ALCOHOLS, PHENOLS AND ETHERS

Topic-1

Alcohols and Phenols: Methods of Preparation, Properties and Uses

Concepts Covered: *Classification of alcohol, General formula, Strucuture and nomenclature, Methods of preparation, Physical and chemical properties, Test for identification, Uses.*

Revision Notes

- **Alcohol:** When one hydrogen atom of alkane is replaced by —OH group, the compounds obtained are called alcohols having general formula $C_nH_{2n+1}OH$.
- **Classification of alcohols:**

(a) Based on number of hydroxyl(-OH) group

(i) Monohydric alcohols: the alcohols which contain one –OH group. CH_3OH, C_2H_5OH, etc.

(ii) Dihydric alcohols: The alcohols which contain two —OH groups , also called diols.

General formula = $C_nH_{2n}(OH)_2$.

e.g., $CHOH_2CHOH_2$

Ethane-1, 2-diol.

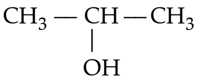
(iii) Trihydric alcohols: The alcohols which contain three hydroxyl (–OH) groups, also called triols. Their general formula is $C_nH_{2n-1}(OH)_3$. e.g.,

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

Propane-1,2,3-triol

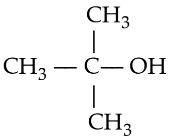
(b) Based on carbon atom attached to -OH group:

- **(i) Primary alcohols:** The alcohol in which –OH group is attached to primary (1°) carbon atom. e.g., CH_3OH, C_2H_5OH, etc.
- **(ii) Secondary alcohols:** The alcohol in which –OH group is attached to secondary (2°) carbon atom. e.g.,



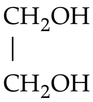
$$CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_3$$ (2-propanol)

- **(iii) Tertiary alcohols:** The alcohol in which —OH group is attached to tertiary (3°) carbon atom

e.g., 

$$CH_3-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-OH$$ or $(CH_3)_3C$-OH (2-methylpropan-2-ol)

Note: Those alcohols which have more than one —OH groups are called polyhydric alcohol. e.g.,



$$\begin{array}{l} CH_2OH \\ | \\ CH_2OH \end{array}$$ Glycol.

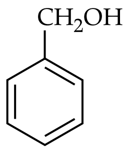
(c) Allylic and vinylic alcohols:

- **(i)** Those alcohols in which —OH group is attached to single bonded *sp*^{3}- hybridised carbon next to carbon-carbon double bond, that is to allylic carbon are called as allylic alcohols, e.g., $CH_2{=}CH{-}CH_2{-}OH$.
- **(ii)** Those alcohols in which —OH group is attached to double bonded *sp*^{2}-hybridised carbon atom are called as vinylic alcohols. They are highly unstable and get tautomerised to form aldehydes. e.g.,

$$CH_2=CHOH \rightleftharpoons CH_3-\overset{\displaystyle O}{\overset{\|}{C}}-H$$

(Vinyl alcohol) (Acetaldehyde)

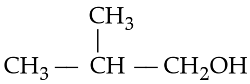
(d) Benzyl alcohol: Those in which —OH group is attached to single bonded *sp*^{3}-hydridised carbon atom attached to aromatic ring are called as benzylic alcohols. e.g.,



(Benzyl alcohol)
Phenyl methanol

- **Isomerism in alcohols:** They show four types of structural isomerism.
  - **(i) Chain isomerism:** These isomers differ in the chain of the carbon atoms attached to the hydroxyl group.

$C_4H_{10}O$ $CH_3-CH_2-CH_2-CH_2-OH$ Butan-1-ol

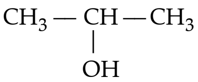


$$CH_3-\overset{\displaystyle CH_3}{\overset{|}{CH}}-CH_2OH$$

2-methylpropan-1-ol

  - **(ii) Position isomerism:** These isomers differ in the position of the hydroxyl group.

C_3H_8O $CH_3-CH_2-CH_2-OH$ Propan-1-ol



$$CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_3$$

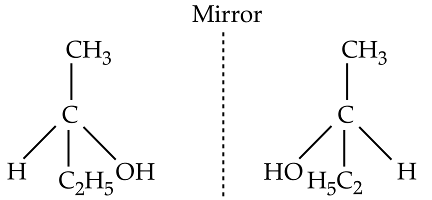
Propan-2-ol

  - **(iii) Functional isomerism:** These isomers differ in the functional group.

C_2H_6O CH_3CH_2-OH Ethanol CH_3-O-CH_3 Dimethlyether

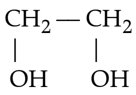
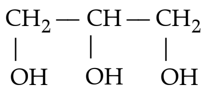
  - **(iv) Optical isomerism:** Monohydric alcohol containing chiral carbon atom show optical isomerism.

$C_4H_{10}O$



d-Butan-2-ol *l*-Butan-2-ol

- **Common and IUPAC Names of Some Alcohols:**

Formula	Common Name	IUPAC Name
CH_3OH	Methyl alcohol	Methanol
CH_3CH_2OH	Ethyl alcohol	Ethanol
$CH_3CH_2CH_2OH$	*n*-Propyl alcohol	Propan-1-ol
$CH_3CHOHCH_3$	*iso*-Propyl alcohol	Propan-2-ol
$(CH_3)_2CH—CH_2OH$	*iso*-Butyl alcohol	2-Methyl propan-1-ol
$CH_3CH_2CHOHCH_3$	*sec*-Butyl alcohol	Butan-2-ol
$(CH_3)_3C—OH$	*tert*–Butyl alcohol	2-Methyl propan-2-ol
 $\underset{OH}{\underset{\vert}{CH_2}}-\underset{OH}{\underset{\vert}{CH_2}}$	Ethylene glycol	Ethane-1, 2-diol
 $\underset{OH}{\underset{\vert}{CH_2}}-\underset{OH}{\underset{\vert}{CH}}-\underset{OH}{\underset{\vert}{CH_2}}$	Glycerol or Glycerine	Propane-1, 2, 3-triol

- **Methods of preparation of Alcohols:**

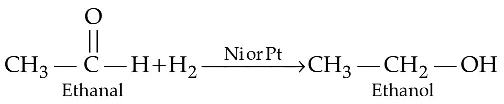
1. **From Haloalkanes:** Haloalkanes are hydrolysed to the corresponding alcohols by treatment with aqueous alkali.

$$CH_3-Cl+KOH\,(aq.) \longrightarrow CH_3—OH+KCl$$

2. **From Aldehydes and Ketones:**

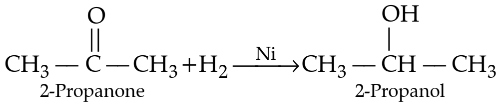
(i) Reduction: Aldehyde and ketones are reduced to primary and secondary alcohols respectively. The common reducing agents are lithium aluminium hydride ($LiAlH_4$), Sodium borohydride ($NaBH_4$) or hydrogen gas in the presence of nickel or platinum as catalyst.

(a)



$$\underset{\text{Ethanal}}{CH_3-\overset{\overset{O}{||}}{C}-H}+H_2 \xrightarrow{\text{Ni or Pt}} \underset{\text{Ethanol}}{CH_3-CH_2-OH}$$

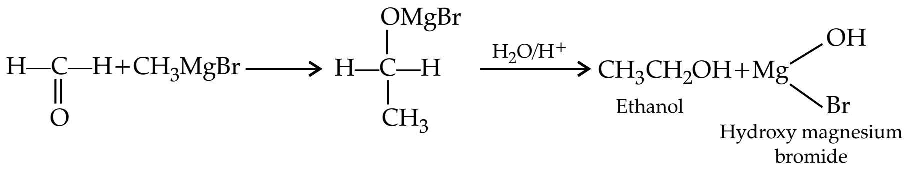
(b)



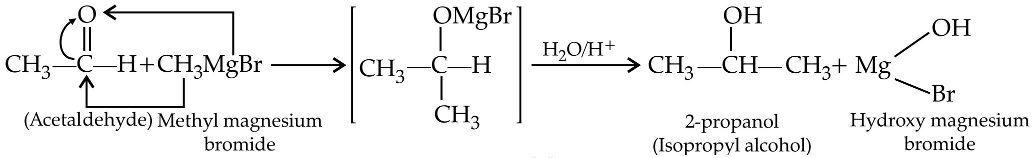
$$\underset{\text{2-Propanone}}{CH_3-\overset{\overset{O}{||}}{C}-CH_3}+H_2 \xrightarrow{\text{Ni}} \underset{\text{2-Propanol}}{CH_3-\overset{\overset{OH}{|}}{CH}-CH_3}$$

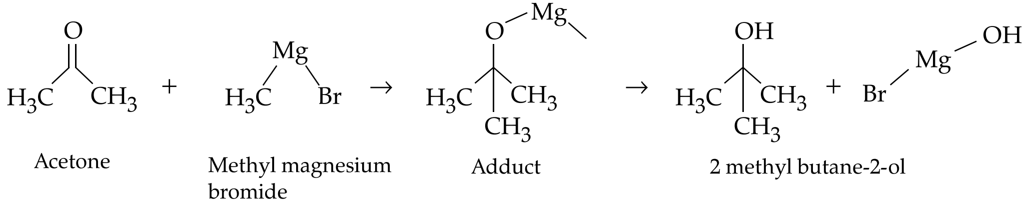
(ii) Using Grignard reagent: This method is used to get all three types of alcohols: Formaldehyde (HCHO) reacts with Grignard reagent to give primary alcohol whereas other aldehydes give secondary alcohols. Ketones give tertiary alcohols. e.g.,

(a)



(b)

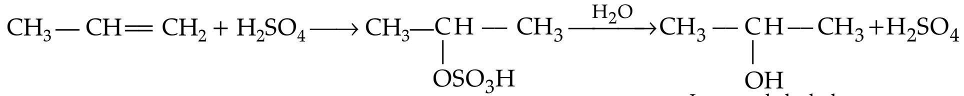




3. From Alkenes:

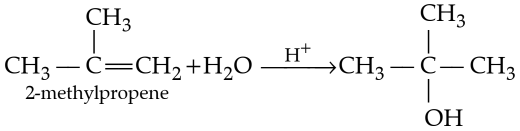
(i) $CH_2{=}CH_2 + H_2SO_4 \longrightarrow CH_3CH_2OSO_3H \xrightarrow{H_2O} CH_3CH_2OH + H_2SO_4$

Ethene Ethanol

(ii) 

$$CH_3-CH{=}CH_2 + H_2SO_4 \longrightarrow CH_3-\underset{OSO_3H}{\underset{|}{C}}H-CH_3 \xrightarrow{H_2O} CH_3-\underset{OH}{\underset{|}{C}}H-CH_3 + H_2SO_4$$

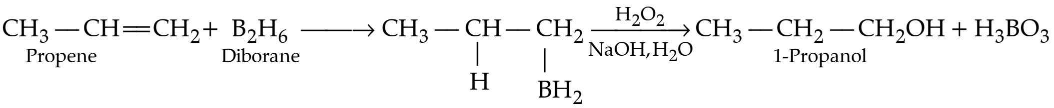
Isopropyl alcohol

(iii) 

$$CH_3-\overset{CH_3}{\overset{|}{C}}{=}CH_2 + H_2O \xrightarrow{H^+} CH_3-\underset{OH}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CH_3$$

2-methylpropene 2-methylpropan-2-ol

4. Hydroboration oxidation: As per anti-Markovnikov's rule –



$$CH_3-CH{=}CH_2 + B_2H_6 \longrightarrow CH_3-\underset{H}{\underset{|}{CH}}-\underset{BH_2}{\underset{|}{CH_2}} \xrightarrow[NaOH,\,H_2O]{H_2O_2} CH_3-CH_2-CH_2OH + H_3BO_3$$

Propene Diborane 1-Propanol

5. Reduction of carboxylic acids and esters: With the help of strong reducing agent, lithium aluminium hydride, carboxylic acids are reduced to primary alcohols.

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

Carboxylic acids 1° alcohol

Commercially, acids are reduced to alcohols by converting them to esters, followed by catalytic hydrogenation.

$$RCOOH \xrightarrow[H^+]{R'OH} RCOOR' \xrightarrow[\text{Catalyst}]{H_2} RCH_2OH + R'OH$$

6. From amines:

$$C_2H_5NH_2 + HNO_2 \longrightarrow C_2H_5OH + N_2 + H_2O$$

Ethanamine Ethanol

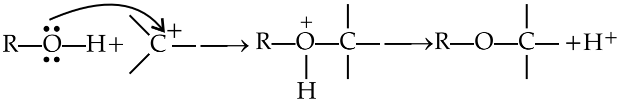
7. By alcoholic Fermentation:

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

(Glucose) (Fructose)

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

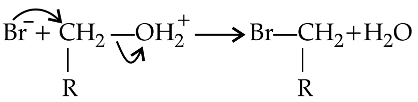
- **Physical properties:**
  - Lower alcohols are colourless liquid members, from C_5-C_{11} are oily liquids and higher members are waxy solids.
  - Characteristic alcoholic odour and burning taste.
  - Polar in nature.
  - Forms intermolecular hydrogen bonding .
  - Soluble in water which decreases with increase in molecular mass.
  - Boiling point is considerably higher than those of corresponding hydrocarbons, haloalkanes, ethers etc. 1° > 2° > 3°.
  - Toxic in nature.
- **Chemical properties:** Alcohols act both as nucleophiles and electrophiles. The bond between O—H is broken when alcohols act as *nucleophiles*.



$$R-\ddot{\underset{..}{O}}-H + \overset{+}{C} \longrightarrow R-\underset{H}{\underset{|}{\overset{+}{O}}}-\underset{|}{\overset{|}{C}}- \longrightarrow R-O-\underset{|}{\overset{|}{C}}- + H^+$$

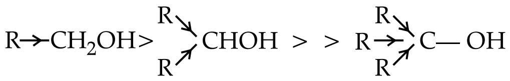
The bond between C—O is broken when they act as *electrophiles*.

$$R-CH_2-OH + \overset{+}{H} \longrightarrow R-CH_2-\overset{+}{O}H_2$$



$$\overset{-}{Br} + \underset{R}{\underset{|}{CH_2}}-\overset{+}{O}H_2 \longrightarrow Br-\underset{R}{\underset{|}{CH_2}} + H_2O$$

➢ **Acidity of alcohols:** The acidic character of alcohols is due to the polar nature of O—H bond. An electron-releasing group ($-CH_3$, $-C_2H_5$) increases electron density on oxygen tending to decrease the polarity of O—H bond. This decreases the acid strength. For this reason, the acid strength of alcohol decreases in the order.



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

Primary Secondary Tertiary

Alcohols can act as Bronsted acids as well as bases due to donation of proton and presence of unshared pair of electrons on oxygen respectively.

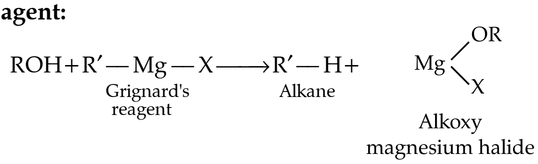
- **Reaction with active metals:**

$$2R-OH+2Na\longrightarrow \underset{\text{Sodium alkoxide}}{2RONa}+H_2\uparrow$$

- **With metal hydrides:**

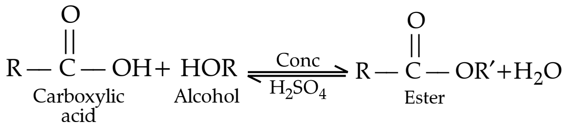
$$2CH_3OH+2NaH\longrightarrow 2CH_3ONa+H_2\uparrow$$

- **With Grignard's reagent:**



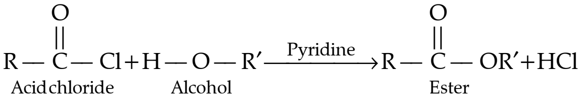
$$ROH+\underset{\text{Grignard's reagent}}{R'-Mg-X}\longrightarrow \underset{\text{Alkane}}{R'-H}+\underset{\text{Alkoxy magnesium halide}}{Mg\begin{matrix}\diagup OR\\ \diagdown X\end{matrix}}$$

- **Esterification:**

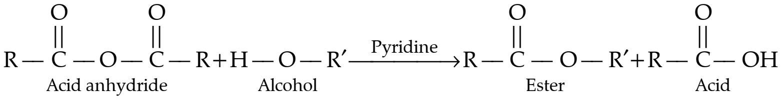


$$\underset{\text{Carboxylic acid}}{R-\overset{\overset{\displaystyle O}{||}}{C}-OH}+\underset{\text{Alcohol}}{HOR}\underset{H_2SO_4}{\overset{\text{Conc}}{\rightleftharpoons}}\underset{\text{Ester}}{R-\overset{\overset{\displaystyle O}{||}}{C}-OR'}+H_2O$$

- **Acylation:**



$$\underset{\text{Acid chloride}}{R-\overset{\overset{\displaystyle O}{||}}{C}-Cl}+\underset{\text{Alcohol}}{H-O-R'}\xrightarrow{\text{Pyridine}}\underset{\text{Ester}}{R-\overset{\overset{\displaystyle O}{||}}{C}-OR'}+HCl$$



$$\underset{\text{Acid anhydride}}{R-\overset{\overset{\displaystyle O}{||}}{C}-O-\overset{\overset{\displaystyle O}{||}}{C}-R}+\underset{\text{Alcohol}}{H-O-R'}\xrightarrow{\text{Pyridine}}\underset{\text{Ester}}{R-\overset{\overset{\displaystyle O}{||}}{C}-O-R'}+\underset{\text{Acid}}{R-\overset{\overset{\displaystyle O}{||}}{C}-OH}$$

- **With hydrogen halides:**

$$R-OH+HX\longrightarrow \underset{\text{Haloalkane}}{R-X}+H_2O$$

- **With phosphorus halides:**

$$\underset{\text{Ethyl alcohol}}{CH_3CH_2OH}+PCl_5\longrightarrow \underset{\text{Chloroethane}}{CH_3CH_2Cl}+\underset{\text{Phosphorus oxychloride}}{POCl_3}+HCl\uparrow$$

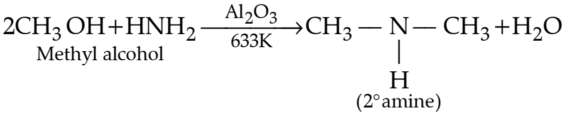
$$\underset{\text{Ethyl alcohol}}{3CH_3CH_2OH}+PCl_3\longrightarrow \underset{\text{Chloroethane}}{3CH_3CH_2Cl}+\underset{\text{Phosphorus acid}}{H_3PO_3}$$

- **With thionyl chloride:**

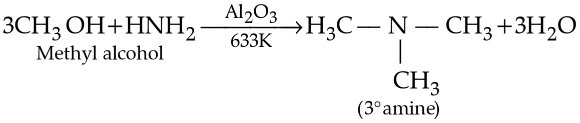
$$R-OH+\underset{\text{Thionyl chloride}}{SOCl_2}\xrightarrow{\text{Pyridine}}\underset{\text{Chloroalkane}}{R-Cl}+SO_2\uparrow+HCl\uparrow\triangleleft$$

- **With NH_3:**

$$CH_3-OH+HNH_2\xrightarrow[633K]{Al_2O_3}\underset{(1^\circ\text{amine})}{CH_3NH_2}+H_2O$$



$$\underset{\text{Methyl alcohol}}{2CH_3OH}+HNH_2\xrightarrow[633K]{Al_2O_3}\underset{(2^\circ\text{amine})}{CH_3-\underset{\underset{\displaystyle H}{|}}{N}-CH_3}+H_2O$$



$$\underset{\text{Methyl alcohol}}{3CH_3OH}+HNH_2\xrightarrow[633K]{Al_2O_3}\underset{(3^\circ\text{amine})}{H_3C-\underset{\underset{\displaystyle CH_3}{|}}{N}-CH_3}+3H_2O$$

- **Dehydration:**

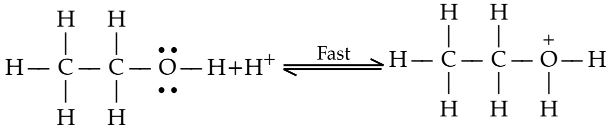
$$\underset{\text{Ethyl alcohol}}{CH_3-CH_2-OH}\xrightarrow[\text{at }443K]{\text{conc.}H_2SO_4}\underset{\text{Ethene}}{CH_2=CH_2}+H_2O$$

$$\underset{\text{Ethyl alcohol}}{2CH_3CH_2OH}\xrightarrow[\text{at }413K]{\text{conc.}H_2SO_4}\underset{\text{Diethyl ether}}{CH_3-CH_2-O-CH_2-CH_3}+H_2O$$

Ease of dehydration of alcohols 3°>2°>1°.

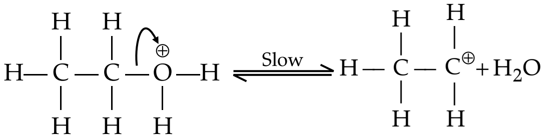
Mechanism of dehydration:

- **Protonation of alcohol:**



$$H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\ddot{\underset{\cdot\cdot}{O}}-H+H^+\xrightleftharpoons{\text{Fast}}H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{+}{O}}-H$$

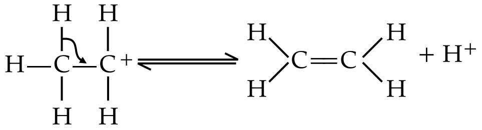
- **Loss of water molecule (Carbocation formation):**



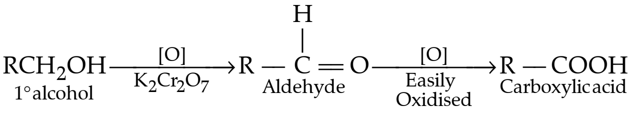
$$H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{\oplus}{O}}-H\xrightleftharpoons{\text{Slow}}H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C^{\oplus}}}+H_2O$$

It is a slowest step and rate determining step.

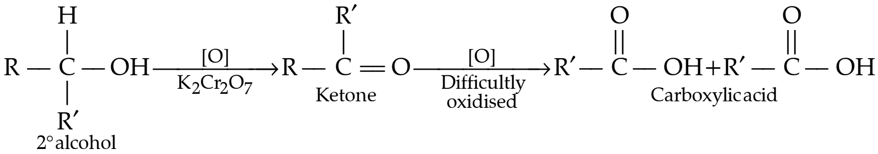
- **Loss of proton**



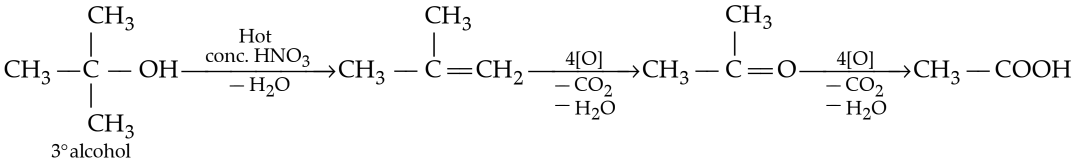
➢ **Oxidation by $Na_2Cr_2O_7$/$K_2Cr_2O_7$/acidified $KMnO_4$:**



$$\underset{1^\circ\text{alcohol}}{RCH_2OH}\xrightarrow[K_2Cr_2O_7]{[O]}\underset{\text{Aldehyde}}{R-\overset{H}{C}=O}\xrightarrow[\text{Easily Oxidised}]{[O]}\underset{\text{Carboxylic acid}}{R-COOH}$$



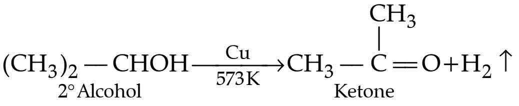
$$\underset{2^\circ\text{alcohol}}{R-\underset{R'}{\overset{H}{C}}-OH}\xrightarrow[K_2Cr_2O_7]{[O]}\underset{\text{Ketone}}{R-\overset{R'}{C}=O}\xrightarrow[\text{Difficultly oxidised}]{[O]}\underset{\text{Carboxylic acid}}{R'-\overset{O}{\overset{\|}{C}}-OH+R'-\overset{O}{\overset{\|}{C}}-OH}$$



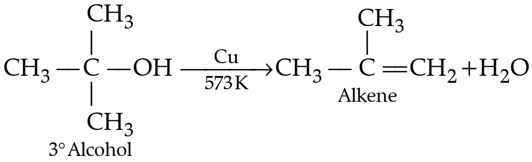
$$\underset{3^\circ\text{alcohol}}{CH_3-\underset{CH_3}{\overset{CH_3}{C}}-OH}\xrightarrow[-H_2O]{\text{Hot conc. }HNO_3}CH_3-\overset{CH_3}{C}=CH_2\xrightarrow[-CO_2,\ -H_2O]{4[O]}CH_3-\overset{CH_3}{C}=O\xrightarrow[-CO_2,\ -H_2O]{4[O]}CH_3-COOH$$

➢ **Dehydrogenation:**

$$\underset{1^\circ\text{Alcohol}}{CH_3-CH_2OH}\xrightarrow[573K]{Cu}\underset{\text{Aldehyde}}{CH_3-CHO}+H_2\uparrow$$

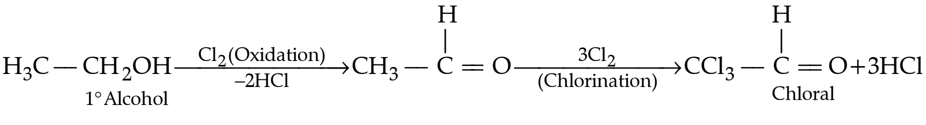


$$\underset{2^\circ\text{Alcohol}}{(CH_3)_2-CHOH}\xrightarrow[573K]{Cu}\underset{\text{Ketone}}{CH_3-\overset{CH_3}{C}=O}+H_2\uparrow$$

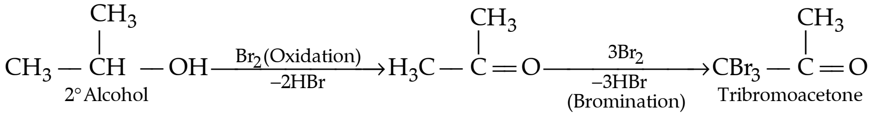


$$\underset{3^\circ\text{Alcohol}}{CH_3-\underset{CH_3}{\overset{CH_3}{C}}-OH}\xrightarrow[573K]{Cu}\underset{\text{Alkene}}{CH_3-\overset{CH_3}{C}=CH_2}+H_2O$$

➢ **Reaction with halogens:**



$$\underset{1^\circ\text{Alcohol}}{H_3C-CH_2OH}\xrightarrow[-2HCl]{Cl_2(\text{Oxidation})}CH_3-\overset{H}{C}=O\xrightarrow[(\text{Chlorination})]{3Cl_2}\underset{\text{Chloral}}{CCl_3-\overset{H}{C}=O}+3HCl$$



$$\underset{2^\circ\text{ Alcohol}}{CH_3-\overset{\overset{CH_3}{|}}{CH}-OH}\xrightarrow[-2HBr]{Br_2(\text{Oxidation})}H_3C-\overset{\overset{CH_3}{|}}{C}=O\xrightarrow[\substack{-3HBr\\(\text{Bromination})}]{3Br_2}\underset{\text{Tribromoacetone}}{CBr_3-\overset{\overset{CH_3}{|}}{C}=O}$$

3° alcohols are not oxidised by halogens.

- **Preparation of methanol by Bosch process:** Firstly water gas $(CO+H_2)$ will be prepared from coal at 1270 K.

$$\underset{\text{Coal}}{C}+H_2O\longrightarrow CO+H_2$$

Methanol (CH_3OH) is prepared from water gas by adding ZnO/Cr_2O_3 catalyst.

$$CO+2H_2\longrightarrow CH_3OH$$

- Preparation of ethanol by fermentation of sugar present in molasses, sugarcane or fruits like grapes. Sugar on fermentation in presence of invertase is converted to glucose and fructose which on further fermentation in presence of zymase enzyme gives ethanol.

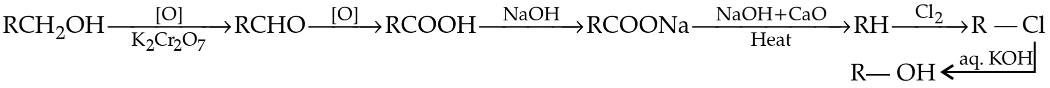
$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}}+H_2O\xrightarrow{\text{Invertase}}\underset{\text{Glucose}}{C_6H_{12}O_6}+\underset{\text{Fructose}}{C_6H_{12}O_6}$$

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

- **Uses of alcohol:**
  - Methanol and ethanol are used as solvents for paints, varnishes, etc.
  - Methanol is used for making formaldehyde.
  - Ethanol is used in preparation of large number of compounds.
- **Distinction between primary, secondary and tertiary alcohols by Lucas Test:** Alcohols on treatment with Lucas reagent (conc. $HCl+ZnCl_2$) form corresponding halides which are insoluble and produce turbidity. Tertiary alcohol gives turbidity immediately, secondary alcohol within five minutes and primary alcohols do not give turbidity at room temperature.
- **Conversion of lower alcohol to a higher alcohol:**

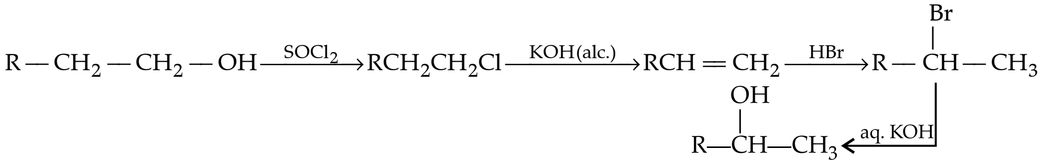
$$R-OH\xrightarrow[-H_2O]{HI}RI\xrightarrow[-KI]{KCN}RCN\xrightarrow[\text{Reduction}]{4[H]}RCH_2NH_2\xrightarrow{HNO_2}RCH_2OH$$

- **Conversion of higher alcohol to a lower alcohol:**



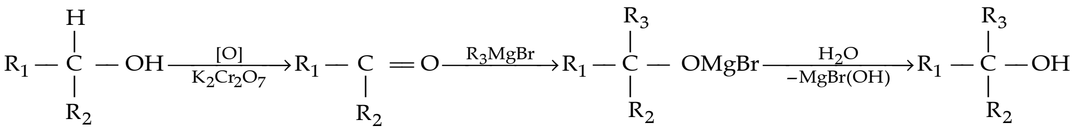
$$RCH_2OH\xrightarrow[K_2Cr_2O_7]{[O]}RCHO\xrightarrow{[O]}RCOOH\xrightarrow{NaOH}RCOONa\xrightarrow[\text{Heat}]{NaOH+CaO}RH\xrightarrow{Cl_2}R-Cl$$
$$R-OH\xleftarrow{aq.\ KOH}R-Cl$$

- **Conversion of primary alcohol to a secondary alcohol:**



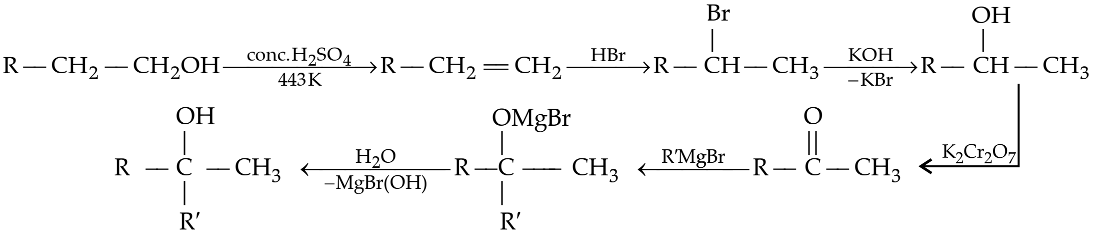
$$R-CH_2-CH_2-OH\xrightarrow{SOCl_2}RCH_2CH_2Cl\xrightarrow{KOH(alc.)}RCH=CH_2\xrightarrow{HBr}R-\overset{\overset{Br}{|}}{CH}-CH_3$$
$$R-\overset{\overset{OH}{|}}{CH}-CH_3\xleftarrow{aq.\ KOH}$$

- **Conversion of secondary alcohol to a tertiary alcohol:**



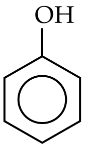
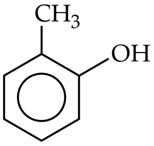
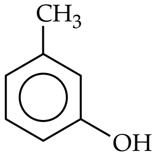
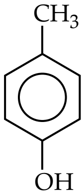
$$R_1-\overset{\overset{H}{|}}{\underset{\underset{R_2}{|}}{C}}-OH\xrightarrow[K_2Cr_2O_7]{[O]}R_1-\underset{\underset{R_2}{|}}{C}=O\xrightarrow{R_3MgBr}R_1-\overset{\overset{R_3}{|}}{\underset{\underset{R_2}{|}}{C}}-OMgBr\xrightarrow[-MgBr(OH)]{H_2O}R_1-\overset{\overset{R_3}{|}}{\underset{\underset{R_2}{|}}{C}}-OH$$

- **Conversion of primary alcohol to a tertiary alcohol:**

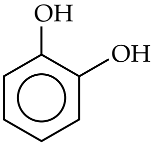
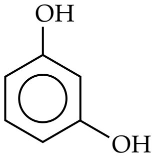
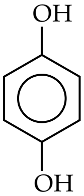


$$R-CH_2-CH_2OH\xrightarrow[443K]{conc.H_2SO_4}R-CH_2=CH_2\xrightarrow{HBr}R-\overset{\overset{Br}{|}}{CH}-CH_3\xrightarrow[-KBr]{KOH}R-\overset{\overset{OH}{|}}{CH}-CH_3$$
$$R-\overset{\overset{OH}{|}}{\underset{\underset{R'}{|}}{C}}-CH_3\xleftarrow[-MgBr(OH)]{H_2O}R-\overset{\overset{OMgBr}{|}}{\underset{\underset{R'}{|}}{C}}-CH_3\xleftarrow{R'MgBr}R-\overset{\overset{O}{||}}{C}-CH_3\xleftarrow{K_2Cr_2O_7}$$

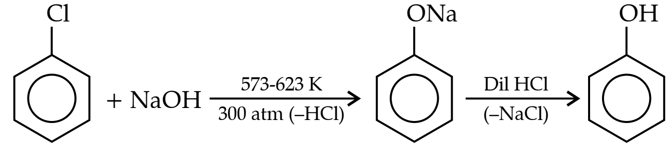
- **Nomenclature of phenols:** Phenol is the monohydroxy derivative of benzene. Substituents in phenol compounds are identified by the position, in which they are attached to the hydroxyl group in the benzene ring called as *ortho*-(1,2-disubstituted), *meta*-(1,3-disubstituted) and *para*-(1, 4-disubstituted).

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

- Dihydroxy derivatives of benzene are known as 1, 2-, 1, 3- or 1, 4-benzenediol.

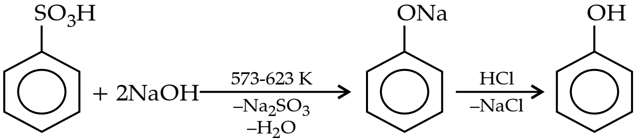
			
Common name	Catechol	Resorcinol	Hydroquinone or quinol
IUPAC name	Benzene-1,2-diol	Benzene-1,3-diol	Benzene-1,4-diol

- **Preparation of phenols:**
  - **Dow's process:** Phenol is prepared by heating chlorobenzene with 10% NaOH solution at 623 K under 300 atm followed by hydrolysis.



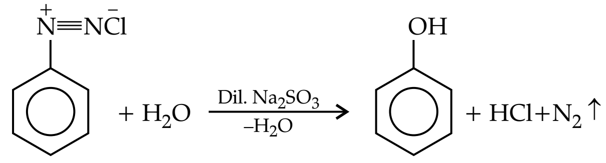
Chlorobenzene Phenol

  - **From salts of benzene sulphonic acid:**



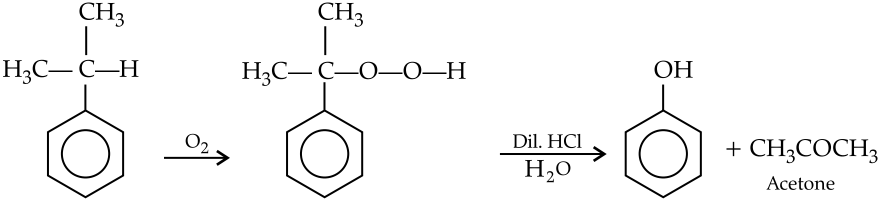
Benzene sulphonic acid Phenol

  - **From diazonium salts:**



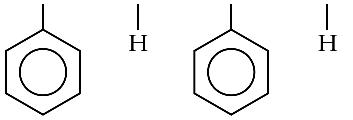
Benzene diazonium chloride Phenol

  - **From cumene (for commercial preparation):**



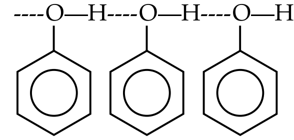
Cumene Cumene hydroperoxide Phenol Acetone

- **Physical Properties:**
  - Colourless liquids or crystalline solids with low melting point.
  - Phenol and few di and trihydric phenols are fairly soluble in water due to their ability to form intermolecular hydrogen bonding with water.



Solubility of phenol in water is much lower than that of alcohols due to presence of large hydrophobic benzene ring.

- Boiling points of phenols are higher than the arenes, aryl halides and aryl ethers of comparable molecular masses. It is due to the presence of intermolecular hydrogen bonding which results in molecular association.

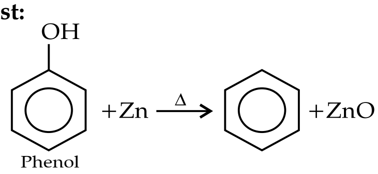


➢ Chemical Properties:

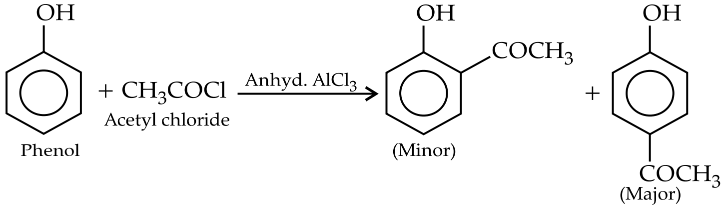
- **Phenol acts as weak acid.**

$$2C_6H_5OH + 2Na \longrightarrow 2C_6H_5ONa + H_2$$
$$C_6H_5OH + NaOH \longrightarrow C_6H_5ONa + H_2O$$

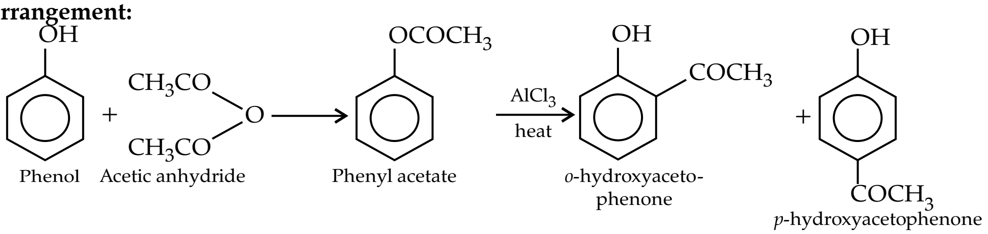
- **Reaction with Zn dust:**



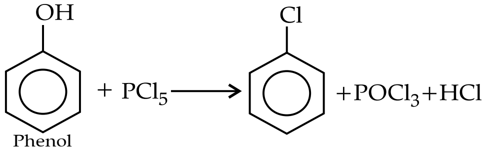
- **Friedel-Crafts reaction:**



- **Fries rearrangement:**

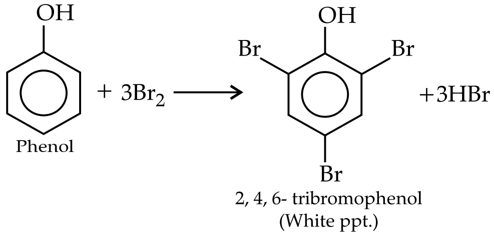


- **With PCl_5:**

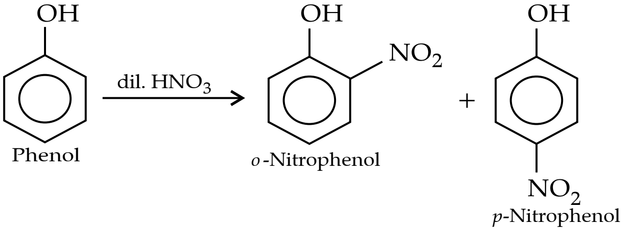


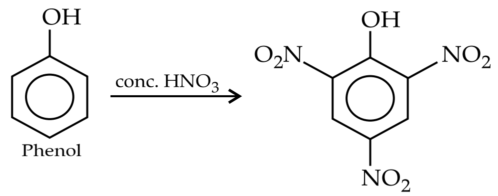
- **Electrophilic substitution reaction:**

(i) Bromination:



(ii) Nitration: In presence of HNO_3 (dil.), it gives *ortho* and *para* product but with HNO_3 (conc.) it forms picric acid.

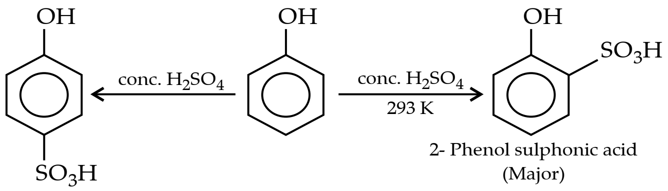




Phenol

2,4,6- Trinitrophenol
(Picric acid)

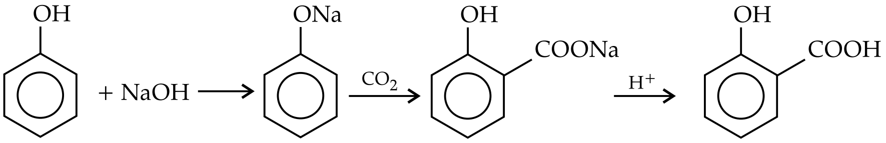
(iii) Sulphonation:



4- Phenol sulphonic acid
(Major)

2- Phenol sulphonic acid
(Major)

- **Kolbe's reaction:**

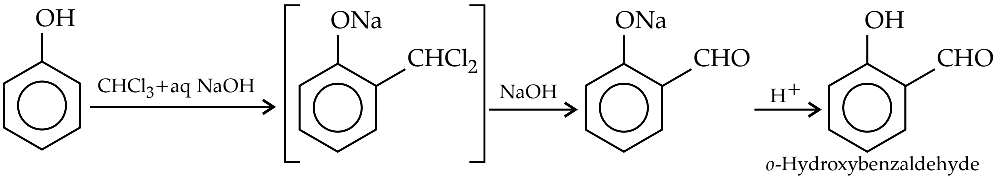


Sodium phenoxide

Sodium salicylate

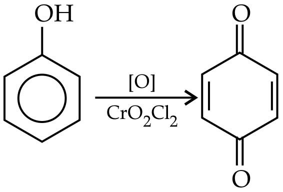
2-hydroxybenzoic acid (Salicylic acid)

- **Reimer-Tiemann reaction:**



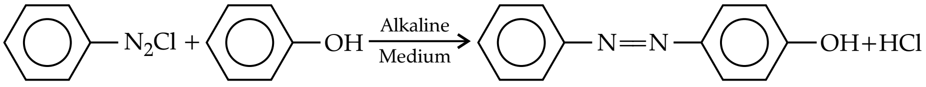
o-Hydroxybenzaldehyde
(Salicylaldehyde)

- **Oxidation:**



p-Benzoquinone

- **Coupling reaction:**



Diazonium salt

Phenol

4-hydroxyazobenzene
(Azo dye)

➢ **Uses of phenol:**

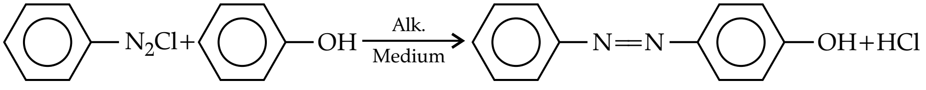
- In perfume.
- In the production of dyes, plastics, etc.

➢ **Test for phenol:**

- **$FeCl_3$ test:** Unlike alcohols, phenols react with neutral $FeCl_3$ to give violet coloured water soluble complex.

$$6C_6H_5OH + FeCl_3 \rightarrow \underset{\text{Violet complex}}{[Fe(OC_6H_5)_6]^{3-}} + 3HCl + 3H^+$$

- **Azo dye test:** Phenol reacts with benzene diazonium chloride in presence of an alkaline medium to give an orange coloured compound azo dye.



4-hydroxyazobenzene
(Azo dye)

Key Terms

- **Wood spirit:** Methanol is known as wood spirit as it is prepared by destructive distillation of wood.
- **Methylated spirit:** Denatured ethyl alcohol which is unfit for drinking purpose is called methylated spirit.
- **Fusel oil:** In the fermentation of starch, ethyl alcohol is prepared but in small amount. Some higher alcohol also forms like isopentyl alcohol or isoamyl alcohol. This mixture is quite often called fusel oil.
- **Power alcohol:** It is the mixture of 20% alcohol and 80% petrol with ether, benzene or tetralin. It is used as a substitute for petrol for running internal combustion engines in cars, scooters, etc.
- **Lederer-Manasse reaction:** Phenol condenses with formaldehyde in presence of acid or base to give bakelite (polymer). The reaction is known as Lederer-Manasse reaction.
- **Rectified Spirit:** It contains about 95.5 percent alcohol.
- **Electrophile:** Positively charged or neutral species which is electron deficient e.g., H^+, H_3O^+, Cl^+, etc.
- **Nucleophile:** Negatively charged or neutral species with lone pair of electrons e.g., Br^-, CN^-, etc.
- **Substitution reaction:** Reaction in which an atom or group of atoms is replaced by some other atom or group of atoms without any change in the structure of the remaining part of the molecule. e.g.,

$$CH_3 — CH_2 — OH + HBr \rightarrow CH_3 — CH_2 — Br + H_2O$$

- **Addition reaction:** When a molecule is added across a double or triple bond to form single product is called addition product, such reactions are called addition reactions. e.g.,

$$CH_2 = CH_2 + HCl \rightarrow CH_3 — CH_2 — Cl$$

- **Oxonium ion:** The ion which is formed by reaction of alcohol or ether with H^+. The oxygen atom in this ion has positive charge.
- **Absolute alcohol:** It is 100% ethanol. It is obtained by fractional distillation of 95% ethanol and little amount of benzene.

Mnemonics

Formation of Alcohols

1. **Mnemonics:** **F**ourth **GR**ade **H**igh income **P**er **A**nnuam

   Interpretation.

   Formaldehyde reacts with Grignard reagent followed by hydrolysis to form Primary Alcohol.

2. **Mnemonics:** **AGR**a **H**ai **B**harat ki **S**h**A**n

   Interpretation.

   Acetaldehyde reacts with Grignard reagent followed by hydrolysis to form Secondary Alcohol.

Reaction of Alcohols with Lucas reagent

1. **Mnemonics:** **TA**ta namak vs **L**aho**RI** namak

   Interpretation.

   Tertiary alcohols react with Lucas reagent to form turbidity immediately.

2. **Mnemonics:** **SAL**e main **5**% off hain

   Interpretation.

   Secondary alcohols react with Lucas reagent to form turbidity within 5 minutes.

3. **Mnemonics: PAL RuNneR Tha**

   Interpretation.

   Primary alcohols do not react with Lucas reagent at room temperature.

Test for phenols

Mnemonic : Feel cool and drink **violet** cool

$FeCl_3$ ↓

violet coloured complex

Alkji ne liyo **golanamak** our banaya **dye**

↓ ↓ ↓

Alkaline medium — diazonium salt — azodye

Topic-2

Ethers: Methods of Preparation, Properties and Uses

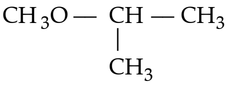
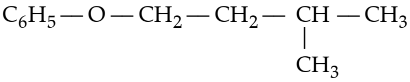
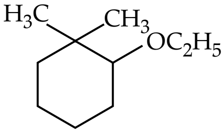
Concepts Covered: *Nomenclature of ether, General formula, Methods of preparation, Physical and chemical properties, Uses.*

Revision Notes

- **Ethers:** Ethers are organic compounds in which alkyl or aryl groups are attached to a divalent oxygen known as etheral oxygen. Compounds with general formula $C_nH_{2n+2}O$. They are represented by general structure, R–O–R′.
- **Nomenclature of Ethers:** Ethers are named from names of alkyl/aryl group written as separate words in alphabetical order and adding the word 'ether' at the end. If both the alkyl groups are the same, the prefix '*di*' is added before the alkyl group. For example, $C_2H_5OC_2H_5$ is diethyl ether. These types of ethers are called symmetrical ethers. If both the alkyl groups are the different, for example, $CH_3OC_2H_5$ is ethylmethyl ether.

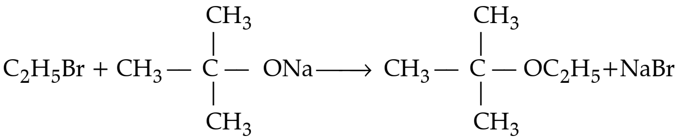
These types of ethers are called unsymmetrical ethers. During naming ethers, the larger alkyl group is chosen as the parent hydrocarbon.

Common and IUPAC names of some Ethers are:

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-Methoxy propane
$C_6H_5OCH_3$	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
 $CH_3O—\underset{\displaystyle CH_3}{\underset{\vert}{CH}}—CH_3$	Methyl isopropyl ether	2-Methoxypropane
 $C_6H_5—O—CH_2—CH_2—\underset{\displaystyle CH_3}{\underset{\vert}{CH}}—CH_3$	Phenyl isopentyl ether	1-phenoxy 3-methyl butane
$CH_3—O—CH_2—CH_2—OCH_3$	—	1, 2-Dimethoxyethane
	—	2-Ethoxy-1, 1-dimethylcyclohexane

- **Methods of Preparation of Ethers:**

(a) Williamson's synthesis: Only primary alkyl halide reacts with sodium alkoxide, ethers are formed while tertiary alkyl halides give alkene due to steric hindrance. e.g.,



$$C_2H_5Br + CH_3—\overset{\displaystyle CH_3}{\overset{\vert}{\underset{\displaystyle CH_3}{\underset{\vert}{C}}}}—ONa \longrightarrow CH_3—\overset{\displaystyle CH_3}{\overset{\vert}{\underset{\displaystyle CH_3}{\underset{\vert}{C}}}}—OC_2H_5 + NaBr$$

2-ethoxy-2-methylpropane

(b) Dehydration of alcohols: Alcohols are dehydrated to ethers in presence of concentrated sulphuric acid at 413 K. The reaction involves the removal of one molecule of water from two moles of alcohols.

$$\underset{\text{Ethyl alcohol}}{C_2H_5\boxed{OH + H}OC_2H_5} \xrightarrow[413\text{ K}]{\text{conc. }H_2SO_4} \underset{\substack{\text{Diethyl ether}\\ \text{(Ethoxy ethane)}}}{C_2H_5OC_2H_5} + H_2O$$

Alcohol can also be dehydrated by heating with alumina at 523 K and high pressure. This method is not suitable for preparation of unsymmetrical ethers.

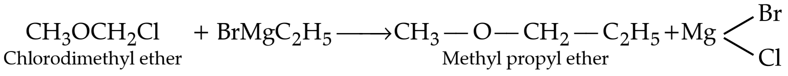
(c) Heating alkyl halides with dry silver oxide: Ethers can be prepared by heating alkyl halides with dry silver oxide (Ag_2O).

$$2C_2H_5Cl + Ag_2O \xrightarrow{\text{heat}} C_2H_5—O—C_2H_5 + 2AgCl$$

$$CH_3Cl + Ag_2O + C_2H_5Cl \longrightarrow CH_3—O—C_2H_5 + 2AgCl$$

Mixed ether or unsymmetrical ether can be prepared by this method.

(d) Reaction of lower halogenated ethers with Grignard reagent: Higher homologues ethers can be prepared by action of Grignard reagent on lower halogenated ethers.

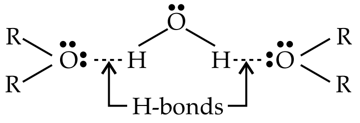


$$\underset{\text{Chlorodimethyl ether}}{CH_3OCH_2Cl} + BrMgC_2H_5 \longrightarrow \underset{\text{Methyl propyl ether}}{CH_3—O—CH_2—C_2H_5} + Mg\begin{matrix} \diagup Br \\ \diagdown Cl \end{matrix}$$

(e) Action of diazomethane on alcohols: Ethyl methyl ether can be prepared by action of diazomethane on alcohols in the presence of catalysts like BF_3.

$$C_2H_5OH + CH_2N_2 \xrightarrow{BF_3} \underset{\text{Ethyl methyl ether}}{C_2H_5OCH_3} + N_2$$

- **Physical properties of ethers:**
  - **Boiling points:** Ethers are weakly polar molecules due to weak dipole-dipole attraction. Thus, their boiling points are comparable to the alkenes of similar molecular mass. Boiling points of ethers are much lower than the corresponding alcohols due to the presence of H-bonding in alcohols.
  - **Miscibility:** Lower ethers (upto three carbon atoms) are soluble in water and their miscibility with water is similar to alcohols of the same molecular masses. This is due to the formation of H-bonds with water molecule.



- **Chemical properties of ethers:**
  - **With chlorine:**

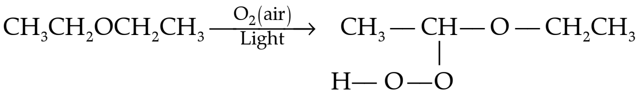
$$\underset{\text{Ether}}{R'CH_2-O-R} + Cl_2 \xrightarrow{\text{Dark}} \underset{\text{Chloroalkylether}}{R'CHCl-O-R} + HCl$$

$$\underset{\text{Diethyl ether}}{CH_3-CH_2-O-CH_2-CH_3} + \underset{\text{Excess}}{10Cl_2} \xrightarrow[\text{-10HCl}]{\text{Light}} \underset{\text{Perchlorodiethyl ether}}{CCl_3-CCl_2-O-CCl_2-CCl_3} + 10HCl$$

  - **Combustion:**

$$\underset{\text{Diethyl ether}}{C_2H_5-O-C_2H_5} + 6O_2 \longrightarrow 4CO_2 + 5H_2O$$

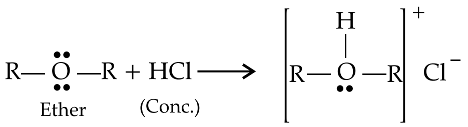
  - **Oxidation:**



$$CH_3CH_2OCH_2CH_3 \xrightarrow[\text{Light}]{O_2(\text{air})} CH_3-\underset{\substack{|\\ H-O-O}}{CH}-O-CH_2CH_3$$

1-ethoxyethyl-hydroperoxide

  - **With cold conc. H_2SO_4 or HCl:**



$$\underset{\text{Ether}}{R-\ddot{\underset{\cdot\cdot}{O}}-R} + \underset{\text{(Conc.)}}{HCl} \longrightarrow \left[R-\overset{\overset{H}{|}}{\underset{\cdot\cdot}{O}}-R\right]^+ Cl^-$$

Dialkyloxomium chloride

  - **With halogen acids (H*X*):**

$$\underset{\text{Ether}}{R-O-R} + \underset{(X=\text{I or Br})}{HX} \xrightarrow{\text{cold}} \underset{\text{Alcohol}}{ROH} + \underset{\text{Alkyl halide}}{RX}$$

$$\underset{\text{Diethyl ether}}{C_2H_5-O-C_2H_5} + 2HI \xrightarrow{\text{cold}} \underset{\text{Iodoethane}}{C_2H_5I} + \underset{\text{Ethanol}}{C_2H_5OH}$$

$$R-O-R + \underset{\text{Excess}}{2HX} \xrightarrow{\Delta} 2RX + H_2O$$

$$C_2H_5-O-C_2H_5 + \underset{\text{Excess}}{2HI} \xrightarrow{\Delta} 2C_2H_5I + H_2O$$

  - **Hydrolysis:**

$$R-O-R + HOH \xrightarrow{\text{Boil}} \underset{\text{Alcohol}}{2R-OH}$$

  - **With PCl_5:**

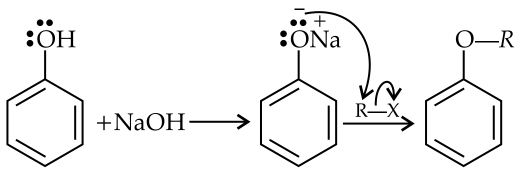
$$R-O-R + PCl_5 \xrightarrow{\Delta} \underset{\text{Alkyl chloride}}{2R-Cl} + POCl_3$$

Mnemonics

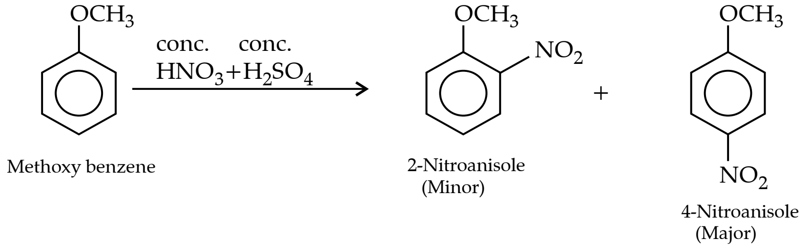
Concept : Preparation of Ethers

1. **Mnemonics: WRE**stling
   Interpretation.
   Williamson Reaction is used to prepare Ethers.
2. **Mnemonics: DAESA**ng award
   Interpretation.
   Dehydration of Alcohols gives Ethers in the presence of conc. Sulphuric acid.

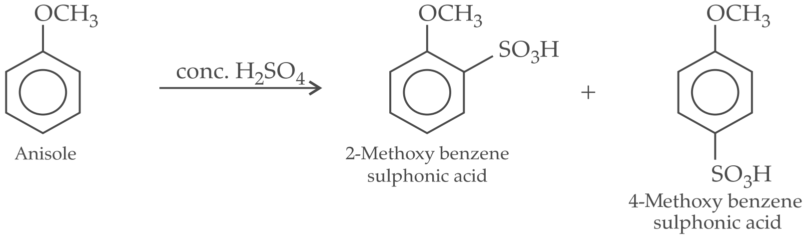
- **Preparation of Aryl Ether:**



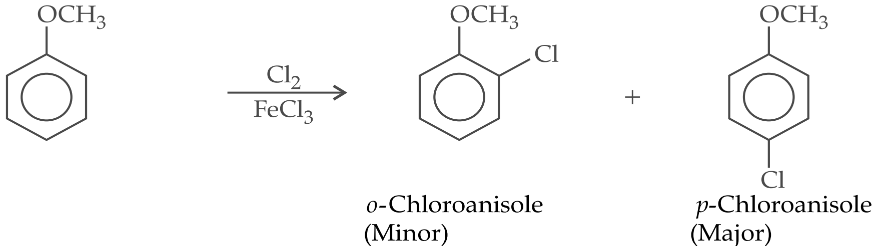
- **Physical properties of aryl ether:**
  Ethers are weakly polar, thus have comparably less boiling points than alcohols due to lack of hydrogen bonding. Similar to alcohols, ethers are miscible with water as they also form hydrogen bonds with water.
  (a) Nitration: Aromatic ethers react with conc. HNO_3 and conc. H_2SO_4 to form nitro compounds.



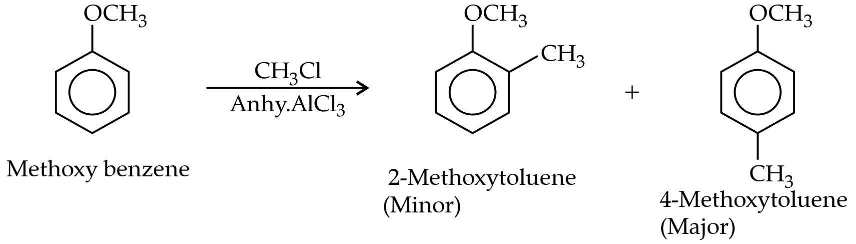
(b) Sulphonation: Aromatic ethers, on reaction with conc. H_2SO_4 form sulphonic acids.



(c) Halogenation: Aromatic ethers, on halogenation forms chloro substituted ethers.



(d) Friedel-Crafts reaction: Aromatic ethers undergo alkylation, when reacted with alkyl halide in presence of anhydrous $AlCl_3$.



- **Uses of ethers:**
  - Diethyl ether is used as inhalation anaesthetic.
  - As industrial solvent for oils, resins, gums, etc.
  - Diphenyl ether acts as a heat strangler medium.

Key Term

- **Grignard reagent:** An organometallic chemical compound formed from reaction of an alkyl or aryl halide with elemental magnesium.

❑❑