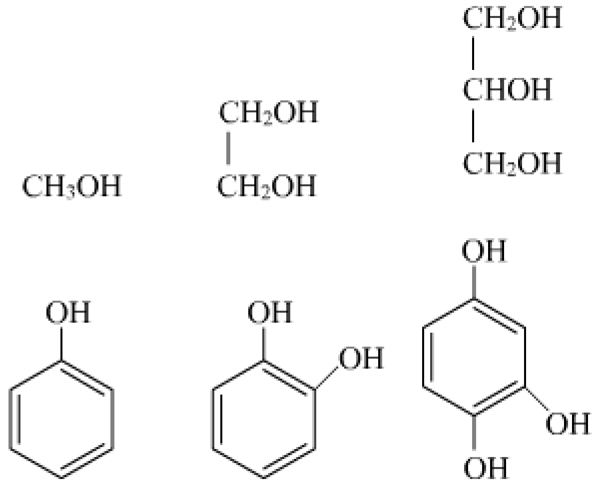
Alcohols, Phenols and Ethers

Classification and Nomenclature of Alcohols, Phenols and Ethers

Classification of Alcohols and Phenols

- On the basis of number of hydroxyl groups
- Monohydric
- Dihydric
- Polyhydric (tri-, tetra-, etc.)



Monohydric Dihydric Trihydric

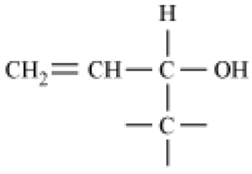
- Monohydric alcohols are classified on the basis of hybridisation of C in C−OH bond.
- Compounds containing C_{sp^3} −OH bond

  Further classified as −

- 1°, 2° and 3° alcohols
- Allylic alcohols

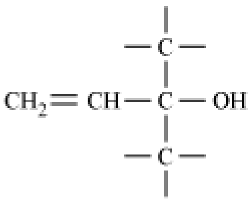
$CH_2{=}CH{-}CH_2{-}OH$

(1°)



$CH_2{=}CH{-}\overset{H}{\underset{-C-}{C}}{-}OH$

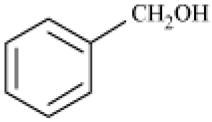
(2°)



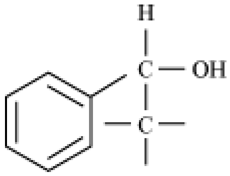
$CH_2{=}CH{-}\overset{-C-}{\underset{-C-}{C}}{-}OH$

(3°)

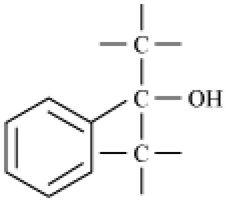
- Benzylic alcohols



(1°)



(2°)



(3°)

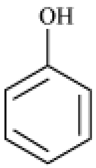
- Compounds containing C_{sp^2} −OH bond

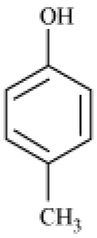
Further classified as –

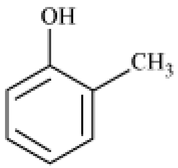
- Vinylic alcohol

$CH_2{=}CH{-}OH$

- Phenols







To test your knowledge of this concept, solve the following puzzle.

Classification of Ethers

Two categories –

- Simple or symmetrical
- The two alkyl or aryl groups attached to the oxygen atom are the same.

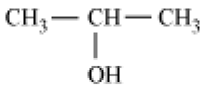
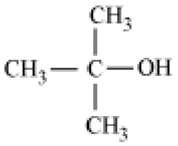
$C_2H_5OC_2H_5$ $C_3H_7OC_3H_7$

- Mixed or unsymmetrical
- The two alkyl or aryl groups attached to the oxygen atom are different.

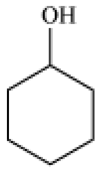
$CH_3OC_3H_7$ $C_2H_5OC_6H_5$

Nomenclature

- **Alcohols**
- The common names are derived from the common name of the alkyl group, with the word alcohol added to it.
- The IUPAC names are derived by substituting 'e' of the alkane (from which the alcohol is derived) with the suffix '–ol'.
- Common and IUPAC names of some alcohols are listed in the given table.

Compound	CH_3OH	 $CH_3-\underset{OH}{\underset{\mid}{CH}}-CH_3$	 $CH_3-\overset{CH_3}{\overset{\mid}{\underset{CH_3}{\underset{\mid}{C}}}}-OH$
Common name	Methyl alcohol	Isopropyl alcohol	*tert*-Butyl alcohol
IUPAC name	Methanol	Propan-2-ol	2-Methylpropan-2-ol

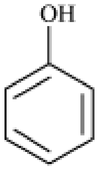
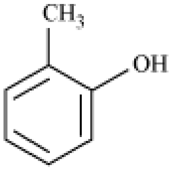
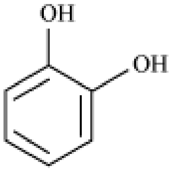
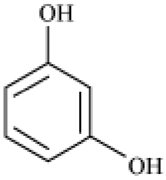
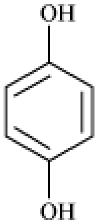
- For naming cyclic alcohols, prefix 'cyclo' is used



Cyclohexanol

- **Phenols**

Common and IUPAC names of some phenols are given below.

Compound	**Common name**	**IUPAC name**
	Phenol	Phenol
	*o*-Cresol	2-Methylphenol
	Catechol	Benzene-1,2-diol
	Resorcinol	Benzene-1,3-diol
	Hydroquinone or Quinol	Benzene-1,4-diol

- **Ethers**

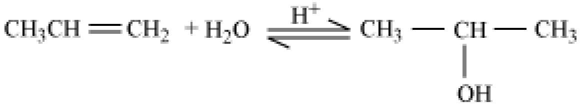
- The common names are derived from the alkyl or aryl groups by writing them as separate words and adding the word ‘ether’ at the end.
- IUPAC names of the ether is written as***"Alkoxy alkane"*** . For example IUPAC name of $CH_3OC_2H_5$ is *methoxyethane*.
- In IUPAC nomenclature of ethers, the longer chain is given priority and *'oxy'* is added to shorter chain.
- Common and IUPAC names are listed in the given table.

Compound	**Common Name**	**IUPAC name**
CH_3OCH_3	Dimethyl ether	Methoxymethane
$CH_3OCH_2CH_2CH_3$	Methyl n-propyl ether	1-Methoxypropane
$C_6H_5OCH_2CH_3$	Ethylphenyl ether	Ethoxybenzene
$C_6H_5OCH_3$	Methylphenyl ether (Anisole)	Methoxybenzene (Anisole)
$C_6H_5O(CH_2)_6 -CH_3$	Heptylphenyl ether	1-Phenoxyheptane

Methods of Preparation of Alcohols and Phenols

Preparation of Alcohols

- **From alkenes**
- By acid-catalysed hydration

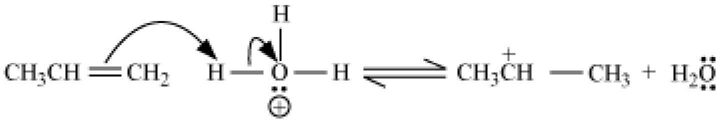


$$CH_3CH=CH_2 + H_2O \overset{H^+}{\rightleftharpoons} CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_3$$

Mechanism:

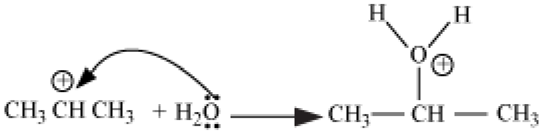
Step 1 – Protonation of alkene by electrophilic attack of H_3O^+ to form carbocation

$$H_2O + H^+ \longrightarrow H_3O^+$$

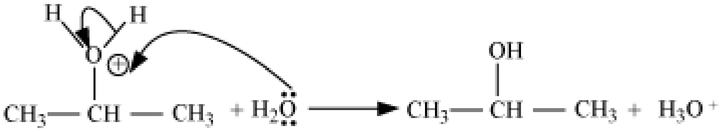


$$CH_3CH=CH_2 \quad H-\overset{\displaystyle H}{\overset{|}{\underset{\oplus}{\ddot{O}}}}-H \rightleftharpoons CH_3\overset{+}{C}H-CH_3 + H_2\ddot{O}$$

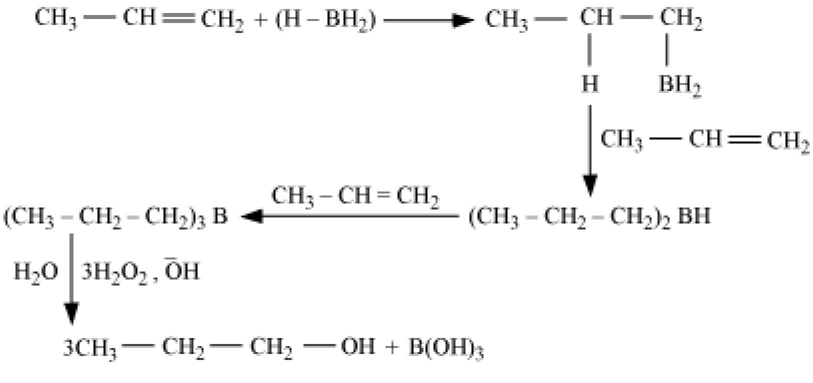
Step 2 – Nucleophilic attack of water on the carbocation



Step 3 – Deprotonation to form alcohol



- By hydroboration–oxidation



Propan-1-ol

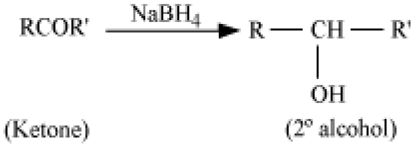
The product so formed looks as if it were formed by the addition of water to the alkene in a way opposite to Markovnikov's rule.

- **From carbonyl compounds**
- By reduction of aldehydes and ketones

Catalysts → finely divided metals such as Pt, Pd or Ni, $NaBH_4$, $LiAlH_4$

Aldehydes give 1° alcohol while ketones give 2° alcohol

$$\underset{\text{(Aldehyde)}}{RCHO} + H_2 \xrightarrow{Pd} \underset{\text{(1°alcohol)}}{RCH_2OH}$$



$$\underset{\text{(Ketone)}}{RCOR'} \xrightarrow{NaBH_4} \underset{\text{(2° alcohol)}}{R-\underset{OH}{\underset{|}{CH}}-R'}$$

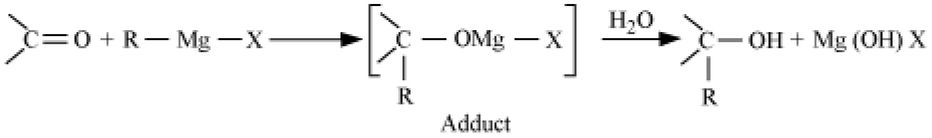
- By reduction of carboxylic acids and esters

$$\underset{\text{(Carboxylic acid)}}{RCOOH} \xrightarrow[\text{(ii) } H_2O]{\text{(i) } LiAlH_4} \underset{\text{(1° alcohol)}}{RCH_2OH}$$

Since $LiAlH_4$ is an expensive reagent, alcohol is produced from carboxylic acid commercially in another manner.

$$\underset{\text{(Carboxylic acid)}}{RCOOH} \xrightarrow[H^+]{R'OH} \underset{\text{(Ester)}}{RCOOR'} \xrightarrow[\text{Catalyst}]{H_2} RCH_2OH + R'OH$$

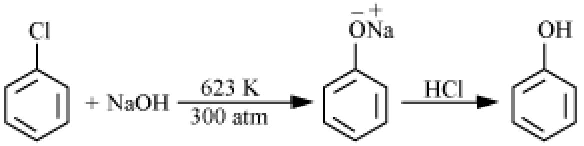
- **From Grignard reagents**



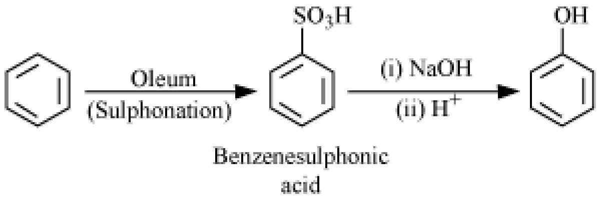
- Methanal gives 1° alcohol
- Other aldehydes give 2° alcohol
- Ketones give 3° alcohol

Preparation of Phenols (Also Known as Carbolic Acid)

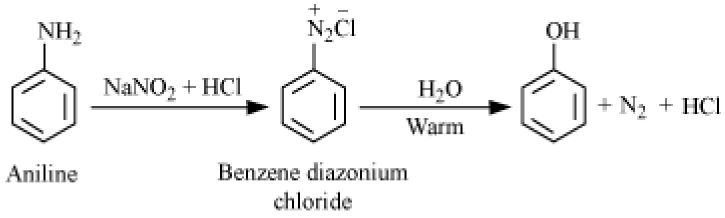
- **From haloarenes**



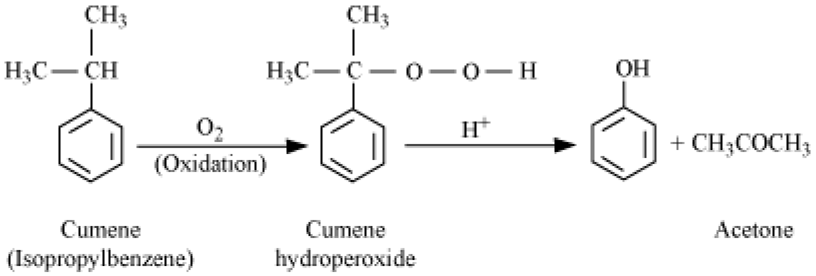
- **From benzenesulphonic acid**



- **From diazonium salts**



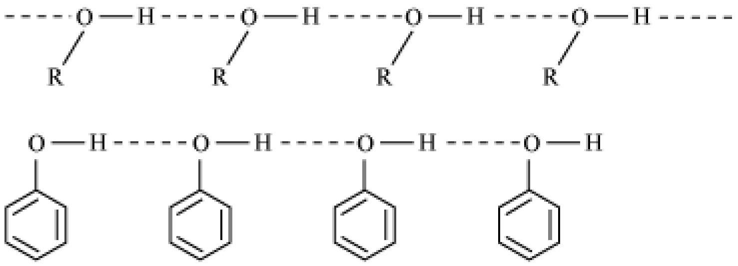
- **From cumene**



Physical Properties of Alcohols and Phenols

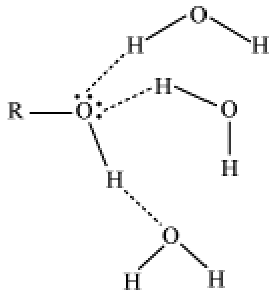
Boiling Points

- Increase with the increase in number of carbon atoms
- Reason − With the increase in the number of carbon atoms, van der Waals forces increase.
- Decrease with increase of branching
- Reason − With the increase in branching, surface area decreases and hence, van der Waals forces decrease.
- Alcohols and phenols have higher boiling points than other classes of compounds (hydrocarbons, ethers, haloalkanes, and haloarenes) of comparable molecular masses.
- Reason − They undergo extensive intermolecular hydrogen bonding resulting in aggregation of molecules.



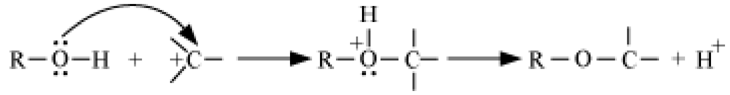
Solubility

- **Soluble in Water**
- Reason – They undergo H-bonding with water molecules.



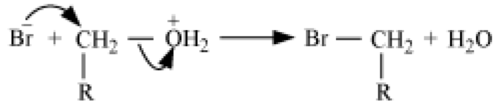
Chemical Reactions of Alcohols and Phenols

- Alcohols act both as nucleophiles and electrophiles.
- Alcohols as nucleophiles



- Protonated alcohols as electrophiles

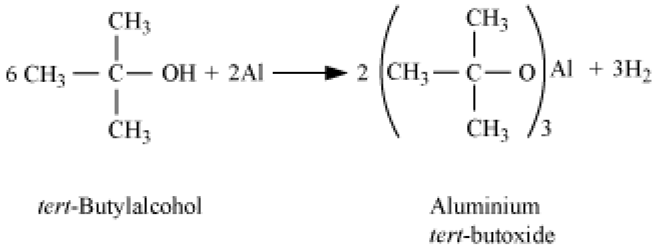
$$R-CH_2-OH + H^+ \longrightarrow R-CH_2-\overset{+}{O}H_2$$

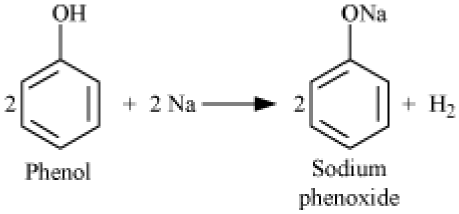


Reactions Involving Cleavage of O–H Bond

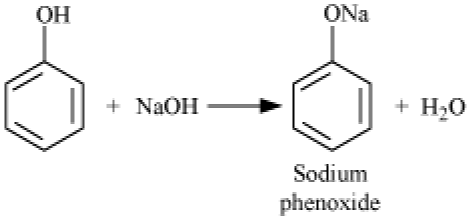
- **Acidity of alcohols and phenols**
- Reaction with active metals such as Na, K and Al

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

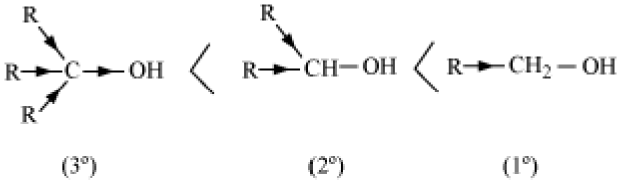




- Phenols react with aq. NaOH to form sodium phenoxides.

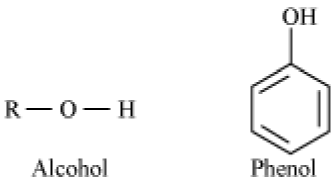


- Acidity of phenols
- Acidic character arises due to the polar nature of O−H
- The acid strength of alcohols increases in the order



- Alcohols are weaker acids than water.
- Alcohols act as Bronsted bases as well.
- Phenols are stronger acids than alcohols.

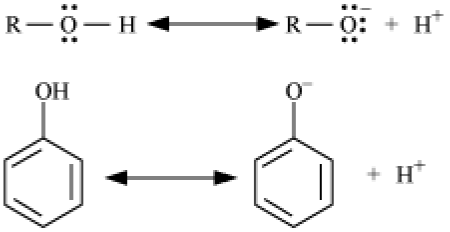
  Reason:



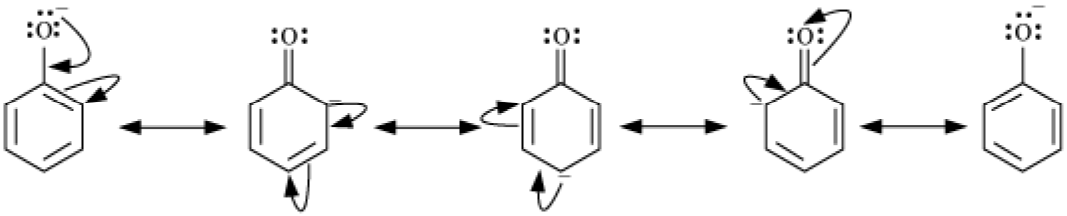
Alcohol Phenol

Let us first go through this video to see which all orbitals are involved in the formation of alcohols

In alcohol, −OH is attached to the *sp*^{3} hybridised carbon whereas in phenol, −OH is attached to the *sp*^{2} hybridised carbon. Since *sp*^{2} hybridised carbon is more electronegative than *sp*^{3}hybridised carbon, electron density on the oxygen atom in phenol decreases. As a result, the polarity of O−H bond increases, and hence, ionisation of phenol increases. This leads to increase in the acidity of phenols.



Phenoxide ion is more stable than alkoxide ion due its resonance stabilisation.



Therefore, phenol is more acidic than alcohol.

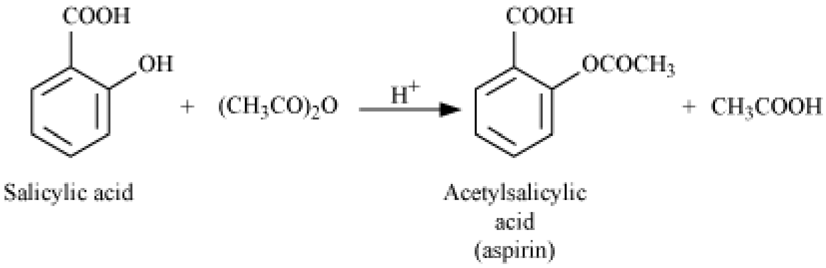
- Electron-withdrawing substituents (especially at *ortho*- and *para*- positions) increase the acidity of phenols whereas electron-donating substituents decrease acidity.
- **Esterification**

$$\mathrm{Ar/R-OH} + \underset{\text{Carboxylic acid}}{\mathrm{R'-COOH}} \xleftrightarrow{H^+} \mathrm{Ar/ROCOR'} + \mathrm{H_2O}$$

$$\mathrm{Ar/R-OH} + \underset{\text{Acid anhydride}}{\mathrm{(R'CO)_2O}} \xleftrightarrow{H^+} \mathrm{Ar/ROCOR'} + \mathrm{R'COOH}$$

- $$\mathrm{Ar/R-OH} + \underset{\text{Acid Chloride}}{\mathrm{R'COCl}} \xleftrightarrow{\text{Pyridine}} \mathrm{Ar/ROCOR'} + \mathrm{HCl}$$

- Example − Acetylation of salicylic acid



Reactions Involving Cleavage of C−O Bond in Alcohols

- **Reaction with hydrogen halides:**

$$\mathrm{R-OH+HX \xrightarrow{ZnCl_2} R-X+H_2O}$$

- Lucas test [test with Lucas regent (conc. HCl and $ZnCl_2$)] − Used for distinguishing the three classes of alcohols.

- **Reaction with phosphorus trihalides:**

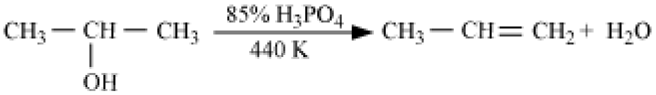
$$\mathrm{3R-OH+PX_3 \longrightarrow 3R-X+H_3PO_3 (X=Cl,Br)}$$

- **Dehydration:**

From 1° alcohol

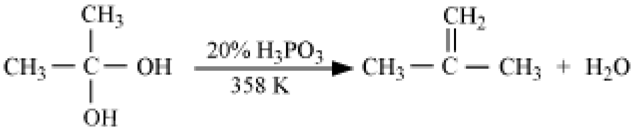
$$\mathrm{C_2H_5OH \xrightarrow[443\ K]{Conc.\ H_2SO_4} CH_2=CH_2+H_2O}$$

From 2° alcohol



$$\mathrm{CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_3 \xrightarrow[440\ K]{85\%\ H_3PO_4} CH_3-CH=CH_2+H_2O}$$

From 3° alcohol



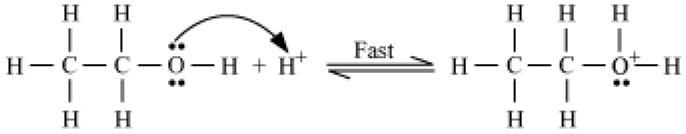
$$\mathrm{CH_3-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle OH}{\underset{|}{C}}}}-OH \xrightarrow[358\ K]{20\%\ H_3PO_3} CH_3-\overset{\displaystyle CH_2}{\overset{\|}{C}}-CH_3+H_2O}$$

Therefore, the order reactivity can be observed as

1° < 2° < 3°

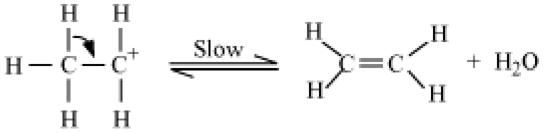
- Mechanism of dehydration

  Step 1 – Formation of protonated alcohols

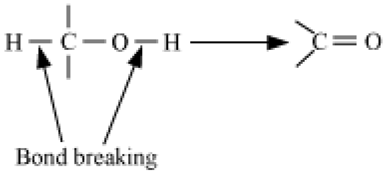


  Step 2 – Formation of carbocation

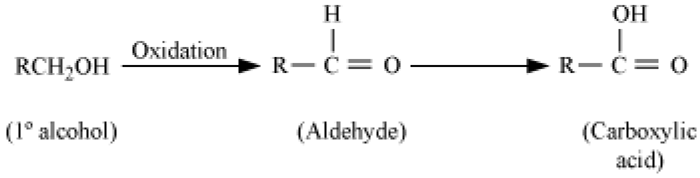
  Step 3 – Formation of alkene by elimination of a proton



- **Oxidation:** Involves formation of a carbon–oxygen double bond, with cleavage of O–H and C–H bonds



- Also known as dehydrogenation as dihydrogen is lost.
- Depending on the oxidising agent, a primary alcohol is oxidised to aldehydes and then to carboxylic acid.



Oxidising agents such as potassium dichromate converts primary alcohol to aldehydes and resist further oxidation.

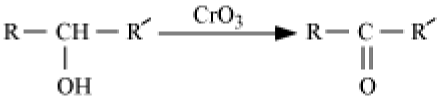
- Strong oxidising agents such as acidified $KMnO_4$ convert alcohols directly into carboxylic acid.

$$RCH_2OH \xrightarrow{\text{acidefied } KMnO_4} RCOOH$$

- Reagents such as CrO_3 in anhydrous medium, PCC (pyridinium chlorochromate) are used for isolation of aldehydes.

$$RCH_2OH \xrightarrow{CrO_3} RCHO$$
$$CH_3-CH=CH-CH_2OH \xrightarrow{PCC} CH_3-CH=CH-CHO$$

- 2° alcohols are converted into ketones by CrO_3

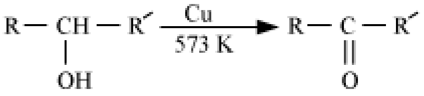


$$R-\underset{\underset{OH}{|}}{CH}-R' \xrightarrow{CrO_3} R-\underset{\underset{O}{||}}{C}-R'$$

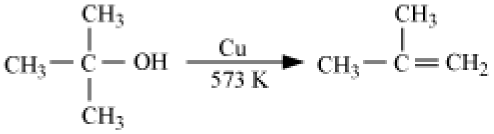
- 3° alcohols do not undergo oxidation; however, under strong oxidising agents such as $KMnO_4$ and high temperature, a mixture of carboxylic acids containing lesser number of carbon atoms is formed.

- Reaction with heated copper at 573 K

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



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



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

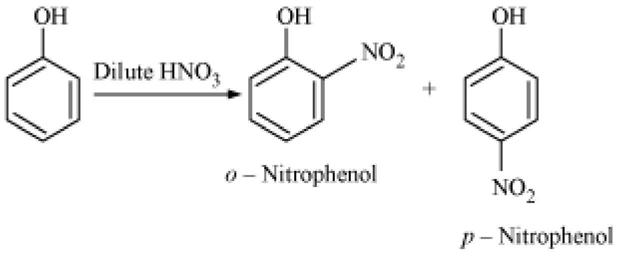
Reactions of Phenols

Electrophilic Aromatic Substitution

- The −OH group activates the benzene ring towards electrophilic substitution and directs the incoming group to *ortho*- and *para*- positions.

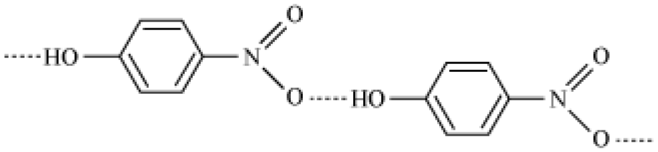
- **Nitration**

- With dilute HNO_3

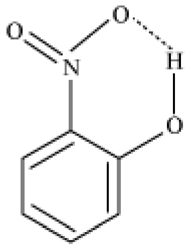


The *o*- and *p*-isomers can be separated by steam distillation.

Reason: *p*-nitrophenol is less volatile due to the association of molecules by intermolecular H-bonding, while *o*-nitrophenol is steam volatile due to intramolecular H-bonding.

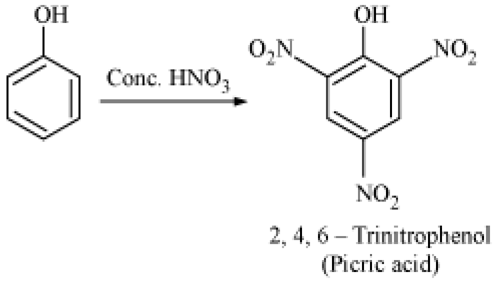


Intermolecular H–bonding in *p*–Nitrophenol

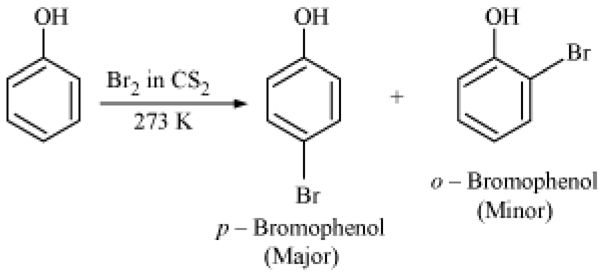


Intramolecular H–bonding in *o*–Nitrophenol

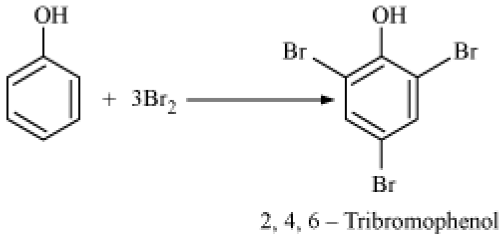
- With concentrated HNO_3:



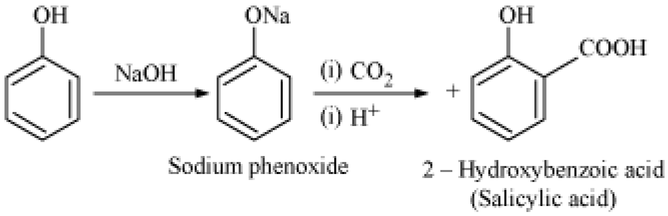
- **Halogenation**
- Reaction carried out in solvents such as CS_2 or $CHCl_3$:



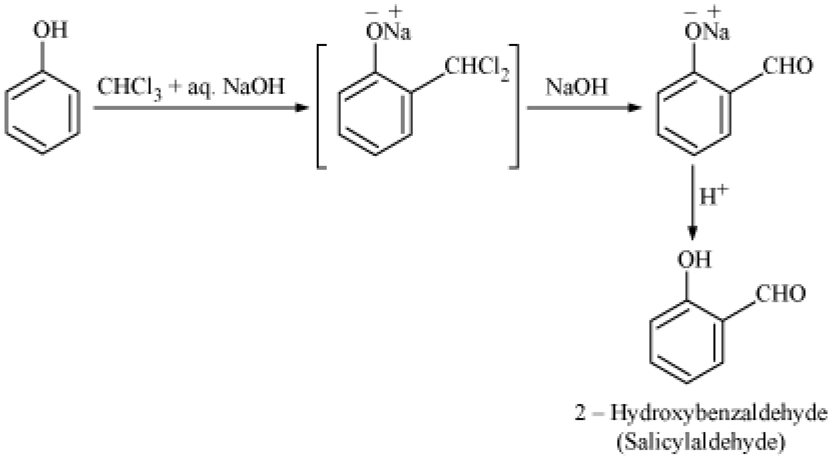
- With bromine water:



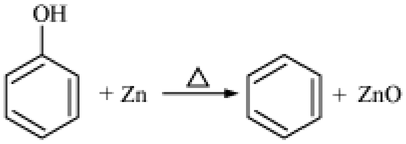
Kolbe's Reaction



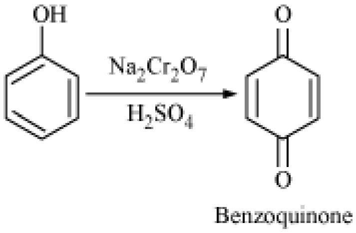
Reimer-Tiemann Reaction



Reaction with Zinc Dust



Oxidation



The presence of phenol can be confirmed by converting it to phenolphthalein which turns pink in basic solution.

Some Commercially Important Alcohols

Classification of Alcohols

- On the basis of the number of − OH groups:
- One −OH group: Monohydric alcohol, for example, methanol (CH_3OH)
- Two −OH groups: Dihydric alcohol, for example, glycol ($OH-CH_2CH_2-OH$)
- Three −OH groups: Trihydric alcohol, for example, glycerol ($HO-CH_2-CH(OH)-CH_2-OH$)

Methanol (CH_3OH)

- Known as wood spirit
- Preparation
- Earlier produced by destructive distillation of wood
- Nowadays, it is produced by catalytic hydrogenation of carbon monoxide

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

- **Properties**
  - Colourless liquid

  - Boiling point = 337 K
  - Highly poisonous – Small quantities cause blindness and large quantities cause even death.
- **Uses**
  - As a solvent in paints and varnishes
  - In the preparation of formaldehyde (HCHO)

Ethanol or Ethyl alcohol, CH_3CH_2OH

Ethanol is commonly known as alcohol. It is an active ingredient of all alcoholic beverages, namely beer, wine, whisky, rum etc.It is also referred to as spirit of wine It is also present in digestive and cough syrups. It is a neutral compound and has no effect on litmus paper. In industries, ethanol is produced by the fermentation of sugar and hence known as grain alcohol. Intake of even a small quantity of pure ethanol can be lethal. If ethanol is consumed regularly for a very long time, then it can lead to many health problems and can also prove fatal.

Do You Know:

Ethanol is usually obtained from sugarcane. Sugarcane contains a large amount of sucrose. When molasses (a concentrated and dark liquid formed by boiling sugarcane juice) is fermented, ethanol is obtained.

Preparation of Ethanol:

- **Industrial preparation of ethanol by fermentation method:**

Sugarcane juice, juice of fruits or grapes, molasses undergoes fermentation reaction in presence of invertase enzyme to form glucose and fructose.

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

- Laboratory method: By hydrolysis of alkyl halides with dilute hot alkali

$$\mathrm{C_2H_5\,Cl} \xrightarrow[-\mathrm{KCl}]{\Delta,\ \mathrm{aq.\ KOH}} \mathrm{C_2H_5\,OH}$$

- Industrial method: By hydration of ethene using:
  - Concentrated H_2SO_4 at 80 ^{o}C and 30 atm
    - $\mathrm{C_2H_4 + H_2O \xrightarrow[30\ atm]{H_2\,SO_4,\,80\,^{o}C} C_2H_5\,OH}$
  - H_3PO_4 at 300 ^{o}C and 60 atm
    - $\mathrm{C_2H_4 + H_2O \xrightarrow[60\ atm]{H_3\,PO_4,\,300\,^{o}C} C_2H_5\,OH}$

Physical properties:

1. It is a colourless liquid at room temperature, having a pleasant odour and inflammable toxic liquid.

2. It is completely miscible with water in all proportions and in organic solvents as well.

3. It is a very good organic solvent. Therefore, it is used in a lot of medicines, syrups, and tonics.

4. It is lighter than water.

5. Its consumption affects brain, liver and kidney.

Chemical properties:

1. Reaction with sodium: Ethanol reacts with sodium to produce hydrogen gas. Sodium ethoxide is also obtained in the reaction.

$$\underset{\text{Ethanol}}{\mathrm{2CH_3CH_2OH}} + \underset{\text{Sodium}}{\mathrm{2Na}} \rightarrow \underset{\text{Sodium ethoxide}}{\mathrm{2CH_3CH_2O^-Na^+}} + \underset{\text{Hydrogen}}{\mathrm{H_2}}$$

2. Dehydration reaction: When ethanol is heated with concentrated sulphuric acid, it loses one water molecule and gives ethene as a product.

$$\underset{\text{Ethanol}}{\mathrm{2CH_3CH_2OH}} \xrightarrow[\text{Conc.sulphuric acid}]{\Delta} \underset{\text{Ethene}}{\mathrm{2CH_2=CH_2}} + \underset{\text{Water}}{\mathrm{2H_2O}}$$

This reaction is known as dehydration reaction. In a chemical reaction, a substance is said to be dehydrated if it loses one or more water molecules. In this reaction, concentrated sulphuric acid acts as a dehydrating agent and removes water molecules from ethanol.

3. Combustion reaction: Combustion of alcohol results in the formation of carbon dioxide and water along with a large amount of heat and light energy.

$$\underset{\text{Ethanol}}{CH_3CH_2OH} + \underset{\text{Oxygen}}{3\,O_2} \rightarrow \underset{\text{Carbon dioxide}}{2\,CO_2} + \underset{\text{Water}}{3\,H_2O} + \text{Heat} + \text{Light}$$

Do You Know:

As a large amount of energy is obtained when alcohol burns, it is used as an additive to petrol in some countries.

It burns to give only carbon dioxide and water. Thus, it is a clean fuel. It does not give out poisonous gases such as sulphur dioxide and nitrogen dioxide. Coal and petroleum contain nitrogen and sulphur, which causes pollution. Hence, they are not clean fuels.

4. Oxidation with acidified $K_2Cr_2O_7$. Alcohols are oxidised by oxidising agent to aldehydes. Further oxidation results in the conversion of the respective aldehydes to corresponding carboxylic acids.

$$CH_3\,OH \xrightarrow[K_2\,Cr_2\,O_7]{[O]} HCHO + H_2O \xrightarrow[K_2\,Cr_2\,O_7]{[O]} HCOOH$$

$$C_2H_5\,OH \xrightarrow[K_2\,Cr_2\,O_7]{[O]} CH_3\,CHO + H_2O \xrightarrow[K_2\,Cr_2\,O_7]{[O]} CH_3\,COOH$$

5. Esterification reaction. This reaction results in the formation of fruity smelling esters by the combination of alcohol and carboxylic acids in the presence of concentrated H_2SO_4.

$$CH_3\,OH + CH_3\,COOH \xrightarrow{\text{conc. } H_2\,SO_4} CH_3\,COOCH_3 + H_2O$$

$$C_2H_5\,OH + CH_3\,COOH \xrightarrow{\text{conc. } H_2\,SO_4} CH_3\,COOC_2\,H_5 + H_2O$$

6. Reaction with phosphorous halide. alkyl halides are formed in this reaction.

$$3\ CH_3\,OH + PCl_3 \longrightarrow 3\ CH_3\,Cl + H_3\,PO_3$$

$$3\,C_2H_5\,OH + PCl_3 \longrightarrow 3\,C_2H_5\,Cl + H_3\,PO_3$$

Uses

- As a solvent in manufacture of paint and a number of carbon compounds

- Denaturation of alcohol – Commercial alcohol becomes unfit for drinking by mixing some copper sulphate (to give it a colour) and pyridine (a foul smelling liquid). This is known as **denaturation** of alcohol.

Commercially Important Forms of Ethanol

- Denatured alcohol:
- Addition of poisonous substances like pyridine, methyl alcohol to pure ethanol for making it unfit for consumption
- Also called methylated spirit
- Contains 5% methyl alcohol
- Used for industrial purposes
- Spurious alcohol:
- Illicit liquor prepared by improper distillation
- Contains large portions of methanol
- Fatal for human consumption
- Used as a solvent for paints and varnishes

Ethers

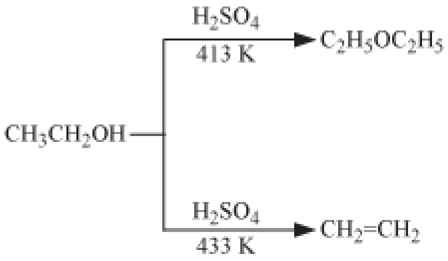
Preparation

- **By dehydration of alcohols**

- Alcohols undergo dehydration in the presence of protic acids like H_2SO_4, H_3PO_4.

- Product may be alkene or ether depending on the reaction conditions.

Example:



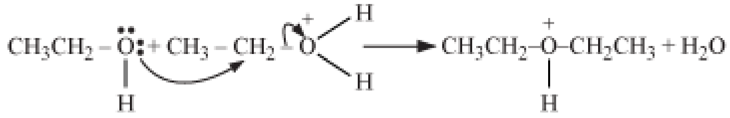
- Mechanism:

Formation of ether follows S_N2 mechanism.

Step 1

$$CH_3-CH_2-\ddot{\underset{\cdot\cdot}{O}}-H + H^+ \longrightarrow CH_3-CH_2-\overset{H}{\overset{|}{\overset{+}{\underset{\cdot\cdot}{O}}}}-H$$

Step 2



$$CH_3CH_2-\underset{H}{\underset{|}{\ddot{O}}}: + CH_3-CH_2-\overset{+}{O}\begin{matrix}H\\H\end{matrix} \longrightarrow CH_3CH_2-\underset{H}{\underset{|}{\overset{+}{O}}}-CH_2CH_3 + H_2O$$

Step 3

$$CH_3CH_2-\underset{H}{\underset{|}{\overset{+}{O}}}-CH_2CH_3 \longrightarrow CH_3CH_2-O-CH_2CH_3 + H^+$$

- This method is applied to prepare ethers having primary alkyl groups only.

- When the alkyl group is 2° or 3°, elimination competes over substitution, and this leads to the formation of alkene.

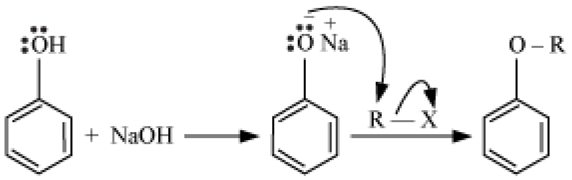
- **Williamson synthesis**

$$R-X + R'-\ddot{\underset{\cdot\cdot}{O}}\ Na \longrightarrow R-\ddot{\underset{\cdot\cdot}{O}}-R' + NaX$$

- Better results are obtained if the alkyl halide is 1°. For 2° and 3° halides, elimination competes over substitution to form alkenes.

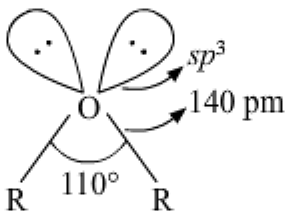
  Reason:Alkoxides are nucleophiles as well as strong bases. They react with alkyl halides, leading to elimination reactions.

- This method can be used for converting phenols to ethers also.



Structure

- Ethers are polar molecules with two alkyl groups attached to the O atom which has two lone pairs of electron on it.
- Just like water molecules, ethers also have bent geometry.
- O atom is sp^3 hybridised.
- C-O bond angle is about 110^0 and the bond length is about 140 pm.



- Bond angle in case of diphenylether is about 124^0. This increase in bond angle is due to repulsion between the two bulky phenyl groups.

Physical Properties

- **Boiling point**

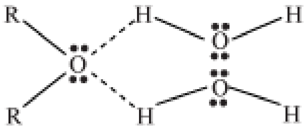
  Comparable to those of alkanes, but much lower than those of alcohols of comparable molecular mass

- Reason: Alcohols undergo intermolecular H−bonding while ethers do not

- **Solubility**

  Soluble in water

- Reason: Form H−bonds with water



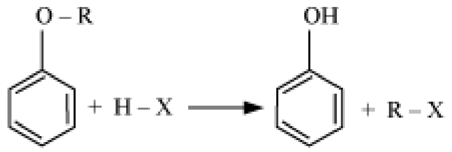
Chemical Reactions

- **Cleavage of C−O bond in ethers**

- React with excess of hydrogen halide under drastic conditions. Dialkyl ethers give two alkyl halide molecules.

$$R-O-R+HX \longrightarrow RX+R-OH$$
$$R-OH+HX \longrightarrow R-X+H_2O$$

- Alkyl aryl ethers react with hydrogen halide to give phenol and alkyl halide. Aryl−oxygen bond is not cleaved due to the high stability of aryl−oxygen bond.

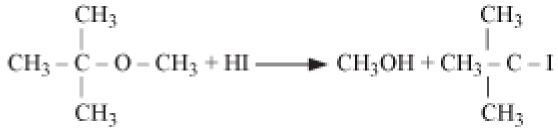


- When the two alkyl groups are different, one alkyl halide molecule and one alcohol molecule is formed.

- The order of reactivity of hydrogen halide is

  HCl < HBr < HI

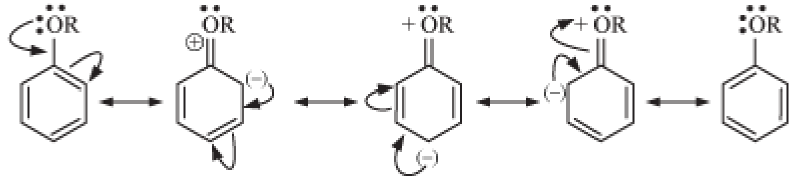
- When one of the alkyl groups is tertiary, the alkyl halide is formed from the tertiary alkyl group.



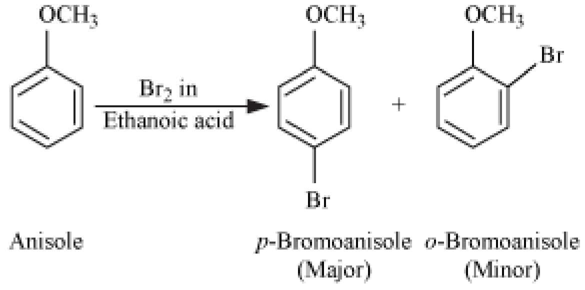
$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-O-CH_3 + HI \longrightarrow CH_3OH + CH_3-\overset{CH_3}{\underset{CH_3}{C}}-I$$

- **Electrophilic substitution**

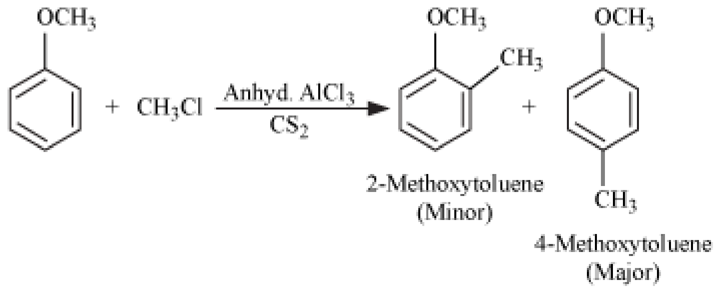
  The alkoxy (−OR) group is *ortho*− and *para*− directing, and activates the aromatic ring towards electrophilic substitution due to resonance.



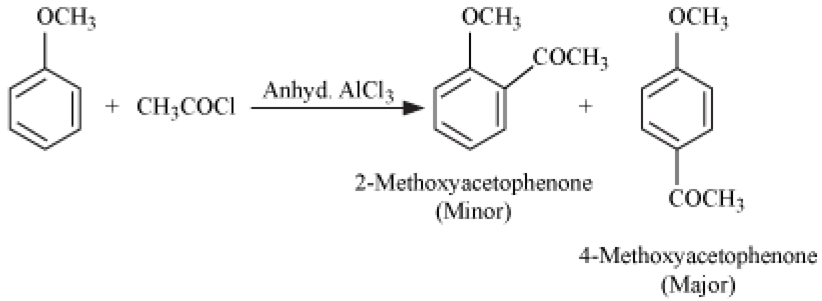
- Halogenation



- Friedel-Crafts alkylation



- Friedel-Crafts Acylation



- Nitration