

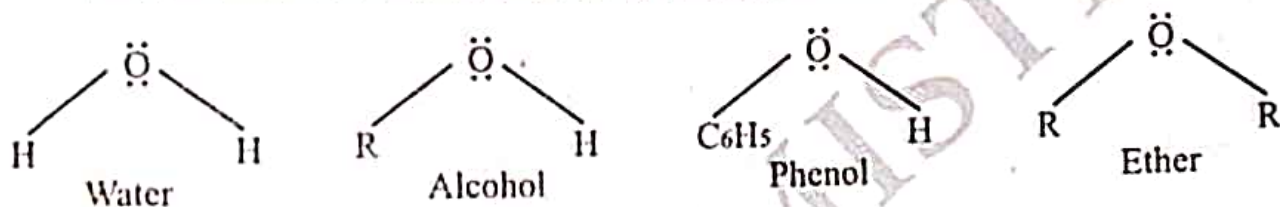
11 CHAPTER

ALCOHOLS, PHENOLS AND ETHERS

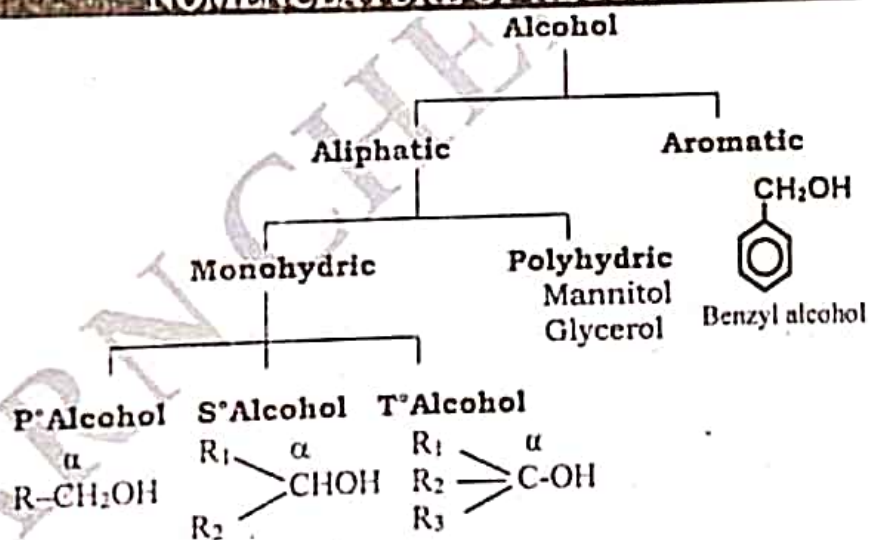
INTRODUCTION

ALCOHOLS

- When H of alkane is replaced by $-OH$ group, then it is called alcohol.
- When the H of benzene ring is replaced by $-OH$ group, then it is called phenol.
- The linkage between two carbon atoms through oxygen atom is called ether.
- Alcohols, phenols and ethers are classes of organic compounds which are much closer to water in structure and hence considered as derivatives of water



NOMENCLATURE OF ALCOHOLS



Common or Trivial Names

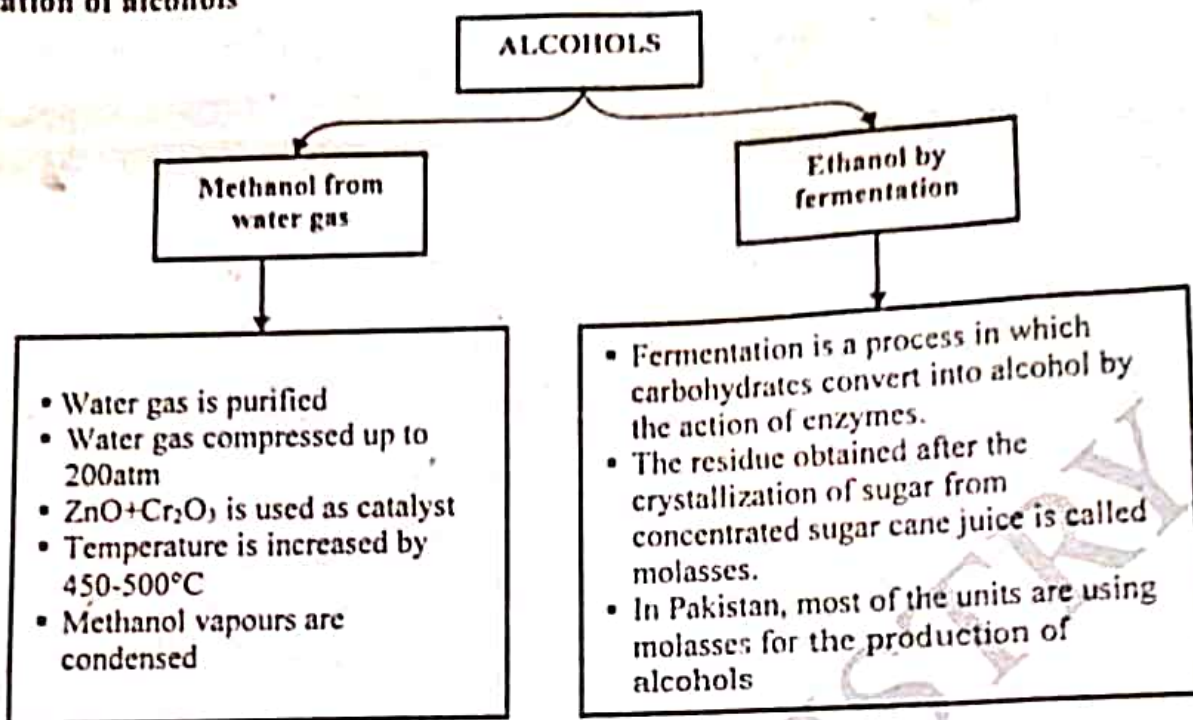
- Alkyl group is prefixed to alcohol. e.g CH_3OH methyl alcohol $\text{C}_2\text{H}_5\text{OH}$ ethyl alcohol etc.

IUPAC Rules

- Select longest carbon chain containing $-OH$ group.
- Start numbering, and give least number to OH group.
- Mention position of $-OH$ group.
- Change the "e" of alkane by "ol".
- If there are more than two-OH groups then use prefix diol, triol, tetraol etc.

If there are unsaturations in longest chain then first write down the position of unsaturated bond and then follow the above rules.

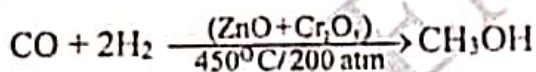
Preparation of alcohols



Industrial Preparation

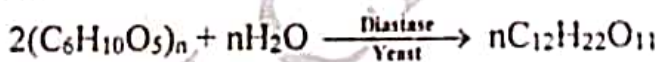
Methanol

- From water gas

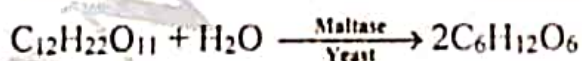


Ethanol

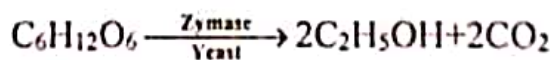
- From starch



Starch Maltose

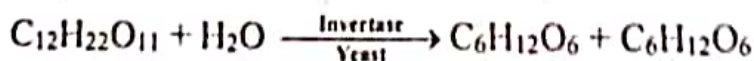


Maltose Glucose

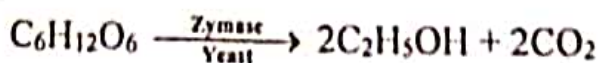


Glucose Ethanol

- From molasses



Molasses Glucose Fructose
(Sucrose)



Glucose Ethanol

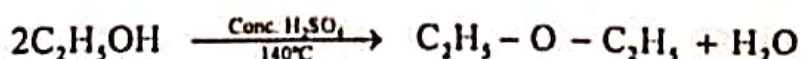
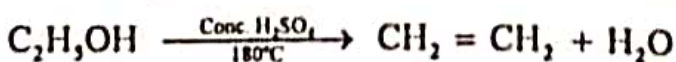
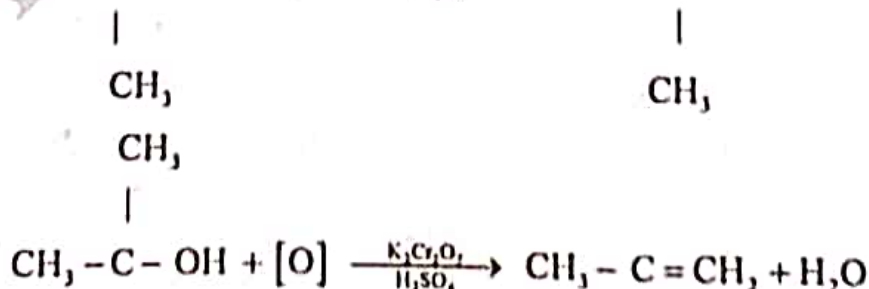
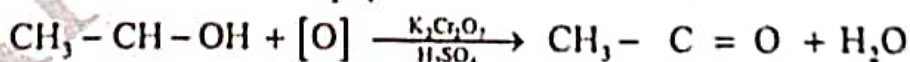
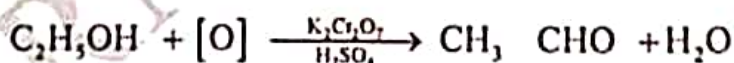
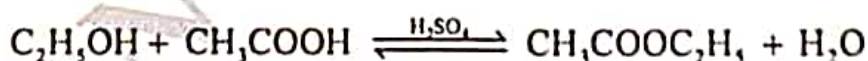
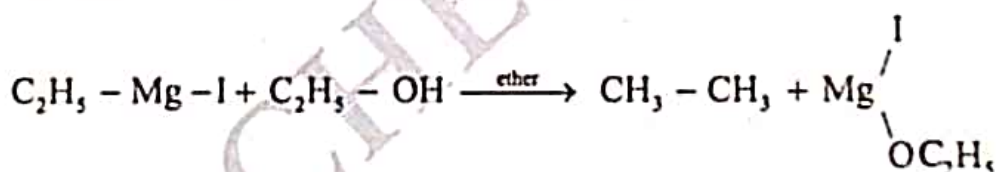
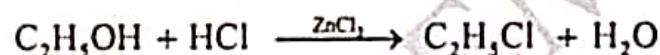
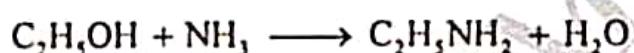
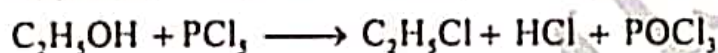
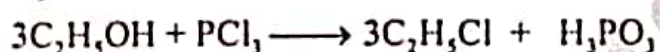
Reactivity of -OH group

- Oxygen atom of the -OH group in alcohols is sp^3 hybridized
- The carbon oxygen bond (C-O) and hydrogen oxygen bond (O-H) are highly polarized.
- The negative charge is present on the oxygen atom of alcohol.

Chemical properties

- Alcohols react with other reagents in two ways
 - Reactions in which C-O bond breaks.
 - Reactions in which O-H bond breaks.
- The order of reactivity of alcohols when C-O bond breaks
Tertiary alcohol > Secondary alcohol > Primary alcohol
- The order of reactivity of alcohols when O-H bond breaks
CH₃OH > Primary alcohol > Secondary alcohol > Tertiary alcohol
- Nucleophile breaks C-O bond of alcohol.
- Attacking electrophile breaks O-H bond of alcohol.
- Catalytic oxidation of primary alcohol and secondary alcohol in presence of K₂Cr₂O₇ and H₂SO₄, converts them into aldehydes and ketones respectively; while same reaction of tertiary alcohol gives alkenes.
- On heating with H₂SO₄ (conc.), alcohol changes to alkene.

Reactions of alcohols

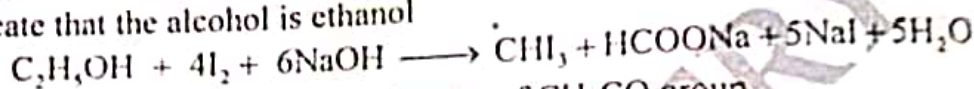


DISTINCTION BETWEEN PRIMARY, SECONDARY AND TERTIARY ALCOHOLS

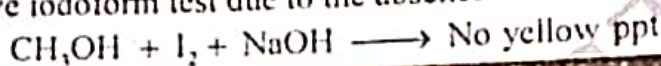
Tests	Primary alcohol	Secondary alcohols	Tertiary alcohols
Lucas Test: To the alcohol add concentrated HCl and ZnCl ₂	Turbidity does not appear but on heating	Turbidity appears after some times (5 - 10 min)	Turbidity appears immediately
Dichromate Test (Oxidation) To the alcohol add a mixture of K ₂ Cr ₂ O ₇ and concentrated H ₂ SO ₄	The orange solution of K ₂ Cr ₂ O ₇ becomes green and aldehydes are produced	The orange solution of K ₂ Cr ₂ O ₇ becomes green and ketones are produced	Solution remains orange as on dehydration alkene is formed

Distinction between methanol and ethanol

Ethanol gives iodoform with iodine in the presence of NaOH. Formation of yellow crystals of iodoform (CHI₃) indicate that the alcohol is ethanol



Methanol does not give iodoform test due to the absence of CH₃CO group.



USES OF ALCOHOLS

Methanol	Ethanol
<ul style="list-style-type: none"> It is used as a solvent for fats, oils, paints and varnishes. It is used as antifreeze in the radiators of automobiles. It is used for denaturing of alcohol. 	<ul style="list-style-type: none"> It is used as a <ul style="list-style-type: none"> Solvent Drink Fuel It is used in pharmaceutical preparations. It is used as a preservative for biological specimen.

PHENOL

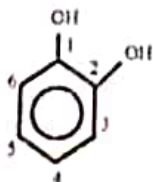
Aromatic compounds which contain one or more -OH groups directly attached with carbon of benzene ring are called Phenols.

Simplest Phenol

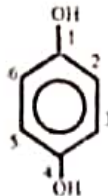
Carbolic acid (Benzenol) (C₆H₅OH). It was first obtained from coaltar by Runge in 1834.



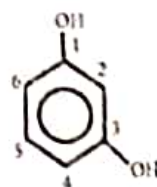
Phenol



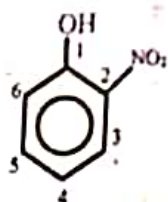
1,2-Dihydroxy benzene
o-Hydroxy phenol
(catechol)



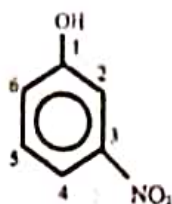
1,4-Dihydroxy benzene
p-hydroxy phenol
(hydroquinone)



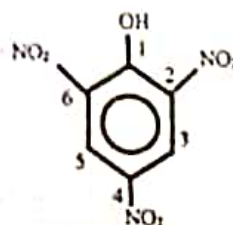
1,3-Dihydroxy benzene
m-dihydroxy phenol
(resorcinol)



2-Nitrophenol
o-Nitrophenol



m-Nitrophenol

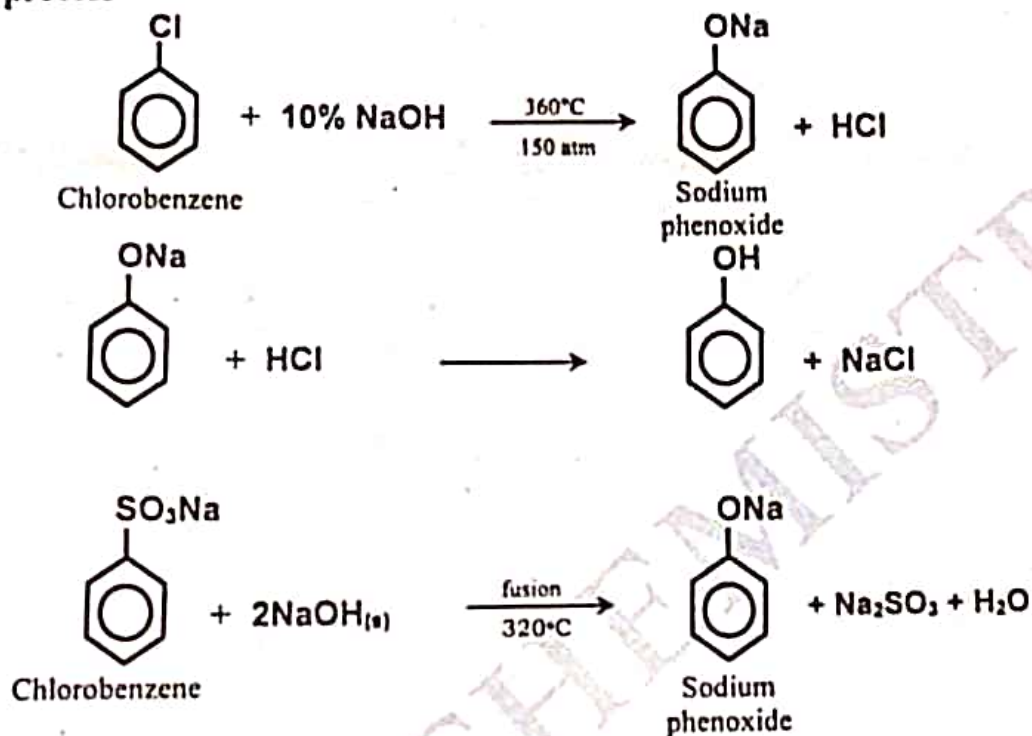


2,4,6-Trinitrophenol
(picric acid)

Preparation of phenol

Source of reactant	Remarks
From chloro benzene(Dow's method)	<ul style="list-style-type: none"> 10% NaOH is used Reaction completes in two steps
From sodium salt of sulphonic acid	Phenol is recovered by distillation

Dow's process



Fusion of sodium benzenesulphonate with solid sodium hydroxide



Physical properties of phenol

- It is a colourless, crystalline, deliquescent solid with characteristic phenolic odour.
- Its melting point is 41°C and boiling point is 182°C .
- It is sparingly soluble in water at room temperature but completely soluble above 68.5°C .

Reactions of phenol

Phenol shows two types of reactions

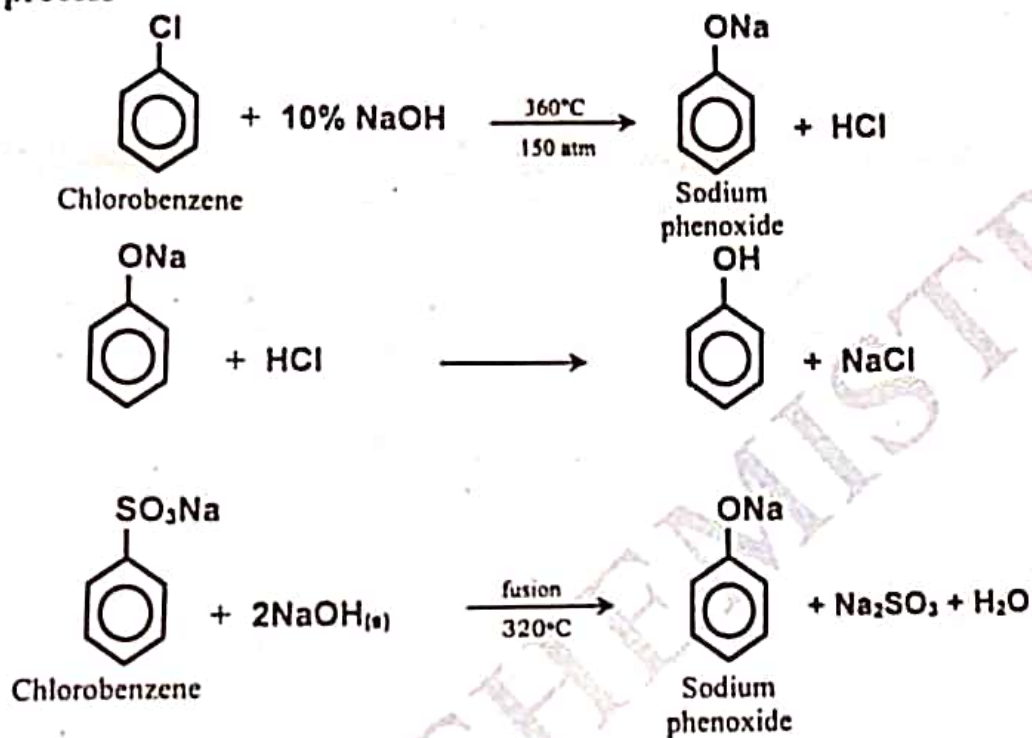
(i) Reaction of phenol due to $-\text{OH}$ group

Nature of reaction	Remarks
Salt formation	Phenoxides are formed
Ester formation	Reaction takes place in basic media
Reduction with Zn	Benzene is obtained

Preparation of phenol

Source of reactant	Remarks
From chloro benzene(Dow's method)	<ul style="list-style-type: none"> 10% NaOH is used Reaction completes in two steps
From sodium salt of sulphonic acid	Phenol is recovered by distillation

Dow's process



Fusion of sodium benzenesulphonate with solid sodium hydroxide



Physical properties of phenol

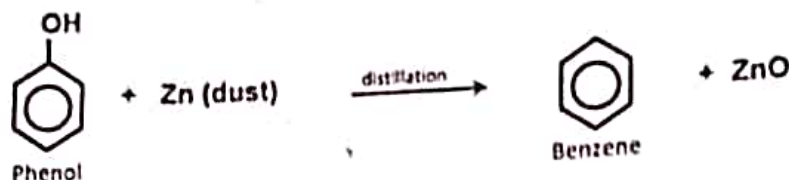
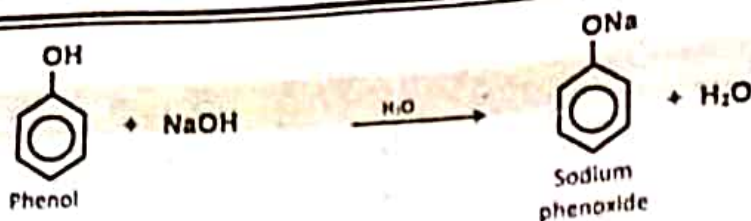
- It is a colourless, crystalline, deliquescent solid with characteristic phenolic odour.
- Its melting point is 41°C and boiling point is 182°C .
- It is sparingly soluble in water at room temperature but completely soluble above 68.5°C .

Reactions of phenol

Phenol shows two types of reactions

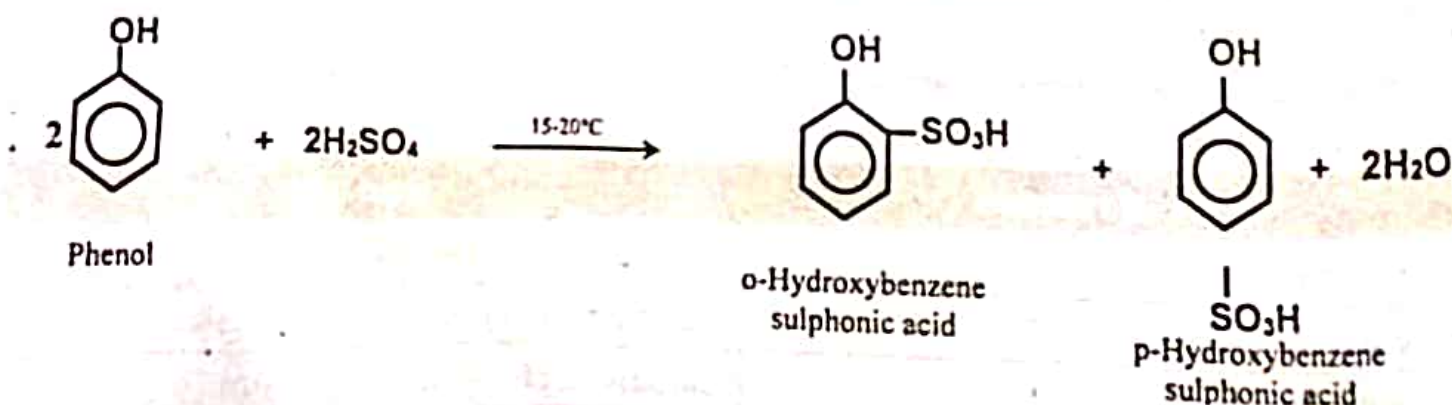
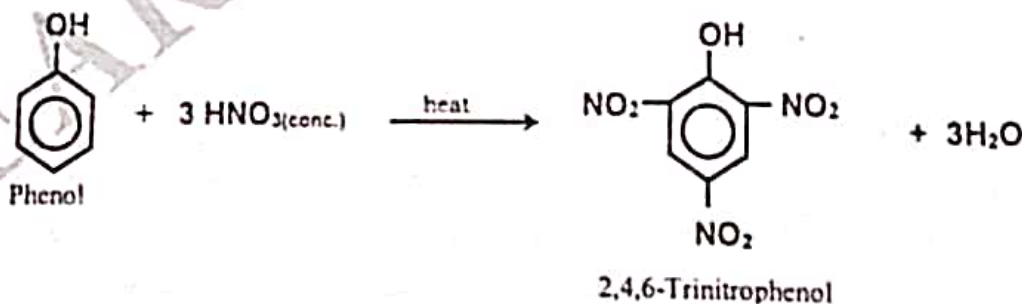
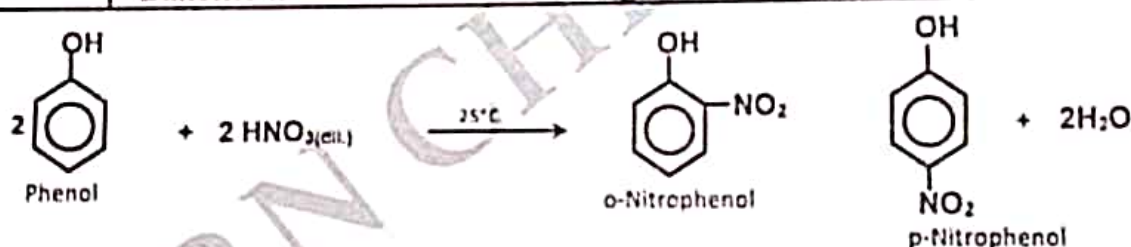
(i) Reaction of phenol due to $-\text{OH}$ group

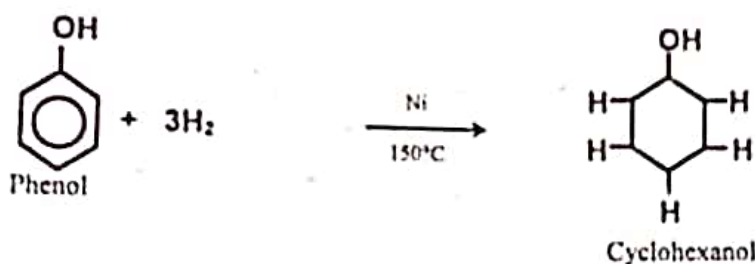
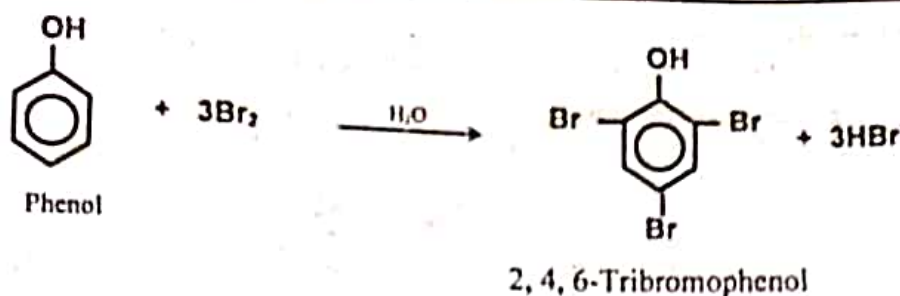
Nature of reaction	Remarks
Salt formation	Phenoxides are formed
Ester formation	Reaction takes place in basic media
Reduction with Zn	Benzene is obtained



REACTION OF PHENOL DUE TO BENZENE RING

Reaction	Remarks
Nitration	<ul style="list-style-type: none"> At room temperature, the product is a mixture of o- and p-nitrophenol with dil. HNO_3 At higher temperature, the product is picric acid with concentrated HNO_3
Sulphonation	Introduction of HSO_3^- is called sulphonation a mixture of ortho and para products at 15 to 20°C
Halogenation	White ppt. of 2,4,6-tribromophenol is obtained
Hydrogenation	Un-saturation of ring is removed
Reaction with formaldehyde	<ul style="list-style-type: none"> This is a condensation polymerization of phenol Formaldehyde polymerizes with phenol to produce bakelite. Bakelite is used for manufacturing of switch buttons



**Acidic nature of phenol:**

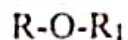
(1) Relative acidic strength of alcohol, phenol, water and carboxylic acid is as follows:
carboxylic acid > phenol > water > alcohol

(2) Phenol is:

- Too weak to affect the litmus paper.
- Unable to evolve CO_2 from carbonates.
- Acidic in nature due to stability of phenoxide ion.
- Its K_a is 1.3×10^{-10} .

ETHERS

Those organic compounds in which an oxygen atom is bonded to two alkyl groups or aryl groups are called ether.

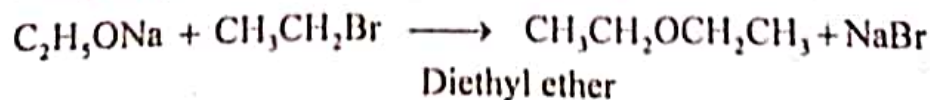
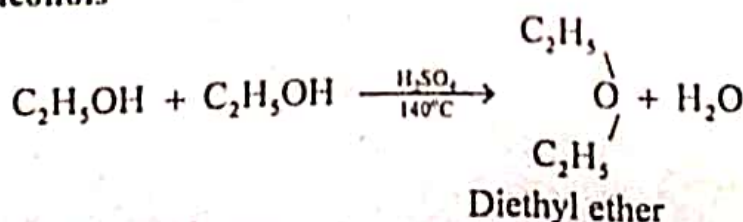


$\text{R} = \text{R}_1$ (symmetrical ethers)

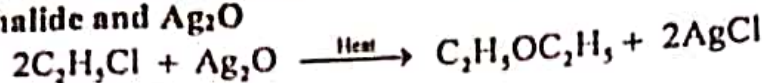
$\text{R} \neq \text{R}_1$ (unsymmetrical ethers)

Nomenclature

Formula	Common Names	IUPAC
CH_3OCH_3	Dimethyl ether	Methoxy methane
$\text{CH}_3\text{OC}_2\text{H}_5$	Methyl ethyl ether	Methoxy ethane
$\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$	Diethyl ether	Ethoxy ethane
$\text{CH}_3\text{OC}_6\text{H}_5$	Methyl phenyl ether (Anisol)	Methoxy benzene

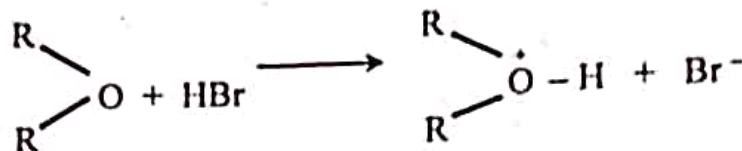
PREPARATION OF ETHER**1. By Williamson's synthesis****2. Condensation of alcohols**

3. Reaction of alkyl halide and Ag₂O

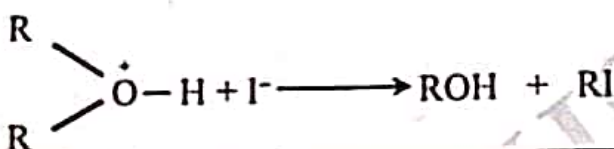
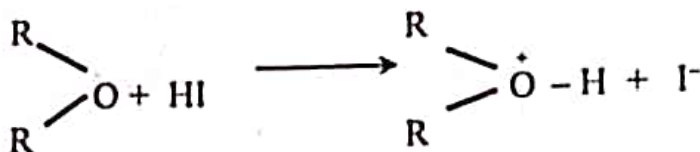


CHEMICAL REACTIVITY OF ETHER

Reaction with acid



Stronger acid



COMPARISON OF PHYSICAL PROPERTIES

Property	Alcohol	Phenol	Ether
Solubility in water	Soluble	Sparingly soluble at room temperature; soluble at 68.5°C	Slightly soluble
Volatile	Volatile	Almost non volatile	More volatile
Hydrogen binding	Present	Present	Absent

ALCOHOLS, PHENOLS AND ETHERS

11 Chapter

PRACTICE EXERCISE

- (1) Which of the following compound does not have $-COOH$ group
(a) Succinic acid (b) Maleic acid
(c) Picric acid (d) Acetic acid
- (2) The rate of esterification of alcohol is more for
(a) C_2H_5OH (b) CH_3OH
(c) $(CH_3)_2CHOH$ (d) $(CH_3)_3COH$
- (3) Alcohol in which hydroxyl is attached to carbon which is further attached to two alkyl groups is
(a) Primary alcohol (b) Tertiary alcohol
(c) Secondary alcohol (d) All of these
- (4) Methanol can be obtained from
(a) Water gas (b) Destructive distillation of wood
(c) Methane (d) All of these
- (5) An alcohol which can be prepared by fermentation is
(a) CH_3OH (b) C_3H_7OH
(c) CH_3-CH_2-OH (d) C_6H_5OH
- (6) Absolute alcohol is obtained when rectified spirit is treated with
(a) $Ca(OH)_2$ (b) $CaCO_3$
(c) $CaCl_2$ (d) CaO
- (7) Which one of the following compound does not have $-OH$ group
(a) Ethylene glycol (b) Glycerol
(c) Picric acid (d) Ethyl acetate
- (8) Which one of the following alcohol has greater boiling point
(a) Ethanol (b) Ethylene glycol
(c) Glycerol (d) Methanol
- (9) The dehydration of alcohol results in:
(a) Alkene (b) Ether
(c) Aldehyde (d) Both (a) and (b)
- (10) What happens when iodine is treated with methyl alcohol in the presence of $NaOH$?
(a) An oily layer is formed immediately
(b) An oily layer of aldehyde is formed
(c) An oily layer of alkyl halide formed on heating
(d) No reaction takes place
- (11) Which one of the following alcohol does not undergo oxidation reaction
(a) Ethanol (b) Propanol
(c) Iso-butanol (d) 2-methyl-2-propanol
- (12) Which one of the following is also known as lactic acid
(a) 3-Hydroxy propanoic acid (b) 2-hydroxy propanoic acid
(c) 2-hydroxy butanoic acid (d) 3-hydroxy butanoic acid
- (13) Which one of the following is also known as tartaric acid
(a) 2, 3-dihydroxy butane-1,4-dioic acid (b) 2,3-dihydroxy butanedioic acid
(c) 2, 3-dihydroxy butanoic acid (d) 2,2-dihydroxy butanoic acid
- (14) Water gas heated at $450^\circ C$ and 200 atm pressure in the presence of $ZnO+Cr_2O_3$ will produce
(a) Methanal (b) Methanol
(c) Carbonic acid (d) Methane

Chapter-11

- (15) From the following which has strongest conjugate base
 (a) Carboxylic acid (b) Phenol
 (c) Water (d) Alcohol
- (16) The formula of starch is
 (a) $C_{12}H_{22}O_{11}$ (b) $C_6H_{10}O_5$
 (c) $(C_6H_{10}O_5)_n$ (d) $C_6H_{12}O_6$
- (17) The process of fermentation of starch involves many enzymes, the sequence of enzymes used are
 (a) Diastase-maltase-zymase (b) Zymase-maltase-diaastase
 (c) Maltase-diaastase-zymase (d) Diaastase-zymase-maltase
- (18) The rectified spirit contains
 (a) 12% alcohol (b) 90% alcohol
 (c) 95% alcohol (d) 100% alcohol
- (19) An ether reacts with HI it forms oxonium ion. Approximate bond angle in oxonium ion is
 (a) 109.5° (b) 107.5°
 (c) 104.5° (d) 102°
- (20) The oxidation of isopropyl alcohol will yield
 (a) Propane (b) Propanol
 (c) Propanone (d) Propanoic acid
- (21) Which alcohol will undergo elimination reaction to give alkene in the presence of acidic potassium dichromate
 (a) Primary alcohol (b) Secondary alcohol
 (c) Tertiary alcohol (d) All of above
- (22) Which compound shows maximum hydrogen bonding
 (a) C_2H_6 (b) C_2H_5Cl
 (c) CH_3OCH_3 (d) C_2H_5OH
- (23) Ethanol can be converted into ethanoic acid by
 (a) Hydrogenation (b) Hydration
 (c) Oxidation (d) Fermentation
- (24) Methyl alcohol is not used
 (a) As a solvent (b) As an antifreezing agent
 (c) As a substitute for petrol (d) For denaturing of ethyl alcohol
- (25) The distinction test for primary, secondary, and tertiary alcohol required to react each of them is
 (a) Conc. HCl and anhydrous $SOCl_2$ (b) Conc. HCl and anhydrous $CaCl_2$
 (c) Conc. HCl and anhydrous PCl_5 (d) Conc. HCl and anhydrous $ZnCl_2$
- (26) Ethanol and methanol can be distinguished by a
 (a) Iodoform test (b) Lucas test
 (c) Benedicts' test (d) Tollen's test
- (27) Which compound is also known by the name of carboic acid
 (a) C_2H_5OH (b) H_2CO_3
 (c) C_6H_5OH (d) H_3PO_3
- (28) The given dissociation constant (K_a) value 1.3×10^{-10} is of
 (a) Alcohol (b) Acetic acid
 (c) Water (d) Phenol
- (29) Heating phenol with Zn will yield
 (a) Benzene (b) Benzoic acid
 (c) Phenoxide (d) Cyclohexane

- (30) When phenol is heated with concentrated nitric acid, the product is
(a) Picric acid
(c) 1, 3, 5-trinitro benzene
(b) o-nitrophenol
(d) p-nitrophenol
- (31) Treating phenol with formaldehyde in the presence of dilute base forms Bakelite. The process involved is
(a) Oxidation
(c) Condensation polymerization
(b) Elimination
(d) Additional polymerization
- (32) Phenol was isolated by Runge from
(a) Vegetable oil
(c) Wood
(b) Coaltar
(d) Molasses
- (33) The hydrogenation of phenol in the presence of Ni and heat gives
(a) Cyclohexane
(c) 1-hexanol
(b) n-hexane
(d) Cyclohexanol
- (34) Which one of the following is more acidic is water
(a) Water
(c) Phenol
(b) Ethanol
(d) Ammonia
- (35) p-nitrophenol is stronger acid than phenol because nitro group is
(a) Electron donating
(c) Electron withdrawing
(b) Basic
(d) Acid
- (36) What is nature of bakelite?
(a) It is a monomer
(b) It is a simple molecule
(c) It is a condensation polyenes of phenol
(d) It is a macromolecule adduct
- (37) Electrophilic substitution in phenol takes place at
(a) o-and p-position
(c) Only at o-position
(b) Only at m-position
(d) Only at p-position
- (38) A methyl phenol is also called
(a) A cresol
(c) Alcohol
(b) Benzyl alcohol
(d) Formaldehyde
- (39) When phenol is treated with an excess of bromine water it gives
(a) m-bromophenol
(c) 2,4-dibromophenol
(b) o-bromophenol
(d) 2,4,6-tribromophenol
- (40) What is correct order for acidity of water, phenol and ethanol
(a) Phenol > Water > Ethanol
(c) Ethanol > Water > Phenol
(b) Phenol > Ethanol > Water
(d) Water > Phenol > Ethanol
- (41) Ethers show functional group isomerism with
(a) Aldehydes
(c) Alcohols
(b) Ketones
(d) Carboxylic acid
- (42) Which ether is symmetrical in nature
(a) Methyl ethyl ether
(c) Methyl n-propyl ether
(b) Diphenyl ether
(d) Methoxy benzene

Chapter-11

- (43) Which substance shows very weak hydrogen bonding with water
 (a) Methanol (b) Ethanol
 (c) Diethyl ether (d) Benzene
- (44) The IUPAC name of $\text{CH}_3\text{OC}_6\text{H}_5$ is
 (a) Methyl phenyl ether (b) Diphenyl ether
 (c) Methyl n-propyl ether (d) Methoxy benzene
- (45) When ethyl alcohol is heated, with NiH_2 in the presence of ThO_2 then
 (a) O - H bond breaks (b) C - O bond breaks
 (c) Ethene is formed (d) Ethane is formed
- (46) Which one is used as dehydrating agent for alcohol
 (a) H_2SO_4 (b) Al_2O_3
 (c) H_3PO_4 (d) All of these
- (47) Diethyl ether can be converted to alcohol by heating with:
 (a) HI (b) NaOH
 (c) Water (d) KMnO_4
- (48) The compound that does not react with sodium is
 (a) $(\text{C}_2\text{H}_5)_2\text{O}$ (b) CH_3COOH
 (c) $\text{CH}_3\text{CHOHCH}_3$ (d) $\text{C}_2\text{H}_5\text{OH}$
- (49) Which is an intermediate when alcohol is treated with Na metal and R - X?
 (a) Ether (b) A ketone
 (c) Alkoxides (d) An arene
- (50) Which of the following is the hybridization of oxygen in ethers?
 (a) sp^2 (b) sp
 (c) dsp^2 (d) sp^3

ANSWER KEY >>>

1	c	11	d	21	c	31	e	41	c
2	b	12	b	22	d	32	b	42	b
3	c	13	a	23	c	33	d	43	c
4	d	14	b	24	c	34	e	44	d
5	c	15	d	25	d	35	c	45	b
6	d	16	c	26	a	36	d	46	d
7	d	17	a	27	e	37	a	47	a
8	c	18	c	28	d	38	a	48	a
9	d	19	b	29	a	39	d	49	c
10	d	20	c	30	a	40	a	50	d