

Organic Chemistry II

FOR CHEMISTRY' STUDENTS, COLLEGE OF ENGINEERING

CREDIT HOURS; 2 (2+0)

Alcohol, Phenols and Ethers

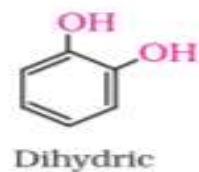
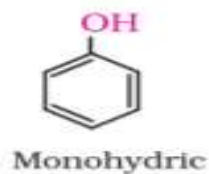
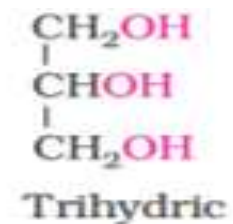
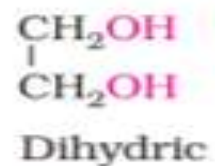
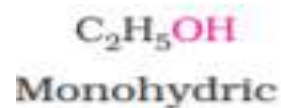
- **Alcohols, phenols and ethers** may be viewed as organic *derivatives of water*.

| | | | | | |
|--------------|--------------|---------------|--------------|---------------|----------------|
| H-O-H | R-O-H | Ar-O-H | R-O-R | R-O-Ar | Ar-O-Ar |
| Water | Alcohol | Phenol | Ether | | |

- **Alcohols and phenols** have a common functional group, *the hydroxyl group, -OH*.
- An **alcohol** contains one or more hydroxyl (OH) group(s) directly attached to carbon atom(s), of an *aliphatic system* (CH₃OH).
- A **phenol** contains -OH group(s) directly attached to carbon atom(s) of an *aromatic system* (C₆H₅OH).
- **Ethers**; the substitution of a hydrogen atom in a hydrocarbon by *an alkoxy*
- or *aryloxy group* (**R-O/Ar-O**) (CH₃OCH₃), the substitution of a hydrogen atom of hydroxyl group of an alcohol or phenol by an alkyl or aryl group.

Classification of Alcohols and Phenols

- Alcohols and phenols may be classified as *mono-, di-, tri- or polyhydric compounds* depending on whether they contain *one, two, three or many hydroxyl groups*, respectively.



Classification of Alcohols and Phenols

➤ **Monohydric alcohols** are classified according to the hybridization of the carbon atom to which the hydroxyl group is attached.

(i) **Compounds containing C_{sp^3} -OH bond**: the -OH group is attached to an sp^3 hybridized carbon atom of an alkyl group.

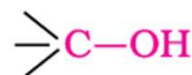
- **Primary, secondary and tertiary alcohols**: the -OH group is attached to primary, secondary and tertiary carbon atom, respectively.



Primary (1°)

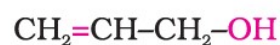


Secondary (2°)

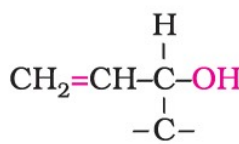


Tertiary (3°)

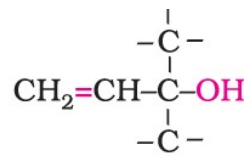
- **Allylic alcohols**: the -OH group is attached to a sp^3 hybridized carbon next to the carbon-carbon double bond.



Primary

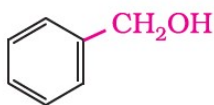


Secondary

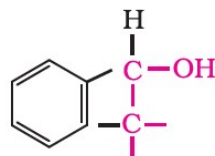


Tertiary

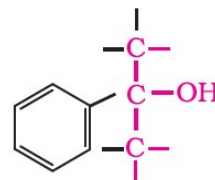
- **Benzylic alcohols**: In these alcohols, the -OH group is attached to a sp^3 -hybridized carbon atom next to an aromatic ring.



Primary



Secondary

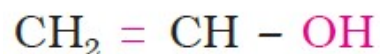


Tertiary

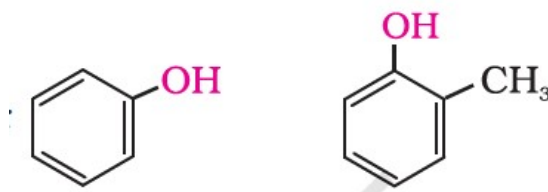
Classification of Alcohols and Phenols

(ii) **Compounds containing C_{sp^2} -OH bond**: these alcohols contain —OH group bonded to a carbon-carbon double bond.

- **vinyl alcohols**: —OH group bonded to a vinylic carbon.



- **Phenols**: —OH group bonded to an aryl carbon.



Classification of Ethers

➤ **Ethers are classified:**

- **Simple or symmetrical ethers**, if the alkyl or aryl groups attached to the oxygen atom are the same.
Example: Diethyl ether, $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$.
- **Mixed or unsymmetrical ethers**, if the alkyl or aryl groups attached to the oxygen atom are different.
Example: $\text{C}_2\text{H}_5\text{OCH}_3$ and $\text{C}_2\text{H}_5\text{OC}_6\text{H}_5$.

Nomenclature of Alcohols

- The **common name** of an alcohol is derived from the common name of the alkyl group and adding the word alcohol to it.
Alkyl alcohol

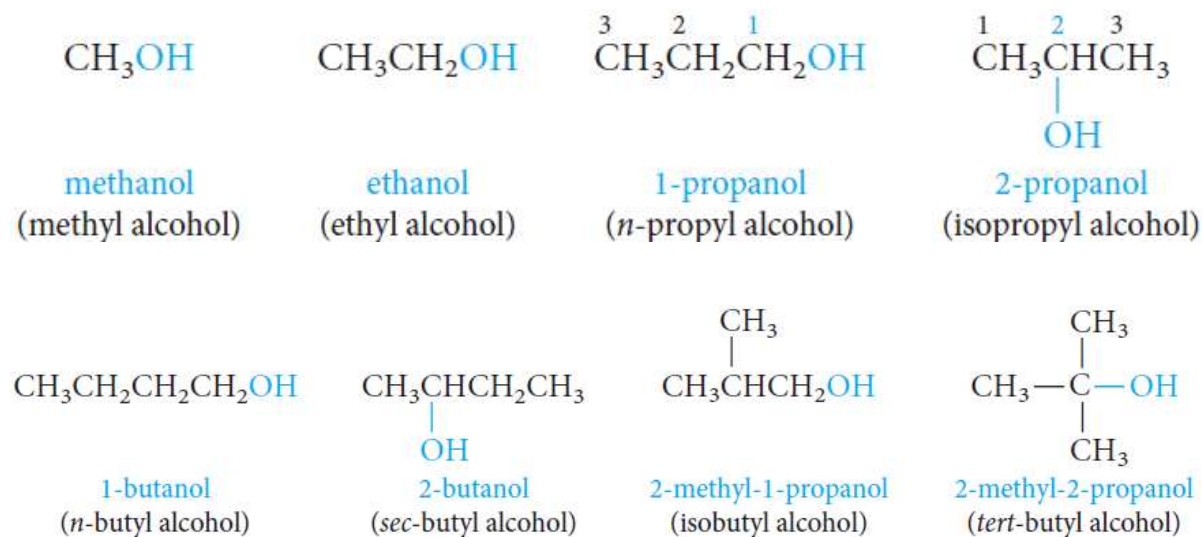
Example: CH₃OH is methyl alcohol.

- In the **IUPAC system**, alcohols are named according to the following rules.

1. Select the **longest continuous carbon chain that contains the -OH group**.

Drop the **-e** ending of the parent alkane and replace it by the suffix **-ol**: **Alkane - e + ol = Alkanol**

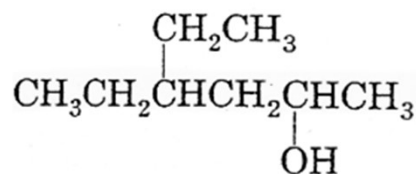
2. When isomers are possible, the chain is numbered so as to give the functional group (-OH) the **lowest possible number**.



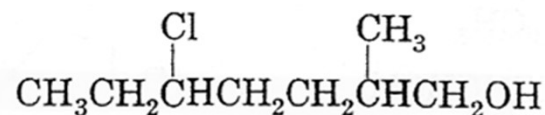
Nomenclature of Alcohols

3. **When alkyl side chains or other groups are present;** they are named alphabetically and their positions are indicated by a number.

The position of the functional group (-OH) is always given the lowest possible number at the end of the name.



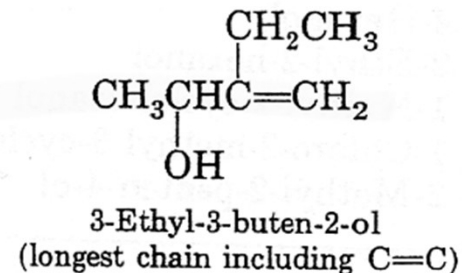
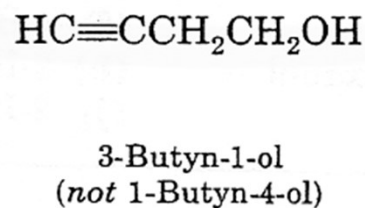
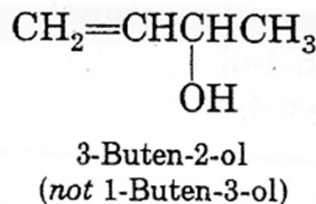
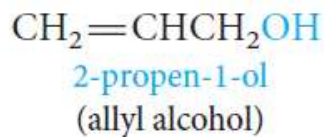
4-Ethyl-2-hexanol
(not 3-Ethyl-5-hexanol)



5-Chloro-2-methyl-1-heptanol
(not 3-Chloro-6-methyl-7-heptanol)

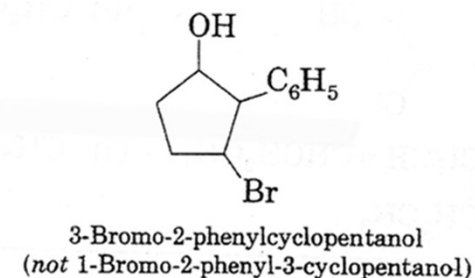
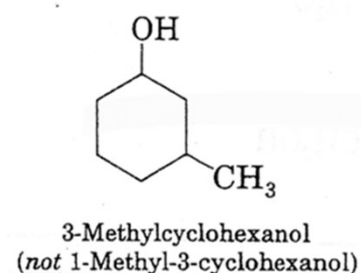
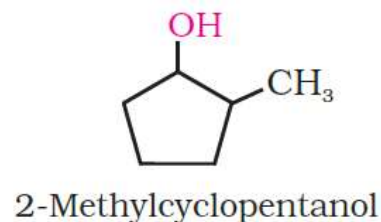
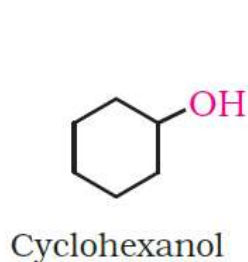
4. **With Unsaturated Alcohols;** If a molecule contains both an -OH group and a C=C or C-C triple bond, the -OH group takes preference before the double or triple bonds in getting the lower number.

The name should include (if possible) both the hydroxyl and the unsaturated groups, even if this does not make the longest chain the parent hydrocarbon.

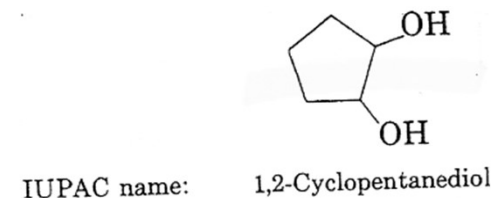
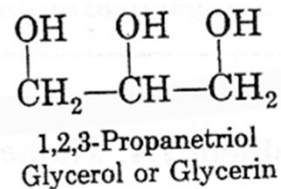
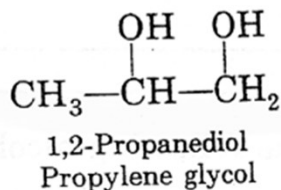
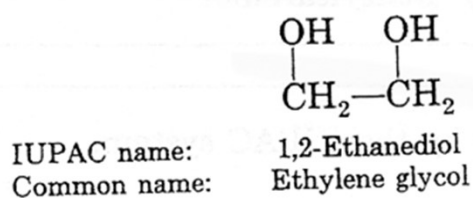


Nomenclature of Alcohols

- **Cyclic alcohols** are named using the prefix *cyclo* and considering the —OH group attached to C-1.

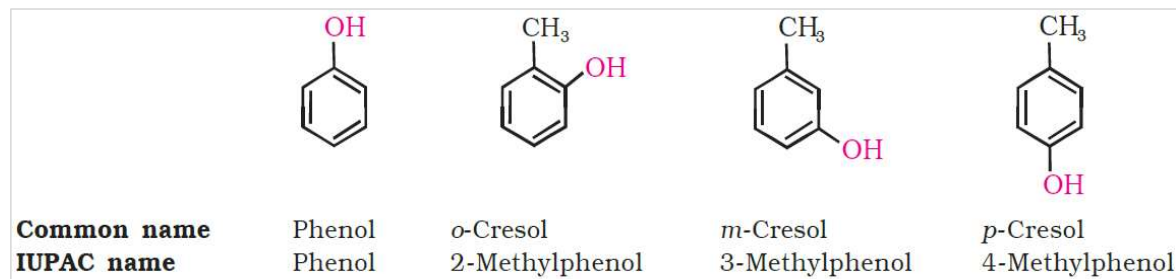


- For naming **polyhydric alcohols**, the 'e' of alkane is retained and the ending 'ol' is added.
 - The number of —OH groups is indicated by adding the multiplicative prefix, di, tri, etc., before 'ol'.
 - The positions of —OH groups are indicated by appropriate locantions
e.g., HO—CH₂—CH₂—OH is named as **ethane-1, 2-diol**.
 - **Compounds with two adjacent alcohol groups** are called **glycols**.

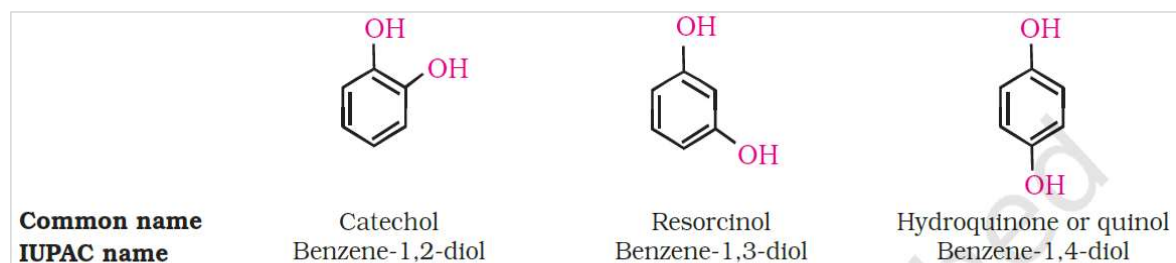


Nomenclature of Phenols

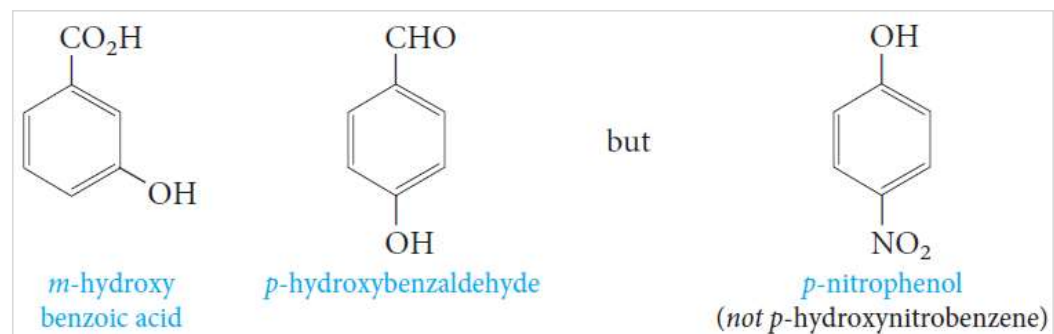
- The simplest hydroxy derivative of benzene is **phenol** and its common name and also an accepted IUPAC name.



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

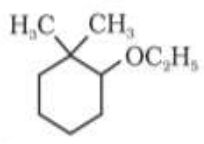


- The **hydroxyl group is named as a substituent** when it occurs in the same molecule with **carboxylic acid**, **aldehyde**, or **ketone** functionalities, which have priority in naming.



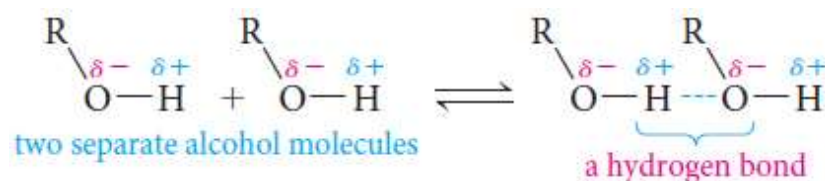
Nomenclature of Ethers

- **Common names** of ethers are derived from the names of **alkyl/aryl groups** written as separate words in **alphabetical order** and adding the word 'ether' at the end. **alkyl/aryl ether**
- If **both the alkyl groups** are the same, the prefix 'di' is added before the alkyl group.
- **IUPAC system**, ethers are regarded as **hydrocarbon derivatives** in which a hydrogen atom is replaced by;
 - an **alkoxy** group ($-OR$) or **aryloxy** group ($-OAr$),
where R and Ar represent alkyl and aryl groups, respectively.
- *The larger (R) group is chosen as the parent hydrocarbon.*

| 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 |
| $CH_3O-\underset{\substack{ \\ CH_3}}{CH}-CH_3$ | Methyl isopropyl ether | 2-Methoxypropane |
| $C_6H_5-O-CH_2-CH_2-\underset{\substack{ \\ CH_3}}{CH}-CH_3$ | Phenyl isopentyl ether | 3- Methylbutoxybenzene |
| $CH_3-O-CH_2-CH_2-OCH_3$ | — | 1,2-Dimethoxyethane |
|  | — | 2-Ethoxy- -1,1-dimethylcyclohexane |

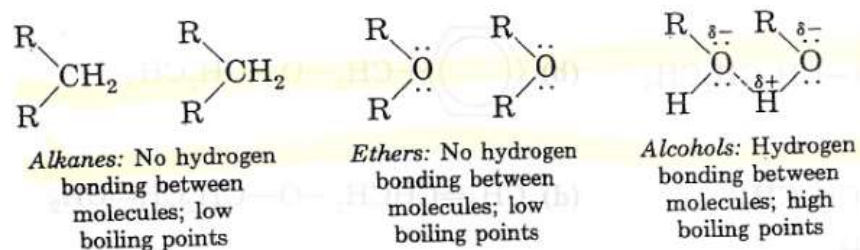
Hydrogen Bonding in Alcohols, Phenols and Ethers

- The O-H bond is polarized by the high electronegativity of the oxygen atom and places a partial positive charge on the hydrogen atom and a partial negative charge on the oxygen atom.

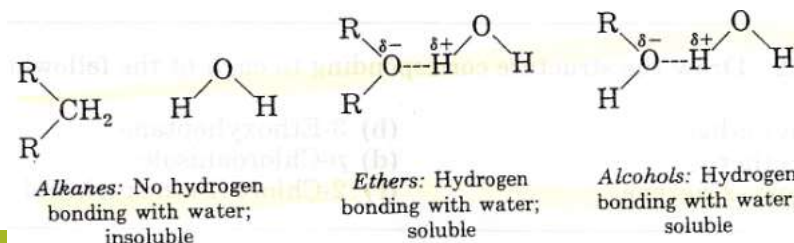


- Two or more alcohol molecules thus become loosely bonded to one another through hydrogen bonds.
- Hydrogen bonds are weaker than ordinary covalent bonds.

- Ether** molecules cannot form hydrogen bonds with one another, as their structures has no O-H bonds.



- The **lower molecular-weight alcohols and ethers** can form H-bond with water molecules.



Physical Properties of Alcohols, Phenols and Ethers

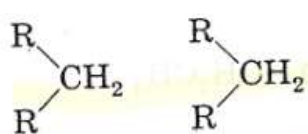
○ Physical State

- The simplest **alcohol**, methanol, is a liquid at room temperature.
In contrast, alkanes from methane to butane are gases.
- **Phenol** is a colorless, crystalline, and low-melting solid and other phenols also are solids.
- **Ethers** are colorless compounds with characteristic, relatively pleasant odors.

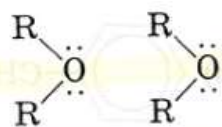
○ Boiling Points

- **Ethers** have lower boiling points (bp's) than **alcohols** with an equal number of carbon atoms.
- **Ether** has nearly the same b.p. as the corresponding hydrocarbon in which a -CH₂- group replaces the ether's oxygen.

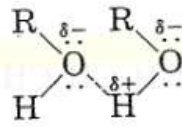
Because of their structures (no O-H bonds), ether molecules cannot form hydrogen bonds with one another.



Alkanes: No hydrogen bonding between molecules; low boiling points



Ethers: No hydrogen bonding between molecules; low boiling points



Alcohols: Hydrogen bonding between molecules; high boiling points

| Compound | Formula | bp | mol wt | Water solubility (g/100 mL, 20°C) |
|---------------|---|-------|--------|-----------------------------------|
| 1-butanol | CH ₃ CH ₂ CH ₂ CH ₂ OH | 118°C | 74 | 7.9 |
| diethyl ether | CH ₃ CH ₂ -O-CH ₂ CH ₃ | 35°C | 74 | 7.5 |
| pentane | CH ₃ CH ₂ -CH ₂ -CH ₂ CH ₃ | 36°C | 72 | 0.03 |

Physical Properties of Alcohols, Phenols and Ethers

○ Boiling Points

- **Series of normal alcohols;** the boiling points increase with increasing molecular weights.
- A comparison of boiling points among **isomeric alcohols;** The boiling points decrease as the number of alkyl branches from the carbinol group increases.

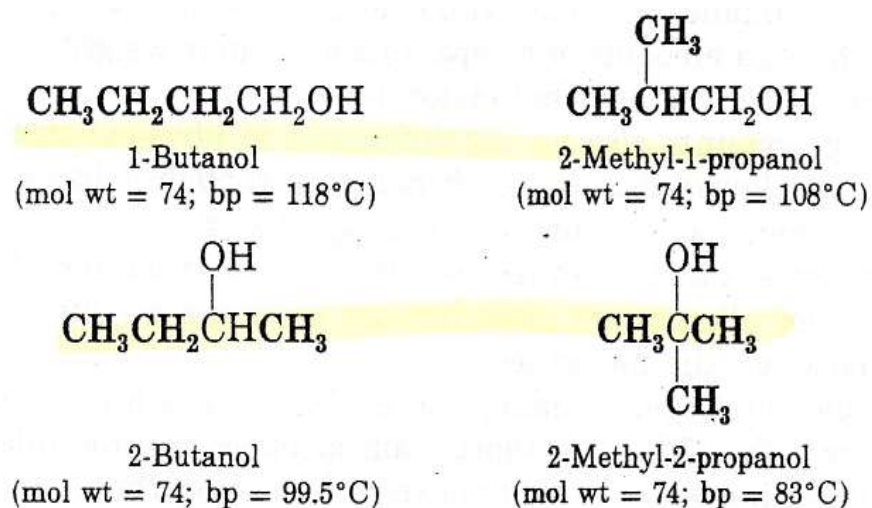


Table 7.1 Boiling Point and Water Solubility of Some Alcohols

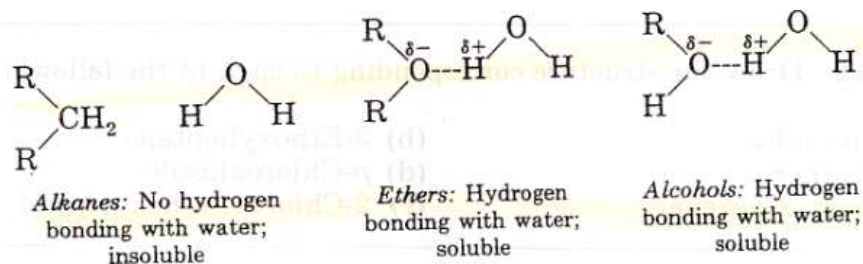
| Name | Formula | bp, °C | Solubility in H ₂ O g/100 g at 20°C |
|------------|--|--------|---|
| methanol | CH ₃ OH | 65 | completely miscible |
| ethanol | CH ₃ CH ₂ OH | 78.5 | completely miscible |
| 1-propanol | CH ₃ CH ₂ CH ₂ OH | 97 | completely miscible |
| 1-butanol | CH ₃ CH ₂ CH ₂ CH ₂ OH | 117.7 | 7.9 |
| 1-pentanol | CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ OH | 137.9 | 2.7 |
| 1-hexanol | CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ OH | 155.8 | 0.59 |

Physical Properties of Alcohols, Phenols and Ethers

○ Solubility

- The **lower alcohols** are completely miscible with water.
- As the number of carbons in the alcohol increases, the solubility in water decreases.
- **Low-molecular-weight ethers**, such as dimethyl ether, are quite soluble in water.

Ether molecules can form hydrogen bonds to water.



| Structure | Name | Mol. wt | Bp (°C) | Solubility in H ₂ O at 20°C |
|--|------------------------|---------|---------|--|
| CH ₃ CH ₂ CH ₃ | propane | 44 | -42 | insoluble |
| CH ₃ OCH ₃ | methyl ether | 46 | -24 | soluble |
| CH ₃ CH ₂ OH | ethanol | 46 | 78 | soluble |
| CH ₃ CH ₂ CH ₂ CH ₃ | <i>n</i> -butane | 58 | -0.5 | insoluble |
| CH ₃ CH ₂ OCH ₃ | ethyl methyl ether | 60 | 8 | soluble |
| CH ₃ CH ₂ CH ₂ OH | 1-propanol | 60 | 97 | soluble |
| CH ₃ (CH ₂) ₃ CH ₃ | <i>n</i> -pentane | 72 | 35 | insoluble |
| CH ₃ CH ₂ OCH ₂ CH ₃ | ethyl ether | 74 | 36 | 7.5 g/100 g |
| CH ₃ (CH ₂) ₂ CH ₂ OH | 1-butanol | 74 | 118 | 7.9 g/100 g |
| CH ₃ (CH ₂) ₅ CH ₃ | <i>n</i> -heptane | 100 | 98 | insoluble |
| CH ₃ (CH ₂) ₂ O(CH ₂) ₂ CH ₃ | <i>n</i> -propyl ether | 102 | 91 | 0.2 g/100 g |
| CH ₃ (CH ₂) ₄ CH ₂ OH | 1-hexanol | 102 | 157 | 0.6 g/100 g |

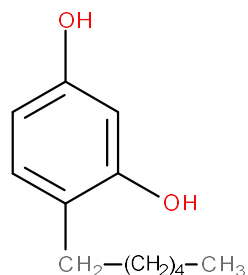
- **Phenol** and most other phenols are slightly soluble in water .

Importance of Alcohols, Phenols and Ethers

- *Alcohols, phenols and ethers are the basic compounds for the formation of detergents, antiseptics and fragrances, respectively.*
- These classes of compounds find wide applications in industry as well as in day-to-day life.
 - The sugar we eat, the cotton used for fabrics, the paper we use for writing, are all made up of compounds containing – OH groups.
 - **Ethanol** is used as a solvent in paint industry and in the preparation of a number of carbon compounds.
 - The **commercial alcohol** is made unfit for drinking by mixing in it some copper sulphate (to give it a color) and pyridine (a foul smelling liquid).
 - Ingestion of **ethanol** acts on the central nervous system.
 - **Methanol** is poisonous in nature. Ingestion of even small quantities of methanol can cause blindness and large quantities causes even death.
 - **Methanol** is used as a solvent in paints, varnishes and chiefly for making formaldehyde.
 - **Ethylene glycol** is used as the “permanent” antifreeze in automobile radiators and as a raw material in the manufacture of Dacron.
 - **Ethylene glycol** is completely miscible with water.
 - **Glycerol** is a syrupy, colorless, water-soluble, high-boiling liquid with a distinctly sweet taste. Its soothing qualities make it useful in shaving and toilet soaps and in cough drops and syrups.

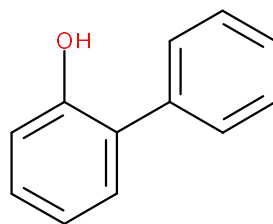
Importance of Alcohols, Phenols and Ethers

Occurrence and uses of phenols



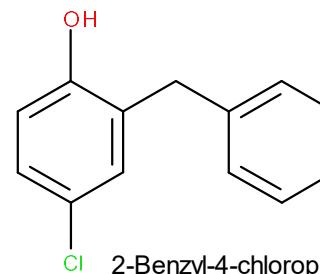
4-Hexylresorcinol

an antiseptic

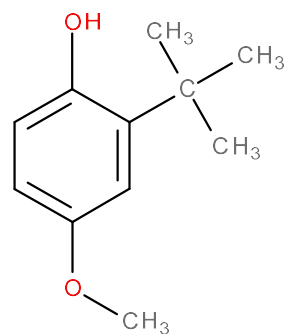


2-Phenylphenol

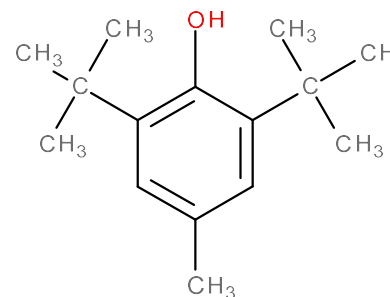
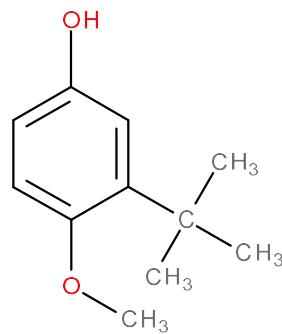
disinfectants



2-Benzyl-4-chlorophenol



BHAs (butylated hydroxyanilines)



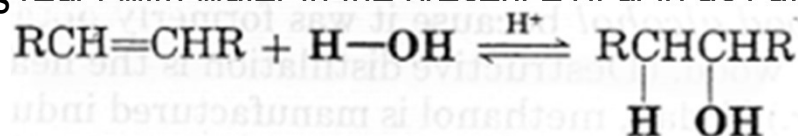
BHT
(butylated hydroxytoluene)

antioxidants

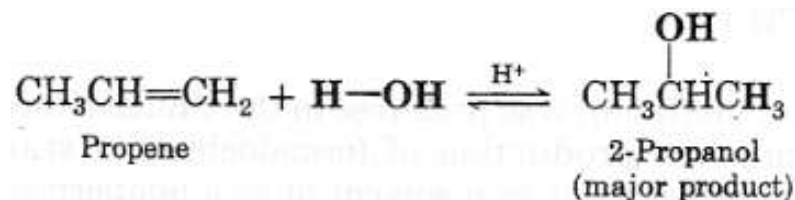
Preparation of Alcohols

From Alkenes

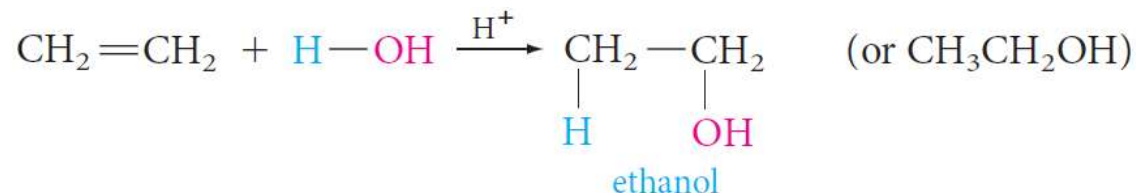
(i) **Hydration of Alkenes:** alkenes react with water in the presence of acid as catalyst to form alcohols.



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



- *It is not possible to prepare primary alcohols* except Ethanol.

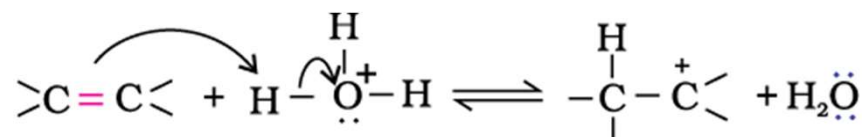
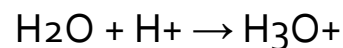


Preparation of Alcohols

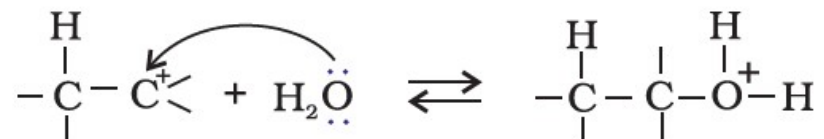
From Alkenes

Hydration of Alkenes; **Mechanism:** *three steps*

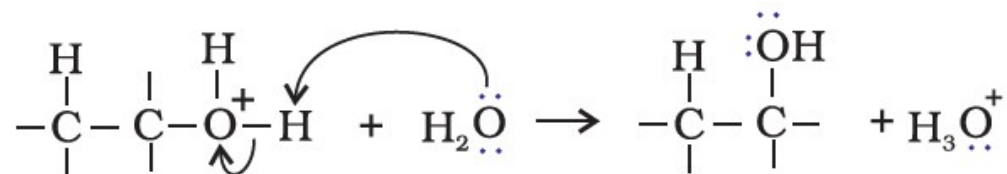
Step 1: Protonation of alkene to form carbocation by electrophilic attack of H_3O^+ .



Step 2: Nucleophilic attack of water on carbocation



Step 3: Deprotonation to form an alcohol.

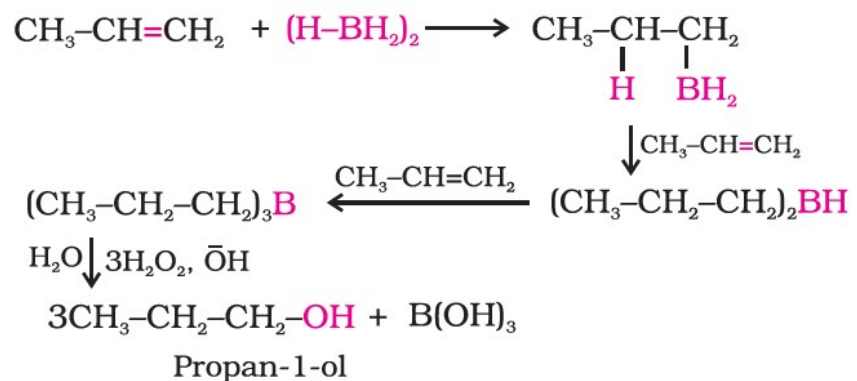


Preparation of Alcohols

From Alkenes

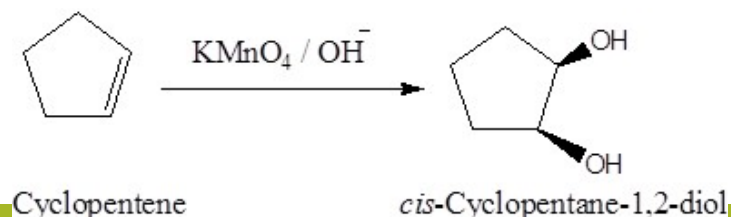
(ii) *Hydroboration-oxidation:*

- Diborane (BH_3)₂ reacts with alkenes to give trialkyl boranes as addition product.
- This is oxidized to alcohol by hydrogen peroxide in the presence of aqueous sodium hydroxide.



The alcohol so formed looks as if it has been formed by the addition of water to the alkene in a way **opposite to the Markovnikov's rule**.

(iii) *Oxidation of Cycloalkenes:* alkenes react with alkaline potassium permanganate to form glycols.

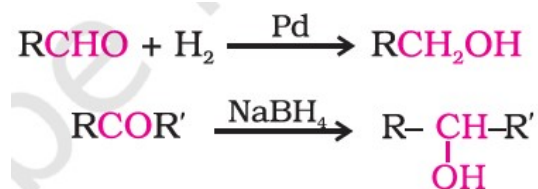


Preparation of Alcohols

From Carbonyl Compounds

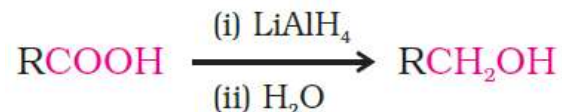
(i) **Reduction of aldehydes and ketones:** aldehydes and ketones are reduced to the corresponding alcohols by addition of hydrogen in the presence of catalysts (catalytic hydrogenation).

- **Catalyst;** metals such as platinum, palladium or nickel, sodium borohydride (NaBH_4) or lithium aluminium hydride (LiAlH_4).
- Aldehydes yield primary alcohols whereas ketones give secondary alcohols.



(ii) **By reduction of carboxylic acids and esters:**

- Carboxylic acids are reduced to primary alcohols by lithium aluminium hydride, a strong reducing agent.



- Commercially, acids are reduced to alcohols by converting them to the esters followed by their reduction using hydrogen in the presence of catalyst (catalytic hydrogenation).

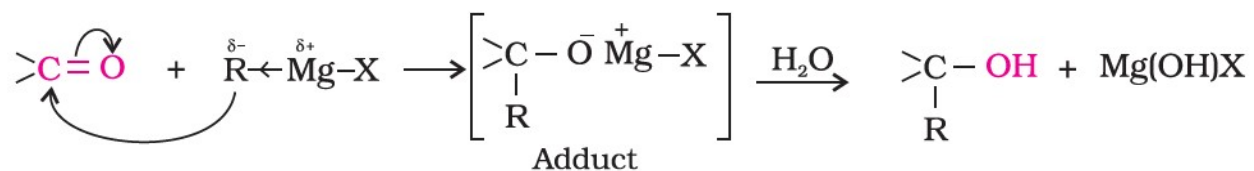


Preparation of Alcohols

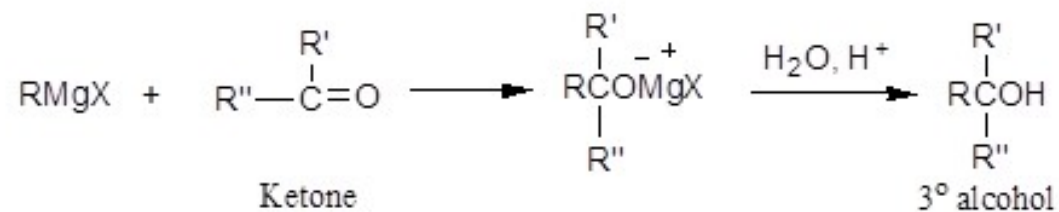
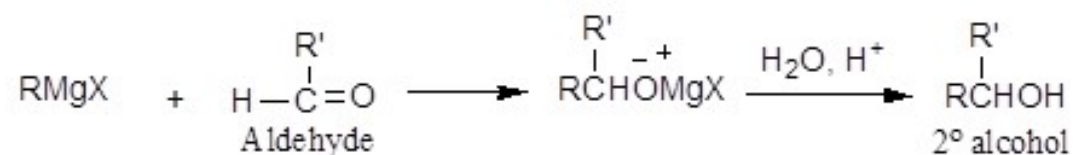
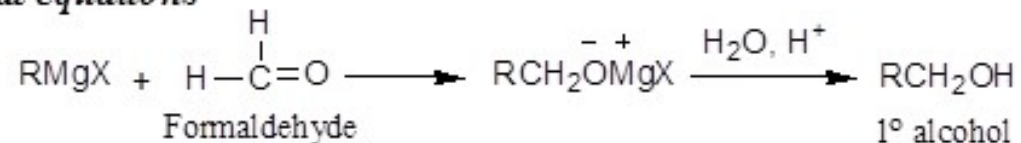
From Carbonyl Compounds

(iii) Addition of Grignard's Reagent to Aldehydes and Ketones:

- **Step 1;** The reaction is the nucleophilic addition of Grignard reagent to the carbonyl group to form an adduct.
- **Step 2;** Hydrolysis of the adduct yields an alcohol.



General equations

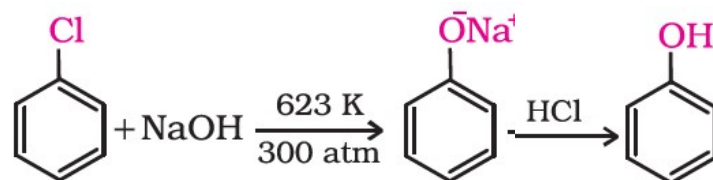


Preparation of Phenols

From Benzene Derivatives

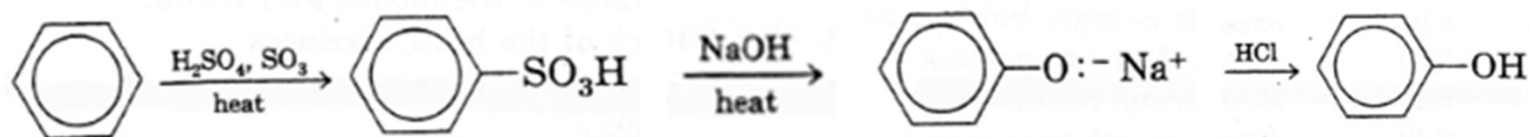
(i) From Haloarenes:

- Chlorobenzene is fused with NaOH at 623K and 320 atmospheric pressure.
- Phenol is obtained by acidification of sodium phenoxide so produced



(ii) From Benzenesulphonic Acid: The Alkali Fusion of Sulphonates

1. **Sulfonation** of an aromatic ring.
2. **Melting (fusion)** of the aromatic sulfonic acid with sodium hydroxide to give a **phenoxide salt**.
3. **Acidification** of the phenoxide with HCl to produce the **phenol**.

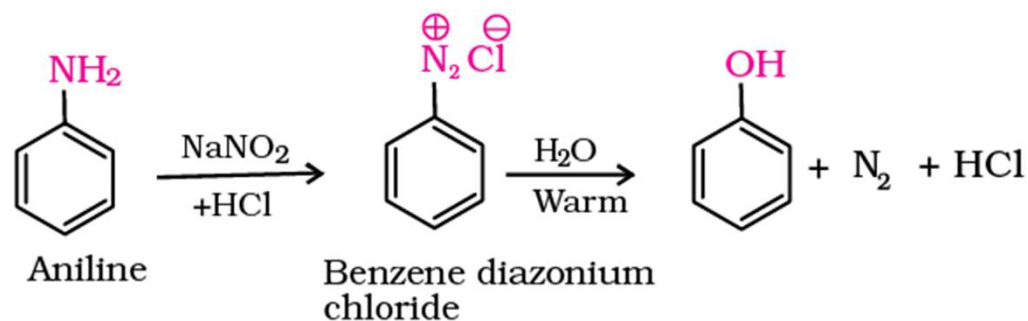


Preparation of Phenols

From Benzene Derivatives

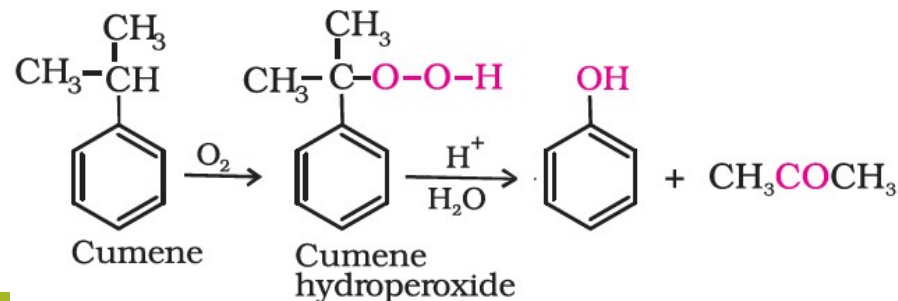
(iii) From Diazonium Salts:

- A diazonium salt is formed by treating an aromatic primary amine with nitrous acid ($\text{NaNO}_2 + \text{HCl}$) at 273-278 K.
- Diazonium salts are hydrolyzed to phenols by warming with water or by treating with dilute acids



(iv) From Cumene:

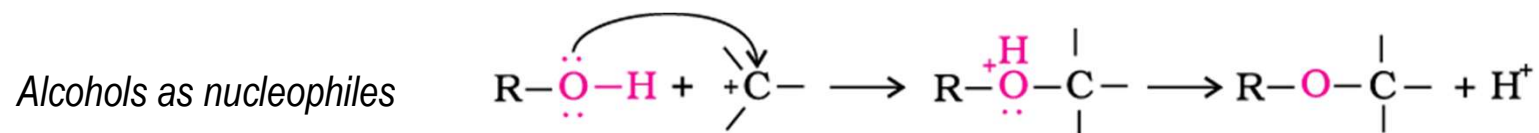
- Cumene (isopropylbenzene) is oxidized in the presence of air to cumene hydroperoxide.
- It is converted to phenol and acetone by treating it with dilute acid.



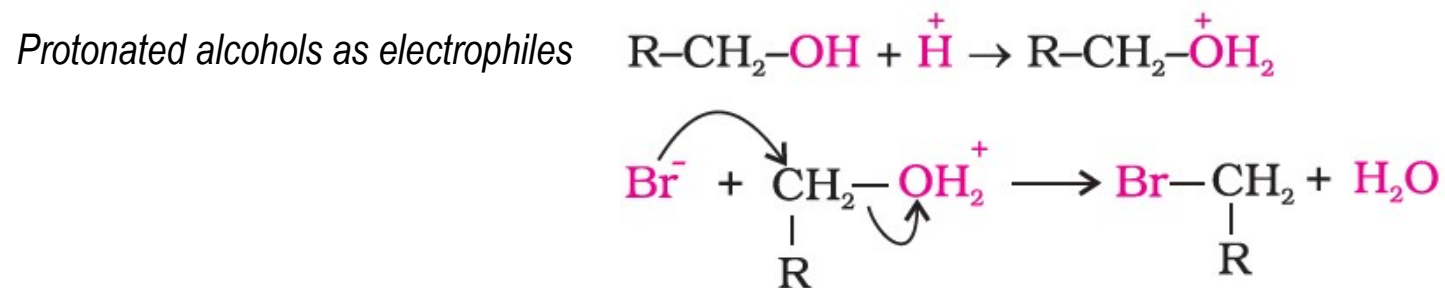
Chemical Reactions of Alcohols and Phenols

- **Alcohols** are versatile compounds. They react both as nucleophiles and electrophiles.

(i) The bond between O–H is broken when alcohols react **as nucleophiles**.



(ii) The bond between C–O is broken when they react **as electrophiles**.



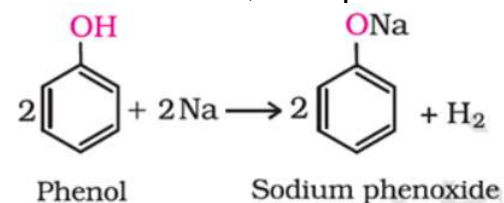
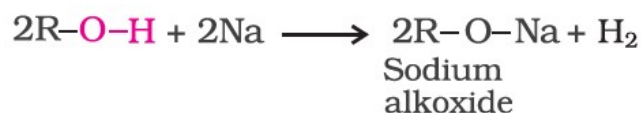
- **Alcohols** undergo two kinds of reactions:
 - Those that involve the **breaking of the oxygen-hydrogen bond (O-H)**.
 - Those that involve **the rupture of the carbon-oxygen bond (C-OH)**.
- **Phenols** do not participate in reactions where the C-OH bond is broken.

Chemical Reactions of Alcohols and Phenols

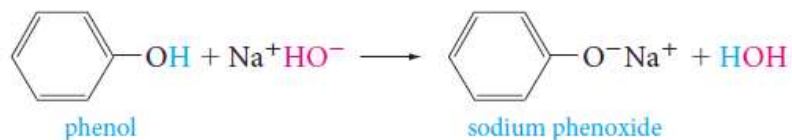
(a) Reactions involving cleavage of O–H bond

1. Acidity of alcohols and phenols

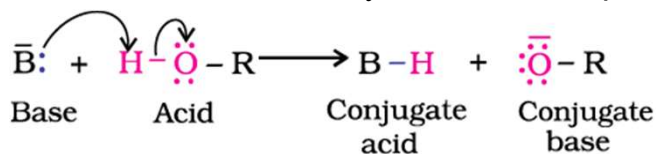
- (i) **Reaction with metals:** alcohols and phenols react with active metals such as sodium, and potassium to yield corresponding **alkoxides/phenoxides** and hydrogen.



- In addition to this, **phenols react with aqueous sodium hydroxide to form sodium phenoxides.**



- The above reactions show that **alcohols and phenols are acidic in nature.**
- In fact, alcohols and phenols are Brønsted acids i.e., they can donate a proton to a stronger base (B:).



Chemical Reactions of Alcohols and Phenols

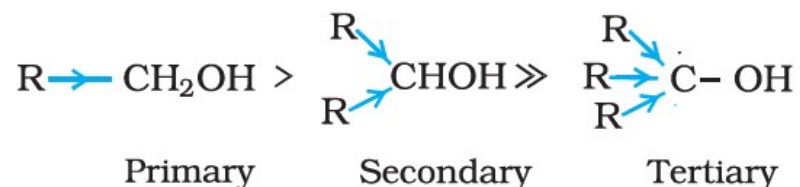
(a) Reactions involving cleavage of O–H bond

1. Acidity of alcohols and phenols

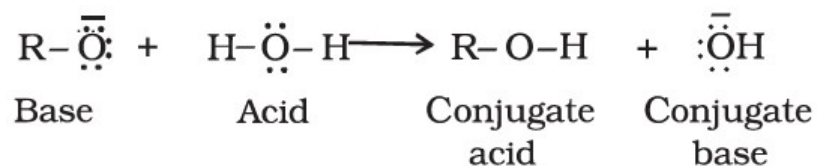
(ii) **Acidity of alcohols:** The acidic character of alcohols is due to the polar nature of O–H bond.

- An *electron-releasing group* ($-\text{CH}_3$, $-\text{C}_2\text{H}_5$) increases electron density on oxygen tending to decrease the polarity of O–H bond.

i.e. This decreases the acid strength.



- Alcohols are, however, weaker acids than water.



- This reaction shows that;
 - water is a better proton donor (i.e., stronger acid) than alcohol.
 - an alkoxide ion is a better proton acceptor than hydroxide ion, which suggests that alkoxides are stronger bases (sodium ethoxide is a stronger base than sodium hydroxide).
- Alcohols act as Bronsted bases as well due to the presence of unshared electron pairs on oxygen.