Alcohols, Phenols and Ethers

toppr

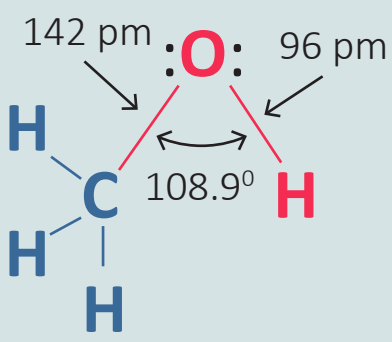
Part - 1

Functional Group- OH
Suffix to be used - ol
Homologous series-

- Methanol (CH_3OH)
- Ethanol (C_2H_5OH)
- Propanol (C_3H_7OH)
- Butanol (C_4H_9OH)
- Pentanol ($C_5H_{11}OH$) and so on

Alcohol

Structure



Methanol

Classification

C_2H_5OH

Monohydric alcohols

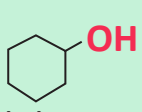
Compounds containing C_{sp^3} -OH bond	Compounds containing C_{sp^2} -OH bond
* Primary, secondary and tertiary alcohols * Allylic alcohols * Benzylic alcohols	* Vinylic alcohol

CH_2OH | CH_2OH — **Dihydric alcohols**

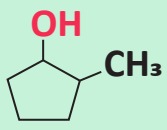
CH_2OH | $CHOH$ | CH_2OH — **Trihydric alcohols**

Nomenclature

Compound	Common name	IUPAC name
CH_3-OH	Methyl alcohol	Methanol
CH_3-CH_2-CH_2-OH	n-Propyl alcohol	Propan-1-ol
CH_3-CH(CH_3)-OH	Isopropyl alcohol	Propan-2-ol
CH_3-CH_2-CH_2-CH_2-OH	n-Butyl alcohol	Butan-1-ol
CH_3-CH_2-CH(OH)-CH_3	sec-Butyl alcohol	Butan-2-ol
CH_3-CH(CH_3)-CH_2-OH	Isobutyl alcohol	2-Methylpropan-1-ol
CH_3-C(CH_3)(CH_3)-OH	tert-Butyl alcohol	2-Methylpropan-2-ol
HO-H_2C-CH_2-OH	Ethylene glycol	Ethane-1,2-diol
CH_2(OH)-CH(OH)-CH_2(OH)	Glycerol	Propane -1,2,3-triol



Cyclohexanol



2-Methylcyclopentanol

Preparatory Methods

R-CH=CH_2 (Markownikoff addition)	H_2O/H^+ / H_2O_2
R-CH=CH_2 (Anti markownikoff addition)	B_2H_6 / H_2O_2/H_2O
R-C(=O)-Cl	N_2/H_2 / Na + C_2H_5OH
RCHO	H_2/Pd / $LiAlH_4$
R-COOH R-COO-R’	i) $LiAlH_4$ / ii) H_2O
For the preparation of - 1º alcohol – HCHO 2º alcohol – RCHO 3º alcohol – R-C(=O)-R	i) RMgX / ii) H_2O/H^+

R-OH

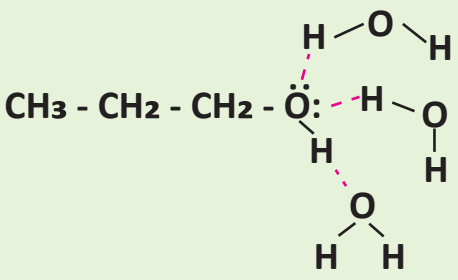
Physical Properties

1. Boiling Point-

* Higher than other organic compounds having equal molecular masses
* The boiling point decreases with an increase in branching in aliphatic carbon chains

2. Solubility-

* The hydroxyl group in alcohol is involved in the formation of intermolecular hydrogen bonding
* The solubility of alcohol in water decreases with the increase in the size of the alkyl group



Chemical Properties

Reactions involving cleavage of O-H bond

Reaction with Metals

$2R\text{-}O\text{-}H + 2Na \longrightarrow 2R\text{-}O\text{-}Na + H_2$ (Sodium alkoxide)

$6\ CH_3\text{-}C(CH_3)(CH_3)\text{-}OH + 2Al \longrightarrow 2(CH_3\text{-}C(CH_3)(CH_3)\text{-}O)_3Al + 3H_2$

tert-Butyl alcohol → Aluminium *tert*-butoxide

$R\text{-}CH_2OH > R_2CHOH >> R_3C\text{-}OH$

Primary > Secondary >> Tertiary

Acidity of Alcohols

Alcohols: Weaker acids than water

$R\text{-}\ddot{O}: + H\text{-}\ddot{O}\text{:-}H \longrightarrow R\text{-}O\text{-}H + :\ddot{O}H$

Base — Acid — Conjugate acid — Conjugate base

Acidity of Alcohols

Esterification

$R\text{-}C(=O)\text{-}OH + H\text{-}O\text{-}R \rightleftharpoons[H^+] R\text{-}C(=O)\text{-}O\text{-}R' + H\text{-}O\text{-}H$

Acid — Alcohol — Ester

Esterification

Reactions involving cleavage of C–O bond

Reaction with hydrogen halides

$ROH + HX \rightarrow R\text{-}X + H_2O$

Dehydrogenation

$RCH_2OH \xrightarrow[573K]{Cu} RCHO$

$R\text{-}CH(OH)\text{-}R' \xrightarrow[573K]{Cu} R\text{-}C(=O)\text{-}R'$

$R\text{-}C(CH_3)(CH_3)\text{-}OH \xrightarrow[573K]{Cu} R\text{-}C(CH_3)=CH_2$

Oxidation

$RCH_2OH \xrightarrow{Oxidation} R\text{-}CHO(=O) \longrightarrow R\text{-}COOH$ (Aldehyde → Carboxylic acid)

$RCH_2OH \xrightarrow{CrO_3} RCHO$

$CH_3\text{-}CH=CH\text{-}CH_2OH \xrightarrow{PCC} CH_3\text{-}CH=CH\text{-}CHO$

$R\text{-}CH(OH)\text{-}R' \xrightarrow{CrO_3} R\text{-}C(=O)\text{-}R'$

Sec- alcohol → Ketone

Reaction with phosphorus trihalides

$3CH_3\text{-}CH_2\text{-}CH_2\text{-}OH + PCl_3 \rightarrow 3CH_3\text{-}CH_2\text{-}CH_2\text{-}Cl + H_3PO_3$

Dehydration

$C_2H_5OH \xrightarrow[443K]{H_2SO_4} CH_2=CH_2 + H_2O$

$CH_3CH(OH)CH_3 \xrightarrow[440K]{85\%H_3PO_4} CH_3\text{-}CH=CH_2 + H_2O$

$CH_3\text{-}C(CH_3)(OH)\text{-}CH_3 \xrightarrow[358K]{20\%H_3PO_4} CH_3\text{-}C(=CH_2)\text{-}CH_3 + H_2O$

The relative ease of dehydration of alcohols follows the following order:

Tertiary > Secondary > Primary

Some Commercially Important Alcohols

Methanol

Preparation

$CO + 2H_2 \xrightarrow[200\text{-}300\ atm,\ 573\text{-}673\ K]{ZnO\text{-}Cr_2O_3} CH_3OH$

Properties

* Methanol is a colourless liquid and boils at 337 K
* It is highly poisonous in nature

Ethanol

Preparation

$C_{12}H_{22}O_{11} + H_2O \xrightarrow{Invertase} C_6H_{12}O_6 + C_6H_{12}O_6$ (Glucose, Fructose)

$C_6H_{12}O_6 \xrightarrow{Zymase} 2C_2H_5OH + 2CO_2$

Properties

* Ethanol is a colourless liquid with boiling point 351 K
* It is used as a solvent in paint industry and in the preparation of a number of carbon compounds

Alcohols, Phenols and Ethers

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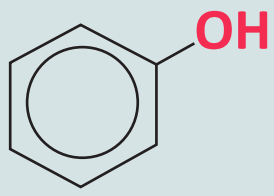
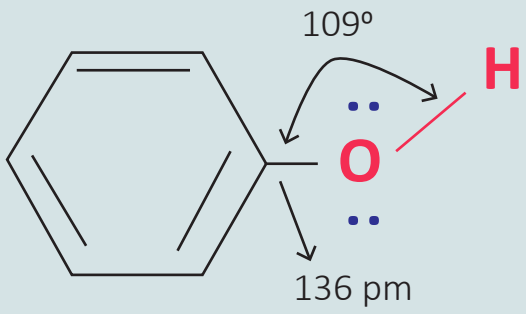
Part - 2

Phenol

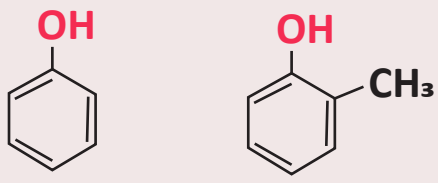
It is a white crystalline compound that has a distinctive odour



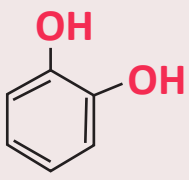
Structure



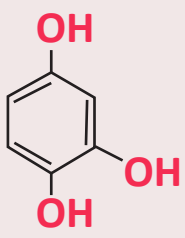
Classification



Monohydric Phenol

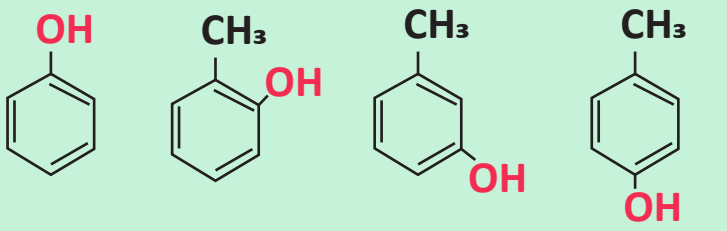


Dihydric Phenol



Trihydric Phenol

Nomenclature

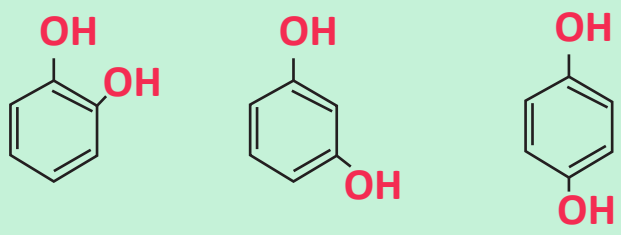


Phenol
Phenol

o-Cresol
2-Methylphenol

m-Cresol
3-Methylphenol

p-Cresol
4-Methylphenol



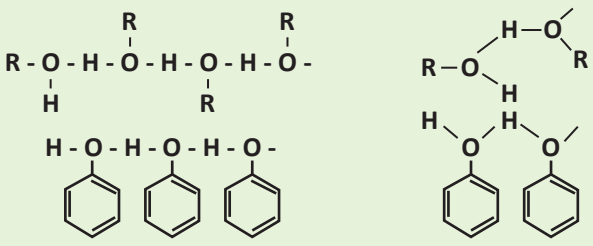
Catechol
Benzene-1,2-diol

Hydroquinone or quinol
Benzene-1,4-diol

Physical Properties

1. Boiling Point-

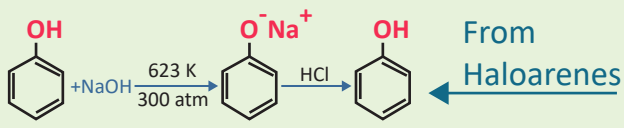
* Phenols have higher boiling points in comparison to other organic compounds having equal molecular masses

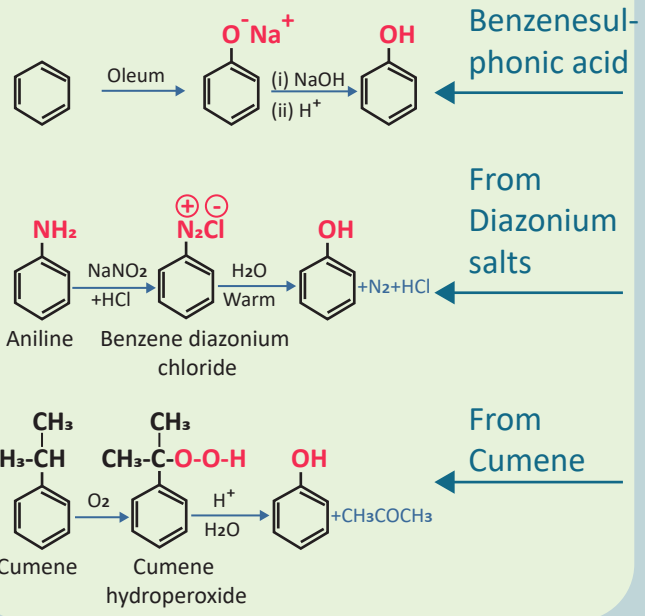


2. Solubility-

* The hydroxyl groups are responsible for the solubility of phenol in water
* The solubility of phenol decreases with the increase in the size of the aryl group

Preparation



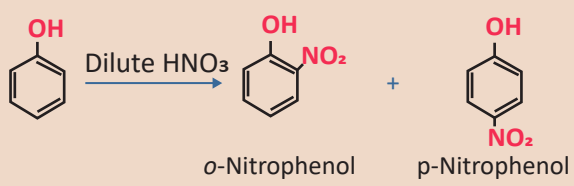


Phenols

Chemical Properties

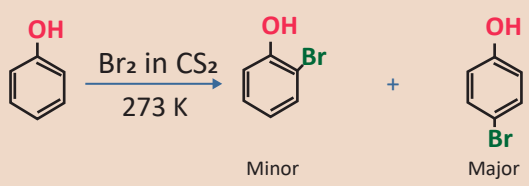
Electrophilic aromatic substitution

1) Nitration



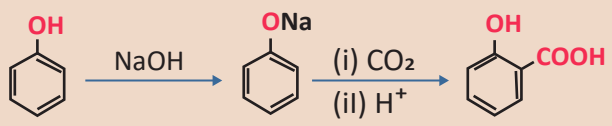
o-Nitrophenol
p-Nitrophenol

2) Halogenation



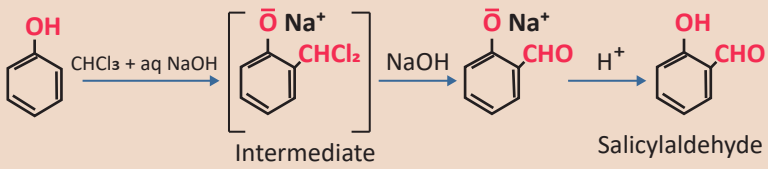
Minor
Major

Kolbe's reaction



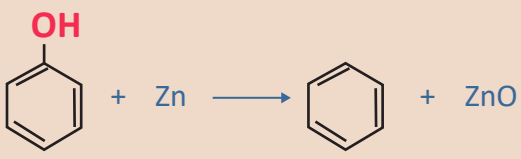
2-Hydroxybenzoic acid
(salicylic acid)

Reimer-Tiemann Reaction

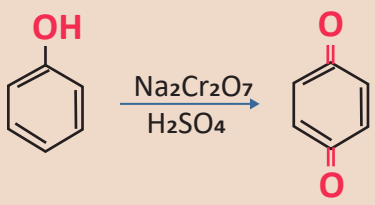


Intermediate
Salicylaldehyde

Reaction of Phenol with zinc dust



Oxidation



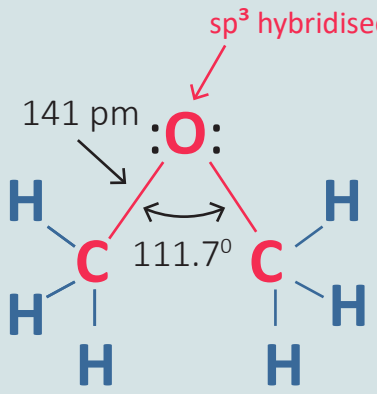
benzoquinne

Alcohols, Phenols and Ethers

Part - 3

Ether

Structure

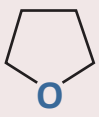


Methoxymethane

Classification

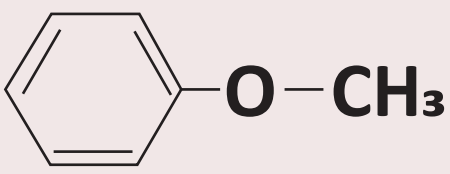
$CH_3\ CH_2$ - O - $CH_2\ CH_3$

diethyl ether



tetrahydrofuran

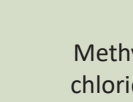
Symmetrical Ethers



methyl phenyl ether

Unsymmetrical Ethers

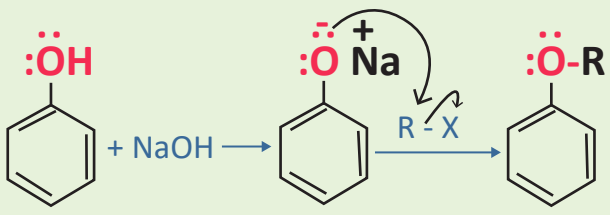
Nomenclature

Compound	Common name	IUPAC name
CH_3OCH_3	Dimethyl ether	Methoxymethane
$C_2H_5OC_2H_5$	Diethyl ether	Ethoxyethane
$CH_3OCH_2CH_2CH_3$	Methyl n-propyl ether	1-Methoxypropane
$C_6H_5OCH_3$	Methyl phenyl ether (Anisole)	Methoxybenzene (Anisole)
$C_6H_5OCH_2CH_3$	Ethyl phenyl ether (Phenetole)	Ehoxybenzene
$C_6H_5O(CH_2)_6$-CH_3	Heptyl phenyl ether	1-Phenoxyheptane
CH_3O-CH-CH_3 (CH_3)	Methyl isopropyl ether	2-Methoxypropane
C_6H_5-O-CH_2-CH_2-CH-CH_3 (CH_3)	Phenyl isopentyl ether	3-Methylbutoxybenzene
CH_3-O-CH_2-CH_2-OCH_3		1,2-Dimethoxyethane
		2-Ethoxy- -1,1-dimethylcyclohexane

Preparation

1. By dehydration of alcohol

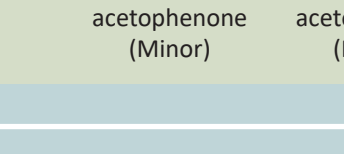
2. Williamson synthesis



Physical Properties

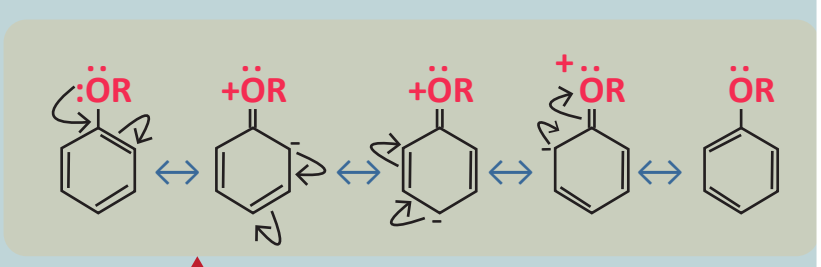
1. Miscibility

Miscibility with water resembles those of alcohols of the same molecular mass



2. Boiling Points

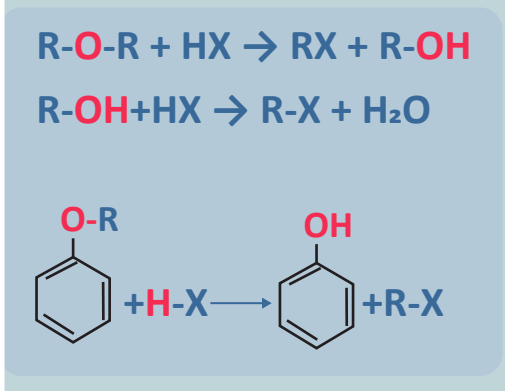
* Lower than alcohols
* This is due to the presence of hydrogen bonding in alcohols which is absent in ethers

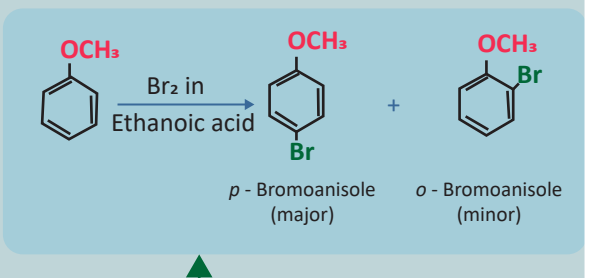


Electrophilic substitution

Chemical Properties

Cleavage of C–O bond in ethers





Halogenation

Friedel-Crafts reaction

Nitration