C? Name the reaction.
- Give equations for the reaction of ethanol with  $PCl_3$  and  $PCl_5$ .
- Explain how the three types of alcohols, primary, secondary and tertiary can be distinguished?

## PHENOLS

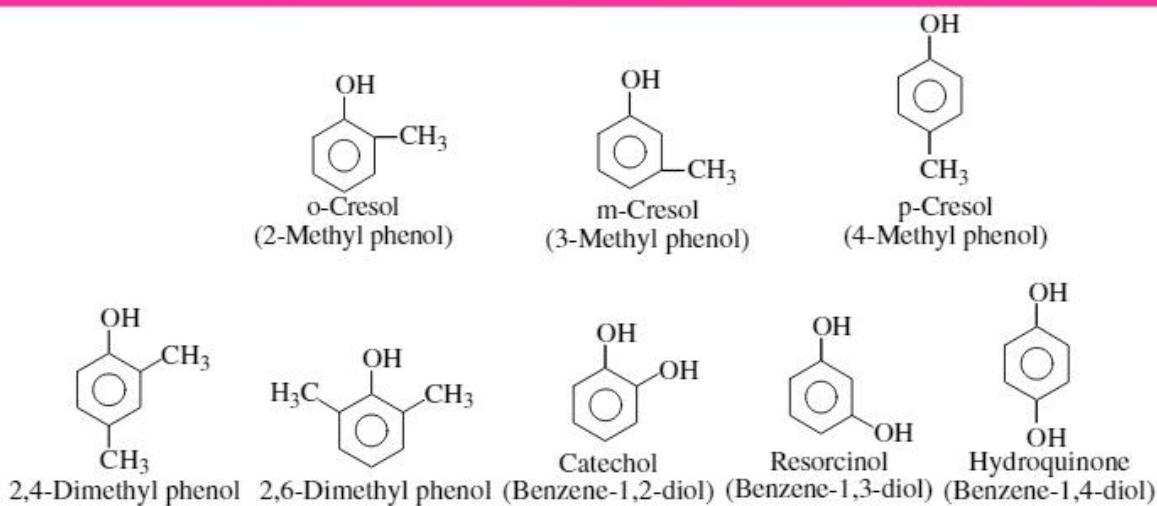
### 2.2.1

#### Nomenclature

**Phenols are called carbolic acids**

Phenols are aromatic hydroxy compounds in which –OH group is bonded directly to the benzene ring. Phenols are called carbolic acids. These are classified as monohydroxy, dihydroxy and trihydroxy compounds.

Monohydroxy benzene is phenol. Methyl phenol is called cresol. Cresol has three position isomers.

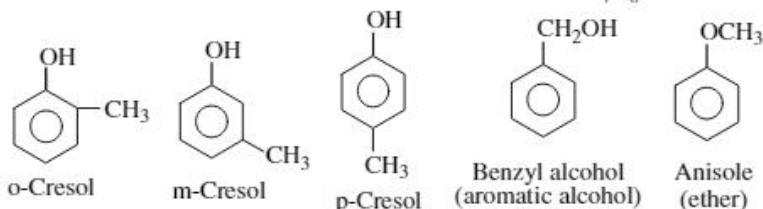


Three trihydroxy derivatives of benzene are known. They are : pyrogallol, hydroxyquinol and phloroglucinol.



**P.2.23** Write the aromatic structures of all isomers with the formula C<sub>7</sub>H<sub>8</sub>O.

**Solution** There are five aromatic structural isomers for the formula C<sub>7</sub>H<sub>8</sub>O.



**P.2.24** What is the tautomer of phenol ? Which is more stable ?

**Solution** The tautomer of phenol is cyclohexadienone. This keto form is unstable.

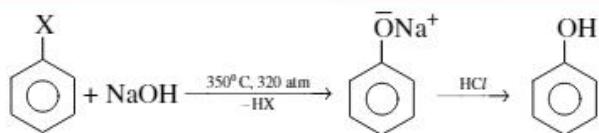
Phenol is more stable because it is aromatic and exists in 100% enol form.

## 2.2.2

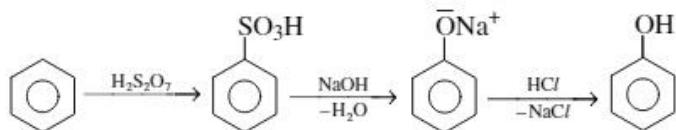
### Preparation

*Fusion of halo benzene with alkali, followed by hydrolysis gives phenol*

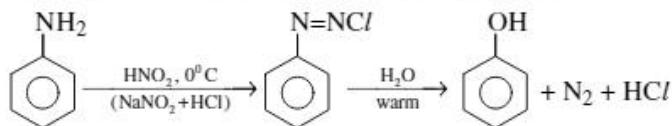
- From coal :** Phenol was first isolated from middle oil fraction of coal tar. After separating naphthalene, the oil is extracted with dilute caustic soda and the aqueous layer is hydrolysed with dilute sulphuric acid. Phenol is separated by fractional distillation.
- From haloarenes :** Phenol is prepared by fusion of halo benzene with NaOH at 350°C and 320 atmospheric pressure. Sodium phenoxide formed is neutralised with dilute hydrochloric acid to give phenol. This is called Dow's process.

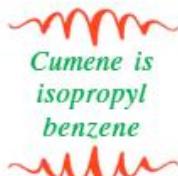


iii) **From benzene sulphonic acid :** Benzene on sulphonation with oleum ( $\text{H}_2\text{S}_2\text{O}_7$ ) gives benzene sulphonic acid. On fusion with sodium hydroxide solid, it gives sodium phenoxide. Acidification of sodium phenoxide produces phenol.

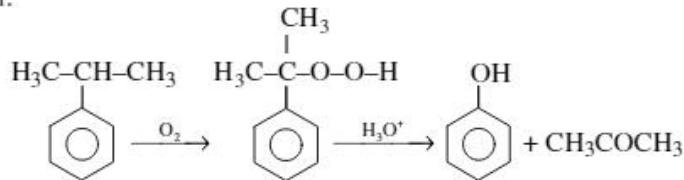


iv) **From diazonium salt :** When treated with sodium nitrite and hydrochloric acid at  $0\text{--}5^\circ\text{C}$ , aniline undergoes diazotisation to give benzene diazonium chloride which on warming with water or dilute acid gives phenol.

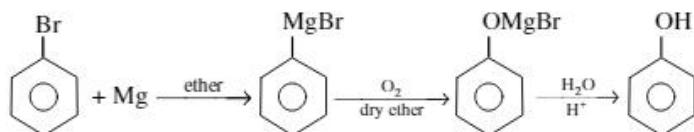


  
Cumene is  
isopropyl  
benzene

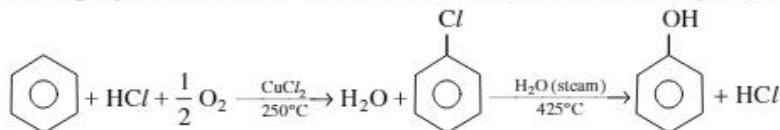
v) **From cumene :** Benzene when treated with propene in presence of  $\text{AlCl}_3$ , isopropyl benzene (cumene) is formed. Cumene is oxidised in presence of air to cumene hydro-peroxide. It is decomposed to phenol and acetone by treating with acid.



vi) **From Grignard reagents :** Chlorobenzene or bromobenzene is first converted into phenyl magnesium halide in presence of dry ether. The Grignard reagents on reaction with oxygen and subsequent hydrolysis by a mineral acid, yield phenol.

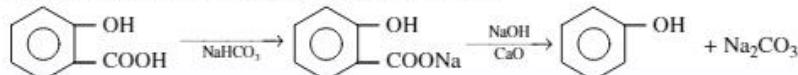


vii) **Raschig process :** Phenol can be manufactured also by heating chlorobenzene with steam of  $425^\circ\text{C}$  in which the chlorobenzene is manufactured from benzene by the Raschig's process. This is one of the latest methods for the synthesis of phenols.



P.2.25 How is salicylic acid converted to phenol?

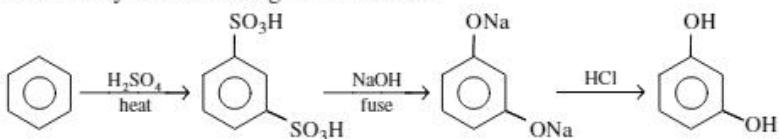
**Solution** Salicylic acid on decarboxylation gives phenol.





**P.2.26** Explain the method of preparation of resorcinol from benzene.

**Solution** Benzene disulphonic acid is obtained by sulphonation of benzene, which on fusion with alkali followed by acidification gives resorcinol.



### 2.2.3

#### Physical properties

Phenol is colourless crystalline solid and turns pink on exposure to air and light. It is slightly soluble in water. Solubility is due to hydrogen bonding with water. Solubility decreases as molecular weight of phenols increase.

Phenol has higher boiling point than hydrocarbons, haloarenes and ethers of comparable molecular mass. This is due to intermolecular hydrogen bonding in phenol.

### 2.2.4

#### Chemical properties

Both alcohols and phenols liberate hydrogen when treated with an active metal like sodium. This shows that both alcohols and phenols are acidic.



However, when treated with an alkali, alcohols do not form salts, only phenols form salts.



Acidic nature of an alcohol is denoted by the following equation.

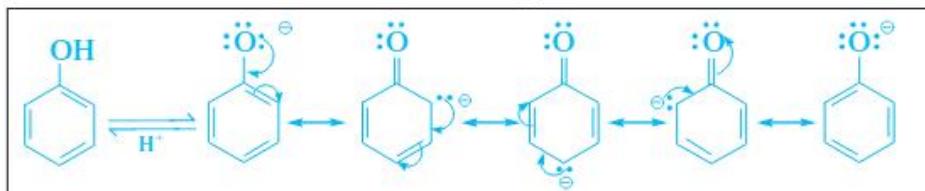


Alkoxyde ion (conjugate base of alcohol) is stronger base. It recombines with  $\text{H}^+$ , backward reaction is fast and hence, alcohol is weak acid.

When compared to alcohols, phenols are stronger acids. Phenoxide ion, the conjugate base of phenol is stabilised by resonance and less basic, correspondingly phenol is a stronger acid. As the stability of conjugate base increases, strength of acid also increases, as backward reaction is suppressed.

*Phenol is stronger acid than ethyl alcohol*

*Phenol is acidic, because phenoxide ion is resonance stabilised*



Presence of electron withdrawing groups like  $-\text{NO}_2$  increases the acidic strength of phenols. While electron releasing groups like  $-\text{CH}_3$  decreases acidic strength of phenols.

The greater the dissociation constant  $K_a$  of acid, the stronger is the acid and the smaller is the  $\text{pK}_a$  value. Acidic strengths are denoted with  $\text{pK}_a$  values in Table 2.4.

Table 2.4 pK<sub>a</sub> values of phenols

Compound	Structure	pK <sub>a</sub>	Compound	Structure	pK <sub>a</sub>
Ethyl alcohol	CH <sub>3</sub> -CH <sub>2</sub> -OH	15.9	p-Nitrophenol	NO <sub>2</sub> -C <sub>6</sub> H <sub>4</sub> -OH	7.1
Phenol	C <sub>6</sub> H <sub>5</sub> -OH	10.0	o-Cresol	C <sub>6</sub> H <sub>5</sub> -CH <sub>2</sub> -OH	10.2
o-Nitrophenol	C <sub>6</sub> H <sub>5</sub> -NO <sub>2</sub> -OH	7.2	m-Cresol	C <sub>6</sub> H <sub>5</sub> -CH <sub>3</sub> -OH	10.1
m-Nitrophenol	C <sub>6</sub> H <sub>5</sub> -OH-NO <sub>2</sub>	8.3	p-Cresol	CH <sub>3</sub> -C <sub>6</sub> H <sub>4</sub> -OH	10.2

Acidic strength of some phenols is given as :

Picric acid > 3,5-dinitrophenol > 3-nitrophenol > phenol > 4-methyl phenol.

p-Nitrophenol > o-Nitrophenol > m-Nitrophenol > Phenol

o-Halophenol > m-Halophenol > p-Halophenol

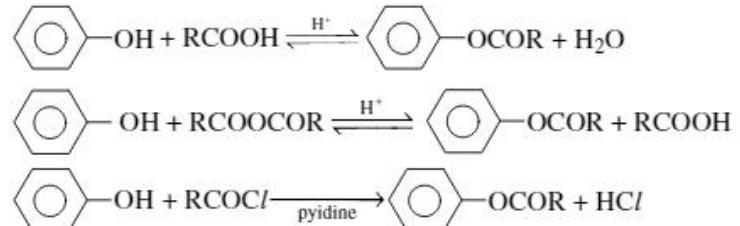
Carbondioxide is a stronger acid than phenol. It displaces phenol from its salt solution. Alcohols do not react with NaOH as they are weak acids. For the same reason, carboxylic acids are more acidic as they readily form salts with NaOH.



Alcohols cannot turn blue litmus to red whereas phenols can turn blue litmus to red. Both phenols and alcohols cannot react with carbonates or bicarbonates to liberate carbon dioxide gas.

### Esterification

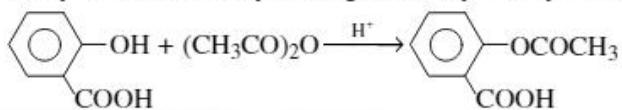
Phenols produce esters with acid and acid derivatives.



In these reactions, the acyl group (R-CO-) is introduced in the place of -H of -OH group of phenol. This reaction is commonly called acylation. The reaction with carboxylic acid and acid anhydride is carried out in the presence of a small amount of concentrated sulphuric acid. The reaction is reversible and water is removed as soon as it is formed. The reaction with acid chloride is carried out in the presence of a base (pyridine) so as to neutralise HCl which is formed during the reaction and backward reactions prevented.

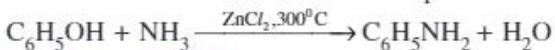
  
*Acetylation of  
salicylic acid  
gives aspirin*  


Salicylic acid on acetylation gives acetyl salicylic acid, called aspirin.



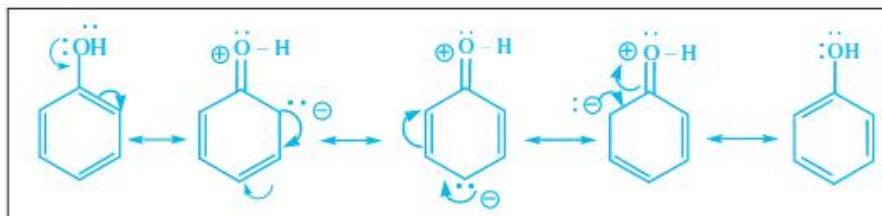
### Reactions involving C–O cleavage

Alcohols react with hydrogen halides to give alkyl halides, but phenols do not. However, phenol reacts with halogen carriers to give halobenzene. Phenol reacts with ammonia at  $300^\circ\text{C}$  under reduced pressure and zinc chloride to give aniline.



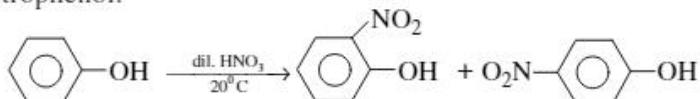
### Electrophilic substitution

Electrophilic aromatic substitution is a characteristic property of phenol due to the aromatic ring. In phenol, the  $-\text{OH}$  group releases electrons by  $+M$  effect and increases the  $\pi$  electron density at ortho and para positions. Therefore electrophilic substitution occurs at position 2 or position 4 of the phenol. Substitution at para position is slightly more preferred.



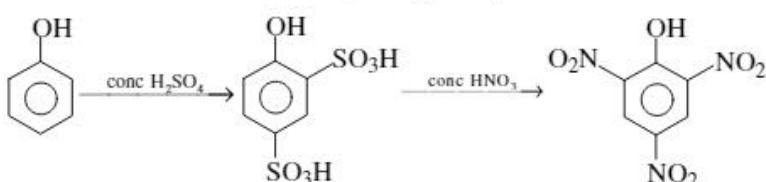
Phenol is more reactive than benzene, as the ring in phenol is activated by  $+M$  effect of  $-\text{OH}$  group. So electrophilic substitution takes place more easily in phenol than in benzene.

**Nitration :** With dilute nitric acid, phenol gives a mixture of o-nitrophenol and p-nitrophenol.



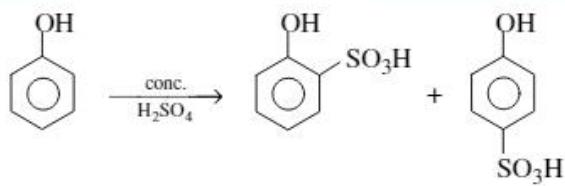
*o*-Nitrophenol can be separated from *p*-nitrophenol by steam distillation. Orthonitrophenol is steam volatile due to intramolecular hydrogen bonding, while in *p*-nitrophenol, molecular association occurs due to intermolecular hydrogen bonding.

If phenol is treated with conc.  $\text{H}_2\text{SO}_4$  and conc.  $\text{HNO}_3$ , picric acid is formed. 2,4,6-Trinitrophenol is called picric acid, which can also be obtained from phenol by nitration with conc. nitric acid, though the yield is less.



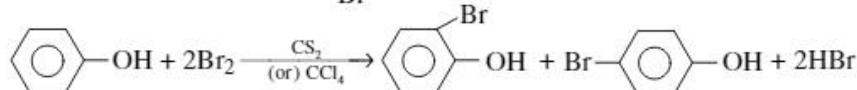
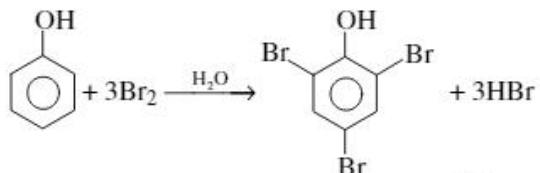
When phenol is treated with concentrated  $\text{H}_2\text{SO}_4$  at room temperature nearly equal amounts of *o*- and *p*-derivatives are formed and at  $100\text{--}110^\circ\text{C}$ , *p*-derivative is the major product.

  
*o-Nitrophenol  
is steam volatile  
due to intramo-  
lecular hydrogen  
bonding*  

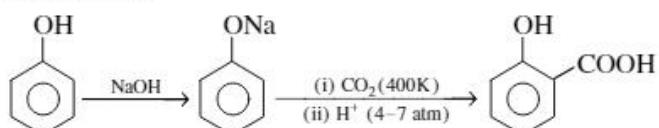
Lewis acid is not required in the bromination of phenol

**Halogenation :** Aqueous bromine converts phenol into 2,4,6-tribromophenol, a white solid. With bromine in carbon disulphide, phenol gives ortho and para bromo-phenols. Lewis acid is not required as phenol is highly reactive.



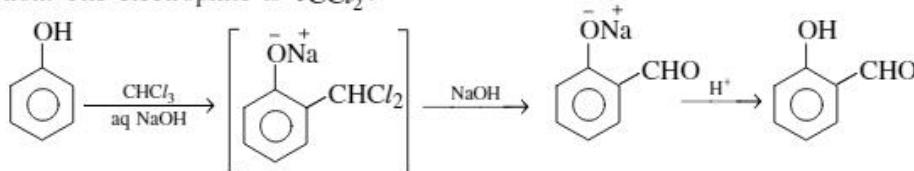
#### Kolbe's reaction

When phenol is treated with sodium hydroxide, sodium phenoxide is formed. Phenoxide ion is even more reactive than phenol towards electrophilic substitution. Hence, it undergoes electrophilic substitution with carbon dioxide, a weak electrophile. o-Hydroxy benzoic acid is formed as the main product. This is called Kolbe's reaction.



#### Reimer-Tiemann reaction

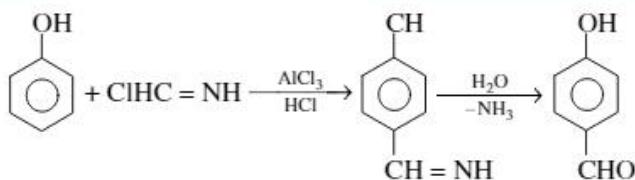
Phenol when treated with chloroform in the presence of sodium hydroxide, a  $-\text{CHO}$  group is introduced at ortho position of benzene ring forming salicylaldehyde. The intermediate substituted benzal chloride is hydrolysed in the presence of alkali to produce ortho hydroxy benzaldehyde. This reaction is known as Reimer-Tiemann reaction. The electrophile is  $\text{:CCl}_2$ .



In the above reaction instead of  $\text{CHCl}_3$  if  $\text{CCl}_4$  is used, salicylic acid will be formed.

**Gattermann formylation reaction :** Phenol, when treated with liquid hydrogen cyanide and hydrochloric acid gas in presence of anhydrous  $\text{AlCl}_3$  yields mainly p-hydroxybenzaldehyde.



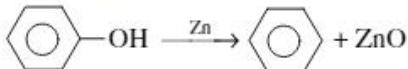
**Liebermann nitroso reaction**

**Phenol can be tested based on the Liebermann nitroso reaction**

When phenol is dissolved in conc.  $\text{H}_2\text{SO}_4$  and treated with aqueous  $\text{NaNO}_2$  solution in the cold condition, a deep blue or green colour is produced which turns red on careful addition of water. When the solution is made alkaline with aqueous  $\text{NaOH}$  solution, blue or deep green colour reappears. This reaction is known as Liebermann nitroso reaction and a test for phenol.

**Other reactions**

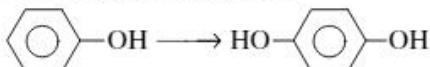
**Reduction :** Phenol on distillation with zinc dust gives benzene.



**Oxidation :** Phenol is slowly oxidised in air. Phenol on treating with chromic acid gives dark brown coloured para-benzoquinone.

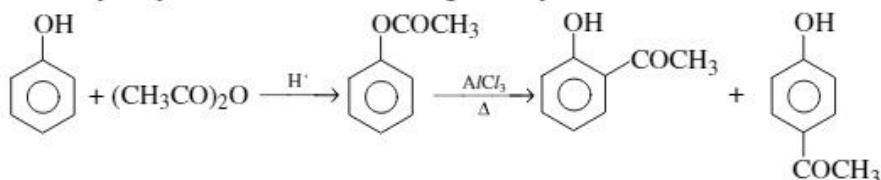


On oxidation with  $\text{K}_2\text{S}_2\text{O}_8$  in alkaline solution, quinol is formed. This is called Elbs persulphate oxidation.

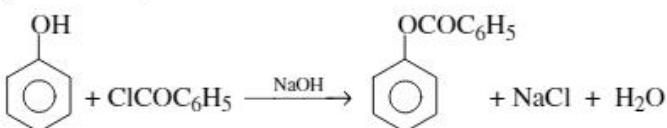


**Phenolic esters undergo Fries rearrangement with hot  $\text{AlCl}_3$  to give hydroxy acetophenones**

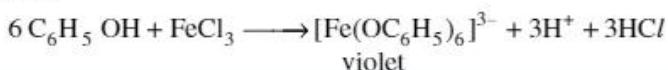
**Fries rearrangement :** Phenolic esters undergo rearrangement on heating with anhydrous  $\text{AlCl}_3$  and give ortho-hydroxy and para-hydroxy acetophenones. This is known as Fries rearrangement. Migration of acyl group from phenolic oxygen to ortho and para positions of aromatic ring takes place.



Phenol reacts with benzoyl chloride in presence of aqueous  $\text{NaOH}$  to form phenyl benzoate, an ester. This reaction is called Schotten-Bauman reaction.



**Reaction with ferric chloride :** Phenol reacts with aqueous  $\text{FeCl}_3$  solution, a violet colour is developed due to the formation of a complex. This colour may be violet, blue, green or red depending upon the structure of phenol. This is a diagnostic test for most phenols. Enolic ( $=\text{C}-\text{OH}$ ) group also responds to this test but not alcohols.



**Uses of phenol**

- A 0.2% aqueous phenol is used as an antiseptic.
- Phenol and substituted phenols are used to prepare dyes, drugs and pharmaceuticals, (salicylic acid, phenacetin, aspirin, salol)
- Phenol on reaction with urea and formaldehyde gives condensation polymers, bakelite.

**P.2.27**

**Q.** Phenol decolorises reddish brown colour of bromine, though it is not unsaturated compound. Explain.

**Solution** Phenol is highly reactive with  $\text{Br}_2\text{-H}_2\text{O}$  and forms 2, 4, 6-tribromophenol. The reaction is electrophilic substitution with liberation of HBr.

Hence, the colour of bromine disappears.

**P.2.28**

**Q.** Write the decreasing order of acidic strengths of the following :

A : Phenol, B : p-nitrophenol, C: p-chlorophenol, D : p-cresol and E : p-methoxy phenol.

**Solution** Most acidic in the given list of phenols is p-nitrophenol.

Least acidic in the given list of phenols is p-methoxy phenol.

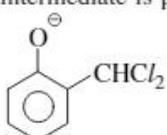
The order of acidic strength is : B > C > A > D > E.

**P.2.29**

**Q.** Write the electrophile and intermediate in Reimer-Tiemann reaction.

**Solution**  $\text{Cl}-\ddot{\text{C}}-\text{Cl}$  (dichlorocarbene) is the electrophile.

The intermediate is phenoxy dichloromethane.

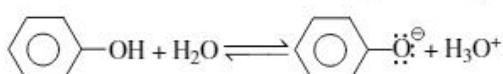
**P.2.30**

**Q.** What is the reason for the formation of tribromo phenol when phenol is treated with aqueous bromine?

**Solution** In aqueous solution, phenol exists as phenoxide ion.

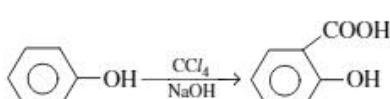
It highly activates the ring and is responsible for the accumulation of negative charge at ortho- and para- positions.

Three bromine atoms are introduced at 2, 4 and 6 - positions of the ring.

**P.2.31**

**Q.** Phenol is treated with  $\text{CCl}_4$  in presence of  $\text{NaOH}$ . What happens ?

**Solution** Like in the Reimer-Tiemann reaction, ortho substitution occurs. Orthohydroxy benzoic acid, called salicylic acid is formed.

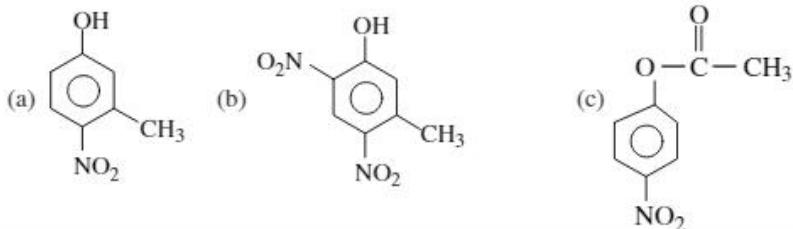




**P.2.32** Write the structures of the major products expected from the following reactions.

- Mononitration of 3-methylphenol
- Dinitration of 3-methyl phenol
- Mononitration of phenyl methanate

**Solution** The  $-OH$  group on benzene ring is strongly activating but  $-CH_3$  group is weakly activating. Hence substitution takes place as per the directing influence of the  $-OH$  group



### EXERCISE - 2.1.2

- How is phenol prepared? Write the properties of phenol.
- Explain the electrophilic substitution reactions of phenol. Write two uses of phenol.
- Write short notes on the following:
  - Reimer-Tiemann reaction and (b) Kolbe's reaction.
- Discuss the acidic nature of phenols compared to alcohols.
- Compare the acidic nature of phenol, cresols and nitrophenols.
- Phenol is less stable than pheroxide ion. Why?
- Arrange the following in the increasing order of acidic nature and discuss the reason : (a) Phenol, (b) p-nitrophenol and (c) p-cresol.
- Discuss the bromination of phenol in aqueous solution and  $CS_2$  (or)  $CHCl_3$  solvent.

## ETHERS

Ethers are alkyl or aryl derivatives of alcohols or phenols, anhydrides of alcohols. They are formed by the substitution of  $-H$  in  $-OH$  group of alcohol or phenol. Ethers are also treated as dialkyl derivatives of water. The general formula of ethers is  $R-O-R'$ , where  $R$  and  $R'$  are alkyl, alkenyl or aryl groups. If  $R$  and  $R'$  are same, the ether is said to be simple or symmetrical. If  $R$  and  $R'$  are different, the ether is said to be mixed or unsymmetrical.

### 2.3.1

#### Nomenclature

*IUPAC name of  
aliphatic  
saturated ether  
is alkoxyalkane*

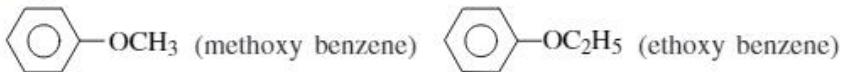
The common names are also called radico functional names. The names of the two alkyl groups surrounding ethereal oxygen are written in alphabetical order followed by the word 'ether'. If both the alkyl groups  $R$  and  $R'$  are same, the prefix 'di' is included before the name of the alkyl group. The simplest ether is dimethylether and the commonest ether is diethylether, also called sulphuric ether.

In the IUPAC system, ethers are named as alkoxyalkanes (Table 2.5). The smaller alkyl group along with  $-O-$  is named as alkoxy group and the name of the parent hydrocarbon of the other alkyl group succeeds it. Position of alkoxy group in the parent is indicated.

Table 2.5 Common and IUPAC names of some ethers

Compound	Common name	IUPAC name
$\text{CH}_3\text{OCH}_3$	Dimethyl ether	Methoxymethane
$\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$	Diethyl ether	Ethoxyethane
$\text{CH}_3\text{OCH}_2\text{CH}_2\text{CH}_3$	Methyl n-propyl ether	1-Methoxypropane
$\text{CH}_3\text{OCH}(\text{CH}_3)_2$	Methyl isopropyl ether	2-Methoxypropane
$\text{C}_6\text{H}_5\text{OCH}_3$	Methyl phenyl ether (Anisole)	Methoxybenzene (Anisole)
$\text{C}_6\text{H}_5\text{OCH}_2\text{CH}_3$	Ethyl phenyl ether (Phenetole)	Ethoxybenzene
$\text{C}_6\text{H}_5\text{O}(\text{CH}_2)_6\text{CH}_3$	n-Heptylphenyl ether	1-Phenoxyheptane
$\text{C}_6\text{H}_5\text{O}-\text{CH}_2-\text{CH}_2-\text{CH}(\text{CH}_3)_2$	Phenyl isopentyl ether	3-Methylbutoxybenzene

**Aromatic ethers :** Methyl phenyl ether is called anisole. Its IUPAC name is methoxy benzene.



**Unsaturated ethers :** Allyl methyl ether is 3-methoxypropene. ( $\text{CH}_2=\text{CH}-\text{CH}_2\text{OCH}_3$ )

**Cyclic ethers :** Ethylene oxide, also called epoxide is a cyclic ether,  $\text{CH}_2-\text{CH}_2-\text{O}$

*Ethylene oxide  
is a cyclic ether,  
called epoxide*

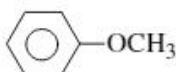
### 2.3.2

#### Isomerism

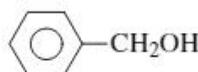
Ethers exhibit functional isomerism with alcohols.

$\text{CH}_3\text{O}-\text{CH}_3$  and  $\text{CH}_3\text{CH}_2\text{OH}$  are functional isomers.

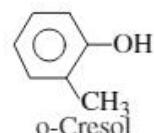
$\text{C}_2\text{H}_5\text{O}-\text{C}_2\text{H}_5$  and  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$  are also functional isomers. Aromatic ethers and phenols also are functional isomers.



Anisole



Benzyl alcohol



o-Cresol

Ethers exhibit metamerism. Metamers differ in the alkyl groups attached to the bivalent functional group.

$\text{C}_2\text{H}_5\text{O}-\text{C}_2\text{H}_5$  and  $\text{CH}_3\text{O}-\text{CH}_2\text{CH}_2\text{CH}_3$  are metamers.

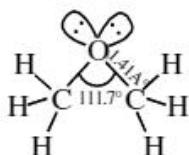
There are six ethers and eight alcohols with the molecular formula,  $\text{C}_5\text{H}_{12}\text{O}$ .

Among these, one ether and three alcohols have enantiomers.

### 2.3.3

#### Structure

The central atom in ethers assumes  $\text{sp}^3$  hybrid state. Two of the hybrid orbitals of oxygen are used in forming sigma bonds with the surrounding alkyl groups. The other two  $\text{sp}^3$  hybrid orbitals of oxygen contain lone pairs of electrons. The electron pairs (lone pairs as well as bond pairs) surrounding oxygen atom, assume tetrahedral arrangement. However, the bond angle around oxygen is not exactly equal to  $109^\circ 28'$ . The deviation in angle is caused by the repulsive interactions between the alkyl groups. Bulkier the alkyl groups, greater will be the repulsive interactions and consequently, larger will be deviation in angle. COC angle in dimethyl ether is  $111.7^\circ$ .



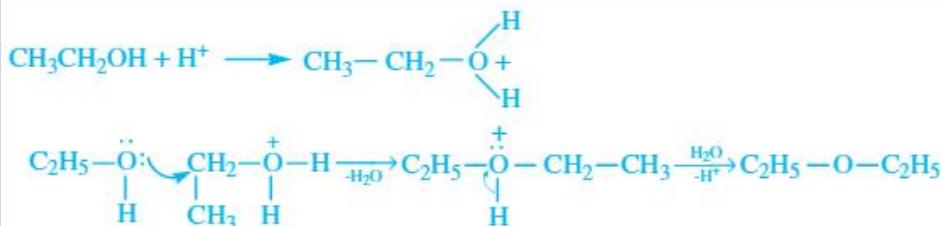
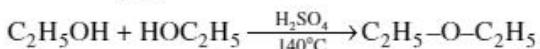
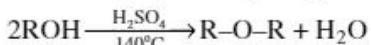
The C–O bond length in ethers is  $1.41\text{ \AA}$  which is almost same as that in alcohols. Thus ethers have bent structure and their dipole moment is greater than zero. Hence their molecules are polar in nature. Net dipole moment of diethyl ether is 1.18 and that of dimethyl ether is 1.3D.

### 2.3.4

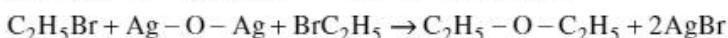
#### Preparation

**Symmetrical ethers can be prepared by dehydration of alcohols**

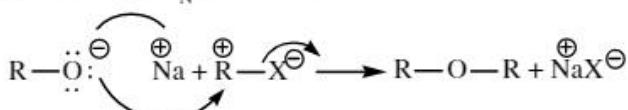
**From Alcohols :** Ethers are prepared by heating alcohol with conc.  $\text{H}_2\text{SO}_4$  at  $140^\circ\text{C}$  or with  $\text{Al}_2\text{O}_3$  at  $260^\circ\text{C}$ . The reaction involves dehydration. Only symmetrical ethers can be prepared by dehydration of alcohols.



**From alkyl halides :** Ethers are prepared by heating alkyl halide with dry silver oxide.



**Williamson's synthesis :** Ethers are prepared commonly by the action of alkali metal alkoxide on an alkyl halide. The method involves nucleophilic substitution. Alkoxide is strong base and entering group. Halide ion is the leaving group. The reaction involves  $\text{S}_{\text{N}}2$  mechanism.



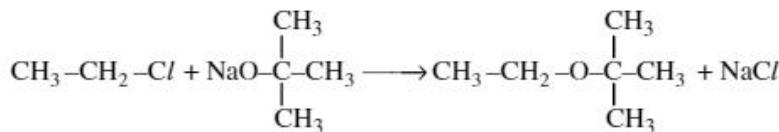
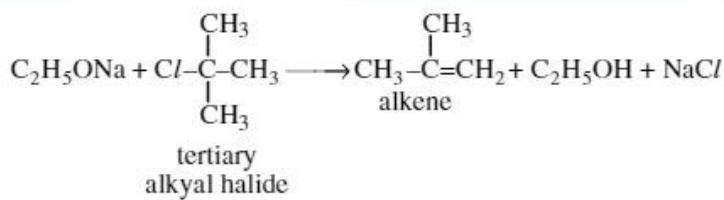
Both symmetrical ethers as well as unsymmetrical ethers can be prepared by Williamson's method.



If one of the alkyl groups in ethers is tertiary alkyl group, it is prepared by taking tertiary alkoxide and a primary or secondary alkyl halide. Tertiary alkyl halide should not be taken as it undergoes elimination. It is because alkoxides are not only nucleophiles but also strong bases. They react with alkyl halides leading to elimination reactions.

**Williamson's method is used for the synthesis of both simple and mixed ethers**

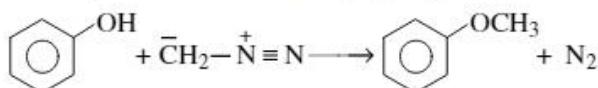
**Tertiary alkyl halide on elimination gives alkene**



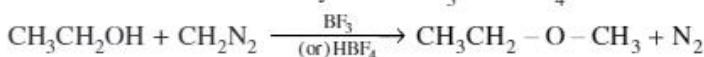
Aryl ethers are prepared by taking a phenoxide and an alkyl halide. Anisole is obtained from a phenoxide and methyl halide.



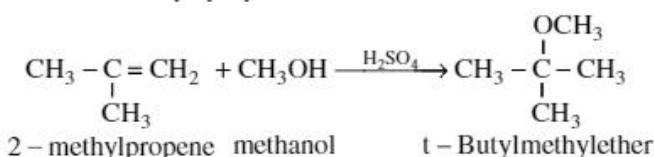
**From diazomethane :** Phenol being more acidic than alcohols, diazomethane reacts with phenols to form methyl phenyl ethers.



In case of alcohols, a catalyst like  $\text{BF}_3$  or  $\text{HBF}_4$  is needed.



**Addition of alcohols to alkenes :** Ethers can be prepared by the addition of alcohols to alkenes in presence of  $\text{H}_2\text{SO}_4$  or  $\text{H}_3\text{PO}_4$ . Usually methanol or ethanol are employed for this purpose. t-Butyl methyl ether is manufactured by the addition of methanol to 2-methyl propene. The addition occurs according to Markonikov rule.



### 2.3.5

#### Physical properties

Ethers are colourless liquids with characteristic odour. Diethyl ether has pleasant odour.

Ethers have lower boiling points than alcohols as they cannot form inter molecular hydrogen bonds due to lack of 'H' atoms on ethereal oxygen. The C–O bonds in ethers are polar and thus ethers have a net dipole moment. Boiling point of diethyl ether is  $34.5^\circ\text{C}$  and that of ethyl alcohol is  $78.2^\circ\text{C}$ .

Ethers are less soluble in water. Diethyl ether is almost immiscible with water. Diethyl ether is less dense than water. Ether cannot form extensive hydrogen bonds like alcohol with water. Ether is more soluble in organic solvents.

### 2.3.6

#### Chemical properties

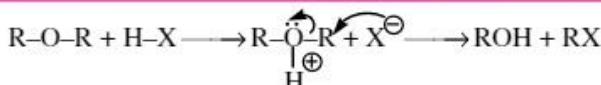
Ethers are less reactive than alcohols, because they do not have active hydrogen atoms.

##### Properties due to C–O bond fission

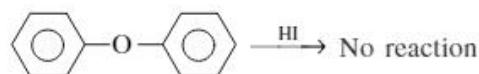
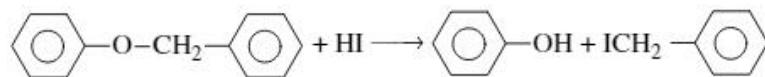
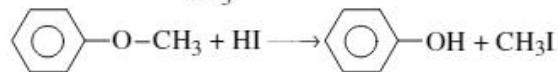
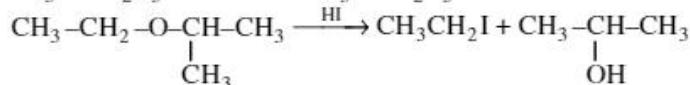
- With  $\text{HI}$  : Ethers react with  $\text{HX}$  to form alcohol and alkyl halide in cold, when concentration of hydrogen halide is less.

## CHEMISTRY IIB

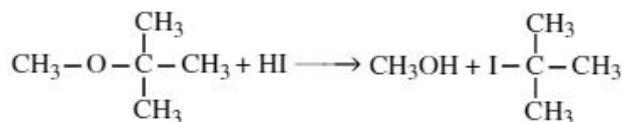
  
With cold, dil HI,  
diethyl ether gives  
ethyl alcohol and  
ethyl iodide  

The reaction mechanism with HI is  $S_N2$ .  $X^-$  is bonded to alkyl group having less steric crowding.



Iodide cannot attack on phenoxide due to repulsion with  $\pi$  electron cloud of the ring. But if one of the alkyl groups is tertiary, the reaction proceeds via  $S_N1$  mechanism and iodide goes with bulky tertiary alkyl group.



The carbocation formed in this reaction is most stable. If the ether is heated with HI or HI is taken in excess, only alkyl iodide is formed.

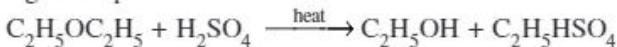


Order of reactivity of HX with ether : HI > HBr > HCl

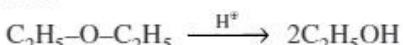
  
Reactivity of HX  
with ethers is  
in the order:  
HI > HBr > HCl  


  
With steam, ether  
gets hydrolysed  
to give ethyl  
alcohol  


b) With  $H_2SO_4$  : Ether on heating with concentrated sulphuric acid gives alkyl hydrogen sulphate.



c) Hydrolysis : Ether undergoes hydrolysis with dilute acids or steam to give alcohol.

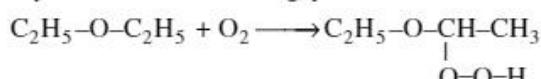


d) Formation of esters : Ethers form esters with acid chloride and acid anhydride.



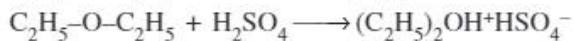
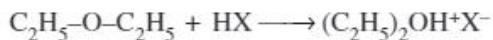
### Reaction of ethereal oxygen

Formation of peroxide : When exposed to air, ethers form explosive peroxides. A sample of ether containing peroxide cannot be used as an anaesthetic.



*Ether is a Lewis base. It forms oxonium salts with cold mineral acids*

**Formation of oxonium salts :** At low temperature, ethers form oxonium salts with concentrated mineral acids.



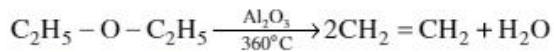
Ether acts as an electron pair donor. Hence it is a Lewis base. Ether also acts proton acceptor. Hence it is a Bronsted base.

#### Other reactions

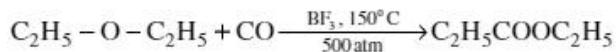
**Oxidation :** On Oxidation with acidified dichromate, diethyl ether gives acetaldehyde and acetic acid.



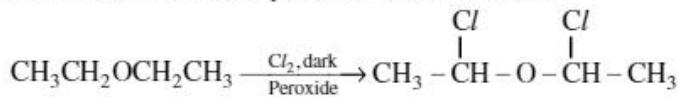
**Dehydration :** On heating with  $\text{Al}_2\text{O}_3$  at  $360^\circ\text{C}$ , diethyl ether gives ethylene.



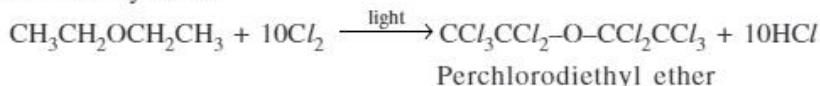
**Addition :** When heated with CO in presence of boron trifluoride catalyst at  $150^\circ\text{C}$  under pressure, diethyl ether forms ethyl propionate.



**Halogenation :** Ethers can be halogenated at the  $\alpha$ -carbon by treatment with chlorine or bromine in the presence of an initiator.

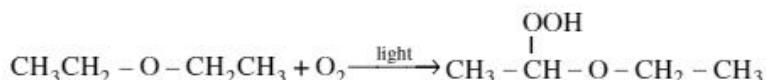


In the presence of light, diethyl ether reacts with excess of chlorine to form perchlorodiethyl ether



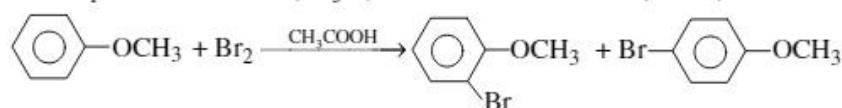
*Atmospheric oxidation of ethers forms peroxide*

**Oxidation and peroxide formation :** Ethers add up atmospheric oxygen or ozonized oxygen through coordination of one of the lone pair of ethereal oxygen to form peroxides in presence of sunlight or ultraviolet light. The peroxide of diethyl ether is unstable and decomposes vigorously on heating.

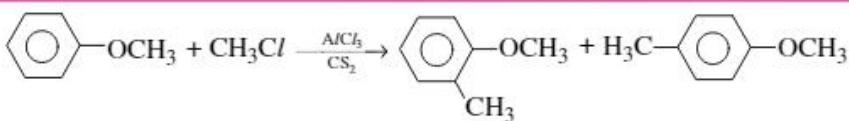


*Electrophilic substitution on anisole is ortho and para directing*

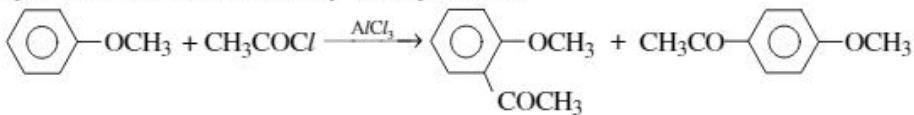
**Electrophilic substitution :** Alkoxy group is electron releasing by  $+M$  effect when connected to benzene ring. Electrophilic substitution on anisole is ortho and para directing. In these reactions, the ring is activated by  $-\text{OCH}_3$  group. The reactivity of anisole is more than that of benzene. Bromination of anisole gives a mixture of p-bromo anisole (major) and o-bromo anisole (minor).



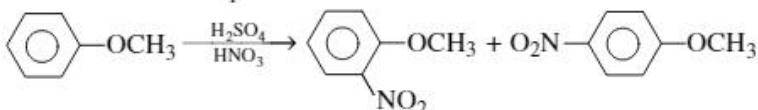
Friedel-Craft's methylation gives a mixture paramethoxy toluene and ortho-methoxy toluene.



Friedel-Craft's acetylation of anisole gives a mixture of paramethoxy acetophenone and orthomethoxy acetophenone.



Anisole reacts with a mixture of concentrated sulphuric and nitric acids to yield a mixture of ortho and para nitroanisole.



In all the above electrophilic substitution reactions of anisole, para product is the major product and ortho product is the minor product.

#### Uses of diethyl ether

Diethyl ether is used as general anaesthetic in surgery without effecting heart, lungs. A mixture of diethyl ether and dry ice ( $\text{CO}_2$ ) is used as refrigerant. It produces a temperature of as low as  $-110^\circ\text{C}$ . A mixture of diethylether and ethanol under the name natallite is used as substitute for petrol.

Ether is used as a solvent for fats, oils and plastics. Dry ether is used as medium for Grignard and Wurtz reaction. Ether is used to separate organic compounds from their aqueous solution by solvent extraction. Aromatic ethers have very good odour. They are used as flavouring agents in perfumes.

  
Halothane,  
 $\text{CF}_3\text{CHClBr}$  is  
anaesthetic  
  
Aromatic ethers  
have good  
flavours



P.2.33

Dehydration of alcohols is suitable for preparing ethers having primary alkyl groups only. Comment.

#### Solution

During dehydration of alcohol the alkyl group should be unhindered and the temperature be kept low. Otherwise the reaction favours the formation of alkene. The reaction follows  $\text{S}_{\text{N}}^1$  pathway when the alcohol is secondary or tertiary.

However, the dehydration of secondary and tertiary alcohols to give corresponding ethers is unsuccessful as elimination competes over substitution and as a consequence, alkenes are easily formed.



P.2.34

Give one example of an ether which cannot be decomposed by HI.

#### Solution

Diphenylether,  $\text{C}_6\text{H}_5-\text{O}-\text{C}_6\text{H}_5$  cannot be decomposed by HI. Iodide cannot attack the ring carbon as nucleophile.



P.2.35

Ether can be dried over sodium, but not alcohol. Why?

#### Solution

Alcohol contains acidic hydrogen and so reacts with sodium metal and releases hydrogen.



Ether has no  $-\text{OH}$  group and does not react with sodium metal. Hence ether can be dried over sodium, but not alcohol.



P.2.36

Chloroethane, 2-chloropropane and chloroethene are treated with methoxide. Which is more reactive towards Williamson's synthesis?

#### Solution

Chloroethane is more reactive.

2-Chloropropane is being  $2^\circ$  halide, is less reactive due to  $+I$  effect.

Chloroethene has stronger C–Cl bond and so is less reactive.



**P.2.37** Diphenyl ether cannot be cleaved by treatment  $\text{HI}$ . Why?

**Solution** In diphenyl ether, oxygen atom is bonded to phenyl ring and both bonds are strong. They cannot be cleaved by  $\text{HI}$ .



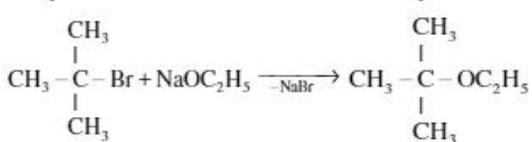
**P.2.38** How is ether distinguished from ethanol using iodine and alkali?

**Solution** Ethanol gives yellow coloured solid iodoform with iodine and alkali. Ether does not form iodoform.

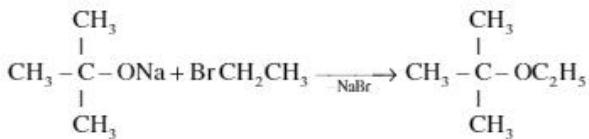


**P.2.39** What product is expected when tertiary butyl bromide is reacted with sodium ethoxide? Why that product is not formed and how that product can be obtained?

**Solution**

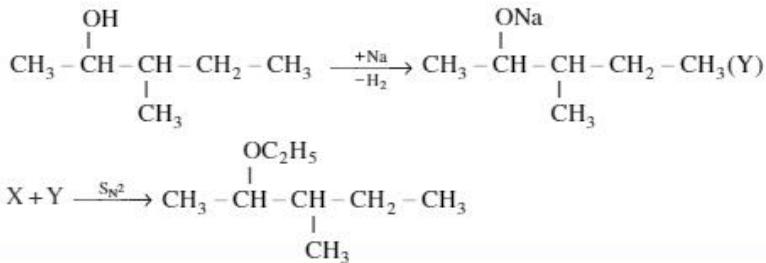


The expected product is shown above. But the major product is 2-methyl-1-propene. This is because sodium ethoxide is a strong nucleophile as well as a strong base. Thus elimination reaction predominates over substitution. The product in the reaction can be obtained as

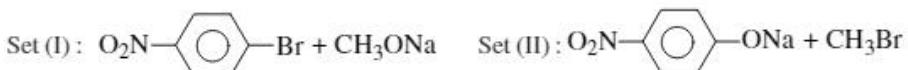


**P.2.40** Write the reactions involved in Williamson synthesis of 2-ethoxy-3-methylpentane, starting from ethanol.

**Solution**  $\text{CH}_3\text{CH}_2\text{OH} \xrightarrow[-\text{SO}_2,\text{HCl}]{+\text{SOCl}_2} \text{CH}_3\text{CH}_2\text{Cl} (\text{X})$



**P.2.41** Which of the following is an appropriate set of reactants for the preparation of 1-methoxy-4-nitrobenzene. Why?



**Solution** Reactants in set (II) is suitable and appropriate for the preparation of the product 1-methoxy-4-nitrobenzene but not those of set I.

This is because aryl halides are very less reactive in nucleophilic substitution reaction.

### EXERCISE - 2.1.3

1. Compare the physical properties of an alcohol and ether of comparable molecular mass.
2. How is diethyl ether prepared? Write its important properties.

3. Explain Williamson's method of preparation of diethyl ether.
4. Explain the action of HI on diethyl ether.
5. Give the structures and names of monohydric phenols with formula  $C_7H_8O$ .
6. What is the action of dil.  $H_2SO_4$  and conc.  $H_2SO_4$  on diethyl ether?
7. Write the important uses of ethers.
8. Explain why ortho nitrophenol is more acidic than ortho methoxyphenol?
9. Metallic sodium reacts with 'X' to form 'Y'. Ethyl chloride and 'Y' react together to give diethyl ether. What are 'X' and 'Y'?
10. How methyl magnesium bromide is converted to 2-methyl-2-propanol?



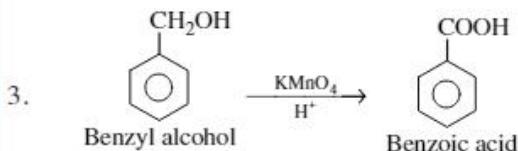
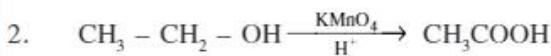
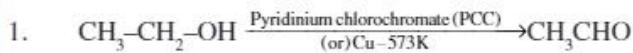
1. Alcohols and phenols are hydroxy compounds. Phenols have -OH group connected to benzene ring.
2. Alcohols are prepared by hydration of alkenes in acid medium.
3. Alcohols are also prepared by the action of Grignard reagent on aldehydes and ketones followed by hydrolysis or by the reduction of aldehydes and ketones.
4. Phenol is prepared by the hydrolysis of benzene sulphonic acid or by heating benzene diazonium chloride with water.
5. Phenol is also prepared by the oxidation of cumene followed by hydrolysis.
6. Diethylether is prepared by heating ethyl alcohol with con  $H_2SO_4$  at 140°C or with  $Al_2O_3$  at 260°C.
7. Ether is also prepared by the action of alkali metal alkoxide on alkyl halides in Williamson's method.
8. Alcohols and phenols are acidic in nature. Phenols are more acidic than alcohols. Phenols are soluble in NaOH and are regenerated by  $CO_2$ . Alcohols are insoluble in NaOH.
9. Phenol gives violet colour with neutral ferric chloride.
10. Alcohols have higher boiling points than hydrocarbons, aldehydes, ketones and ethers due to intermolecular hydrogen bonding.
11. Alcohols are more soluble in water due to the formation of intermolecular hydrogen bonding with water.
12. Alcohols give aldehydes, ketones and carboxylic acids on oxidation.
13. Alcohols form esters with acids and also with acid derivatives.
14. Alcohols give alkyl halides on reaction with HX,  $PCl_5$ ,  $PCl_3$  or  $SOCl_2$ .

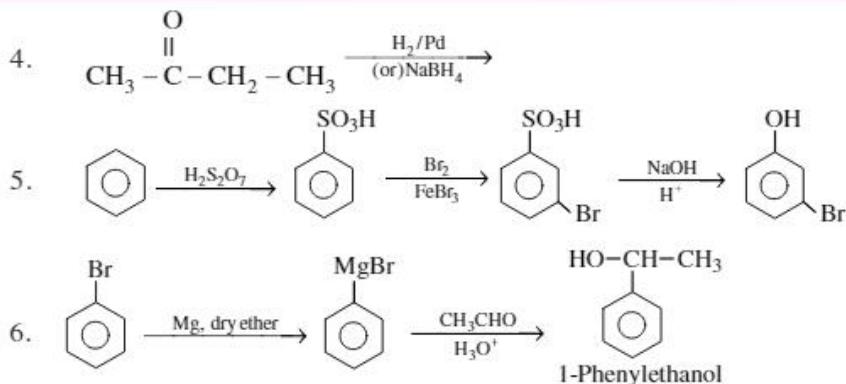
15. Dehydration of alcohols produces alkenes and reduction of alcohols with HI/P gives alkanes.
16. Phenols are aromatic hydroxy compounds in which –OH group is attached to benzene ring.
17. Phenols are more acidic than alcohols.
18. Phenols undergo halogenation, nitration and sulphonation more easily than benzene. The –OH group in phenols is ortho and para orienting and activating.
19. Phenol gives salicylaldehyde with chloroform and salicylic acid with  $\text{CO}_2$  in alkali medium.
20. On heating with zinc dust, phenol gives benzene.
21. Both alcohols and phenols release hydrogen with active metals. Ethers cannot release hydrogen with sodium.
22. Ethers are degraded by HI to alcohol and alkyl iodide. On hydrolysis with dil. acid, ether gives alcohols.
23. Both hydroxy and alkoxy groups connected to benzene ring are ortho and para-orienting.
24. The peroxide formed by the oxidation of ether is destroyed by shaking with  $\text{FeSO}_4$ .
25. The three types of alcohols can be distinguished with Lucas reagent or in Victor Meyer test.
26. Ethanol is used in beverages, solvent, antiseptic and as a component in fuel.
27. Diethylether is used as solvent, medium, anaesthetic and also as refrigerant.

## CONVERSIONS

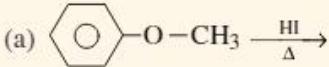
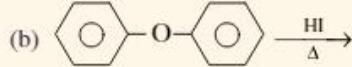
1. Primary alcohol to aldehyde
2. Primary alcohol to carboxylic acid
3. Benzyl alcohol to benzoic acid
4. Butan–2–one to butan–2–ol
5. Benzene to m–bromophenol
6. Bromobenzene to 1–phenylethanol

### ANSWERS to CONVERSIONS



**EXERCISE - 2.2**

- How the three types of alcohols are distinguished?
- Explain Reimer-Tiemann reaction and Kolbe's reaction.
- Differentiate between an alcohol from a phenol, though both contain same functional group.
- What evidence that you can give to say that oxygen atom in phenol is  $\text{sp}^2$  hybridised.
- Why phenols are stronger acids than alcohols?
- Can phenols react with  $\text{NaHCO}_3$  to liberate  $\text{CO}_2$ ?
- tert-Butyl alcohol is more stable than n-butyl alcohol in water. Explain.
- Explain the steps involved in the conversion of starch into ethyl alcohol.
- Give the sequence of reactions to prepare 2-butanol starting from 1-butene.
- Discuss on the relative reactivity of different alcohols with a given carboxylic acid towards esterification.
- Among isomeric alcohols which reacts fastest with metallic sodium? Why?
- Write the importance of isotopic oxygen ( $\text{O}^{18}$ ) in the mechanism of esterification. Give suitable examples.
- Arrange the following in the increasing acidic strength :  
Phenol, o-chlorophenol, m-chlorophenol and p-chlorophenol.
- What are the products formed when  $(\text{CH}_3)_3\text{C}-\text{CH}=\text{CH}_2$  is subjected to (a) hydration in presence an acid, (b) hydroboration oxidation and (c) oxym汞uration-demercuration.
- Optically active 2-butanol recemizes in presence of dilute sulphuric acid. Explain.
- Explain how  $-\text{OH}$  group in phenol is ortho- and para- orienting?
- Why tribromophenol is formed when phenol is treated with bromine water?
- Dehydration of secondary and tertiary alcohols is not convenient to prepare ethers. Why?
- Williamson's synthesis cannot be carried out with tertiary alkyl chloride. Why?
- Reaction of 2-pentanol or 3-pentanol on reaction with  $\text{HCl}$  give both 2-chloropentane and 3-chloropentane. Explain.

21. Give an examples of ether which can not be decomposed by the use of hydrogen iodide.
22. Phenol is more reactive than benzene towards electrophilic substitution. Substantiate.
23. What happens when phenol is treated with carbontetrachloride, in the presence of NaOH?
24. Give the sequence of reactions to convert benzene into p-hydroxyacetophenone.
25. What is dichlorocarbene? Write the reaction in which dichlorocarbene is involved.
26. An alkoxy group connected to benzene ring is ortho- and para- orienting. Explain.
27. How is benzene converted to phenol via Friedel-Crafts reaction?
28. Tertiary alkyl halides are not suitable for preparation of ethers by Williamson's synthesis. Explain.
29. Write the product(s) of the following reactions :
- (a)   $\xrightarrow[\Delta]{\text{HI}}$
- (b)   $\xrightarrow[\Delta]{\text{HI}}$
30. How a mixture of phenol and ethyl alcohol can chemically be separated?
31. Write the phenolic isomer of the compound  $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$ . (Ans : Cresol)
32. Williamson's method is not useful for preparation of diphenyl ether. Why?
33. Salicyladehyde  $\longleftrightarrow$  Phenol  $\longrightarrow$  Salicylic acid. How are these conversions made?
34. 'X' reacts with  $\text{PCl}_5$  to give 'Y'. 'Y' reacts with aqueous KOH to give back 'X'. If the molecular formula of 'X' is  $\text{C}_2\text{H}_6\text{O}$ , what are 'X' and 'Y'?
35. Natallite is a mixture of two compounds A and B, both are organic. How are these distinguished? Write the reactions. (Ans : using Na)
36.  $\text{C}_2\text{H}_4 + \text{HCl} \xrightarrow{\text{AlCl}_3} \text{A} \xrightarrow{\text{H}_2\text{O}, \text{OH}^-} \text{B} \xrightarrow{\text{H}_2\text{SO}_4, 140^\circ\text{C}} \text{C} \xrightarrow{\text{steam}} \text{B}$ . Discuss the reactions.
37.  $\text{A} \xrightarrow[\text{aqueous}]{\text{KOH}} \text{B} \xrightarrow[140^\circ\text{C}]{\text{conc. H}_2\text{SO}_4} \text{C} \xrightarrow[\text{HI}]{\text{hot}} \text{C}_2\text{H}_5\text{I} + \text{H}_2\text{O}$  what are A, B and C?
38.  $\text{C}_2\text{H}_5\text{OH} \xrightarrow{\text{Na}} \text{X}; \text{C}_2\text{H}_5\text{OH} \xrightarrow{\text{PCl}_5} \text{Y}$ . Organic products, X and Y react together to give another organic compound Z. Write the normal chain functional isomer of Z. (Ans : Butanol)
39.  $\text{C}_6\text{H}_5\text{NH}_2 \xrightarrow{\text{HNO}_2, \text{HCl}, 0^\circ\text{C}} \text{A} \xrightarrow{\text{steam}} \text{B} \xrightarrow[\Delta]{\text{Zn}} \text{C}$ . What is compound 'C'? (Ans : Benzene)
40.  $\text{C}_2\text{H}_5\text{CHOHCH}_3 \xrightarrow[-\text{H}_2\text{O}]{\text{H}_2\text{SO}_4} \text{X} \xrightarrow{\text{O}_3, \text{H}_2\text{O}, \text{Zn}} \text{Y} + \text{Z}$ . Are the organic products Y and Z different? (Ans : No)

