ALCOHOLS, PHENOLS AND ETHERS

ALCOHOLS

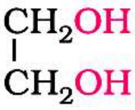
- Alcohols are compounds containing the hydroxyl group attached to the alkyl group.
- These are regarded as hydroxyl derivatives of hydrocarbons.
- Alcohols are represented by the general formula $R—OH$.
- Eg:CH_3OH, C_2H_5OH etc

CLASSIFICATION OF ALCOHOLS

- Alcohols are classified further as monohydric, dihydric and trihydric alcohols, according to the presence of 1, 2 or 3 hydroxyl groups in their molecules.

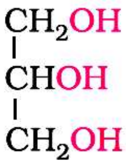
C_2H_5OH

Monohydric



$$\begin{array}{c} CH_2OH \\ | \\ CH_2OH \end{array}$$

Dihydric



$$\begin{array}{c} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array}$$

Trihydric

CLASSIFICATION OF MONOHYDRIC ALCOHOLS

- Monohydric alcohols are further classified as 1^0, 2^0 and 3^0 alcohols depending on whether, the hydroxyl group is attached to a primary, secondary or a tertiary carbon atom.

1. PRIMARY ALCOHOLS (1^0)

- It contains one or no alkyl groups on the carbon bonded to –OH group.
- It is represented by the general formula $R—CH_2OH$.

2. SECONDARY ALCOHOLS (2^0)

- It contains two alkyl groups on the carbon bonded to —OH group.
- It is represented by the general formula $R_2—CHOH$.

3. TERTIARY ALCOHOLS (3^0)

- It contains three alkyl groups on the carbon bonded to —OH group.
- It is represented by the general formula $R_3—COH$.

CLASSIFICATION BASED ON HYBRIDISATION

- Monohydric alcohols may be further classified according to the hybridization of the carbon atom to which the hydroxyl group is attached.

1. COMPOUNDS CONTAINING $C_{sp3}—OH$

- In these types of alcohols, the —OH group is attached to an sp^3 hybridised carbon atom of the alkyl group.
- Eg: $R—CH_2OH$, $R_2—CHOH$, $R_3—COH$.

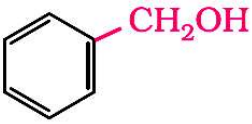
A. ALLYLIC ALCOHOLS

- In these types of alcohols, the —OH group is attached to an sp^3 hybridised carbon atom next to the C—C double bond. i.e. to an allylic carbon.

- Eg: $CH_2=CH-CH_2OH$

B. BENZYLIC ALCOHOLS

- In these types of alcohols, the —OH group is attached to an sp^3 hybridised carbon atom next to an aromatic ring.

Eg: 

1. COMPOUNDS CONTAINING C_{sp2}—OH

- In these types of alcohols, the —OH group is attached to an sp^2 hybridised carbon atom of the alkyl group.

A. VINYLIC ALCOHOLS

- In these types of alcohols, the —OH group is bonded to a c=C double bond. i.e., to a vinylic carbon.
- Eg: $CH_2=CH—OH$

NOMENCLATURE OF ALCOHOLS

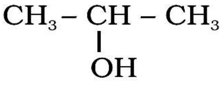
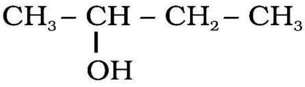
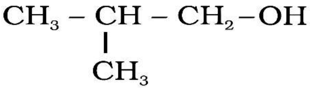
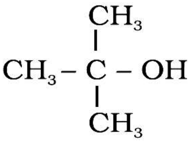
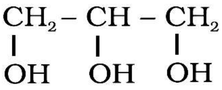
COMMON SYSTEM

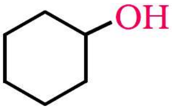
- Alcohols are named as alkyl alcohols.

IUPAC SYSTEM

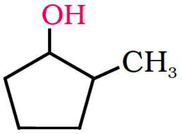
- Alcohols are named by replacing 'e' in the name of the parent alkane by 'ol'.
- The position of the 'C' atom carrying the —OH group is specified by a number.
- Cyclic alcohols are named using the prefix 'cyclo' and considering the —OH group attached to carbon-1.

EXAMPLES

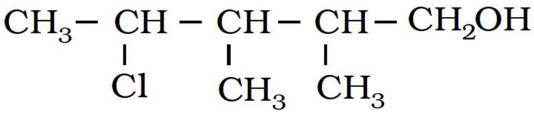
Compound	Common name	IUPAC name
CH_3-OH	Methyl alcohol	Methanol
$CH_3-CH_2-CH_2-OH$	*n*-Propyl alcohol	Propan-1-ol
 $CH_3-\underset{\underset{OH}{\vert}}{CH}-CH_3$	Isopropyl alcohol	Propan-2-ol
$CH_3-CH_2-CH_2-CH_2-OH$	*n*-Butyl alcohol	Butan-1-ol
 $CH_3-\underset{\underset{OH}{\vert}}{CH}-CH_2-CH_3$	*sec*-Butyl alcohol	Butan-2-ol
 $CH_3-\underset{\underset{CH_3}{\vert}}{CH}-CH_2-OH$	Isobutyl alcohol	2-Methylpropan-1-ol
 $CH_3-\overset{\overset{CH_3}{\vert}}{\underset{\underset{CH_3}{\vert}}{C}}-OH$	*tert*-Butyl alcohol	2-Methylpropan-2-ol
$HO-H_2C-CH_2-OH$	Ethylene glycol	Ethane-1,2-diol
 $\underset{\underset{OH}{\vert}}{CH_2}-\underset{\underset{OH}{\vert}}{CH}-\underset{\underset{OH}{\vert}}{CH_2}$	Glycerol	Propane -1, 2, 3-triol



Cyclohexanol

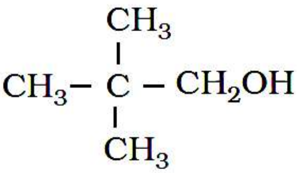


2-Methylcyclopentanol



$CH_3-\underset{Cl}{CH}-\underset{CH_3}{CH}-\underset{CH_3}{CH}-CH_2OH$

4-Chloro-2,3-dimethylpentan-1-ol



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

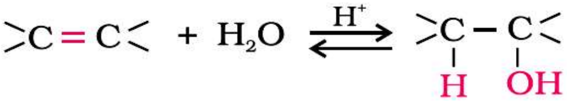
2,2-Dimethylpropan-1-ol

PREPARATION OF ALCOHOLS

1. FROM ALKENES

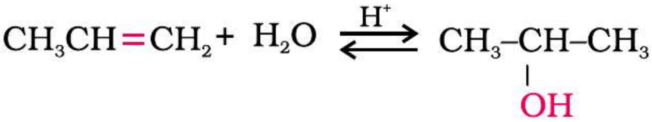
BY ACID CATALYSED HYDRATION

- Alkenes react with water in the presence of acid as catalyst to form alcohols.



$$>C=C< + H_2O \overset{H^+}{\rightleftharpoons} >\underset{H}{C}-\underset{OH}{C}<$$

- In the case of unsymmetrical alkenes, the addition reaction takes place in accordance with Markovnikov's rule.

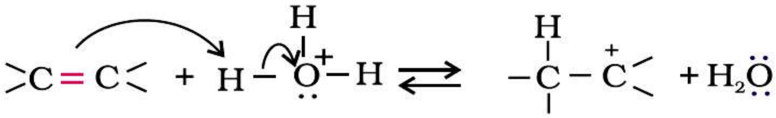


$$CH_3CH=CH_2 + H_2O \overset{H^+}{\rightleftharpoons} CH_3-\underset{OH}{CH}-CH_3$$

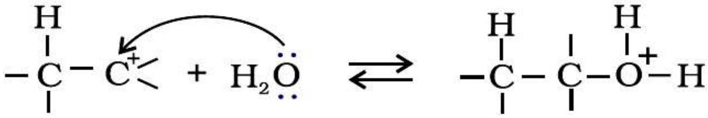
MECHANISM

STEP 1: Protonation of alkene to form a carbocation by electrophilic attack of H_3O^+

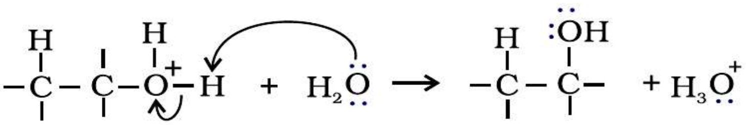
$$H_2O + H^+ \rightarrow H_3O^+$$



STEP 2: Nucleophilic attack of water on carbocation.



STEP 3: Deprotonation to form an alcohol

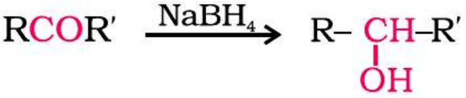


2. FROM CARBONYL COMPOUNDS

A. BY THE REDUCTION OF ALDEHYDES AND KETONES

- Aldehydes and ketones are reduced to 1^0 and 2^0 alcohols respectively by reducing agents such as $LiAlH_4$, $NaBH_4$ or H_2 gas in the presence of Ni or Pt as catalyst.

$$RCHO + H_2 \xrightarrow{Pd} RCH_2OH$$



$$RCOR' \xrightarrow{NaBH_4} R-\underset{\displaystyle OH}{\underset{|}{CH}}-R'$$

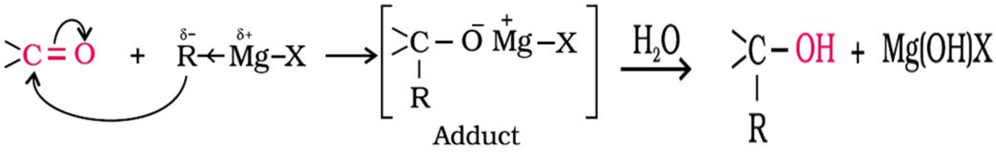
B. BY THE REDUCTION OF CARBOXYLIC ACIDS

- Carboxylic acids are reduced to primary alcohols by treating with strong reducing agents like $LiAlH_4$, $NaBH_4$.

$$RCOOH \xrightarrow[\text{(ii) } H_2O]{\text{(i) } LiAlH_4} RCH_2OH$$

3. FROM GRIGNARD REAGENT

- Aldehydes and ketones are converted to alcohols by the reaction with Grignard reagent in the presence of ether.
- **MECHANISM**
- **STEP 1:** Nucleophilic addition of Grignard reagent to carbonyl compounds to form an adduct.
- **STEP 2:** Hydrolysis of the adduct gives an alcohol.



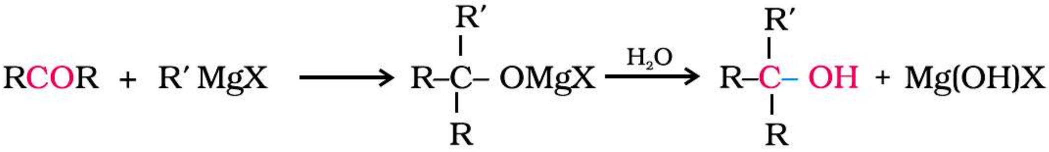
- Formaldehyde gives a primary alcohol

$$HCHO + RMgX \rightarrow RCH_2OMgX \xrightarrow{H_2O} RCH_2OH + Mg(OH)X$$

- Aldehyde other than formaldehyde gives secondary alcohol.

$$RCHO + R'MgX \xrightarrow{H_2O} R-\overset{\displaystyle R'}{\overset{|}{CH}}-OMgX \xrightarrow{H_2O} R-\overset{\displaystyle R'}{\overset{|}{CH}}-OH + Mg(OH)X$$

- Ketones gives tertiary alcohol



$$RCOR + R'MgX \longrightarrow R-\underset{\displaystyle R}{\underset{|}{\overset{\displaystyle R'}{\overset{|}{C}}}}-OMgX \xrightarrow{H_2O} R-\underset{\displaystyle R}{\underset{|}{\overset{\displaystyle R'}{\overset{|}{C}}}}-OH + Mg(OH)X$$

PHYSICAL PROPERTIES OF ALCOHOLS

- The lower alcohols are colourless liquids with a characteristic smell and burning taste.
- The higher members are colourles, odourless, wax like solids.
- The lower alcohols are readily soluble in water.
- The solubility decreases with increase in molar mass.
- The higher solubility of lower alcohols in water is due to the formation of hydrogen bond with water molecule.

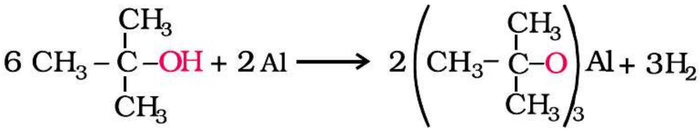
CHEMICAL PROPERTIES OF ALCOHOLS

1. REACTIONS INVOLVING THE CLEAVAGE OF O—H BOND

A. REACTION WITH METALS

- Alcohols react with metals like Na, K, Al etc to form metal alkoxide with the liberation of Hydrogen.

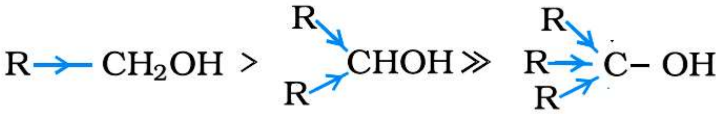
$$2R{-}O{-}H + 2Na \longrightarrow 2R{-}O{-}Na + H_2$$



$$6\ CH_3-\underset{CH_3}{\overset{CH_3}{C}}-OH + 2\,Al \longrightarrow 2\left(CH_3-\underset{CH_3}{\overset{CH_3}{C}}-O\right)_3 Al + 3H_2$$

B. ACIDITY OF ALCOHOLS

- The acidic character of alcohols is due to the polar nature of O—H bond.
- An electron releasing group increases the electron density on oxygen.
- It leads to the decrease in the polarity of O—H bond.
- This decreases the acid strength of alcohols.
- The acid strength of alcohols decreases in the following order.



$$R \rightarrow CH_2OH > \begin{matrix} R \searrow \\ R \nearrow \end{matrix} CHOH \gg \begin{matrix} R \searrow \\ R \rightarrow \\ R \nearrow \end{matrix} C-OH$$

C. ESTERIFICATION

- Alcohols react with organic acids in the presence of Conc. H_2SO_4 or dry HCl to form esters.

$$RCOOH + HOR \xrightleftharpoons[Conc.H_2SO_4]{} RCOOR + H_2O$$

$$CH_3COOH + C_2H_5OH \xrightleftharpoons[Conc.H_2SO_4]{} CH_3\text{-}COO\text{-}C_2H_5 + H_2O$$

2. REACTIONS INVOLVING THE CLEAVAGE OF CARBON—OXYGEN BOND

A. REACTION WITH HYDROGEN HALIDES

- Alcohols react with hydrogen halides in the presence of anhy. $ZnCl_2$ to form alkyl halides and water.

$$ROH + HX \xrightarrow{anhy.ZnCl_2} RX + H_2O$$

$$C_2H_5OH + HX \xrightarrow{anhy.ZnCl_2} C_2H_5Cl + H_2O$$

B. REACTION WITH PHOSPHOROUS HALIDES

- Alcohols react with phosphorous halides to form alkyl halides.

$$C_2H_5OH + PCl_5 \longrightarrow C_2H_5Cl + HCl + POCl_3$$

$$3C_2H_5OH + PBr_5 \longrightarrow 3C_2H_5Br + H_3PO_3$$

C. REACTION WITH THIONYL CHLORIDE

- Alcohols react with thionyl chloride in the presence of pyridine to form alkyl chlorides.

$$ROH + SOCl_2 \xrightarrow{\text{Pyridine}} RCl + HCl + SO_2$$

$$C_2H_5OH + SOCl_2 \xrightarrow{\text{Pyridine}} C_2H_5Cl + HCl + SO_2$$

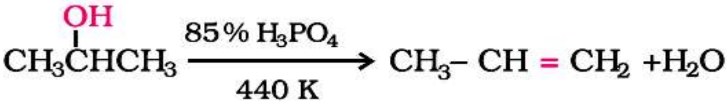
3. REACTIONS INVOLVING BOTH ALKYL AND HYDROXYL GROUPS

A. ACIDIC DEHYDRATION

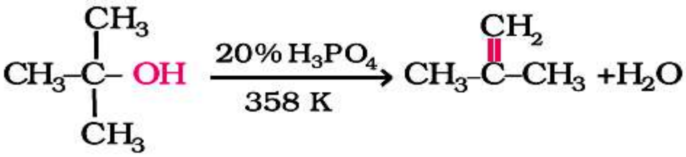
- On heating with Conc. H_2SO4 or H_3PO_4 at 443 K, alcohols get dehydrated to form alkenes.

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

- Secondary and tertiary alcohols are dehydrated under milder conditions.



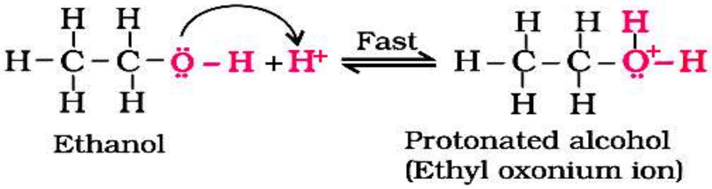
$$CH_3\overset{OH}{C}HCH_3 \xrightarrow[440\text{ K}]{85\%\ H_3PO_4} CH_3-CH=CH_2 + H_2O$$



$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-OH \xrightarrow[358\text{ K}]{20\%\ H_3PO_4} CH_3-\overset{CH_2}{\overset{\|}{C}}-CH_3 + H_2O$$

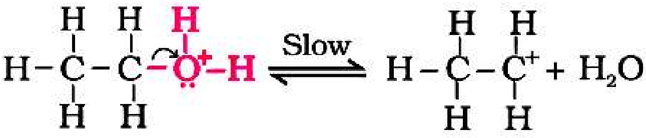
MECHANISM

- **STEP 1: Formation of protonated alcohols.**

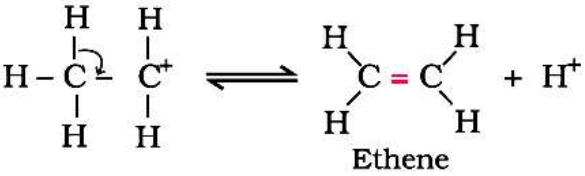


- **STEP 2: Formation of carbocation**

It is the slowest step and hence the rate determining step of the reaction.

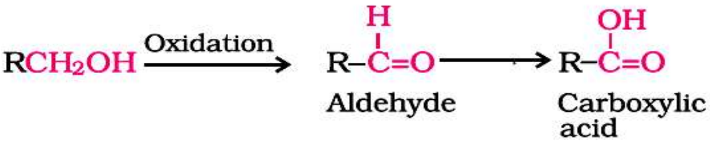


- **STEP 3: Formation of ethane by the elimination of a proton**



B. OXIDATION

- The reagents such as aqueous, alkaline or acidified $KMnO_4$, acidified $K_2Cr_2O_7$, HNO_3, chromic acid etc may be used for the oxidation of alcohols.



$$RCH_2OH \xrightarrow{\text{Oxidation}} R-\overset{H}{C}=O \longrightarrow R-\overset{OH}{C}=O$$

Aldehyde

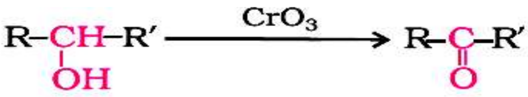
Carboxylic acid

- A 1^0 alcohol is easily oxidized to aldehydes which is further oxidized to a carboxylic acid.

$$RCH_2OH \xrightarrow{CrO_3} RCHO$$

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

- A 2^0 alcohol is easily oxidized to a ketone, which under strong conditions may be further oxidized to form a mixture of acids.



$$\underset{\underset{OH}{|}}{R-CH-R'} \xrightarrow{CrO_3} \underset{\underset{O}{\|}}{R-C-R'}$$

Sec- alcohol Ketone

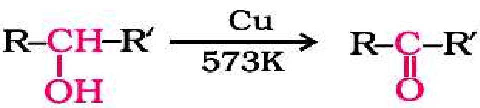
- A 3^0 alcohol cannot be easily oxidized when treated with strong conditions.
- They can be oxidized to ketones and then to acids.

C. DEHYDROGENATION

- Primary alcohols on dehydrogenation gives aldehyde.

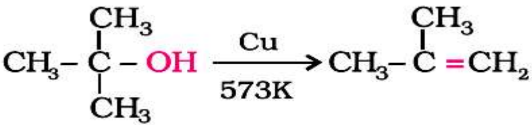
$$RCH_2OH \xrightarrow[573K]{Cu} RCHO$$

- Secondary alcohols are dehydrogenated to form ketones.



$$\underset{\underset{OH}{|}}{R-CH-R'} \xrightarrow[573K]{Cu} \underset{\underset{O}{\|}}{R-C-R'}$$

- 3^0 alcohols on heating with reduced Cu undergo dehydration to form alkenes.



$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-OH \xrightarrow[573K]{Cu} CH_3-\overset{\overset{CH_3}{|}}{C}=CH_2$$

- **LUCAS TEST**
- An alcohol is heated with a mixture of conc. HCl and anhydrous $ZnCl_2$ known as Lucas Reagent.
- Alcohol is converted to an alkyl halide.
- The formation of alkyl halide is indicated by the appearance of cloudiness or turbidity in the reaction mixture.
- A 3^0 alcohol forms turbidity immediately.
- A 2^0 alcohol forms turbidity within five minutes.
- A 1^0 alcohol forms turbidity only upon heating.

SOME COMMERCIALLY IMPORTANT ALCOHOLS

1. METHANOL (CH_3OH)

- Methanol is a colourless liquid with boiling point 337 K.
- It is highly poisonous.
- It is also known as wood spirit because it was produced by the destructive distillation of wood.

MAUFACTURE OF METHANOL

- Prepared by passing a mixture of CO and H_2 over heated Cr_2O_3-ZnO catalyst at 673 K.

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

USES OF METHANOL

Methanol is used

- As a solvent
- As an automobile antifreeze
- For denaturing ethanol
- As an aviation fuel
- In the manufacture of formaldehyde.

2. ETHANOL (C_2H_5OH)

- Prepared industrially by the fermentation of starch or sugar.
- Fermentation is the slow decomposition of complex organic compounds in to simpler compounds by the action of biological catalyst known as enzyme.

PREPARATION OF ETHANOL FROM SUGAR SOLUTION [MOLASSES]

- Molasses is the mother liquor left after the crystallization of sugar from sugar solution.
- It contains about 50% non-crystallisable sugar.
- It is diluted to about 10% solution and yeast is added and kept for about 2-3 days.
- Yeast supplies the enzyme invertase, maltase and zymase.
- The enzyme invertase hydrolyses sucrose to glucose and fructose.
- The enzyme zymase converts glucose and fructose to ethanol and CO_2.

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

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

- The fermented liquid contains about 8-10% ethanol is called **wash.**
- On fractional distillation, it gives rectified spirit which contains 95.6% ethanol.
- Further dehydration with quick lime and distillation with Na or Ca gives 99.8% alcohol.

RECTIFIED SPIRIT

- The fractional distillation of wash gives a constant boiling azeotropic mixture which contains 95.6% ethanol and 4.4% water.

ABSOLUTE ALCOHOL

- Ethanol free from water and other impurities. i.e., 100% pure ethanol is known as absolute alcohol.

PROOF SPIRIT

- 57.1% ethanol by volume is known as proof spirit.

POWER ALCOHOL

- A mixture of 20% ethanol and 80% gasoline used for the purpose of power generation in internal combustion engines is called power alcohol.

METHYLATED SPIRIT OR DENATURED ALCOHOL

- Alcohol for industrial use is made unfit for drinking by adding poisonous materials like methanol, pyridine etc.
- This process is called denaturing and the alcohol so obtained is called denatured spirit.
- Ethanol denatured with methanol is called methylated spirit.

USES OF ETHANOL

Ethanol is used

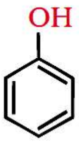
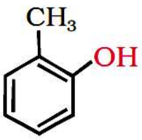
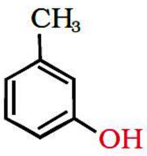
- As a beverage
- As a solvent
- As an antifreeze
- As explosives
- For the manufacture of dyes, detergents etc.

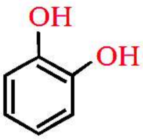
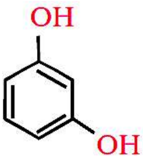
PHENOLS

- Phenols are hydroxy derivatives of aromatic hydrocarbons.
- Hydroxyl group is directly linked to the carbon atom of the aromatic ring.

NOMENCLATURE OF PHENOLS

- The parent member of the family is phenol
- Other members are regarded as derivatives of phenol

				
Common name	Phenol	*o*-Cresol	*m*-Cresol	*p*-Cresol
IUPAC name	Phenol	2-Methylphenol	3-Methylphenol	4-Methylphenol

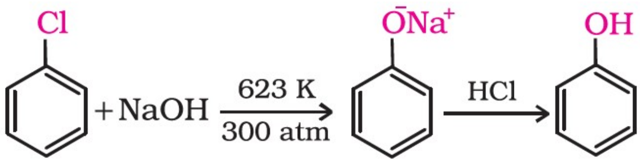
			
Common name	Catechol	Resorcinol	Hydroquinone or quinol
IUPAC name	Benzene-1,2-diol	Benzene-1,3-diol	Benzene-1,4-diol

PREPARATION OF PHENOLS

1. FROM HALOARENES

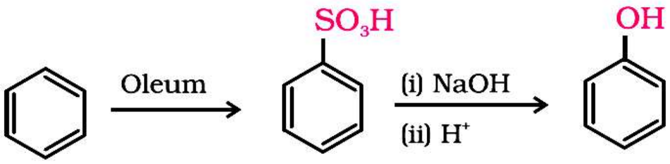
- Chlorobenzene is fused with NaOH at 623 K and 320 atm pressure to form sodium phenoxide.

- Sodium phenoxide on acidification gives phenol.



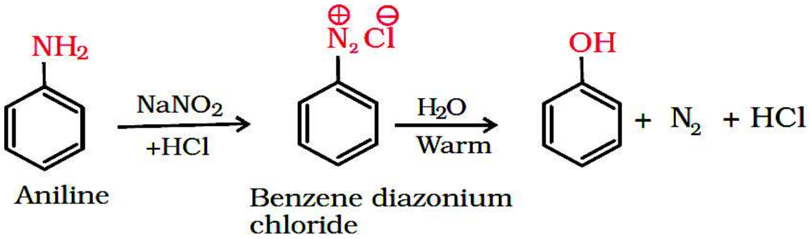
2. FROM BENZENE SULPHONIC ACID

- Benzene is sulphonated with oleum to form benzene sulphonic acid.
- Benzene sulphonic acid on heating with molten sodium hydroxide gives sodium phenoxide.
- This on acidification gives phenol.



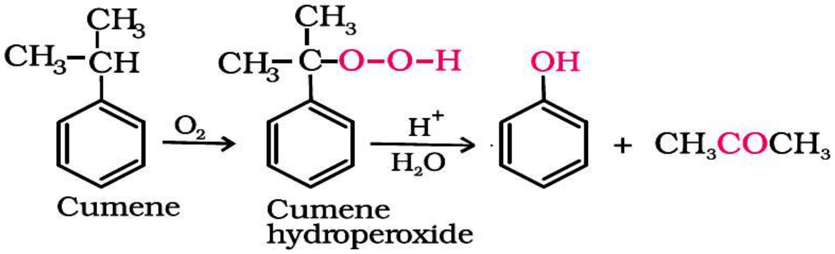
3. FROM DIAZONIUM SALTS

- Aniline reacts with nitrous acid at 273-278 K to form diazonium salt.
- This on warming with water or by treating with dilute acids gives phenols.



4. FROM CUMENES

- Cumene is oxidized in the presence of air to form cumene hydroperoxide.
- Cumene hydroperoxide on treatment with dil. H_2SO_4 gives phenol and propanone.



PHYSICAL PROPERTIES

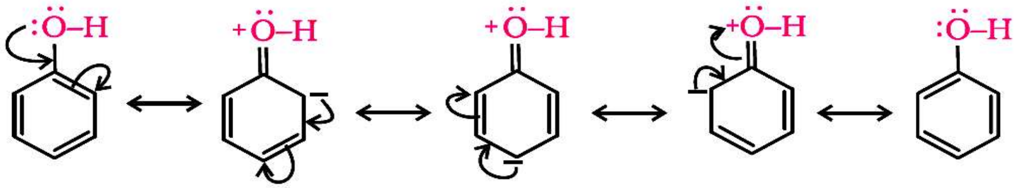
- Phenols are colourless crystalline solids or liquids.
- They have characteristic phenolic odours.
- They are sparingly soluble in water but soluble in alcohols, ethers and also in NaOH.
- The boiling point of phenols is high due to the presence of intermolecular hydrogen bonding which causes molecular association.

CHEMICAL PROPERTIES

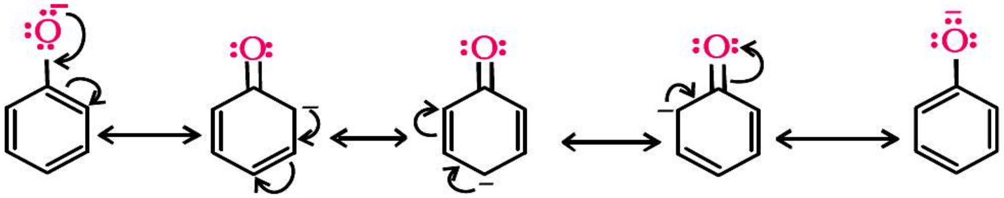
A. REACTIONS OF PHENOLIC GROUP

1. ACIDIC CHARACTER

- Phenols are weakly acidic in nature.
- It turns blue litmus to red.
- It reacts with alkalies to give salts.
- Phenols are more acidic than alcohols.
- The greater acidic character of phenols can be explained on the basis of resonance.

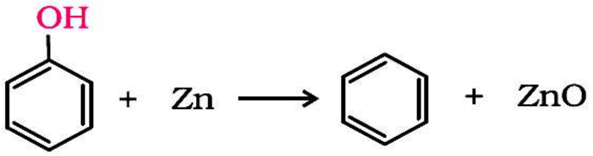


- Similarly, the phenoxide ion is resonance stabilized as follows.



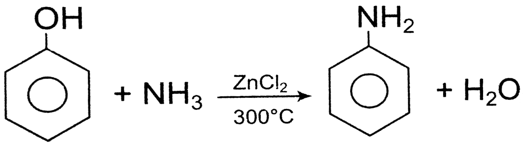
2. REACTION WITH ZINC DUST

- When phenol is heated with zinc dust, benzene is formed.



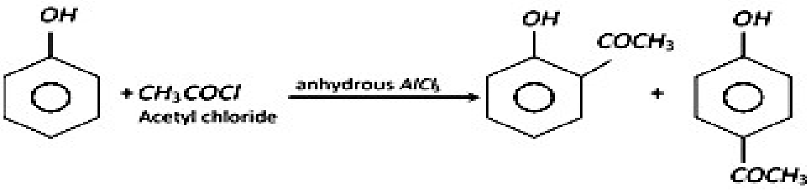
3. REACTION WITH AMMONIA

- Phenol reacts with ammonia in the presence of anhydrous $ZnCl_2$ gives aniline.



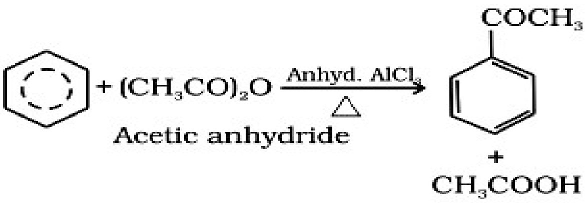
4. REACTION WITH ACID CHLORIDES

- Phenols on treating with acetyl chloride in presence of pyridine gives esters.



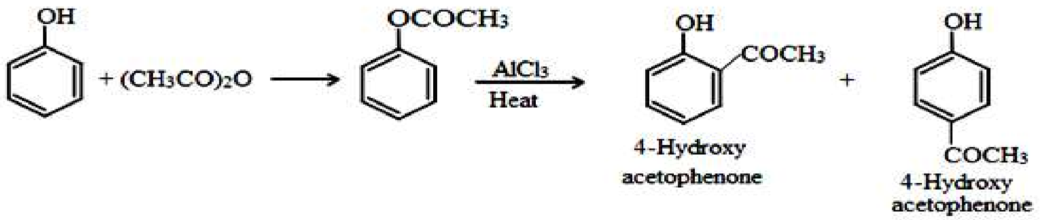
5. REACTION WITH ACID ANHYDRIDES

- Phenols on treating with acetic anhydride in presence of mineral acids gives esters.



FRIES REARRANGEMENT

- On heating with anhy. $AlCl_3$, phenyl acetate undergoes rearrangement in which the acyl group migrates from the phenolic oxygen to an ortho and para postions to form ortho and para ketones.



6. ACTION WITH BENZOYL CHLORIDE

- Phenol react with benzoyl chloride in the presence of aqueous NaOH to form phenyl benzoate.
- This reaction is called Schotten Baumann Reaction.

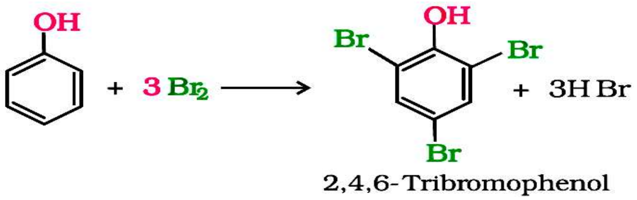
B. REACTIONS OF BENZENE RING

- Phenols undergo aromatic electrophilic substitution.
- —OH group is an activating group.
- It is ortho-para directing.
- Therefore, the incoming group goes to ortho and para position.

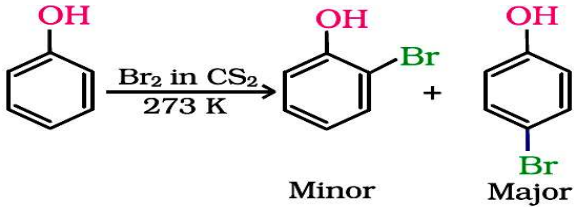
1. ELECTROPHILIC SUBSTITUTION

A. BROMINATION

- Phenol reacts with bromine water to form a white precipitate of 2,4,6-tribromo phenol.

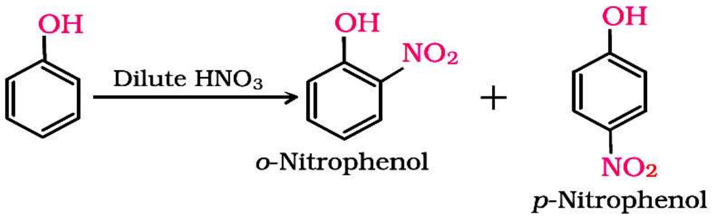


- When the reaction is carried out in CS_2 or CCl_4, a mixture of ortho and para bromo phenol is formed.

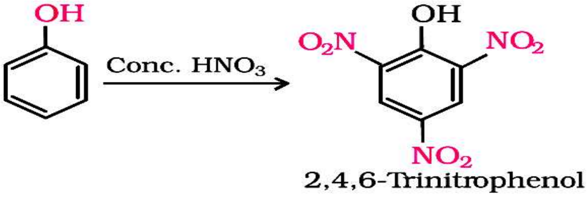


B. NITRATION

- Phenol reacts with dilute HNO3 at low temperature to form a mixture of ortho and para nitro phenols.



- Phenol reacts with conc. HNO_3 in the presence of Conc. H_2SO_4 to form 2,4,6-trinitrophenol

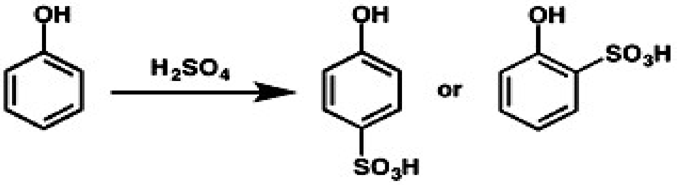


C. ALKYLATION

- On heating with alkyl halides in presence of anhydrous $AlCl_3$, phenols give cresols.
- The reaction is known as Friedel Crafts Reaction.

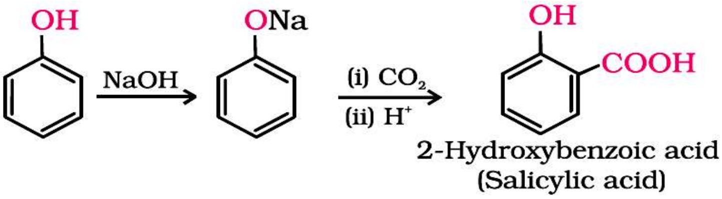
D. SULPHONATION

- When phenol is treated with conc. H_2SO_4, a mixture of ortho and para phenol sulphonic acid is formed.



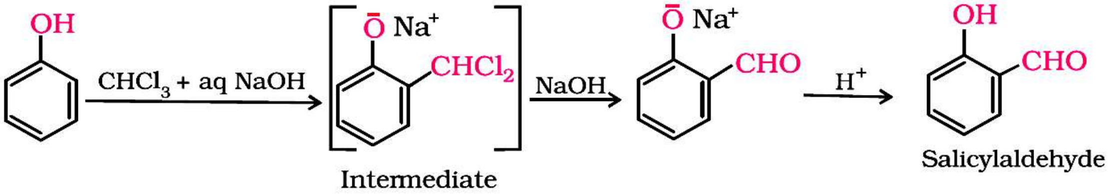
2. KOLBES REACTION

- Phenol reacts with CO_2 at about 400K under pressure to form salicylic acid.



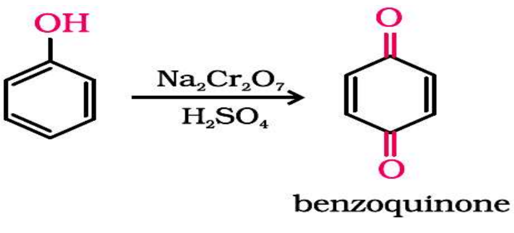
3. REIMER TIEMANN REACTION

- When phenol is treated with chloroform in the presence of sodium hydroxide at 340K, a —CHO group is introduced at ortho position of benzene ring to form ortho Hydroxybenzaldehyde or Salicylaldehyde.



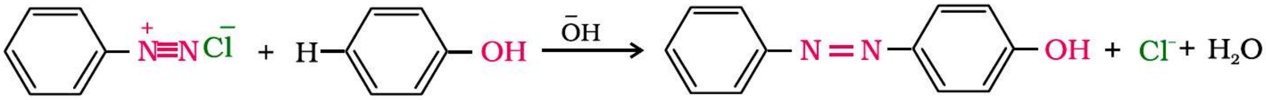
4. OXIDATION

- Phenol on oxidation with chromic acid produces a conjugated diketone known as benzoquinone.



5. COUPLING REACTION

- In alkaline medium, an ice cold solution of phenol combines with an ice cold solution of benzene diazonium chloride to form azo dye.



p-Hydroxyazobenzene (orange dye)

ETHERS

- Ethers are compounds with the general formula R—O—R′.
- R and R′ are alkyl or aryl groups.
- If R and R′ are the same, the ether is said to be a simple ether.
- If R and R′ are different, the ethers is said to be a mixed ether.

NOMENCLATURE

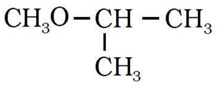
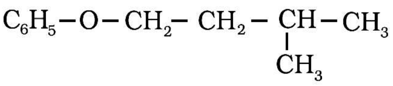
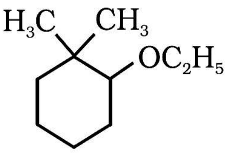
COMMON SYSTEM

- Ethers are named by prefixing the names of the alkyl groups before the word ether.

IUPAC SYSTEM

- Ethers are named as alkoxy derivatives of alkane or arene.
- In the case of mixed ethers, the larger of the two alkyl group is considered as the parent hydrocarbon.

EXAMPLES

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)	Ethoxybenzene
$C_6H_5O(CH_2)_6-CH_3$	Heptyl phenyl ether	1-Phenoxyheptane
 $CH_3O-\underset{\underset{\displaystyle CH_3}{\vert}}{CH}-CH_3$	Methyl isopropyl ether	2-Methoxypropane
 $C_6H_5-O-CH_2-CH_2-\underset{\underset{\displaystyle CH_3}{\vert}}{CH}-CH_3$	Phenyl isopentyl ether	3- Methylbutoxybenzene
$CH_3-O-CH_2-CH_2-OCH_3$	—	1,2-Dimethoxyethane
	—	2-Ethoxy- -1,1-dimethylcyclohexane

PREPARATION OF ETHERS

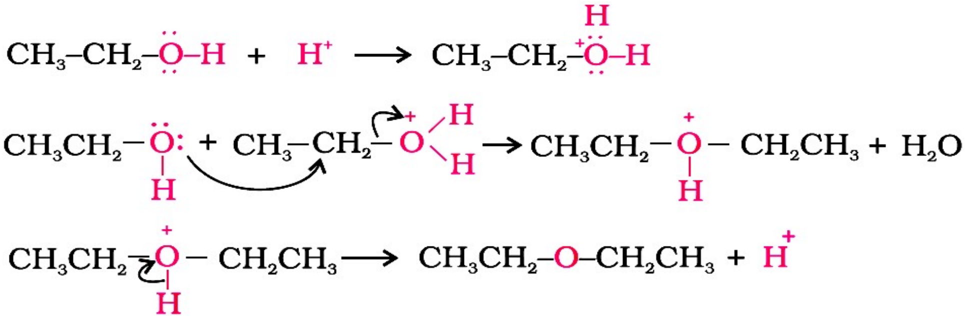
1. BY THE DEHYDRATION OF ALCOHOLS

- Alcohols undergo dehydration when heated with Conc. H_2SO_4 at 413 K to form ethers.

$$2C_2H_5OH \xrightarrow[413\ K]{Conc.H_2SO_4} C_2H_5\text{-}O\text{-}C_2H_5 + H_2O$$

MECHANISM

- The formation of ether is a nucleophilic bimolecular reaction.
- It involves the attack of alcohol molecule on a protonated alcohol.



2. WILLIAMSONS ETHER SYNTHESIS

- An alkyl halide is treated with sodium alkoxide or sodium phenoxide to give ethers.
- This method can be used for the preparation of simple and mixed ethers.

$$R\text{–}X + R'\text{–}\overset{-}{\ddot{O}}\overset{+}{Na} \longrightarrow R\text{–}\ddot{O}\text{–}R' + Na\,X$$

$$2C_2H_5I + NaOC_2H_5 \longrightarrow C_2H_5\text{-}O\text{-}C_2H_5 + NaI$$

$$CH_3I + NaOC_6H_5 \longrightarrow CH_3\text{-}O\text{-}C_6H_5 + NaI$$

CHEMICAL PROERTIES

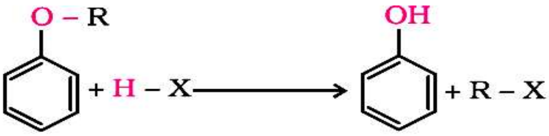
1. CLEAVAGE OF C—O BOND IN ETHERS

- Ethers are the lest reactive of the functional group.
- The cleavage of C—O bond in ethers takes place under drastic conditions with excess of hydrogen halides.
- The reaction of dialkyl ethers gives two alkyl halide molecules.

$$R\text{–}O\text{–}R + HX \longrightarrow RX + R\text{–}OH$$

$$R\text{–}OH + HX \longrightarrow R\text{–}X + H_2O$$

- Alkyl aryl ethers are cleaved at alkyl—oxygen bond due to the more stable aryl—oxygen bond.
- The reaction gives phenol and alkyl halides.



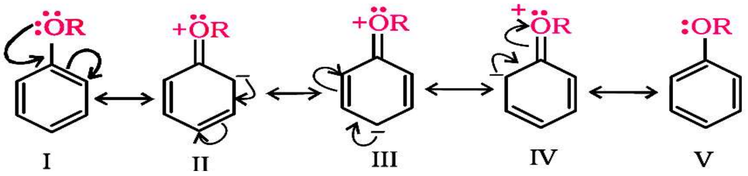
- Ethers with two different alkyl groups are also cleaved in the same manner.

$$R{-}O{-}R' + HX \longrightarrow R{-}X + R'{-}OH$$

The order of reactivity of hydrogen halides is HI > HBr > HCl

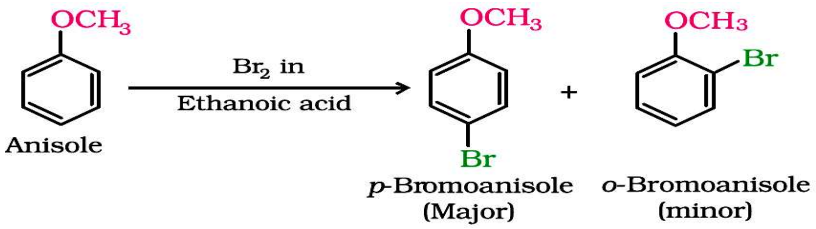
2. ELECTROPHILIC SUBSTITUTION REACTION

- The alkoxy group in ether is ortho para directing. It activates the aromatic ring towards electrophilic substitution in the same way as in phenol.



3. HALOGENATION

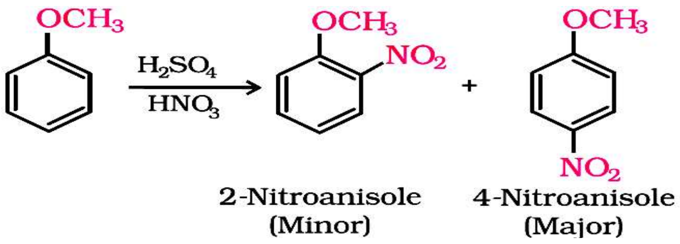
- Anisole undergoes bromination when treated with bromine in ethanoic acid to form ortho and para bromo anisole.



- The nitro group is introduced at ortho and para positions.

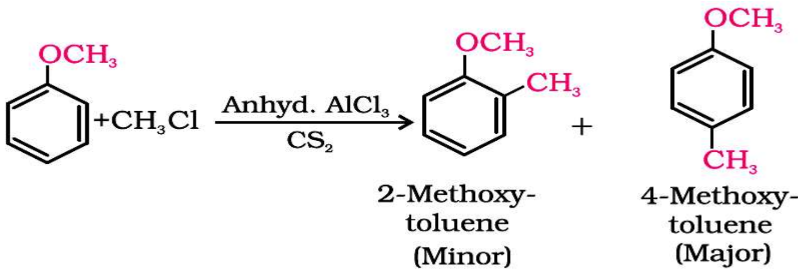
4. NITRATION

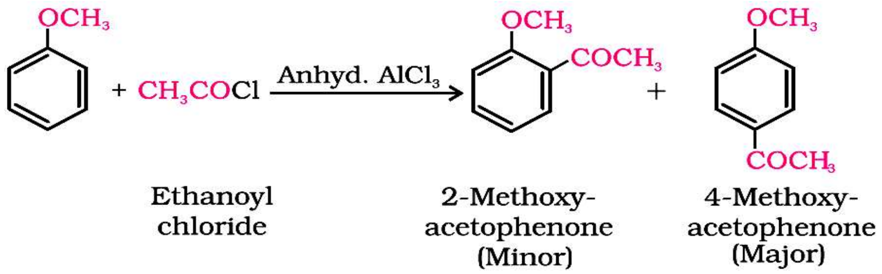
- Anisole reacts with a mixture of Conc. H_2SO_4 and Conc. HNO_3 to give a mixture of ortho and para nitro anisole.



5. FRIEDEL CRAFTS REACTION

- Anisole undergoes Friedel Crafts reaction by treating with an alkyl halide and aryl halide in the presence of anhydrous $AlCl_3$ as catalyst.





USES OF ETHER

Diethyl Ether is used

- as a general anesthetic in surgery.
- as a solvent in industry.