

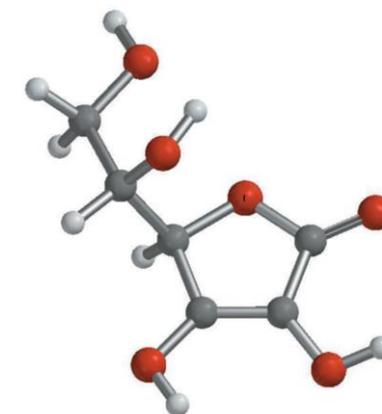
CHEM 241

Organic Chemistry II

FOR CHEMISTRY' STUDENTS, COLLEGE OF SCIENCE

PRE-REQUISITES COURSE; CHEM 240

CREDIT HOURS; 2 (2+0)



Chemistry Department, College of Science, King Saud University

Alcohols, Phenols and Ethers

Based on NCERT

Alcohols, 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).

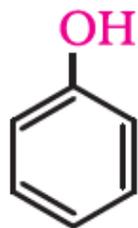
➤ A **phenol** contains -OH group(s) directly attached to carbon atom(s) of an *aromatic system* (C₆H₅OH).

➤ **Ethers**; the substitution of a hydrogen atom in a hydrocarbon by *an alkoxy*

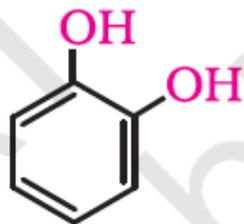
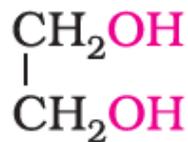
➤ or *aryloxy group* (**R-O/Ar-O**) (CH₃OCH₃), the substitution of a hydrogen atom of hydroxyl group of an alcohol or phenol by an alkyl or aryl group.

Classification of Alcohols and Phenols

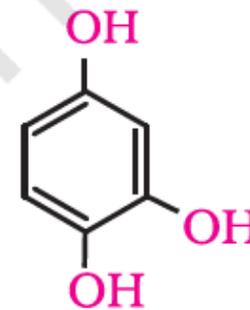
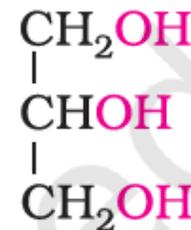
- Alcohols and phenols may be classified as *mono-*, *di-*, *tri-* or *polyhydric compounds* depending on whether they contain *one, two, three or many hydroxyl groups*, respectively.



Monohydric



Dihydric



Trihydric

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.

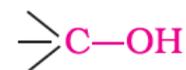
- **Primary, secondary and tertiary alcohols:** the -OH group is attached to primary, secondary and tertiary carbon atom, respectively.



Primary (1°)

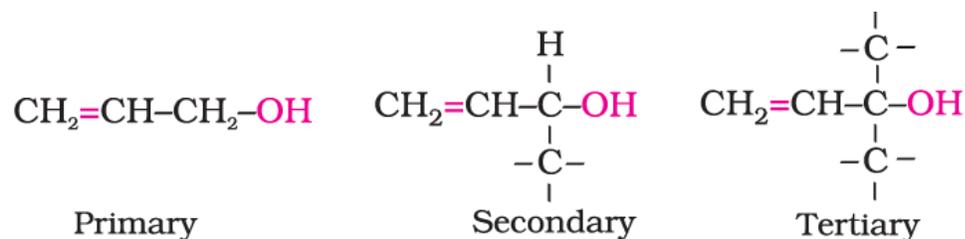


Secondary (2°)

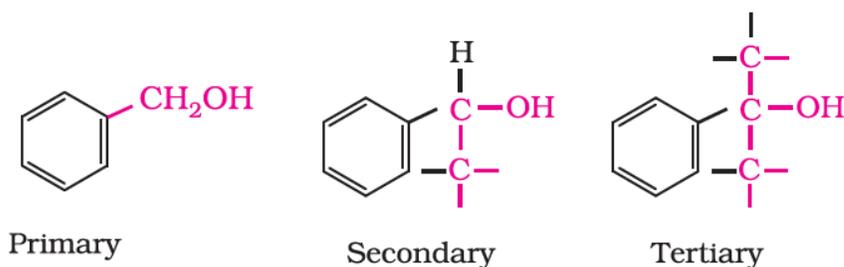


Tertiary (3°)

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



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



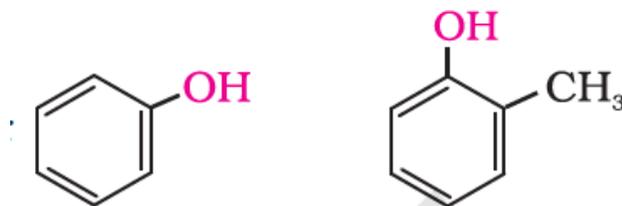
Classification of Alcohols and Phenols

(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

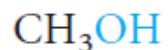
Example: CH₃OH is methyl alcohol.

- 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**

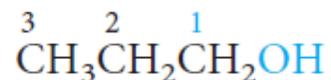
2. When isomers are possible, the chain is numbered so as to give the functional group (-OH) the **lowest possible number**.



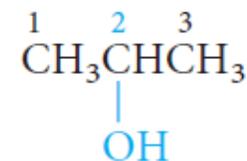
methanol
(methyl alcohol)



ethanol
(ethyl alcohol)



1-propanol
(*n*-propyl alcohol)



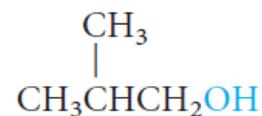
2-propanol
(isopropyl alcohol)



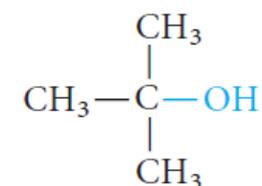
1-butanol
(*n*-butyl alcohol)



$\begin{array}{c} | \\ \text{OH} \end{array}$
2-butanol
(*sec*-butyl alcohol)



2-methyl-1-propanol
(isobutyl alcohol)

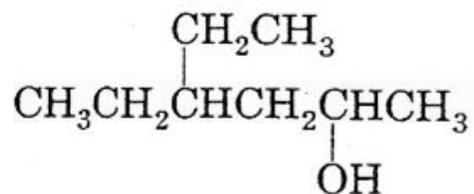


2-methyl-2-propanol
(*tert*-butyl alcohol)

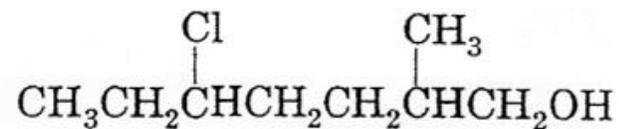
Nomenclature of Alcohols

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.



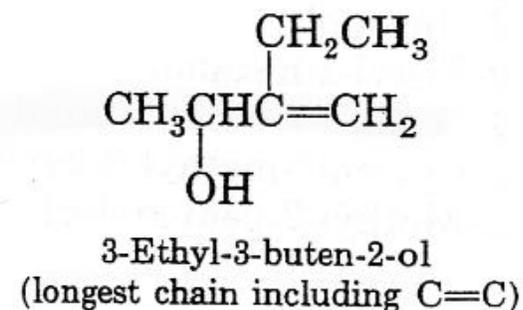
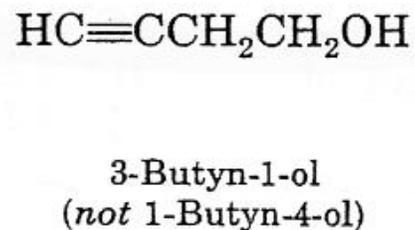
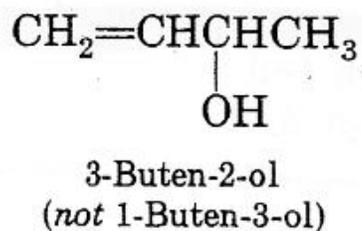
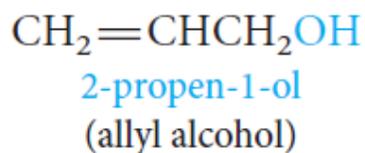
4-Ethyl-2-hexanol
(not 3-Ethyl-5-hexanol)



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

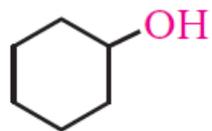
4. With Unsaturated Alcohols; If a molecule contains both an -OH group and a C=C or C-C triple bond, the -OH group takes preference before the double or triple bonds in getting the lower number.

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.

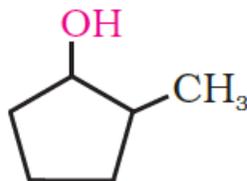


Nomenclature of Alcohols

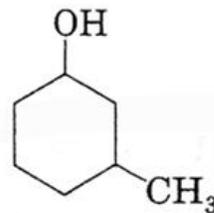
- **Cyclic alcohols** are named using the prefix *cyclo* and considering the —OH group attached to C-1.



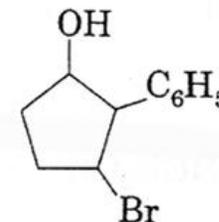
Cyclohexanol



2-Methylcyclopentanol

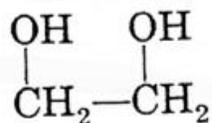


3-Methylcyclohexanol
(not 1-Methyl-3-cyclohexanol)

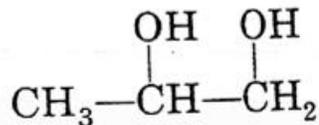


3-Bromo-2-phenylcyclopentanol
(not 1-Bromo-2-phenyl-3-cyclopentanol)

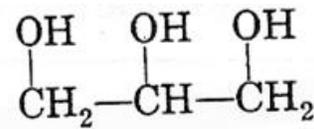
- For naming **polyhydric alcohols**, the 'e' of alkane is retained and the ending 'ol' is added.
 - The number of —OH groups is indicated by adding the multiplicative prefix, di, tri, etc., before 'ol'.
 - The positions of —OH groups are indicated by appropriate locantions
e.g., HO—CH₂—CH₂—OH is named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



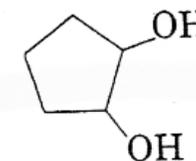
IUPAC name: 1,2-Ethandiol
Common name: Ethylene glycol



1,2-Propanediol
Propylene glycol



1,2,3-Propanetriol
Glycerol or Glycerin



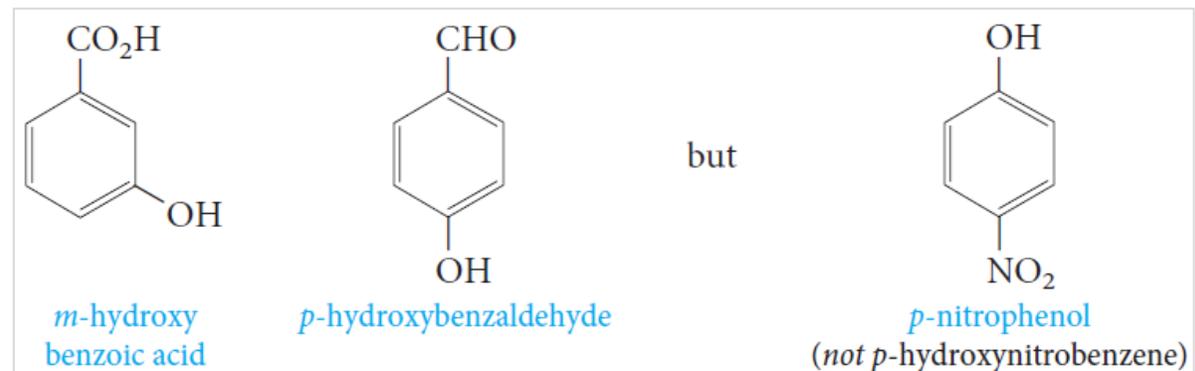
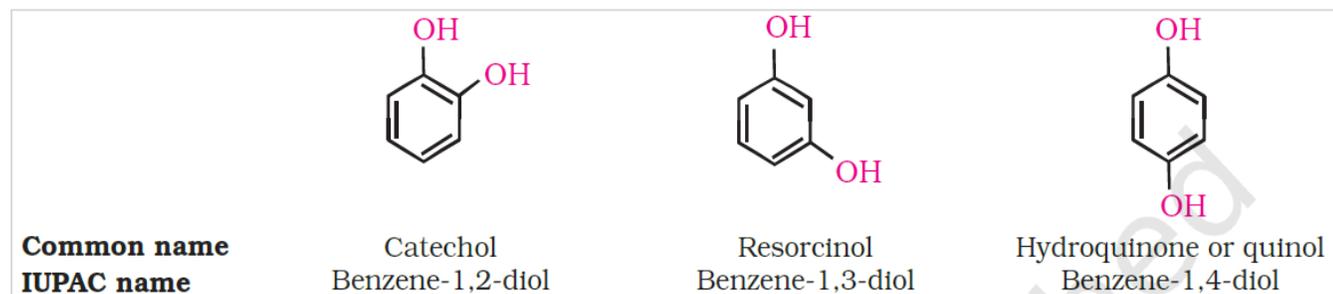
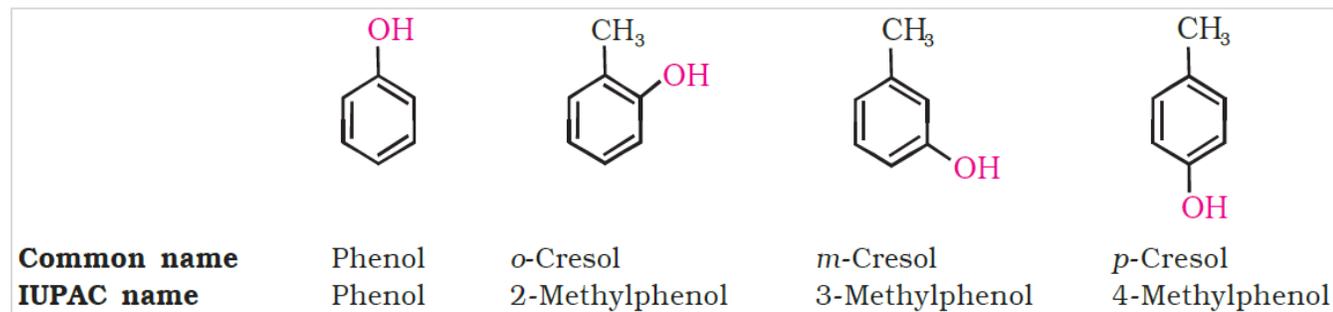
IUPAC name: 1,2-Cyclopentanediol

Nomenclature of Phenols

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

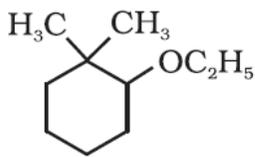
- Dihydroxy derivatives of benzene** are known as 1, 2-, 1, 3- and 1, 4-**benzenediol**.

- 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.



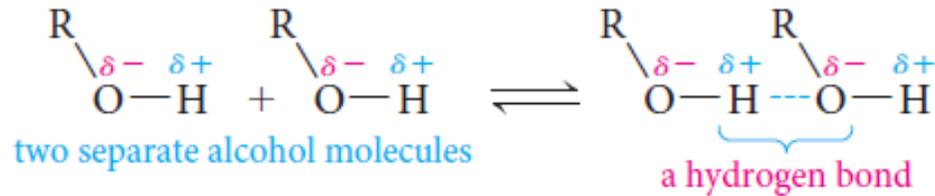
Nomenclature of Ethers

- **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 ($-\text{OR}$) or **aryloxy** group ($-\text{OAr}$), 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
$\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$	Diethyl ether	Ethoxyethane
$\text{CH}_3\text{OCH}_2\text{CH}_2\text{CH}_3$	Methyl n-propyl ether	1-Methoxypropane
$\text{C}_6\text{H}_5\text{OCH}_3$	Methyl phenyl ether (Anisole)	Methoxybenzene (Anisole)
$\text{C}_6\text{H}_5\text{OCH}_2\text{CH}_3$	Ethyl phenyl ether (Phenetole)	Ethoxybenzene
$\text{C}_6\text{H}_5\text{O}(\text{CH}_2)_6-\text{CH}_3$	Heptyl phenyl ether	1-Phenoxyheptane
$\begin{array}{c} \text{CH}_3\text{O}-\text{CH}-\text{CH}_3 \\ \\ \text{CH}_3 \end{array}$	Methyl isopropyl ether	2-Methoxypropane
$\text{C}_6\text{H}_5-\text{O}-\text{CH}_2-\text{CH}_2-\underset{\text{CH}_3}{\text{CH}}-\text{CH}_3$	Phenyl isopentyl ether	3- Methylbutoxybenzene
$\text{CH}_3-\text{O}-\text{CH}_2-\text{CH}_2-\text{OCH}_3$	—	1,2-Dimethoxyethane
	—	2-Ethoxy- -1,1-dimethylcyclohexane

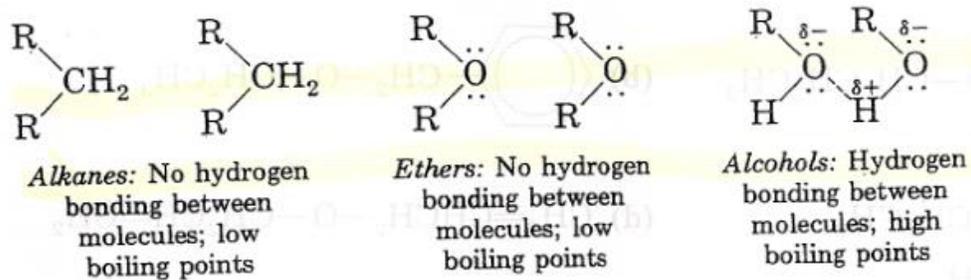
Hydrogen Bonding in Alcohols, Phenols and Ethers

- 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.

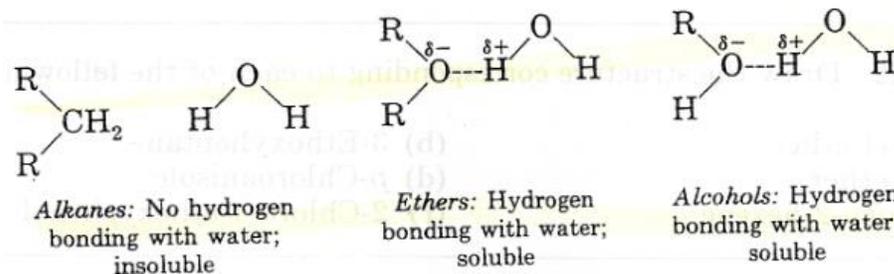


- Two or more alcohol molecules thus become loosely bonded to one another through hydrogen bonds.
- Hydrogen bonds are weaker than ordinary covalent bonds.

- 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

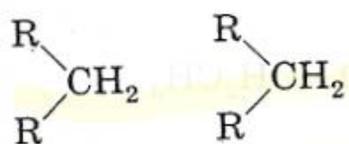
○ Physical State

- 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.

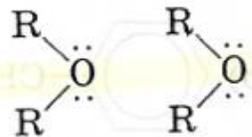
○ Boiling Points

- **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.

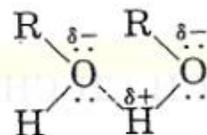
Because of their structures (no O-H bonds), ether molecules cannot form hydrogen bonds with one another.



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.

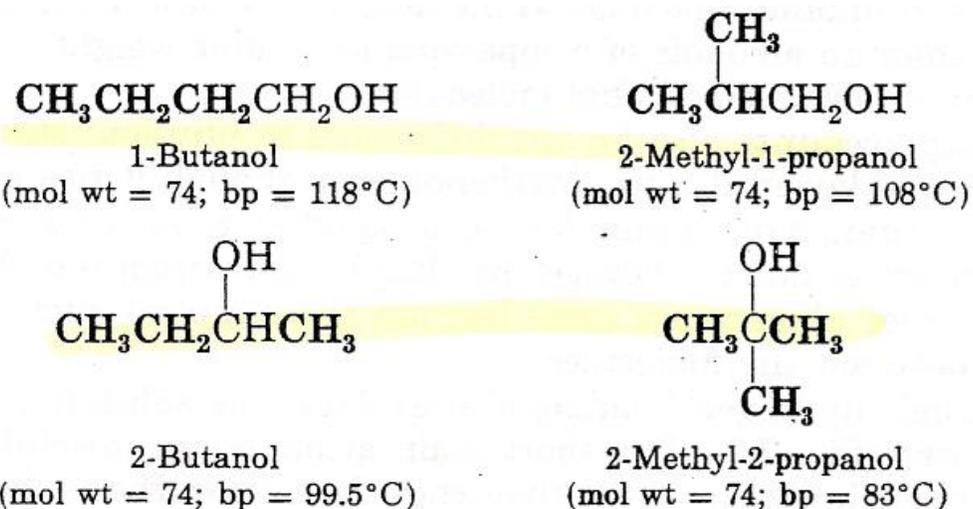


Table 7.1 Boiling Point and Water Solubility of Some Alcohols

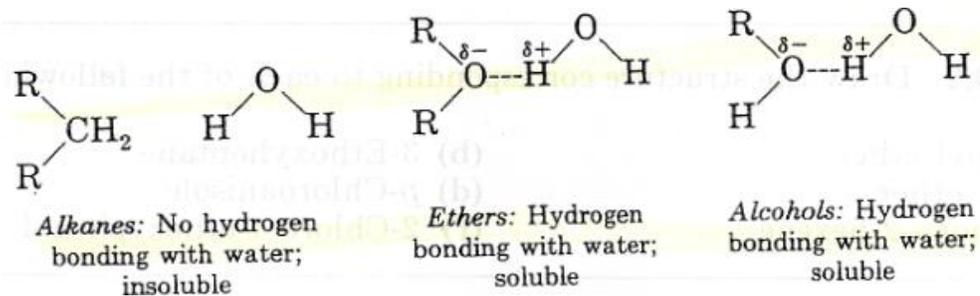
Name	Formula	bp, °C	Solubility in H ₂ O g/100 g at 20°C
methanol	CH ₃ OH	65	completely miscible
ethanol	CH ₃ CH ₂ OH	78.5	completely miscible
1-propanol	CH ₃ CH ₂ CH ₂ OH	97	completely miscible
1-butanol	CH ₃ CH ₂ CH ₂ CH ₂ OH	117.7	7.9
1-pentanol	CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ OH	137.9	2.7
1-hexanol	CH ₃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

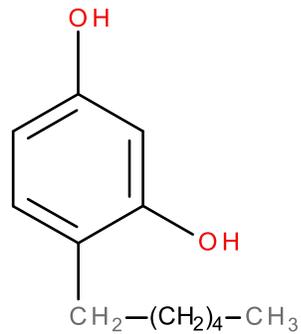
- **Phenol** and most other phenols are slightly soluble in water .

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.

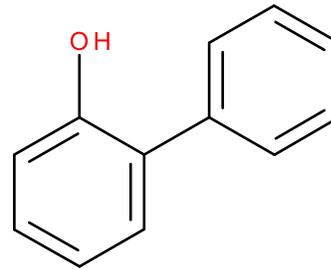
Importance of Alcohols, Phenols and Ethers

Occurrence and uses of phenols



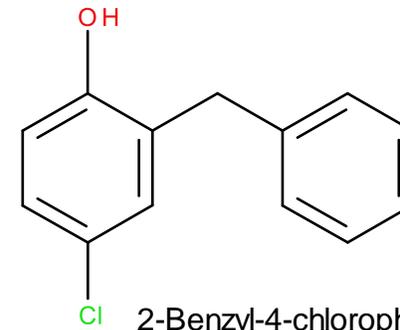
4-Hexylresorcinol

an antiseptic

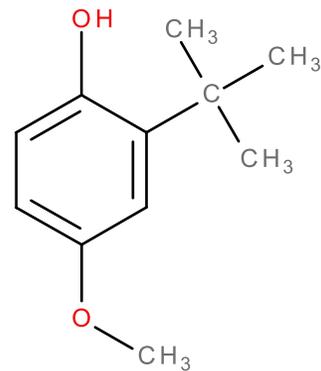


2-Phenylphenol

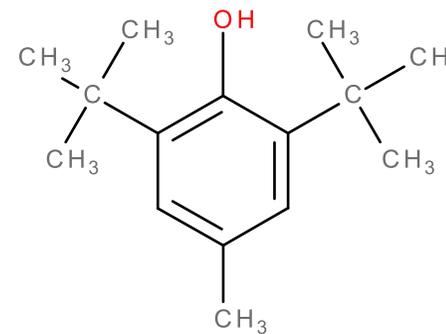
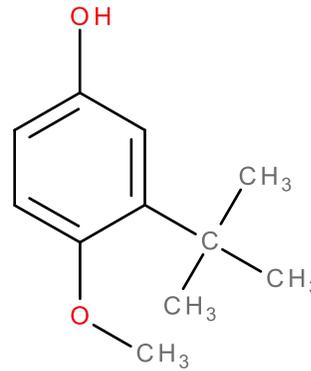
disinfectants



2-Benzyl-4-chlorophenol



BHAs (butylated hydroxyanilines)



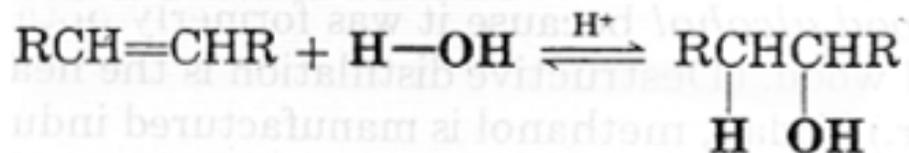
BHT
(butylated hydroxytoluene)

antioxidants

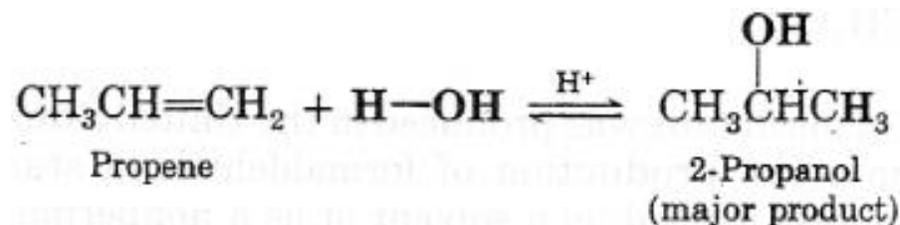
Preparation of Alcohols

From Alkenes

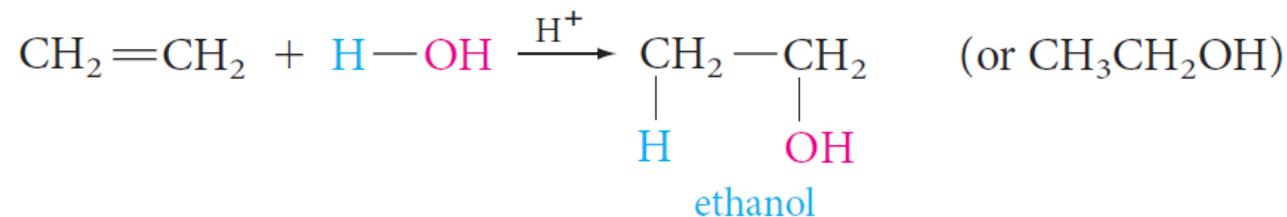
(i) **Hydration of Alkenes:** alkenes react with water in the presence of acid as catalyst to form alcohols.



- 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.

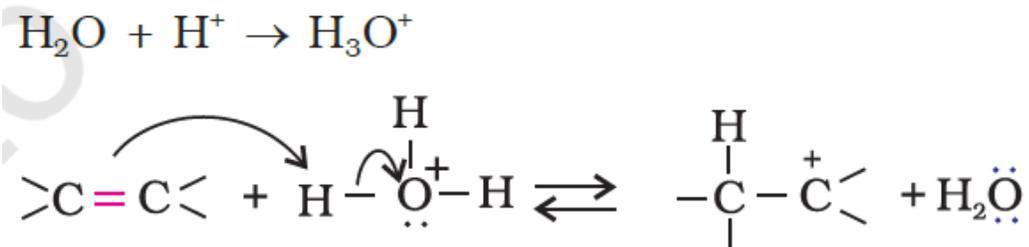


Preparation of Alcohols

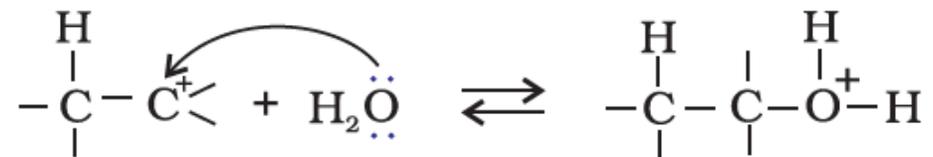
From Alkenes

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

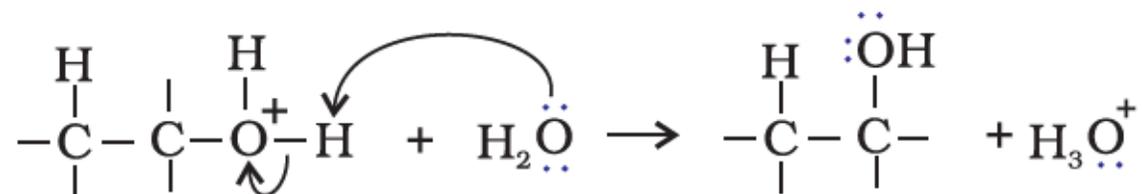
Step 1: Protonation of alkene to form carbocation by electrophilic attack of H_3O^+ .



Step 2: Nucleophilic attack of water on carbocation



Step 3: Deprotonation to form an alcohol.

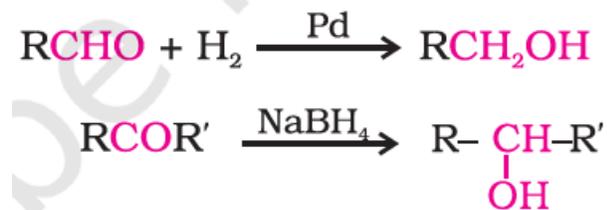


Preparation of Alcohols

From Carbonyl Compounds

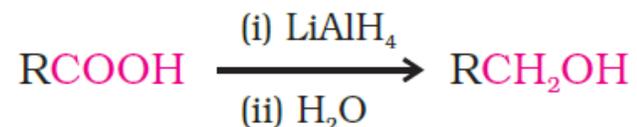
(i) **Reduction of aldehydes and ketones:** aldehydes and ketones are reduced to the corresponding alcohols by addition of hydrogen in the presence of catalysts (catalytic hydrogenation).

- **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).

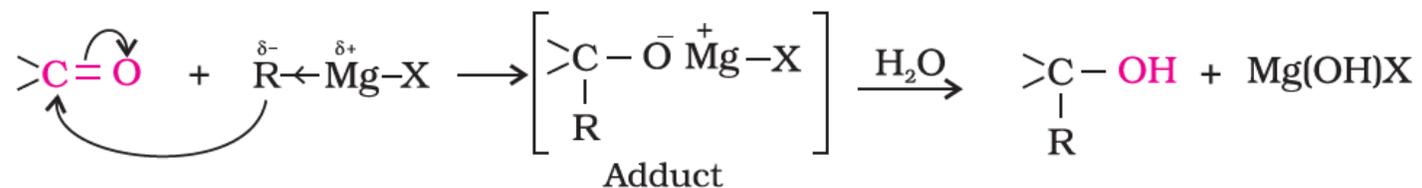


Preparation of Alcohols

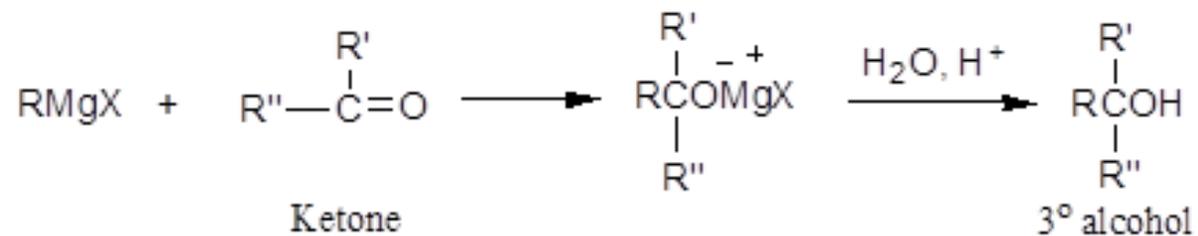
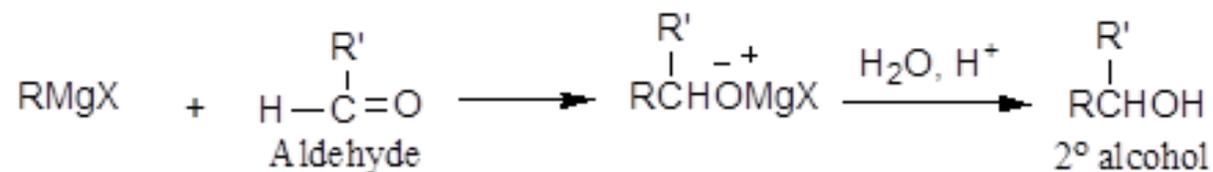
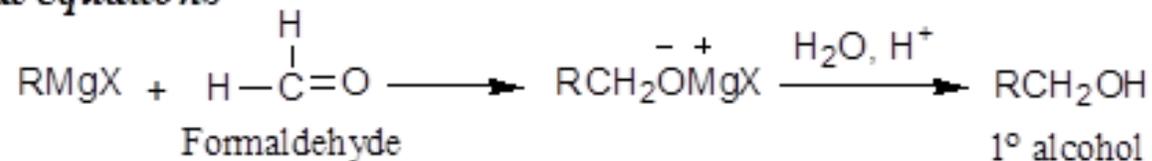
From Carbonyl Compounds

(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

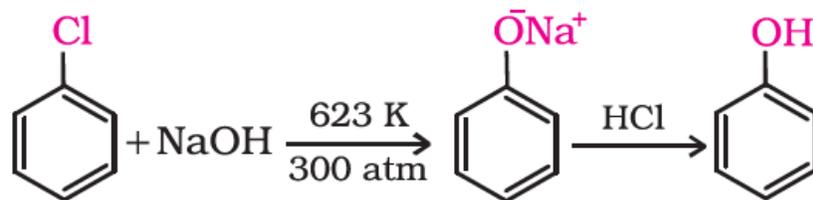


Preparation of Phenols

From Benzene Derivatives

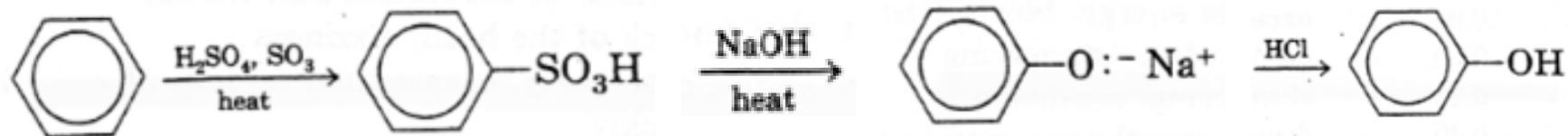
(i) *From Haloarenes:*

- 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 Sulfonates*

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**.

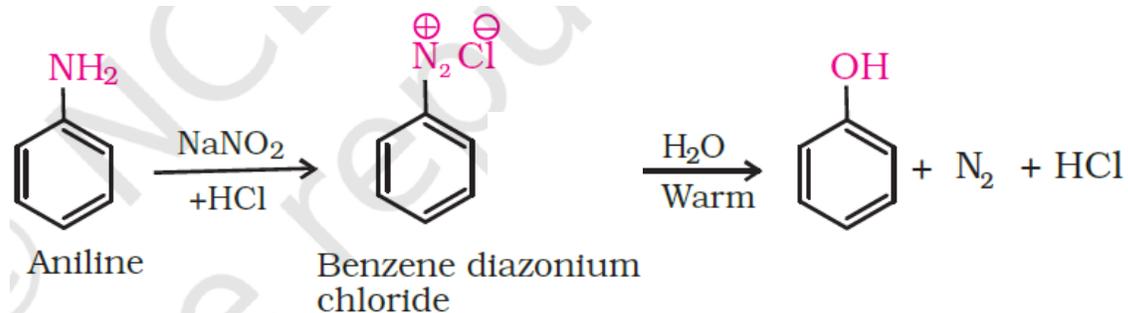


Preparation of Phenols

From Benzene Derivatives

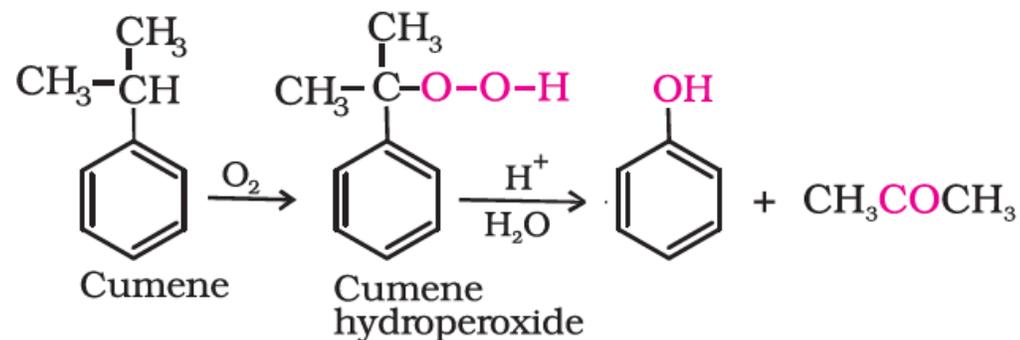
(iii) From Diazonium Salts:

- 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:

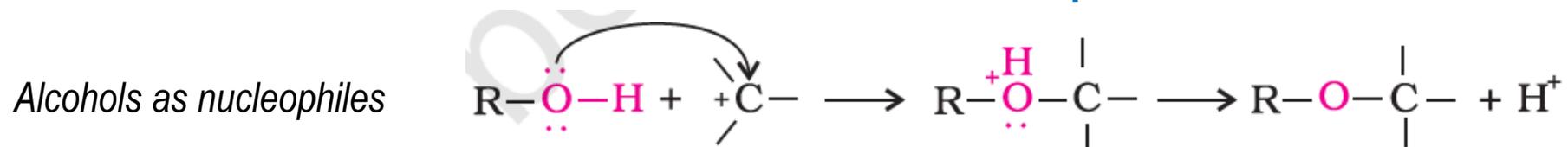
- Cumene (isopropylbenzene) is oxidized in the presence of air to cumene hydroperoxide.
- It is converted to phenol and acetone by treating it with dilute acid.



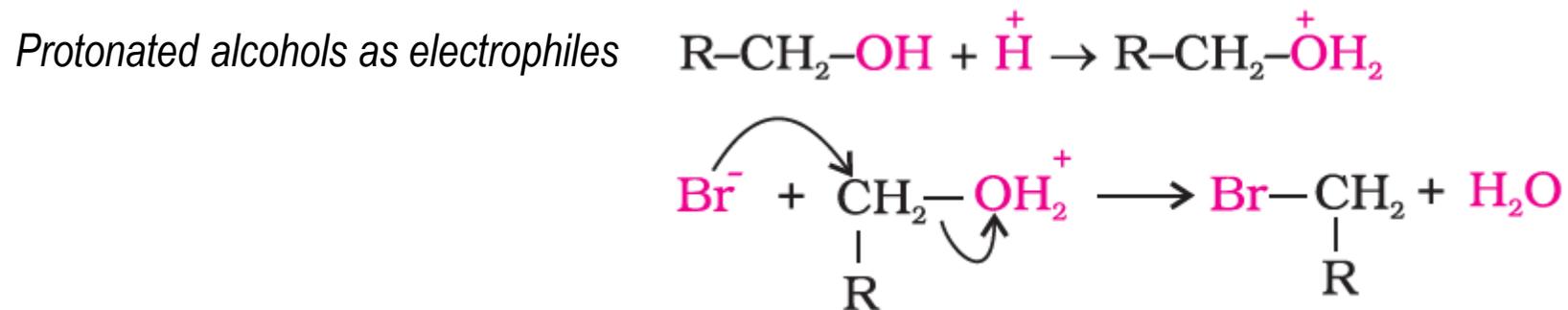
Chemical Reactions of Alcohols and Phenols

- **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**.



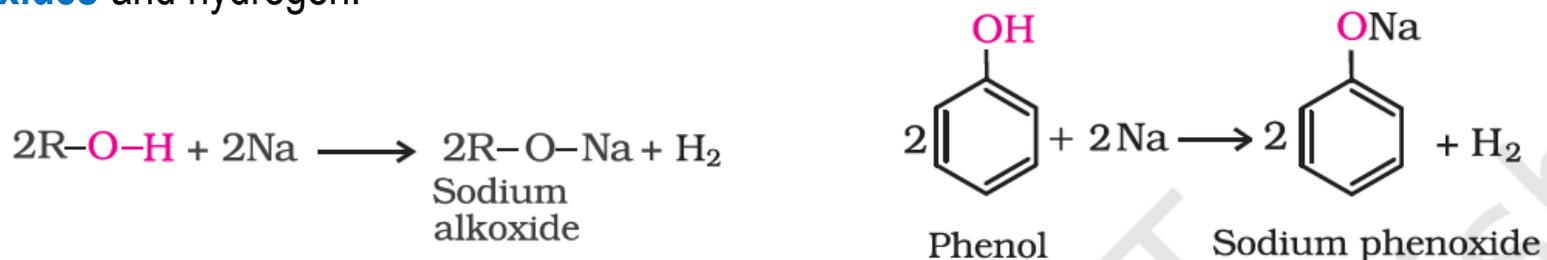
- **Alcohols** undergo two kinds of reactions:
 - Those that involve the **breaking of the oxygen-hydrogen bond (O-H)**.
 - Those that involve **the rupture of the carbon-oxygen bond (C-OH)**.
- **Phenols** do not participate in reactions where the C-OH bond is broken.

Chemical Reactions of Alcohols and Phenols

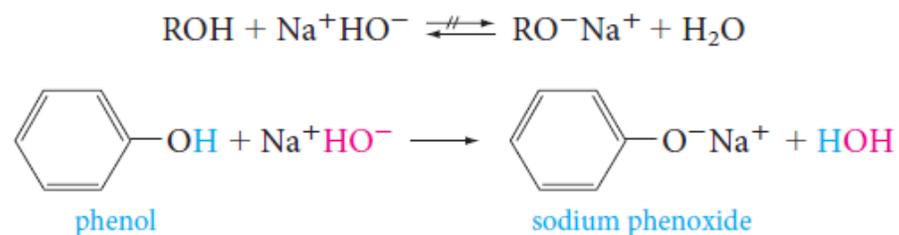
(a) Reactions involving cleavage of O–H bond

1. Acidity of alcohols and phenols

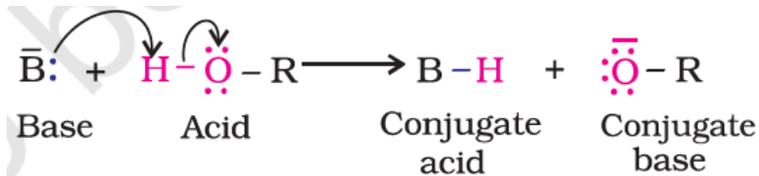
- (i) **Reaction with metals:** alcohols and phenols react with active metals such as sodium, and potassium to yield corresponding **alkoxides/phenoxides** and hydrogen.



- 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

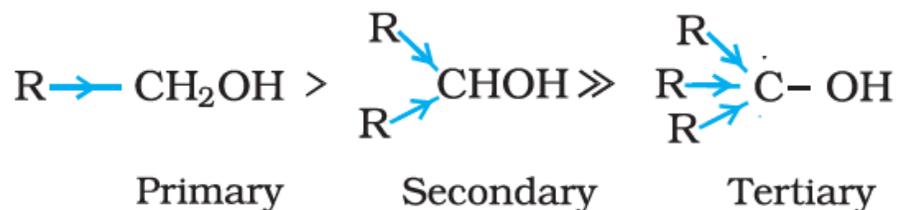
(a) Reactions involving cleavage of O–H bond

1. Acidity of alcohols and phenols

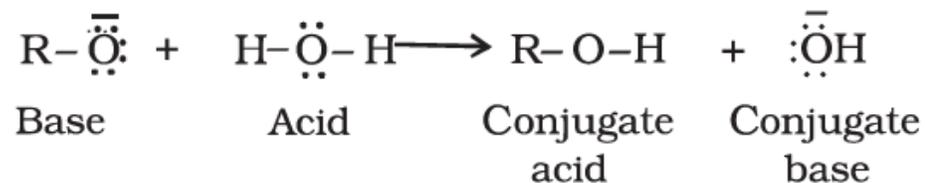
(ii) **Acidity of alcohols:** The acidic character of alcohols is due to the polar nature of O–H bond.

- 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.

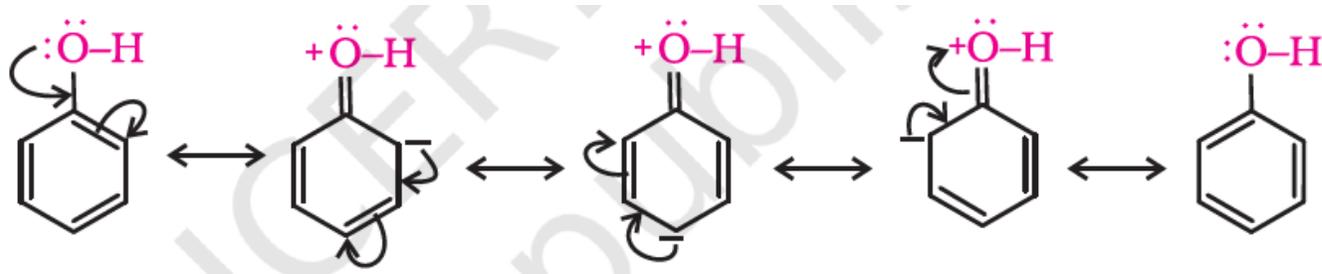
Chemical Reactions of Alcohols and Phenols

(a) Reactions involving cleavage of O–H bond

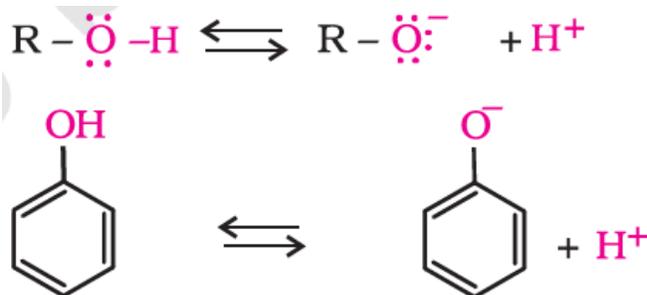
1. Acidity of alcohols and phenols

(iii) **Acidity of phenols:** reactions of phenol with metals (e.g., sodium, aluminium) and sodium hydroxide indicate its acidic nature.

The hydroxyl group, in phenol is directly attached to the sp^2 hybridized carbon of benzene ring which acts as an electron withdrawing group. Due to this, the charge distribution in phenol molecule, as depicted in its resonance structures, causes the oxygen of $-OH$ group to be positive.



- The reaction of phenol with aqueous sodium hydroxide indicates that **phenols are stronger acids than alcohols and water**.
- The ionization of an alcohol and a phenol takes place as follows:

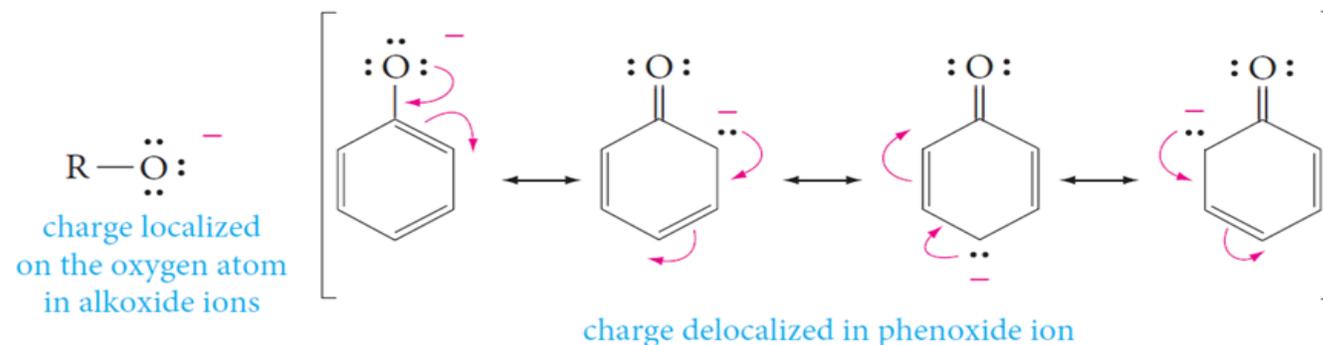


Chemical Reactions of Alcohols and Phenols

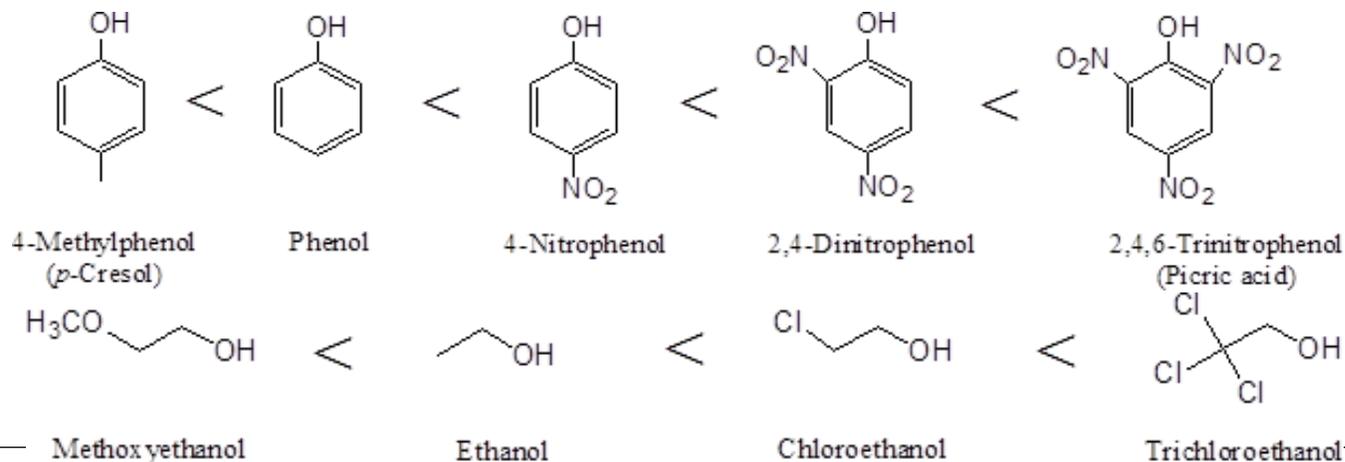
(a) Reactions involving cleavage of O–H bond

1. Acidity of alcohols and phenols

- The stabilities of alkoxide and phenoxide ions. In alkoxide ion, the negative charge is localized on oxygen while in phenoxide ion, the charge is delocalized which makes phenoxide ion more stable and favors the ionization of phenol.



- Electron-withdrawing groups increase acidity by stabilizing the conjugate base.
- Electron-donating groups decrease acidity because they destabilize the conjugate base.

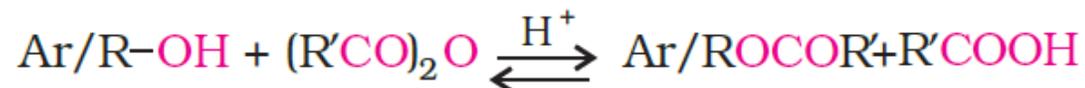


Chemical Reactions of Alcohols and Phenols

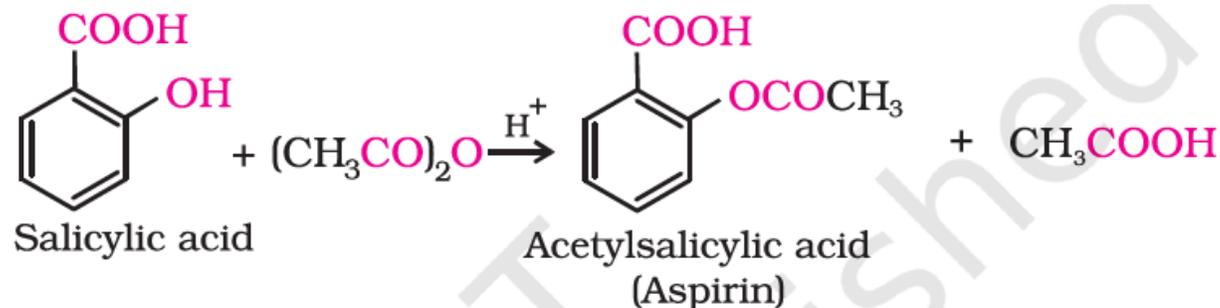
(a) Reactions involving cleavage of O–H bond

2. Esterification

- Alcohols and phenols react with carboxylic acids, acid chlorides and acid anhydrides to form esters.



- Acetylation;** The introduction of acetyl (CH_3CO) group in alcohols or phenols.
Example: Acetylation of salicylic acid produces aspirin.



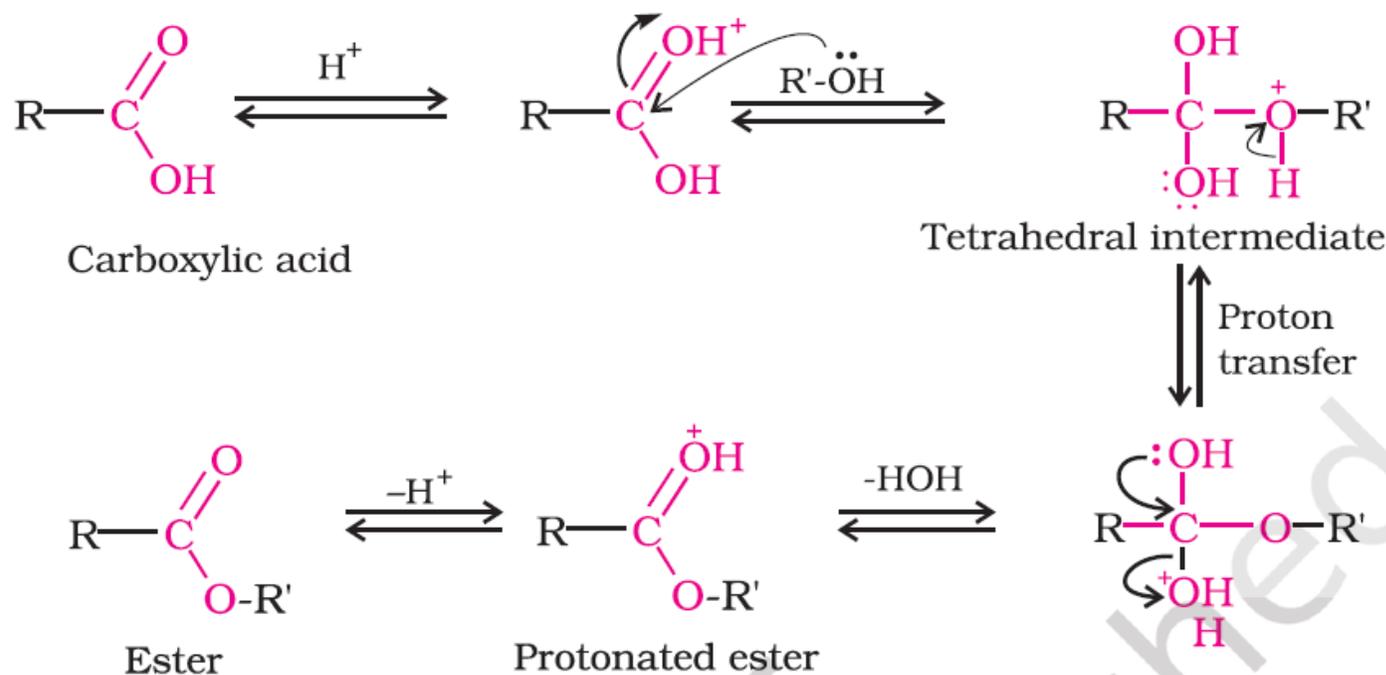
Chemical Reactions of Alcohols and Phenols

(a) Reactions involving cleavage of O–H bond

2. Esterification

Mechanism of esterification of carboxylic acids:

- The esterification of carboxylic acids with alcohols is a kind of **nucleophilic acyl substitution**.
 - Protonation of the carbonyl oxygen activates the carbonyl group towards nucleophilic addition of the alcohol.
 - Proton transfer in the tetrahedral intermediate converts the hydroxyl group into $-^+\text{OH}_2$ group (leaving group).
 - The protonated ester so formed finally loses a proton to give the ester.



Chemical Reactions of Alcohols and Phenols

(b) Reactions involving cleavage of carbon – oxygen (C–O) bond in alcohols

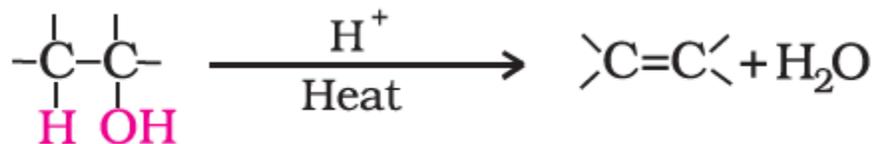
1. Reaction with hydrogen halides: Nucleophilic Substitution Reaction

Alcohols react with hydrogen halides (*HCl*, *HBr* and *HI*) to form alkyl halides.

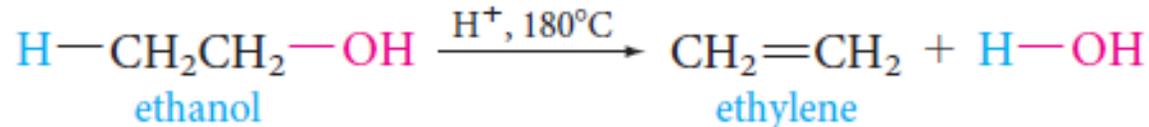


2. Dehydration: Formation of Alkenes

Alcohols undergo dehydration (removal of a molecule of water) to form alkenes on treating with protic acid (concentrated H_2SO_4 or H_3PO_4 , or catalysts such as anhydrous zinc chloride or alumina)



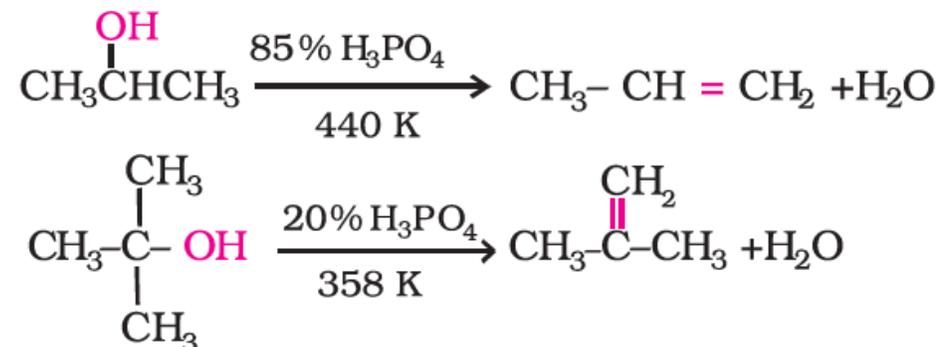
- Ethanol undergoes dehydration by heating it with concentrated H_2SO_4 at 180°C .



Chemical Reactions of Alcohols and Phenols

(b) Reactions involving cleavage of carbon – oxygen (C–O) bond in alcohols

- **Secondary and tertiary alcohols** are dehydrated under milder conditions.



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

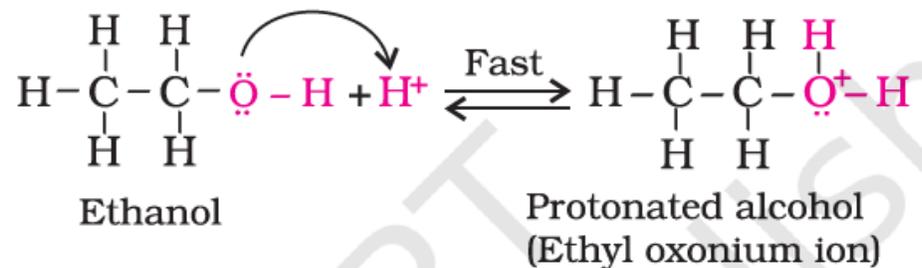
Tertiary > Secondary > Primary

Chemical Reactions of Alcohols and Phenols

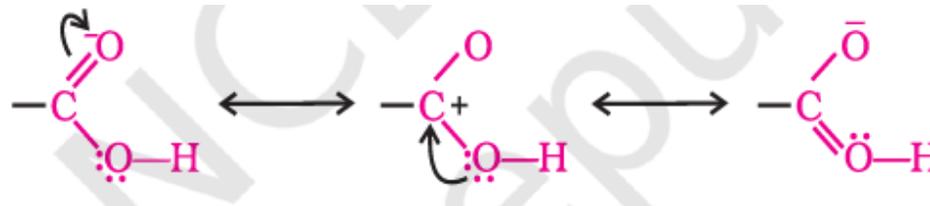
(b) Reactions involving cleavage of carbon – oxygen (C–O) bond in alcohols

Dehydration of ethanol; Mechanism:

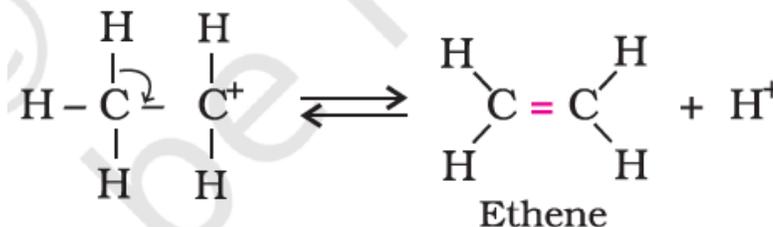
Step 1: Formation of protonated alcohol.



Step 2: Formation of carbocation: It is the slowest step and hence, the rate determining step of the reaction.



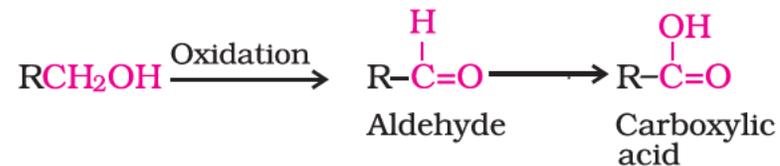
Step 3: Formation of ethene by elimination of a proton.



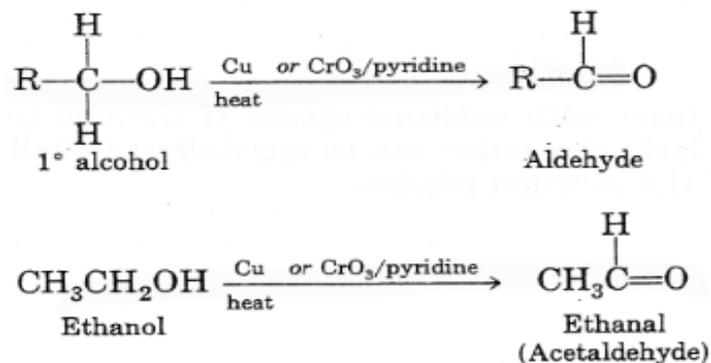
Chemical Reactions of Alcohols and Phenols

(b) Oxidation of alcohols

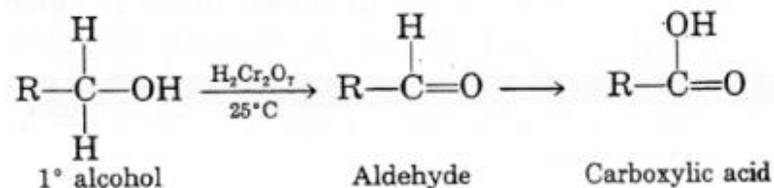
- Depending on the oxidizing agent used, a **primary alcohol** is oxidized to an aldehyde which in turn is oxidized to a carboxylic acid.



- **Primary alcohols** yield **aldehydes** when treated with **mild oxidizing agents** such as **hot metallic copper** or **CrO₃ in pyridine**.



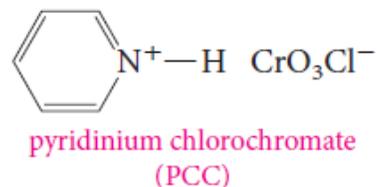
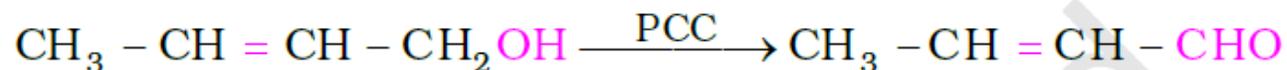
- **Primary alcohols**; when treated with **stronger oxidizing agents**, such as **chromic acid, H₂Cr₂O₇**, or **neutral potassium permanganate, KMnO₄**, the **intermediate aldehydes** formed initially are oxidized further to **carboxylic acids**.



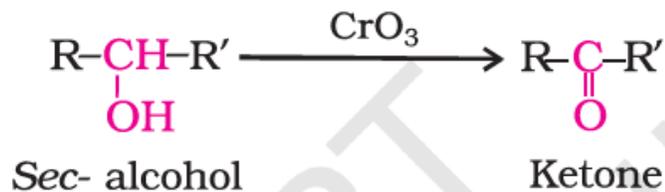
Chemical Reactions of Alcohols and Phenols

(b) Oxidation of alcohols

- A better reagent for oxidation of primary alcohols to aldehydes in good yield is **pyridinium chlorochromate (PCC)**, a complex of chromium trioxide with pyridine and HCl.



- **Secondary alcohols** are oxidized to ketones by chromic anhydride (CrO_3).



- **Tertiary alcohols** do not undergo oxidation reaction.

Chemical Reactions of Alcohols and Phenols

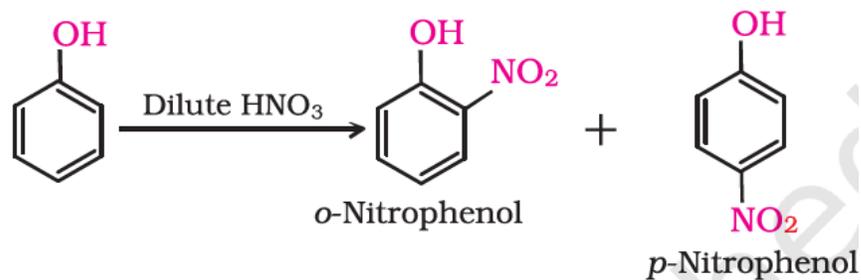
(c) Reactions of Phenols

1. Electrophilic aromatic substitution

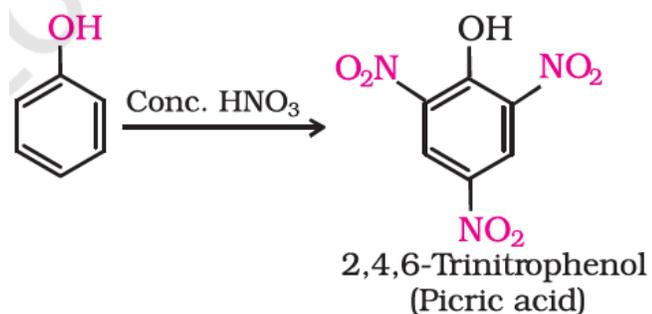
- The $-OH$ group attached to the benzene ring activates it towards electrophilic substitution.
- Also, it directs the incoming group to *ortho* and *para* positions in the ring.

(i) Nitration:

- With dilute nitric acid at low temperature (298 K), phenol yields a mixture of *ortho* and *para*-nitrophenols.



- With concentrated nitric acid, phenol is converted to 2,4,6-trinitrophenol (picric acid).



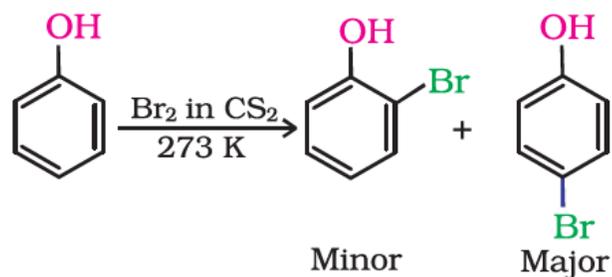
Chemical Reactions of Alcohols and Phenols

(c) Reactions of Phenols

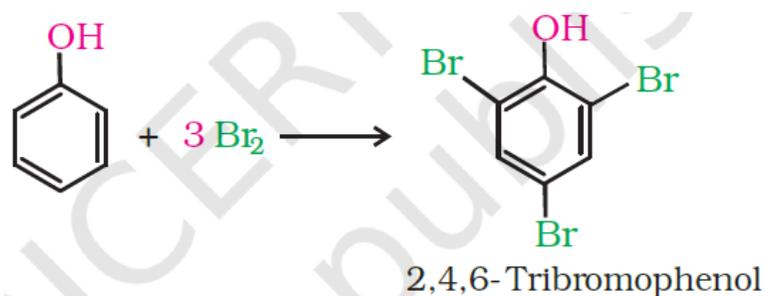
1. Electrophilic aromatic substitution

(ii) Halogenation:

(a) When the reaction is carried out in solvents of low polarity such as CHCl_3 or CS_2 and at low temperature, monobromophenols are formed.



(b) When phenol is treated with bromine water, 2,4,6-tribromophenol is formed as white precipitate.



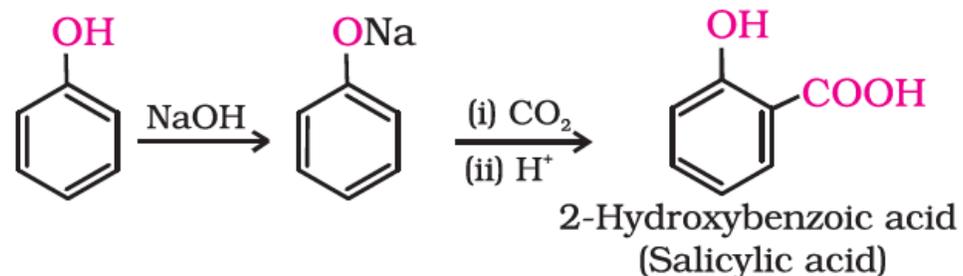
In case of phenol, the polarization of bromine molecule takes place even in the absence of Lewis acid due to the highly activating effect of $-\text{OH}$ group attached to the benzene ring.

Chemical Reactions of Alcohols and Phenols

(c) Reactions of Phenols

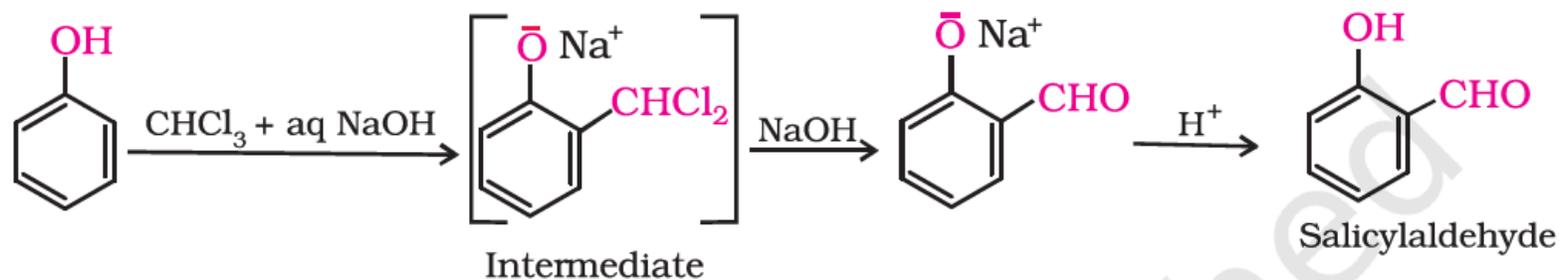
2. Kolbe's reaction

The **synthesis of salicylic acid** by heating a mixture of sodium phenoxide and carbon dioxide under pressure at 180°- 200°C, then treating the product with sulfuric acid.



3. Reimer-Tiemann reaction

- Treatment of phenol with chloroform in the presence of sodium hydroxide, a -CHO group is introduced at o- position of benzene ring.
- The intermediate substituted benzal chloride is hydrolyzed in the presence of alkali to produce salicylaldehyde.

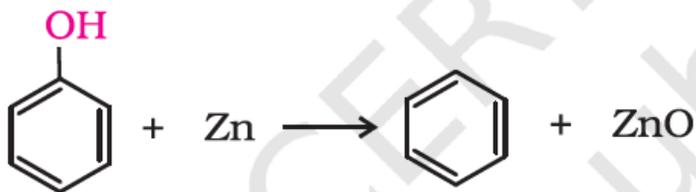


Chemical Reactions of Alcohols and Phenols

(c) Reactions of Phenols

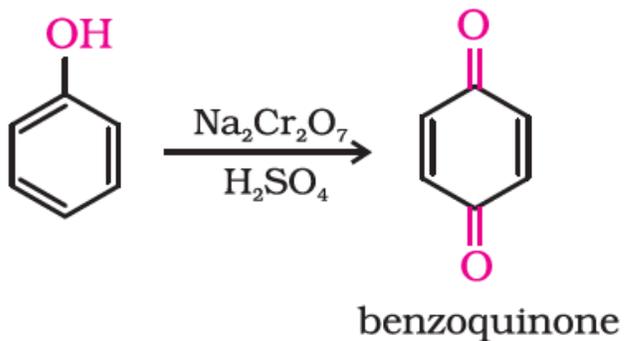
4. Reaction of phenol with zinc dust

Phenol is converted to benzene on heating with zinc dust.



5. Oxidation

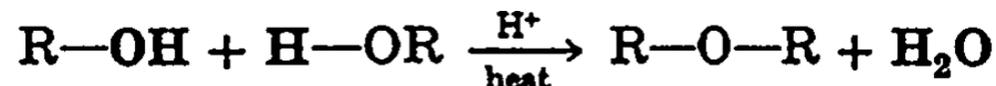
- Oxidation of phenol **with chromic acid** produces a conjugated diketone known as benzoquinone.
- **In the presence of air**, phenols are slowly oxidized to dark colored mixtures containing quinones.



Preparation of Ethers

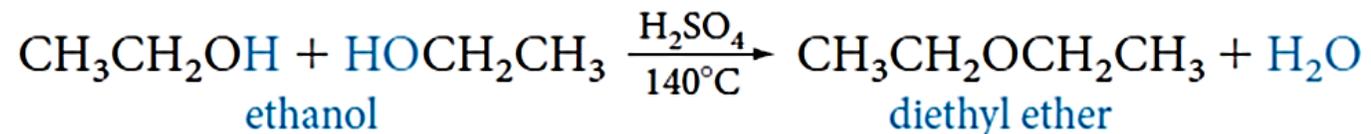
1. Dehydration of Alcohols

- It takes place in the presence of acid catalysts (H_2SO_4 , H_3PO_4) (intermolecular reaction)

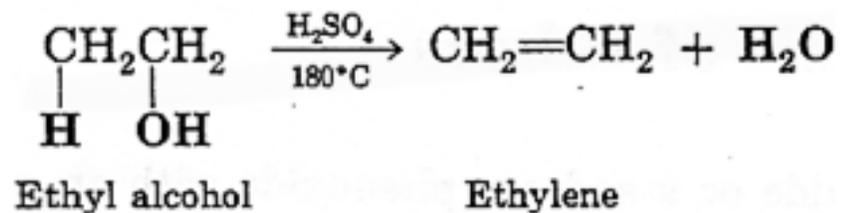


- **Example;**

The most important commercial ether is diethyl ether. It is prepared from ethanol and sulfuric acid.



- When ethyl alcohol is dehydrated by **sulfuric acid at 180°C** , the dominant product is **ethylene**.

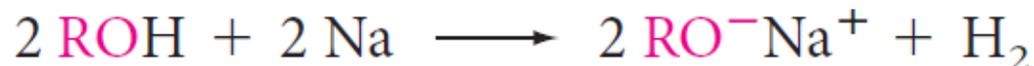


Preparation of Ethers

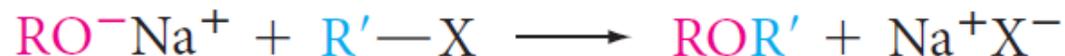
2. Williamson Synthesis

- It is an important laboratory method for the *preparation of symmetrical and unsymmetrical ethers*.
- In this method, an *alkyl halide* is allowed to react with *sodium alkoxide*.
- **This method has two steps;**

1) An alcohol is converted to its alkoxide by treatment with a reactive metal (sodium or potassium).



2) Displacement is carried out between the alkoxide and an alkyl halide.



- To obtain the best yields of mixed dialkyl ethers, we select a 1° rather than a 2° or 3° alkyl halide and react it with a sodium alkoxide
- To prepare an alkyl aryl ether, we must be careful not to pick a combination in which one of the reagents has a halogen directly attached to an aromatic ring.

Preparation of Ethers

2. Williamson Synthesis

○ **Example 1;** Preparation of *t*-butyl methyl ether, $(\text{CH}_3)_3\text{C-O-CH}_3$.

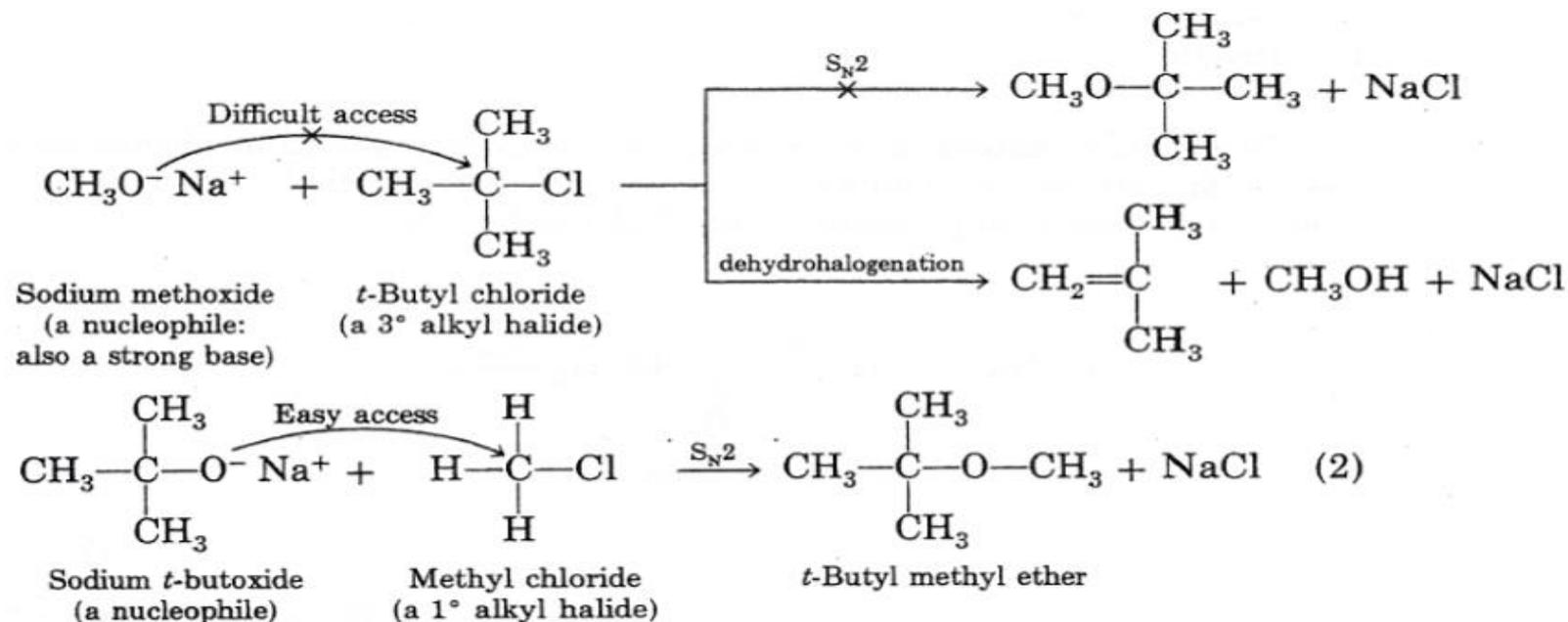
▪ In theory, this could be done by either of two reactions.

1. You could react sodium methoxide, $\text{CH}_3\text{O}^-\text{Na}^+$, with *t*-butyl chloride, $(\text{CH}_3)_3\text{C-Cl}$.

This combination leads to dehydrohalogenation to an alkene, an elimination reaction.

2. You could react sodium *t*-butoxide, $(\text{CH}_3)_3\text{C-O}^-\text{Na}^+$, with methyl chloride, CH_3Cl .

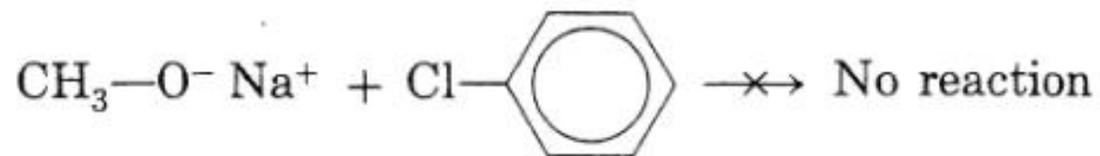
This route gives the desired ether by substitution.



Preparation of Ethers

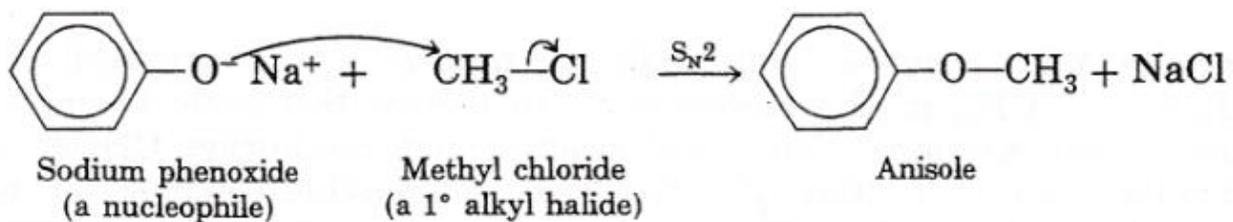
2. Williamson Synthesis

- **Example 2;** Assume you need to synthesize methyl phenyl ether (anisole), $\text{CH}_3\text{-O-C}_6\text{H}_5$, by the Williamson method.
 - *In theory, you could obtain anisole in either of two ways.*



Sodium methoxide
(a nucleophile)

Chlorobenzene
(an aryl halide)



Sodium phenoxide
(a nucleophile)

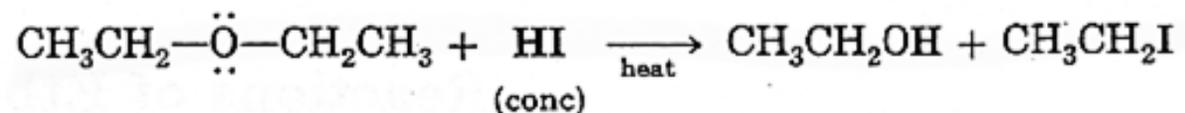
Methyl chloride
(a 1° alkyl halide)

Anisole

Chemical Reactions of Ethers

1. Cleavage of C–O bond in ethers

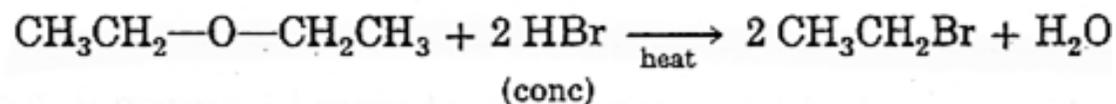
- Ethers are the **least reactive** of the functional groups.
- When **ethers** are heated in concentrated acid solutions, the ether linkage is broken.



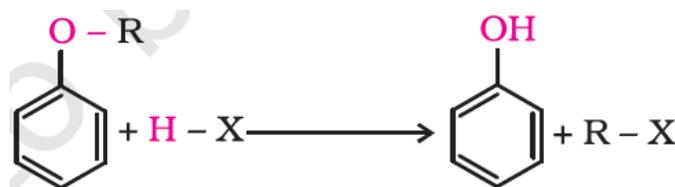
- The acids most often used in this reaction are $\text{HI} > \text{HBr} > \text{HCl}$.
- If an **excess of acid** is present, the alcohol initially produced is converted into an alkyl halide by the reaction.



For example,



- Alkyl aryl ethers** are cleaved at the alkyl-oxygen bond due to the more stable aryl-oxygen bond. The reaction yields *phenol* and *alkyl halide*.



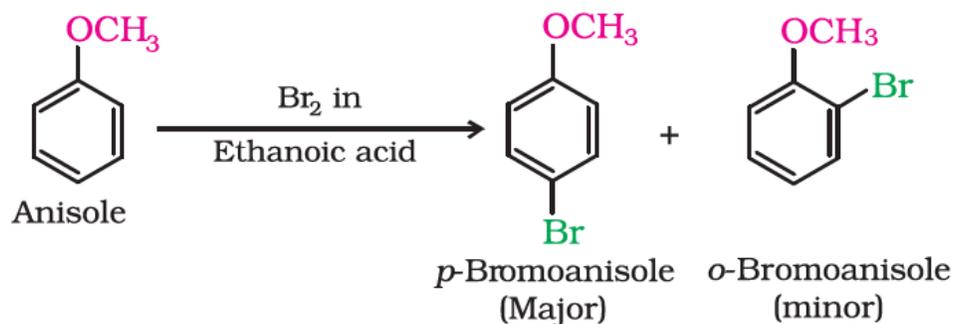
Chemical Reactions of Ethers

2. Electrophilic substitution

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

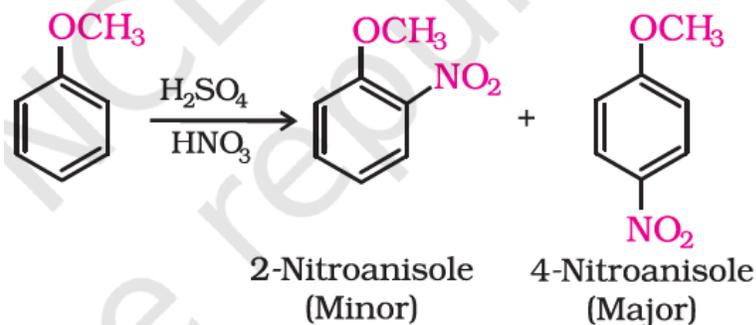
(i) Halogenation:

Anisole undergoes bromination with bromine in ethanoic acid even in the absence of iron (III) bromide catalyst. It is due to the activation of benzene ring by the methoxy group. *Para* isomer is obtained in 90% yield.



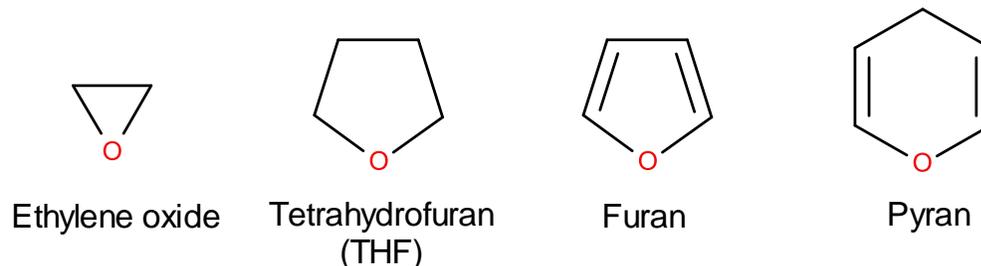
(ii) Nitration:

Anisole reacts with a mixture of concentrated sulphuric and nitric acids to yield a mixture of *ortho* and *para* nitroanisole.



Cyclic Ethers

- **Cyclic ethers** are similar to cycloalkanes/cycloalkenes, but possess an O- atom as part of the ring.



- **Epoxides** are ethers having the oxygen atom in a **three-membered ring**.
- **Epoxides** are also called **oxiranes**.



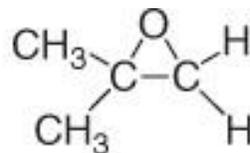
- The C-O-C bond angle for an epoxide must be 60° , a considerable deviation from the tetrahedral bond angle of 109.5° . Thus, epoxides have **angle strain**, making them **more reactive** than other ethers.

Nomenclature of Epoxides

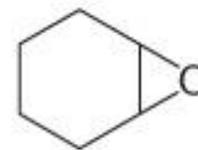
- **Epoxides** bonded to a chain of carbon atoms are named as **derivatives of oxirane**.
- When an epoxide is bonded to a ring, the O atom is considered a substituent, called an epoxy group, bonded to a cycloalkane, and two numbers are used to designate the atoms to which the O atoms are bonded.



oxirane

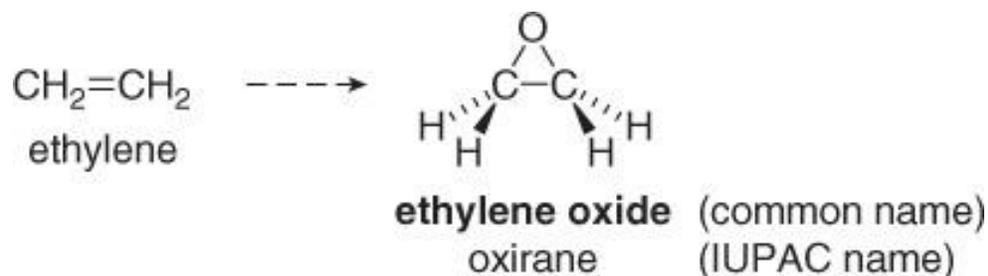


1,1-dimethyloxirane



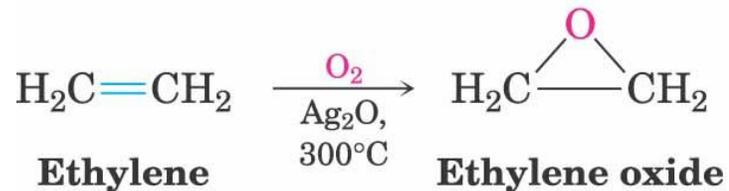
1,2-epoxycyclohexane

- **Epoxides** are also named as **alkene oxides**, because they are often prepared by adding an O atom to an alkene.
- **To name an epoxide in this way:**
 - Mentally replace the epoxide oxygen by a double bond.
 - Name the alkene.
 - Add the word oxide.



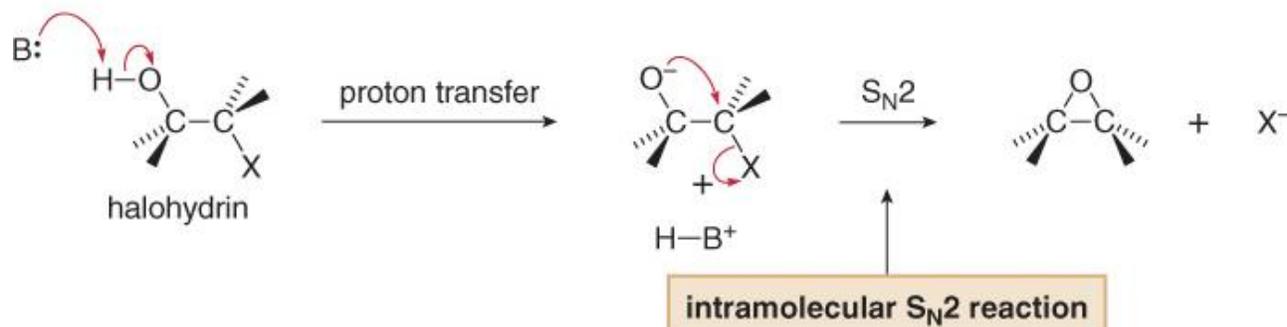
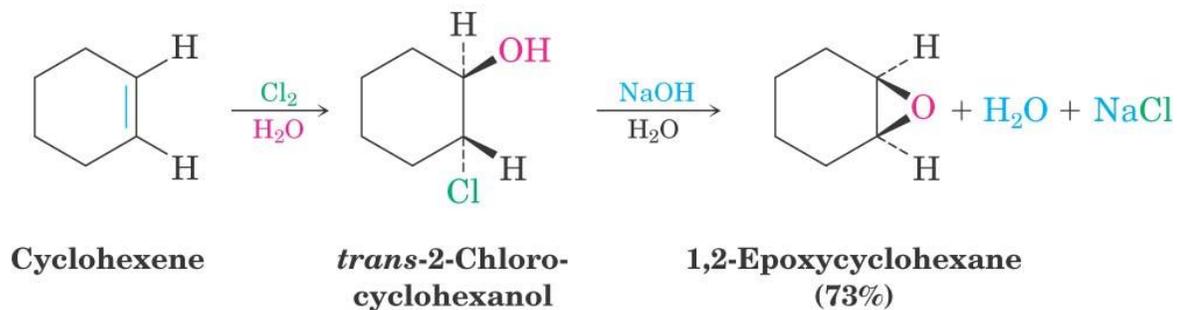
Preparation of Epoxides

- **Ethylene oxide** is prepared commercially by air oxidation of ethylene.



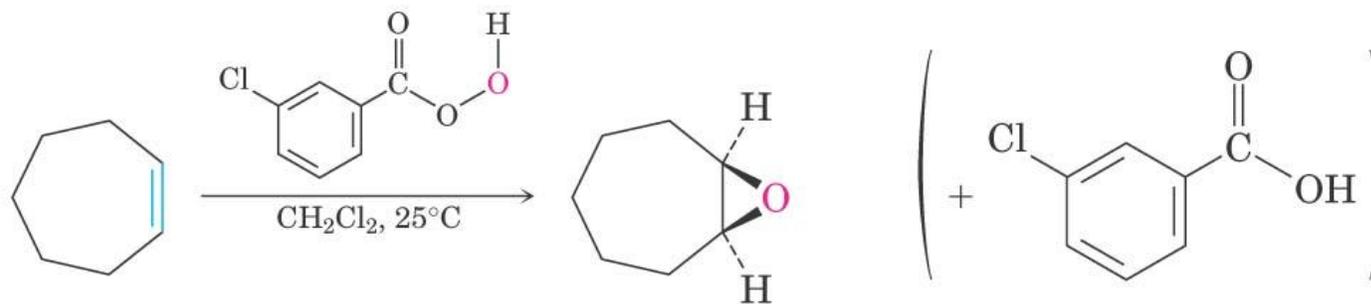
- **Epoxides from Halohydrins**

- Addition of HO-X to an alkene gives a halohydrin
- Treatment of a halohydrin with base gives an epoxide



Preparation of Epoxides

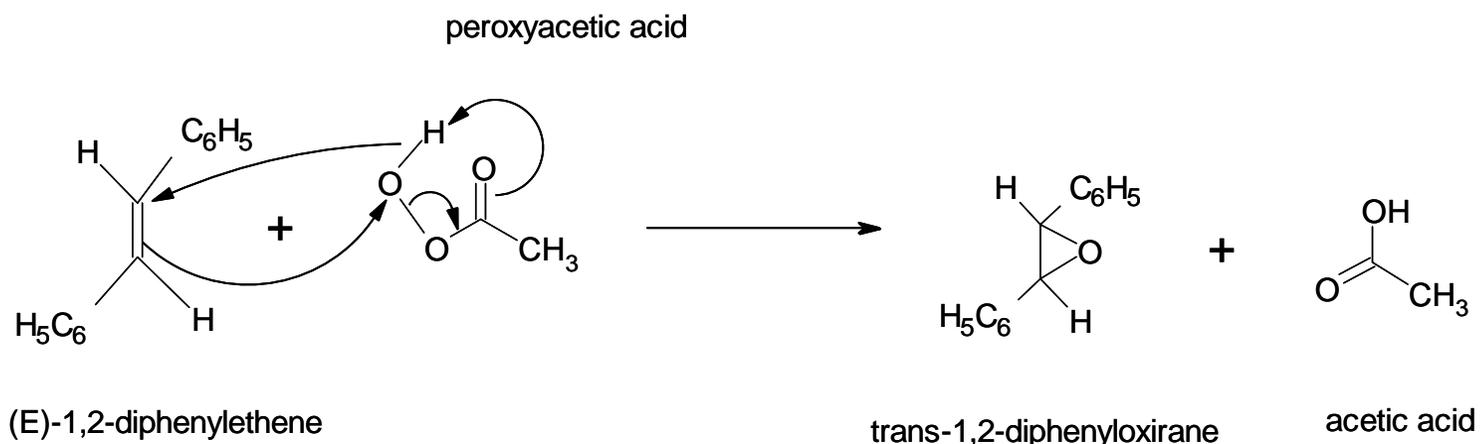
○ Preparation of Epoxides Using a Peroxyacid



Cycloheptene

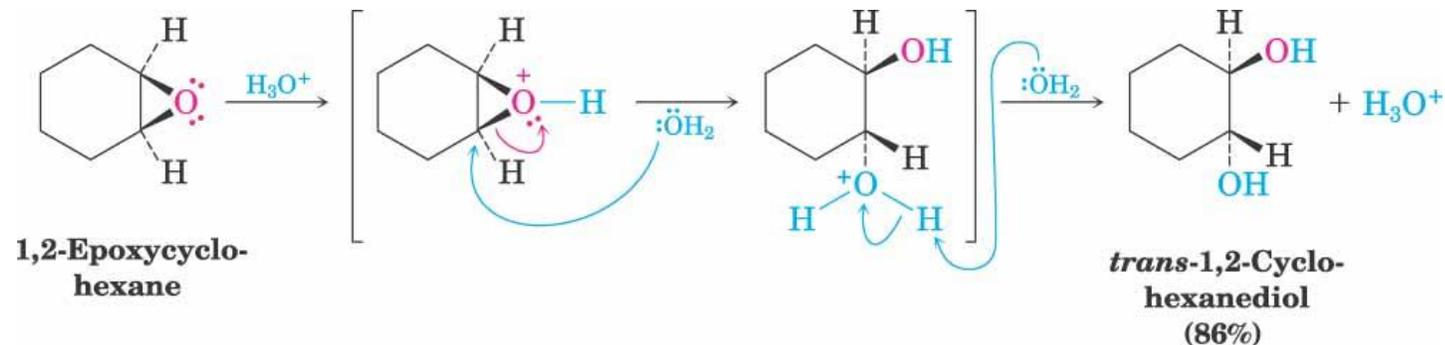
1,2-Epoxycycloheptane
(78%)

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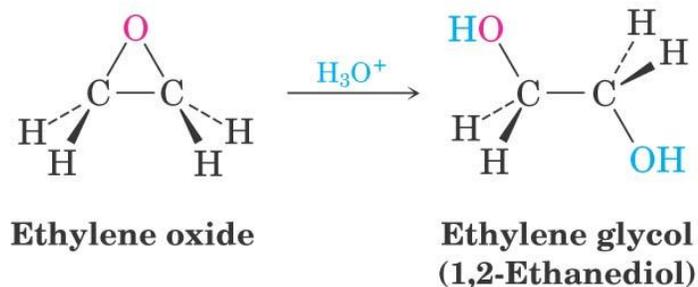


Ring-Opening Reactions of Epoxides

- Common nucleophiles that open the epoxide ring include OH^- , OR^- , CN^- , SR^- and NH_3 .
- With these strong nucleophiles, the reaction occurs by an S_N^2 mechanism
- **Water** adds to epoxides with dilute acid at room temperature
 - Product is a 1,2-diol (on adjacent C's: *vicinal*)
 - Mechanism: acid protonates oxygen and water adds to opposite side (anti-addition)



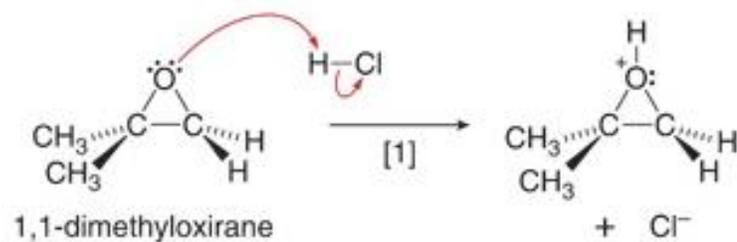
- **Example;** 1,2-ethanediol from acid catalyzed hydration of ethylene



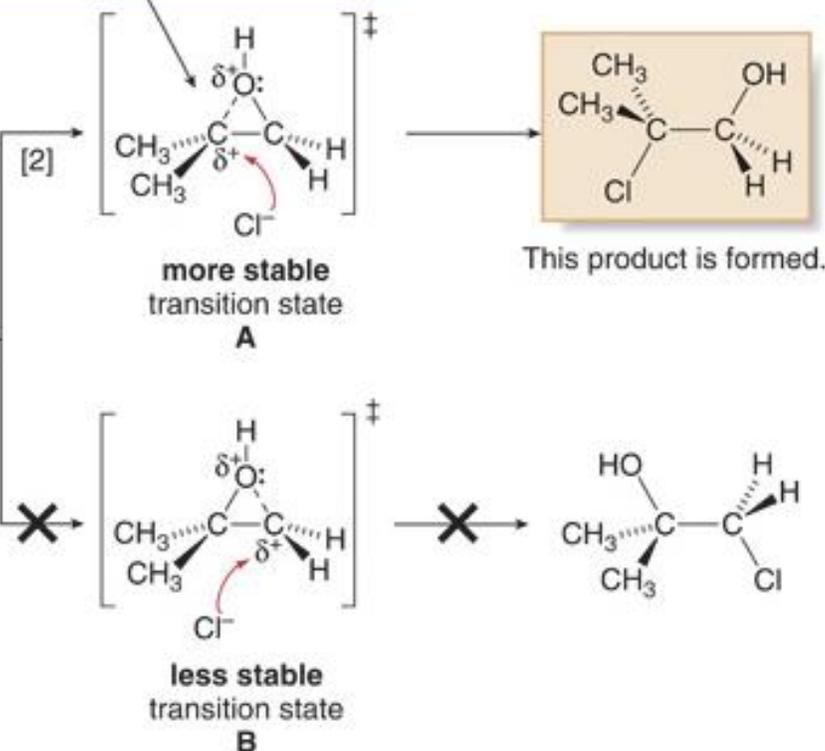
Ring-Opening Reactions of Epoxides

○ Acid-Catalyzed Epoxide Opening

ring opening of an epoxide ring with



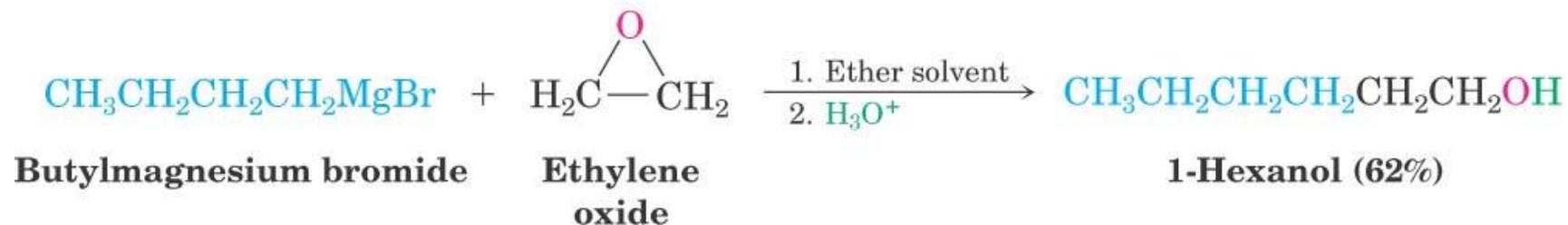
The more substituted C is more able to accept a partial positive charge.



- Transition state **A** is lower in energy because the partial positive charge (δ^+) is located on the more substituted carbon. In this case, therefore, nucleophilic attack occurs from the back side (an S_N2 characteristic) at the more substituted carbon (an S_N1 characteristic).

Ring-Opening Reactions of Epoxides

○ Addition of Grignard to Ethylene Oxide



○ Base-Catalyzed Epoxide Opening

- Hydroxide cleaves epoxides at elevated temperatures to give trans 1,2-diols.

