

# Fundamentals of Organic Chemistry

**CHEM 108**

*King Saud University*

**College of Science, Chemistry Department**

# Alcohols, Phenols and Ethers



- Alcohols, ethers and phenols have a common functional group, the hydroxyl group, -OH.

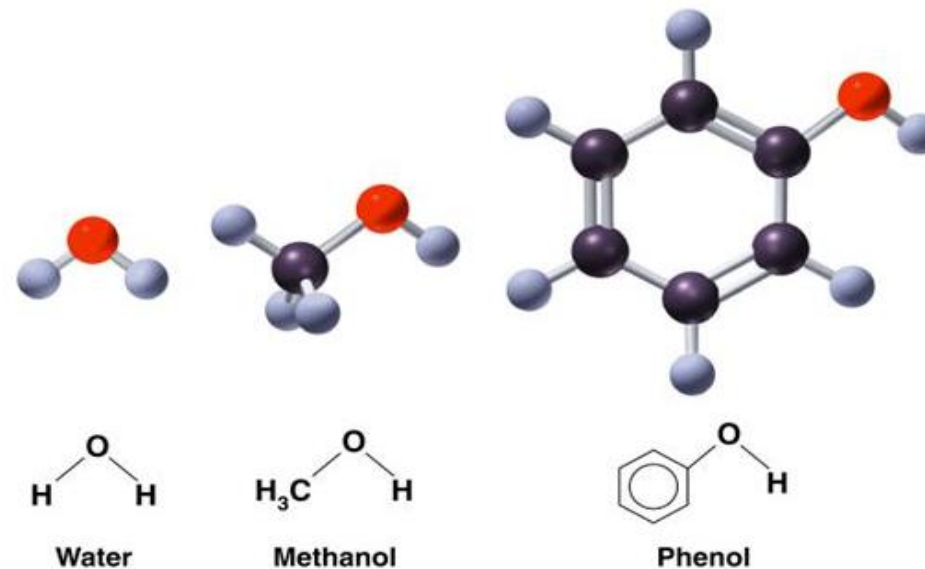
<b>H-O-H</b> Water	<b>R-OH</b> Alcohol	<b>R-O-R</b> Ethers	<b>Ph-O-H</b> Phenol
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- **Alcohols** are compounds whose molecules have a hydroxyl group attached to a *saturated* carbon atom.
- **Phenols** are compounds that have a hydroxyl group attached directly to a *benzene ring*.
- **Ethers** are compounds whose molecules have an oxygen atom bonded to **two** carbon atom.

# Alcohols and Phenols

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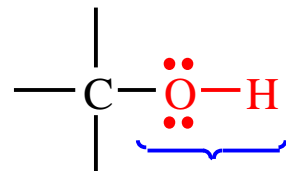
- **Alcohols and phenols** may be viewed as organic *derivatives of water*.



- **Alcohols** have the general formula R-OH, and structurally similar to water, but with one of the hydrogens replaced by an alkyl group.
- **Phenols** have a hydroxyl group attached directly to an aromatic ring.

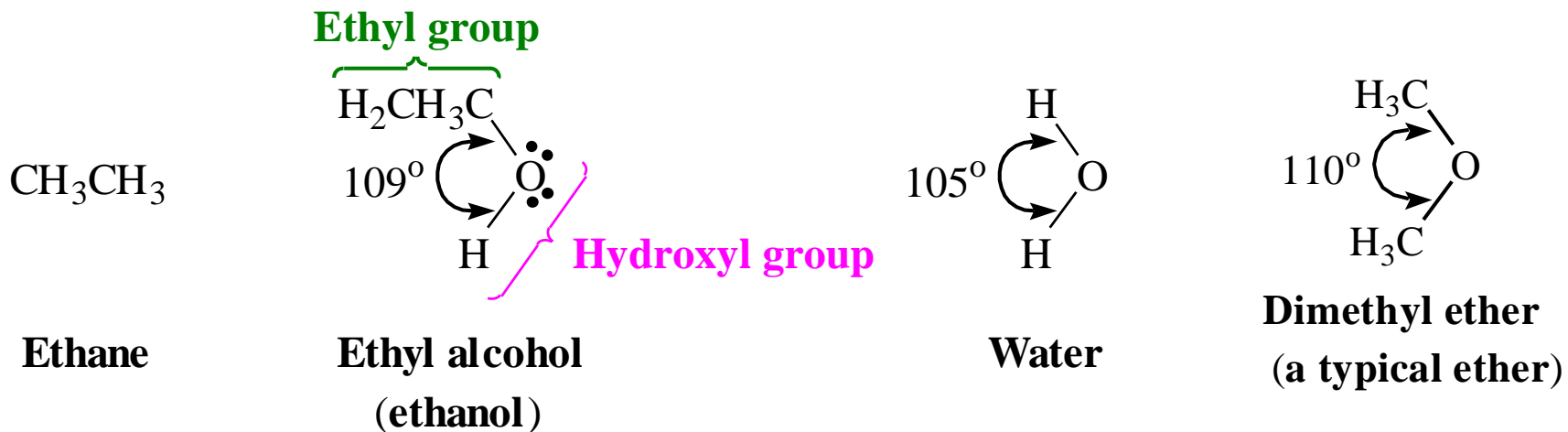
# Alcohols

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This is the functional group of an alcohol

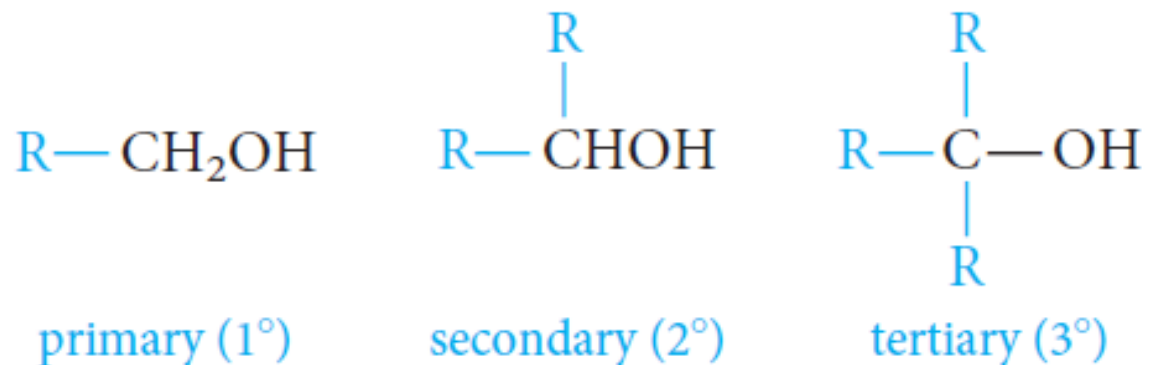
- Alcohols can be viewed in two ways structurally:
  - as **hydroxyl derivatives** of alkanes
  - as **alkyl derivatives** of water.



# Classification of Alcohols

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- **Alcohols** are classified as **primary (1°)**, **secondary (2°)**, or **tertiary (3°)**, depending on whether one, two, or three organic groups are connected to the hydroxyl-bearing carbon atom.



- **Methyl alcohol**, which is not strictly covered by this classification, is usually grouped with the primary alcohols.

# Nomenclature of Alcohols

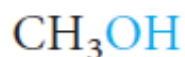
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- The **common names** for the simplest alcohols consist of alkyl group attached to the hydroxyl function followed by the word alcohol: *Alkyl alcohol*.
- In the **IUPAC system**, alcohols are named according to the following rules.

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**: *Alkanol*

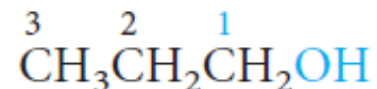
2. When isomers are possible, the chain is numbered so as to give the functional group (-OH) the **lowest possible number**.



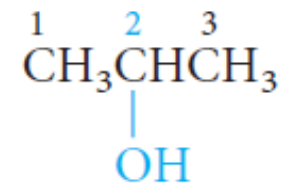
methanol  
(methyl alcohol)



ethanol  
(ethyl alcohol)



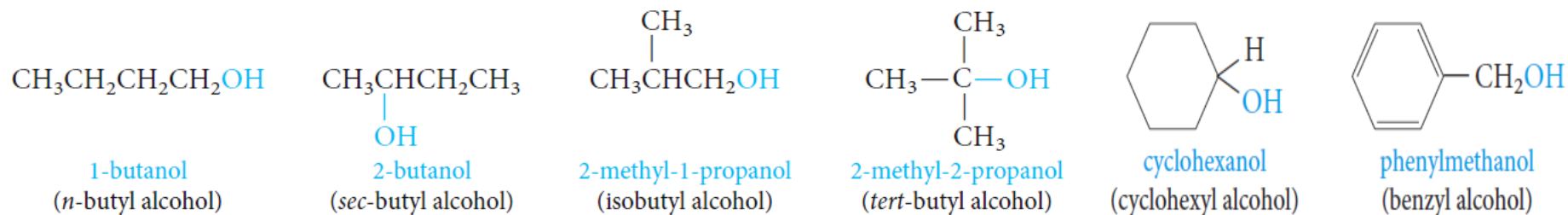
1-propanol  
(*n*-propyl alcohol)



2-propanol  
(isopropyl alcohol)

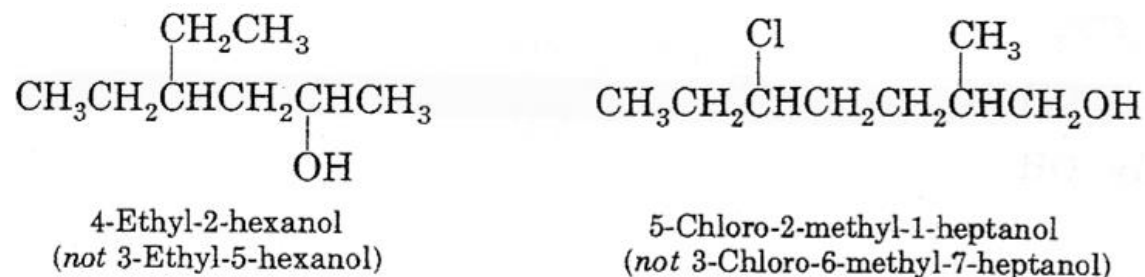
# Nomenclature of Alcohols

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

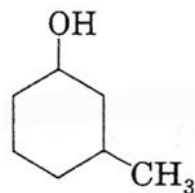
The position of the functional group ( $-\text{OH}$ ) is always given the **lowest possible number** at the end of the name.



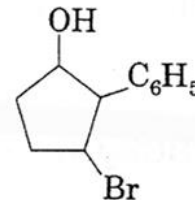
# Nomenclature of Alcohols

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**For cyclic alcohols**, numbering always starts from the carbon bearing the -OH group.



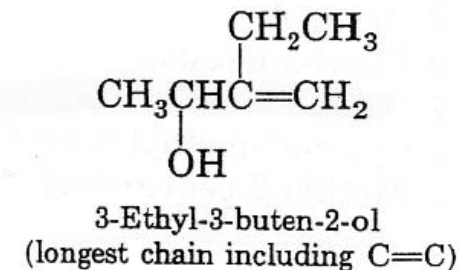
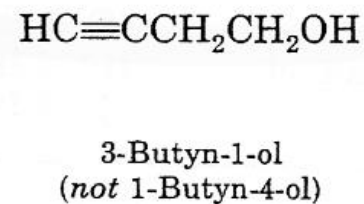
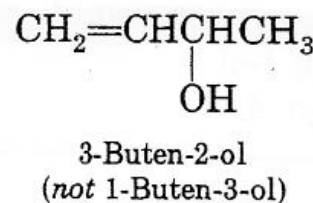
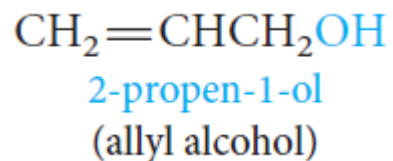
3-Methylcyclohexanol  
(not 1-Methyl-3-cyclohexanol)



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

**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

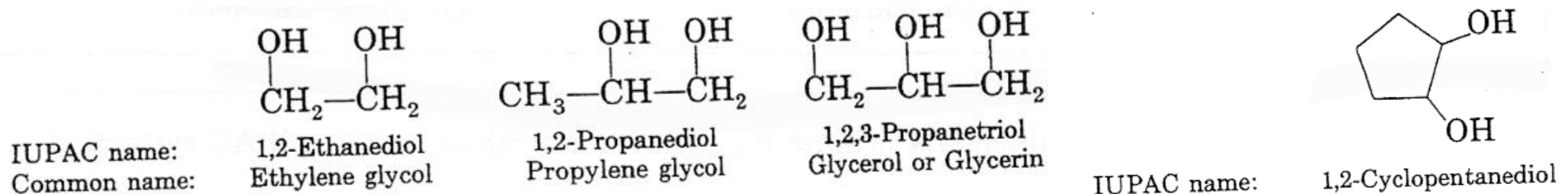
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## Alcohols with More Than One Hydroxyl Group

➤ Compounds with two adjacent alcohol groups are called *glycols*.

*The most important example is ethylene glycol.*

➤ Compounds with more than two hydroxyl groups are also known, and several, such as glycerol and sorbitol, are important commercial chemicals.

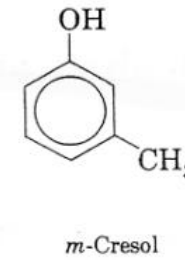
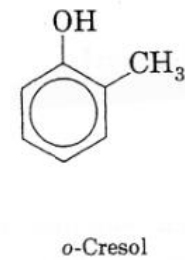
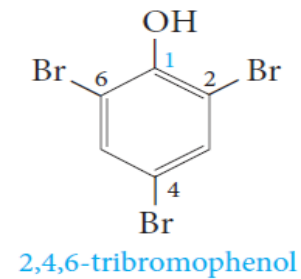
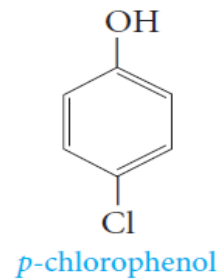
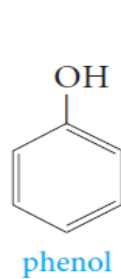


- *Ethylene glycol* is used as the “permanent” antifreeze in automobile radiators and as a raw material in the manufacture of polyester fiber: Dacron.
- *Ethylene glycol* is completely miscible with water.
- *Glycerol* is a syrupy, colorless, water-soluble, high-boiling liquid with a distinctly sweet taste. Its soothing qualities make it useful in shaving and toilet soaps and in cough drops and syrups.

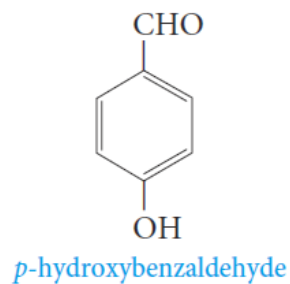
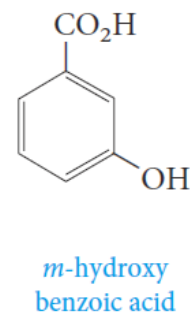
# Nomenclature of Phenols

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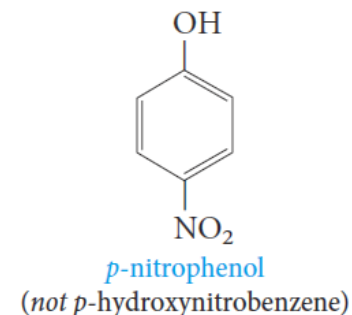
- **Phenols** are usually named as derivatives of the parent compounds.



- 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**.



but



# Physical Properties of Alcohols

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## Physical State

- The simplest alcohol, methanol, is a liquid at room temperature. In contrast, alkanes from methane to butane are gases.

## Solubility

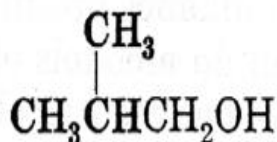
- The lower alcohols are completely miscible with water.
- As the number of carbons in the alcohol increases, the solubility in water decreases.

## Boiling Points

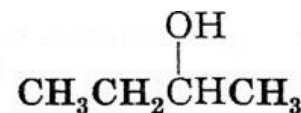
- Series of normal alcohols**; The boiling points increase with increase in molecular weights.
- A comparison of boiling points among **isomeric alcohols**; The boiling points decrease as the number of alkyl branches from the carbinol group increases.



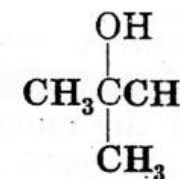
1-Butanol  
(mol wt = 74; bp = 118°C)



2-Methyl-1-propanol  
(mol wt = 74; bp = 108°C)



2-Butanol  
(mol wt = 74; bp = 99.5°C)



2-Methyl-2-propanol  
(mol wt = 74; bp = 83°C)

# Hydrogen Bonding in Alcohols

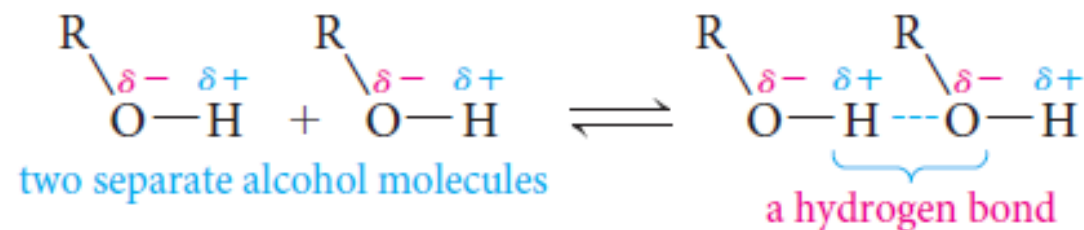
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- The **boiling points** (bps) of alcohols are much higher than those of ethers or hydrocarbons with similar molecular weights.

	CH <sub>3</sub> CH <sub>2</sub> OH	CH <sub>3</sub> OCH <sub>3</sub>	CH <sub>3</sub> CH <sub>2</sub> CH <sub>3</sub>
mol wt	46	46	44
bp	+78.5°C	-24°C	-42°C

**Why?** Because alcohols form hydrogen bonds with one another.

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 Bonding in Alcohols

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- Consequently, alcohols have relatively high boiling points because they must supply enough heat to break the hydrogen bonds before each molecule.
- Hydrogen bonds are weaker than ordinary covalent bonds.
- Water, of course, is also a hydrogen-bonded liquid.
- The lower molecular-weight alcohols can readily replace water molecules in the hydrogen bonded network.
- This accounts for the complete miscibility of the lower alcohols with water.
- However, as the organic chain lengthens and the alcohol becomes relatively more hydrocarbon like, its water solubility decreases.

Table 7.1 Boiling Point and Water Solubility of Some Alcohols

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

# Physical Properties of Phenols



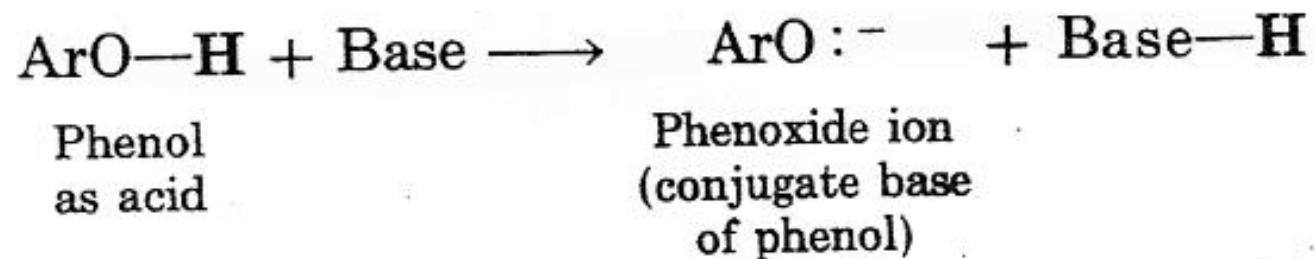
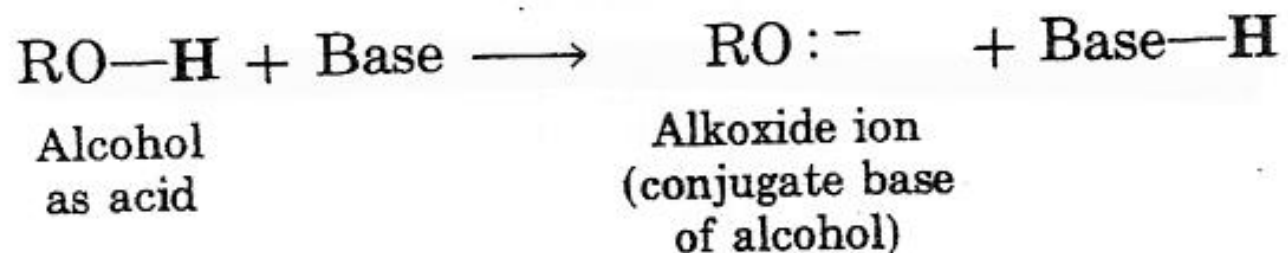
- **Phenol** is a colorless, crystalline, low-melting solid, with a high boiling point, that is moderately soluble in water.
- Most other phenols also are solids, with slight solubility in water and high boiling points.
- The most significant physical property that distinguishes alcohols from phenols is the acidity of phenols.

# The Acidity of Alcohols and Phenols



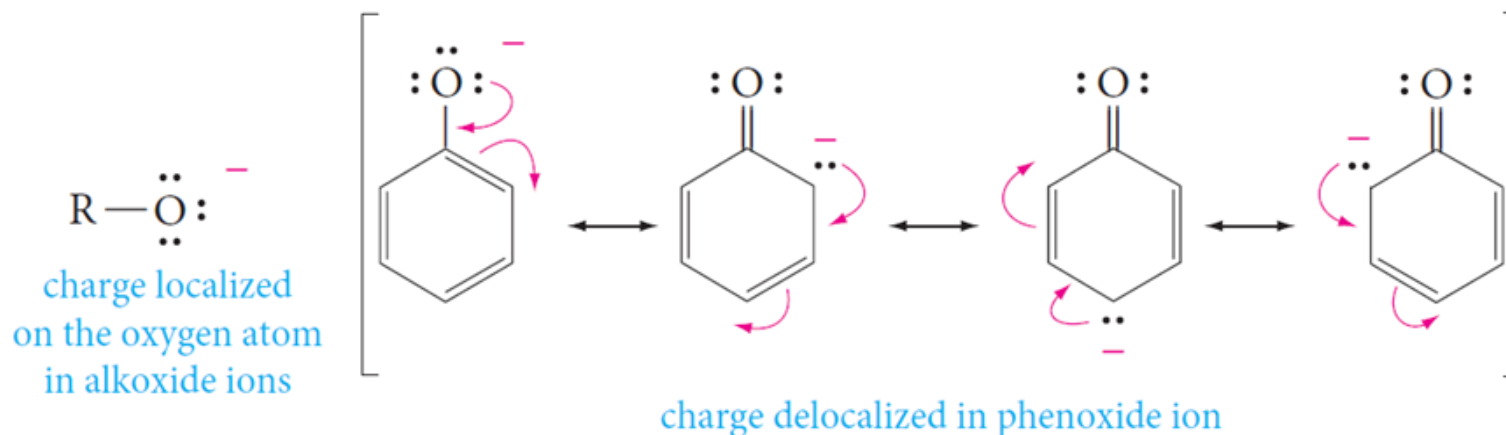
- Like water, alcohols and phenols are weak acids.

*The hydroxyl group can act as a proton donor, and dissociation occurs in a manner similar to that for water*



# The Acidity of Alcohols and Phenols

- **Phenols are stronger acids than alcohols** mainly because the corresponding phenoxide ions are stabilized by resonance.



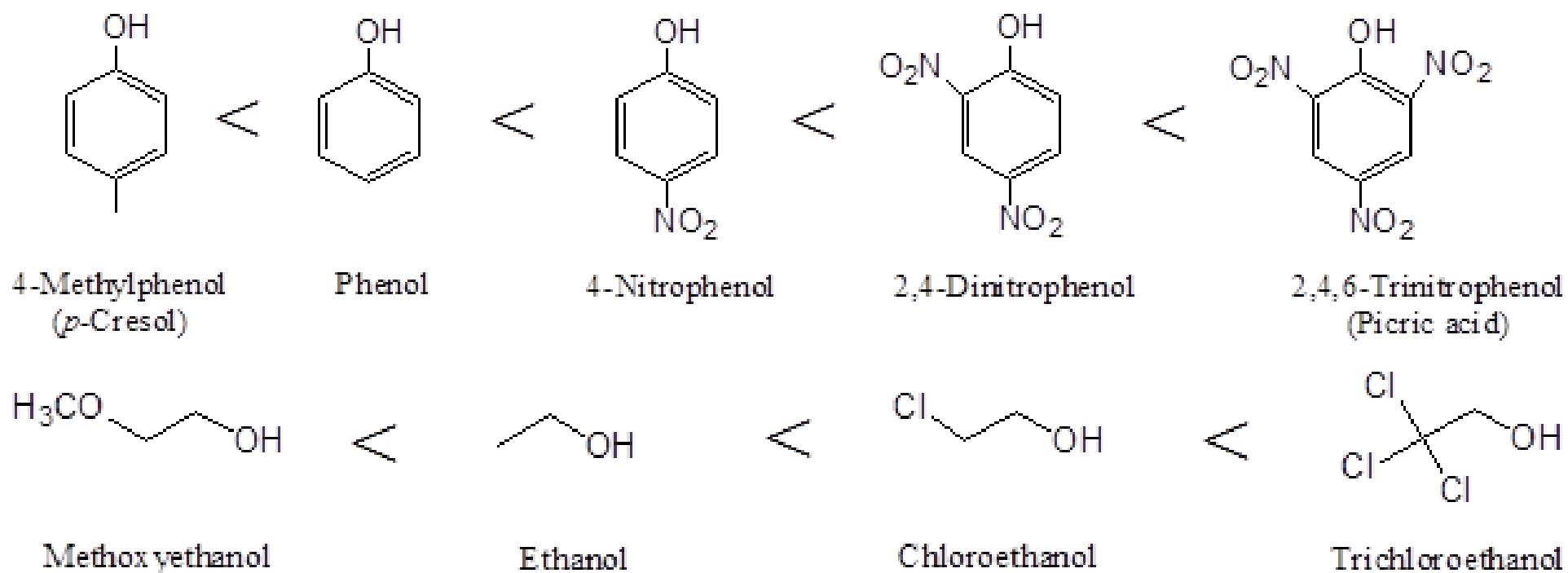
The negative charge of an **alkoxide ion** is concentrated on the oxygen atom, but the negative charge on a phenoxide ion can be delocalized to the ortho and para ring positions through resonance.

Because **phenoxide ions** are stabilized in this way, the equilibrium for their formation is more favorable than that for alkoxide ions



# The Acidity of Alcohols and Phenols

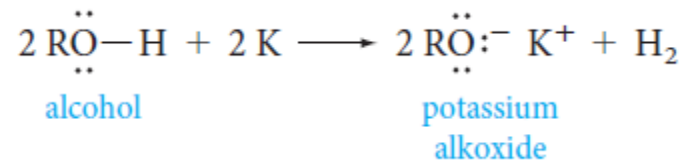
- All **electron-withdrawing groups increase acidity** by stabilizing the conjugate base. **Electron-donating groups decrease acidity** because they destabilize the conjugate base.



# The Acidity of Alcohols and Phenols

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- **Alkoxides**, the conjugate bases of alcohols, can be prepared by the reaction of an alcohol with sodium or potassium metal.

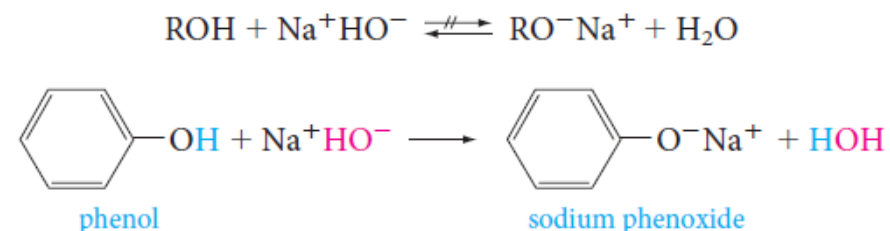


- Treatment of alcohols with sodium hydroxide **does not convert** them to their alkoxides.

*This is because alkoxides are stronger bases than hydroxide ion, so the reaction goes in the reverse direction.*

*Since alcohols are weaker acids than water, it is not possible to form the salt of an alcohol in aqueous alkaline solutions.*

- Treatment of phenols with sodium hydroxide **converts** them to phenoxide ions.



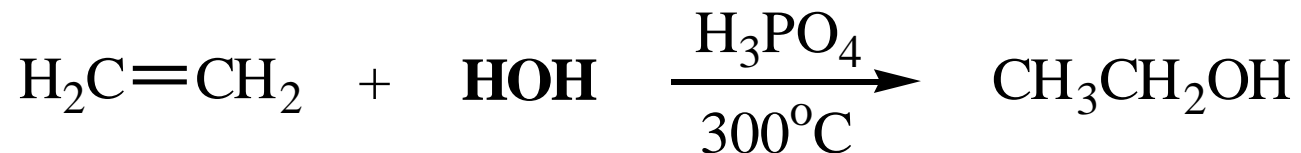
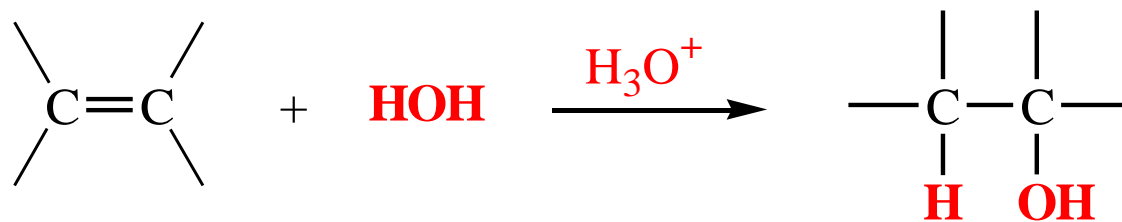
# Preparation of Alcohols

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## ○ From Alkenes

### A. Acid-Catalyzed Hydration of Alkenes

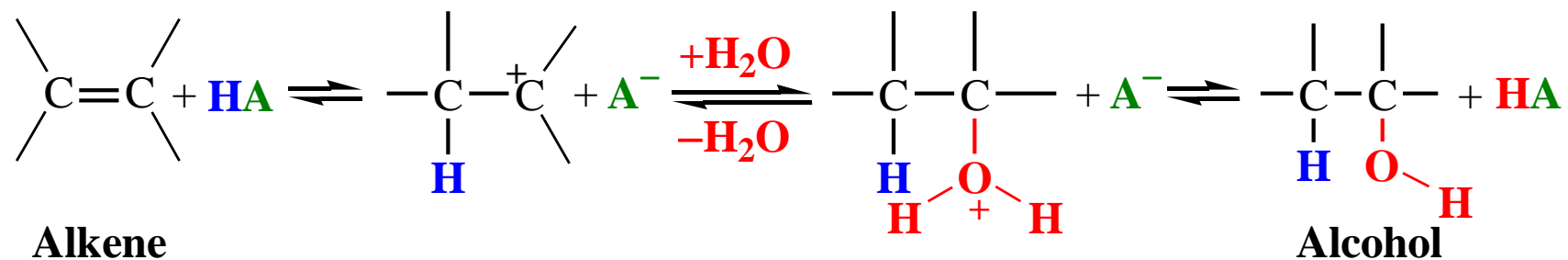
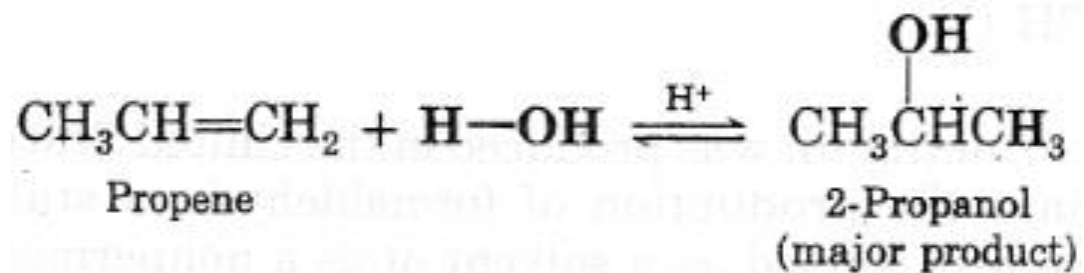
1. Addition of water to a double bond in the presence of an *acid catalyst*,  $H^+$ .



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

## 2. The addition follows *Markovnikov's rule*.

**Mechanism:** Water adds to alkenes in the presence of an acid catalyst following **Markovnikov's rule**, the reaction is reversible.



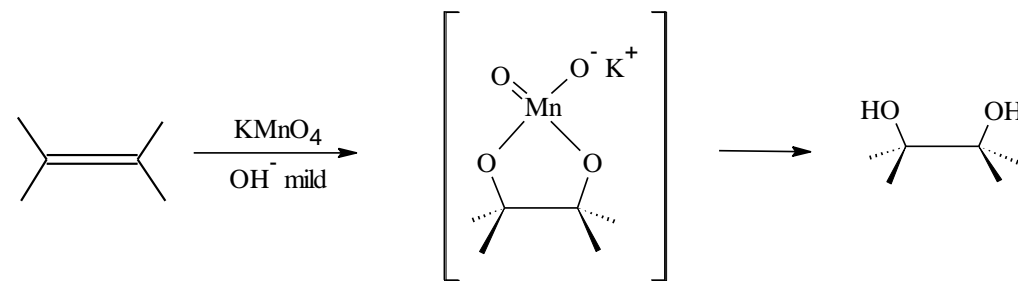
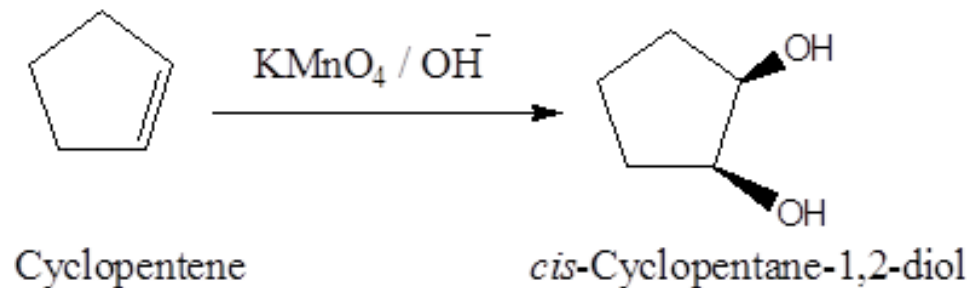
# Preparation of Alcohols

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## ○ From Alkenes

### B. Oxidation of Alkenes and Cycloalkenes

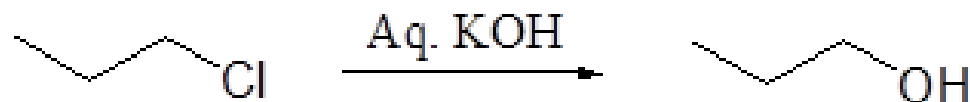
Alkenes react with alkaline potassium permanganate to form glycols (compounds with two adjacent hydroxyl groups).



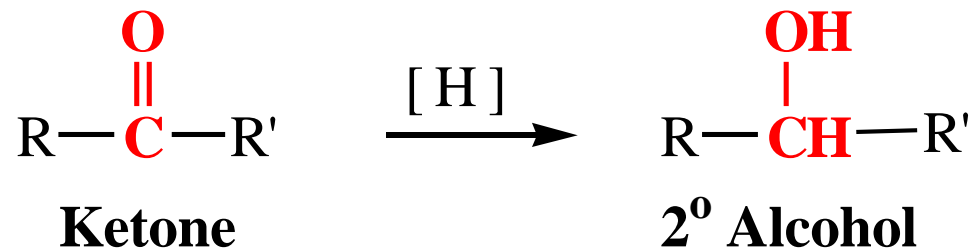
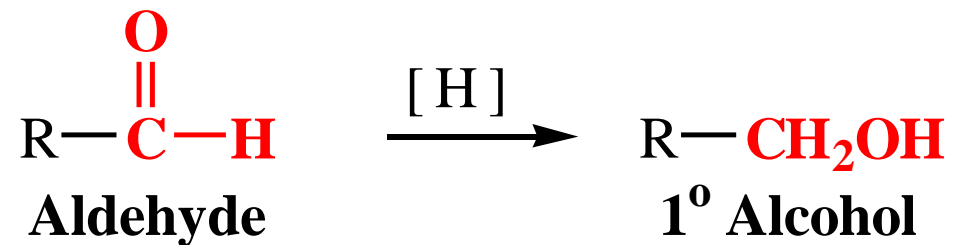
# Preparation of Alcohols

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## ○ Nucleophilic Substitution of Alkyl Halide

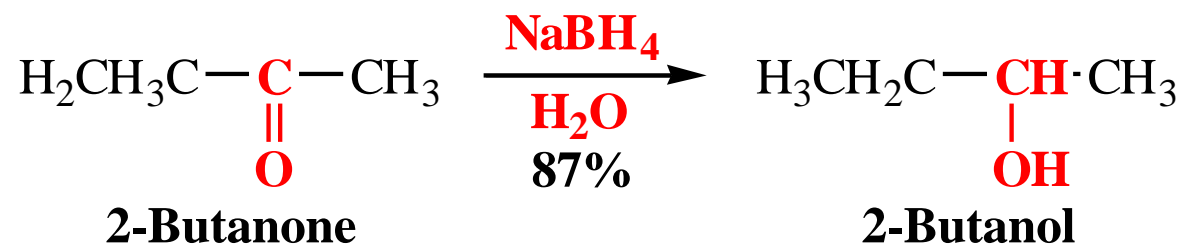
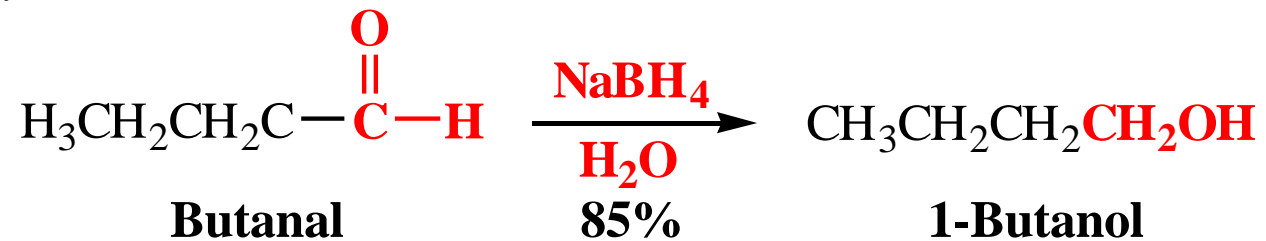


## ○ Reduction of Ketones, and Aldehydes using $\text{LiAlH}_4$ or $\text{NaBH}_4$



## ○ Reduction of Ketones, and Aldehydes

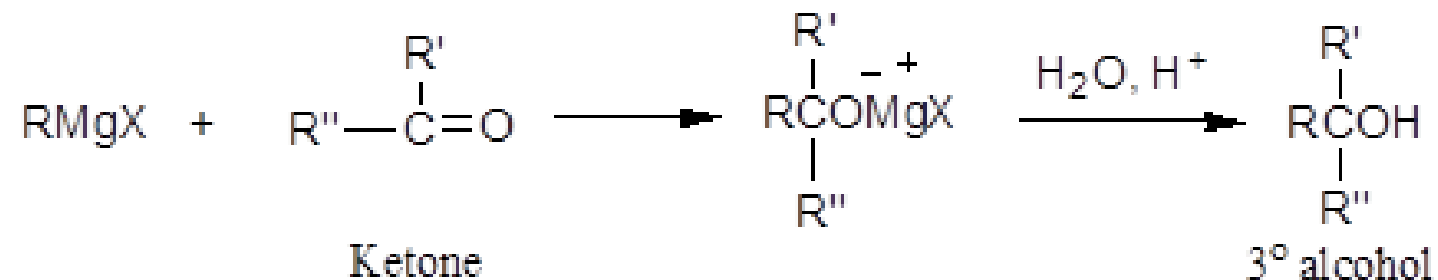
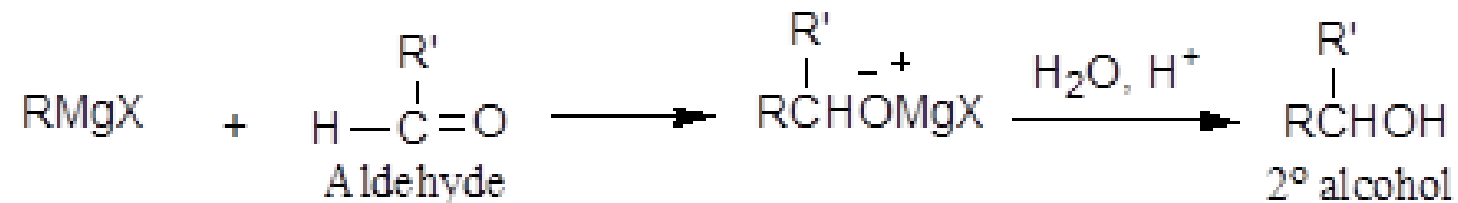
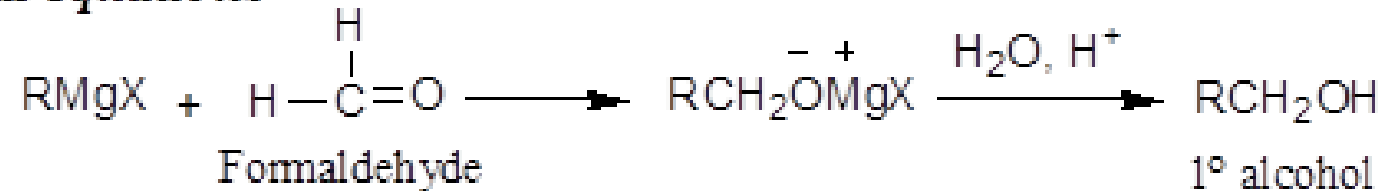
Aldehydes and ketones are easily reduced to primary and secondary alcohols, respectively.



# Preparation of Alcohols

## ○ Addition of Grignard's Reagent to Aldehydes and Ketones

*General equations*





# Reactions of Alcohols and Phenols

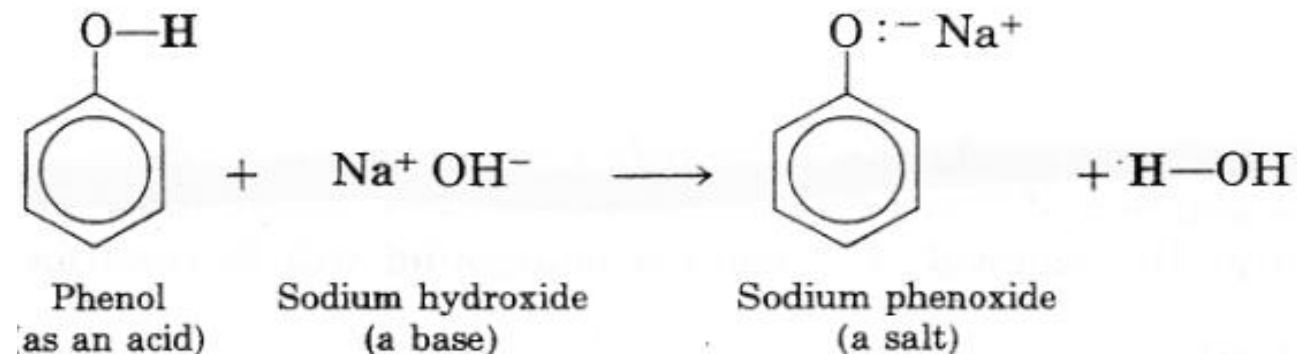
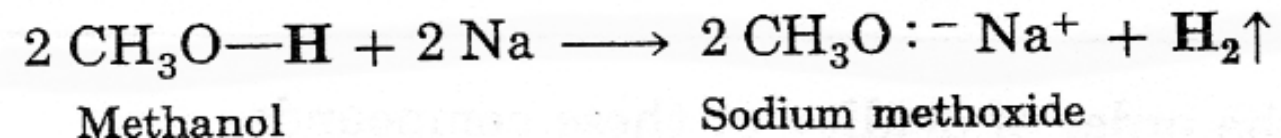
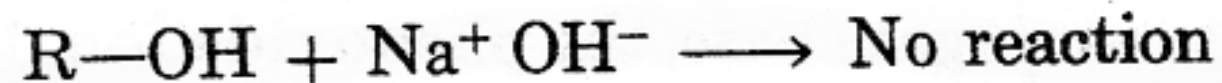


- **Alcohols** undergo two kinds of reactions:
  - Those that involve the breaking of the oxygen-hydrogen bond (CO-H).
  - Those that involve the rupture of the carbon-oxygen bond (C-OH).
- **Phenols** do not participate in reactions where the C-OH bond is broken.

# Reactions of Alcohols

A) Those that involve the breaking of the oxygen-hydrogen bond (CO-H).

## 1) Reactions of Alcohols and Phenols as Acids: Salt Formation.



# Reactions of Alcohols

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**B) Those that involve the rupture of the carbon-oxygen bond (C-OH).**

## **1) The Reaction of Alcohols with Hydrogen Halides: Alkyl Halides**

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

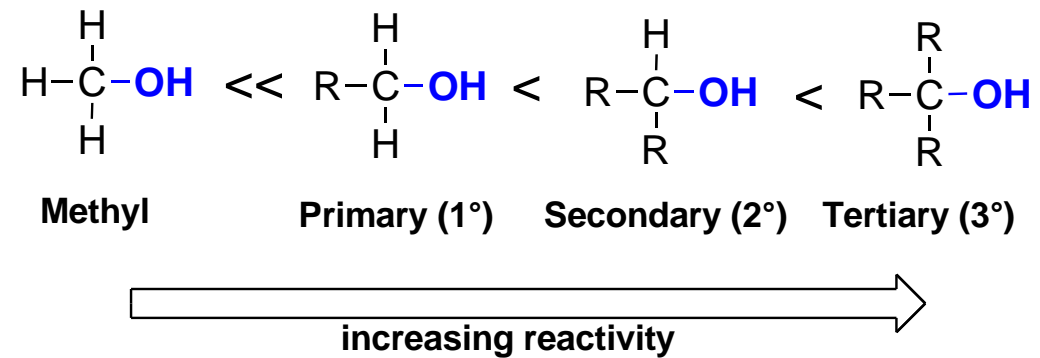


### **Reaction of Primary Alcohols with Hydrogen Halides: The S<sub>N</sub>2 Mechanism:**

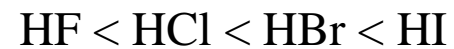
Methyl and primary carbocations are the least stable, and they are not likely to be intermediates in reaction mechanism:



Reactivity of the alcohol:

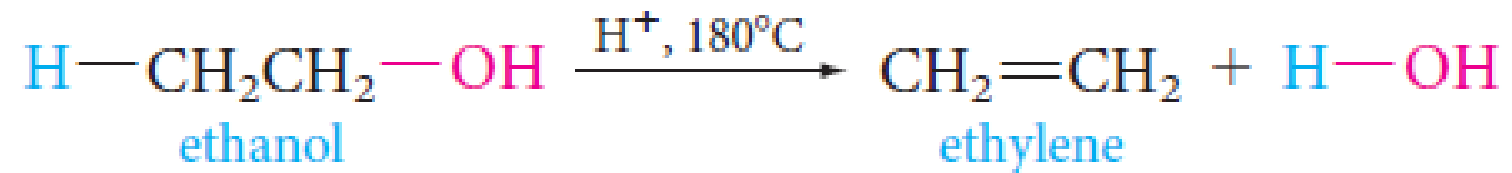


Reactivity of the H-X : parallels the acidity of HX



## 2) Dehydration of Alcohols: Formation of Alkenes

*Alcohols can be dehydrated by heating them with strong acid.*

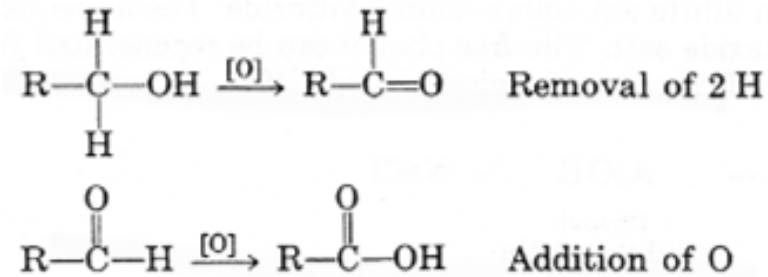


# Reactions of Alcohols

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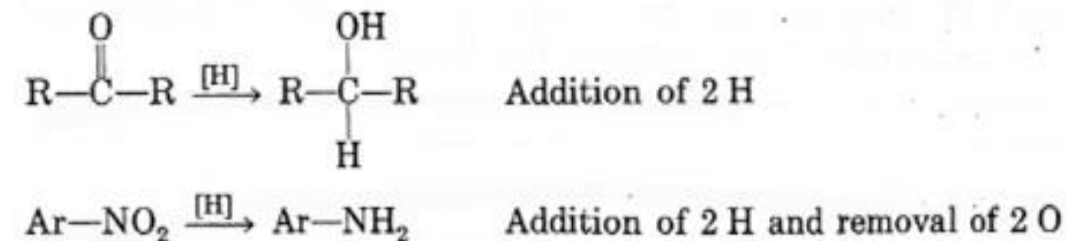
## C) Oxidation Reactions

- **Oxidation** is the **removal of H** from a compound and/or the **addition of O** to a compound.



*An oxidizing agent is the chemical reagent that does the oxidation.*

- **Reduction** is the **addition of H** to a compound and/or the **removal of O** from a compound.



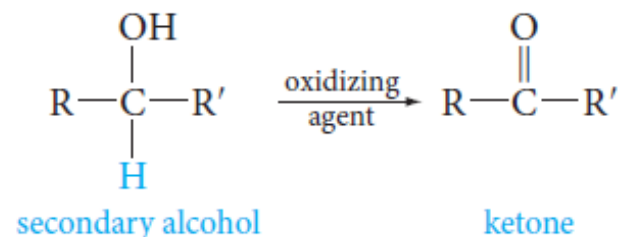
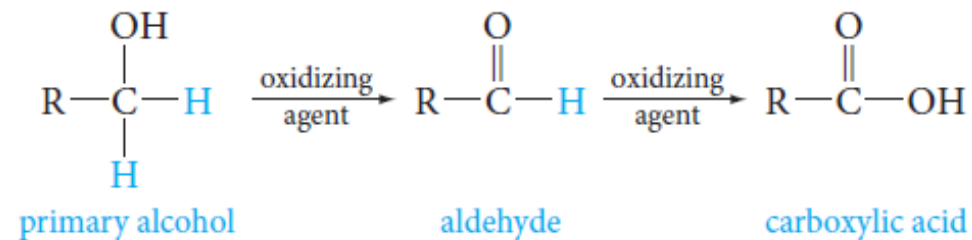
*A reducing agent is a substance that does the reduction.*

# Reactions of Alcohols

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## C) Oxidation Reactions

- Alcohols with at least one hydrogen attached to the hydroxyl-bearing carbon can be oxidized to carbonyl compounds.
- **Primary alcohols** give **aldehydes**, which may be further oxidized to **carboxylic acids**.
- **Secondary alcohols** give **ketones**.
- **Tertiary alcohols**, having no hydrogen atom on hydroxyl-bearing carbon, do not undergo oxidation.

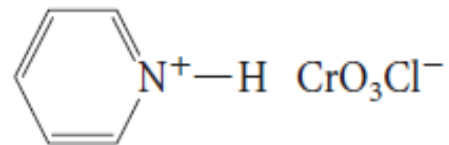
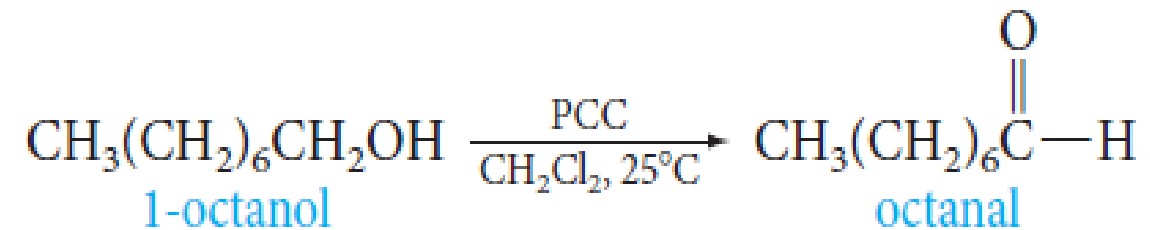


# Reactions of Alcohols

32

## C) Oxidation Reactions

- **Primary alcohols**, oxidation can be stopped at aldehyde stage by special reagents, such as “**pyridinium chlorochromate (PCC)**”.



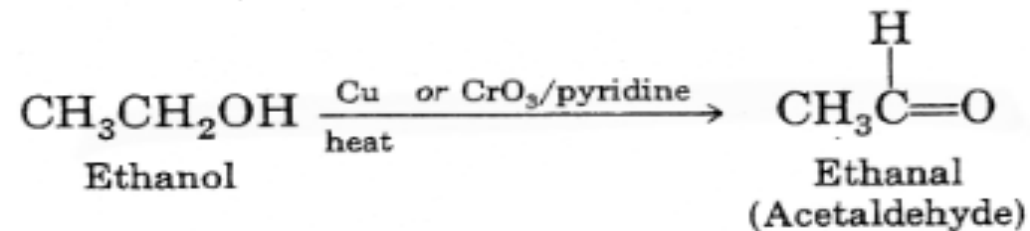
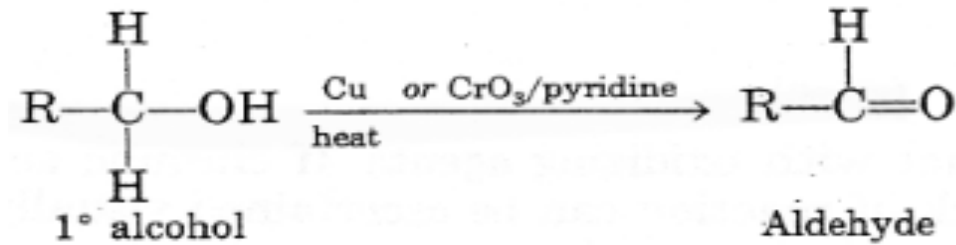
pyridinium chlorochromate  
(PCC)



# Reactions of Alcohols

## C) Oxidation Reactions

- **Primary alcohols** yield **aldehydes** when treated with mild oxidizing agents such as hot metallic copper or  $\text{CrO}_3$  in pyridine.

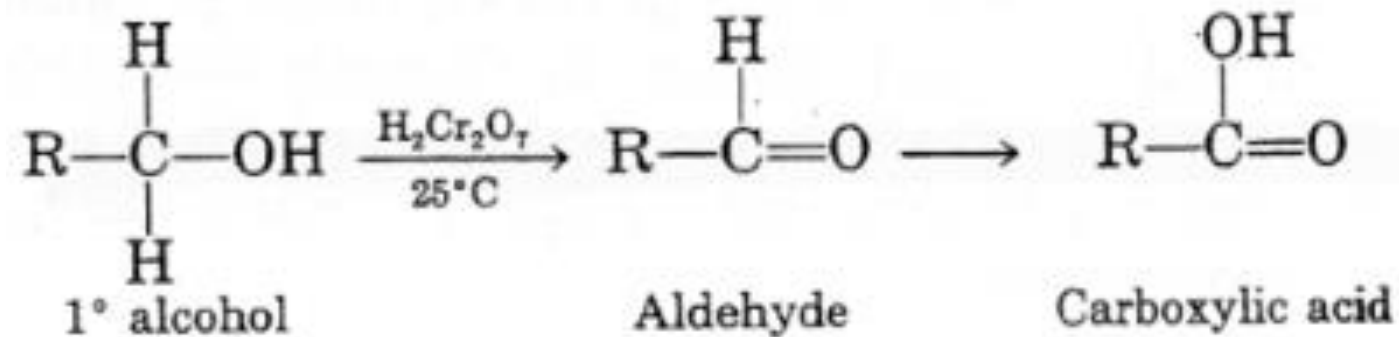


# Reactions of Alcohols

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## C) Oxidation Reactions

- **Primary alcohols** yield **aldehydes** when treated with stronger oxidizing agents, such as **chromic acid,  $H_2Cr_2O_7$** , or **neutral potassium permanganate,  $KMnO_4$** , the **intermediate aldehydes** formed initially are oxidized further to **carboxylic acids**.

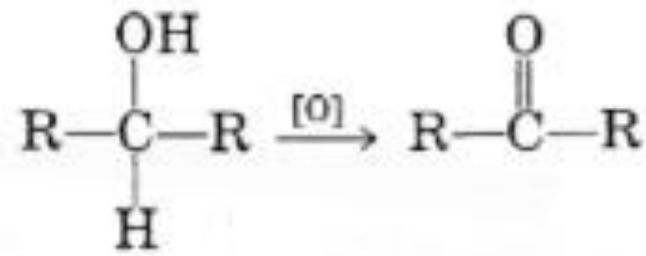


# Reactions of Alcohols

35

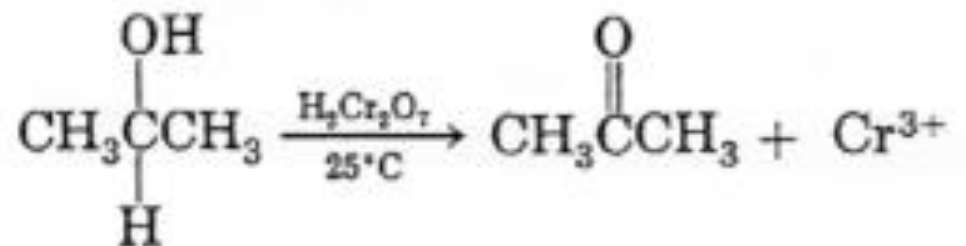
## C) Oxidation Reactions

- **Secondary alcohols**, when treated with *any* of the oxidizing agents mentioned previously, **yield ketones**.



2° alcohol

Ketone



2-Propanol

(orange)

Acetone

(green)

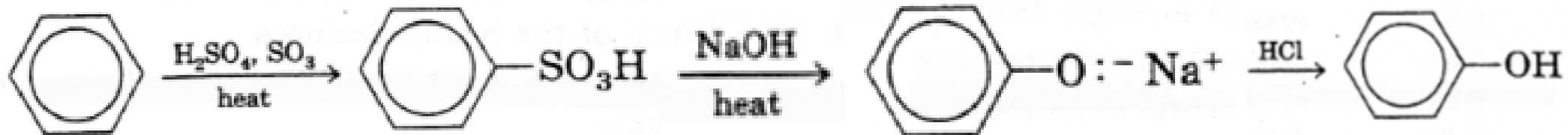
# Preparation of Phenols

36

## ○ *The Alkali Fusion of Sulfonates*

The alkali fusion of sulfonates involves the following steps;

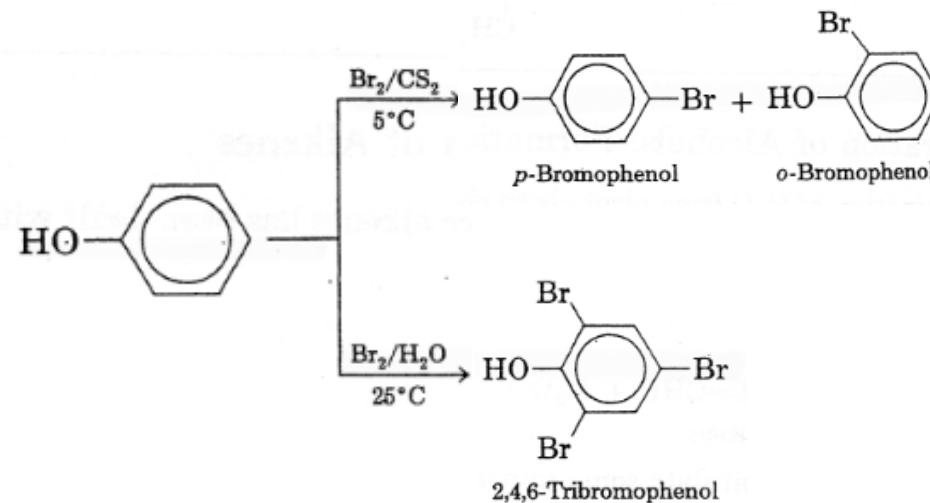
1. **Sulfonation** of an aromatic ring.
2. **Melting (fusion)** of the aromatic sulfonic acid with sodium hydroxide to give a **phenoxide salt**.
3. **Acidification** of the phenoxide with HCl to produce the **phenol**.



# Reactions of Phenols

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- Halogenation takes place *without catalyst*.



➤ **The products depend on the solvent used.**

- In *aprotic solvents* (solvents that do not release protons) ( $\text{CCl}_4$ ,  $\text{CS}_2$ )-bromination gives a mixture of *o*- and *p*-bromophenol.
- In *protic solvents* (solvents that can release protons) ( $\text{H}_2\text{O}$ )-halogenation gives a trisubstituted phenol is produced.



# Ethers

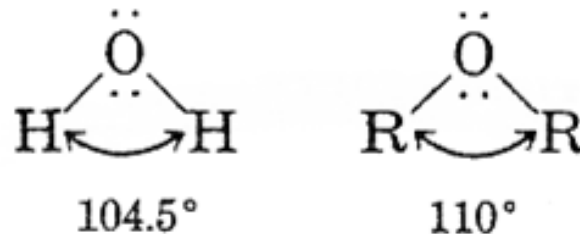
# Structure of Ethers

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- All **ethers** are compounds in which two organic groups are connected to a single oxygen atom.
- The **general formula for an ether** is  $R-O-R'$ , where R and R' may be identical or different, and they may be alkyl or aryl groups



- The geometry of simple ethers is similar to that of water.



# Structure of Ethers

- **The ether is classified as**

- **Symmetrical ethers;**

- When the organic groups attached to the oxygen are **identical**.

- **Unsymmetrical ethers (mixed ethers);**

- When the organic groups attached to the oxygen are **different**.

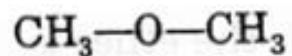


# Nomenclature of Ethers

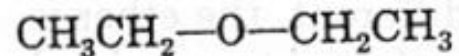
## Common Names

Ethers are usually named by giving the name of each alkyl or aryl group, in alphabetical order, followed by the word *ether*.

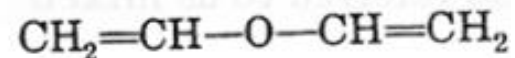
Methyl ether



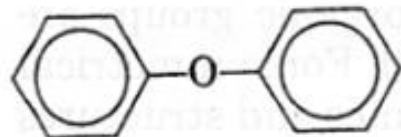
Ethyl ether



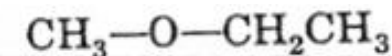
Vinyl ether



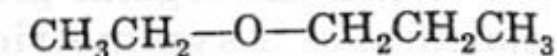
Phenyl ether



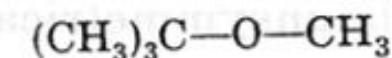
Ethyl methyl ether



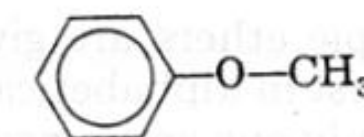
Ethyl-*n*-propyl ether



*t*-Butyl methyl ether



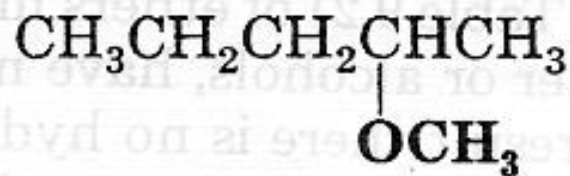
Methyl phenyl ether  
(anisole)



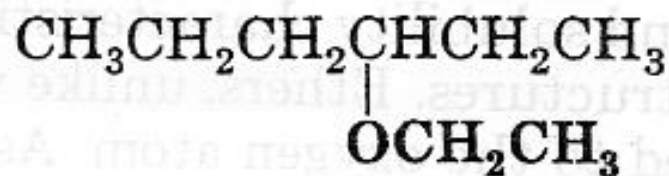
# Nomenclature of Ethers

## IUPAC System

For ethers with more complex structures, it may be necessary to name the -OR group as an alkoxy group. In the IUPAC system, the smaller alkoxy group is named as a substituent.



2-Methoxypentane



3-Ethoxyhexane



2-Methoxyethanol

# Physical Properties of Ethers

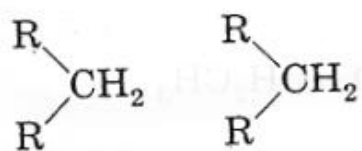
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## Physical State

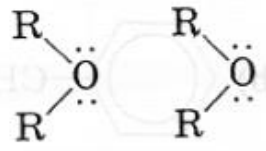
Ethers are colorless compounds with characteristic, relatively pleasant odors.

## Boiling Points

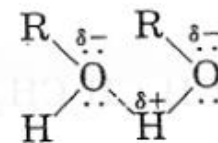
- They have **lower boiling points (bp,s)** than **alcohols** with an equal number of carbon atoms.
- In fact, an ether has nearly the **same bp** as the **corresponding hydrocarbon** in which a -CH<sub>2</sub>- group replaces the ether's oxygen.
- **Because of their structures (no O-H bonds)**, ether 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



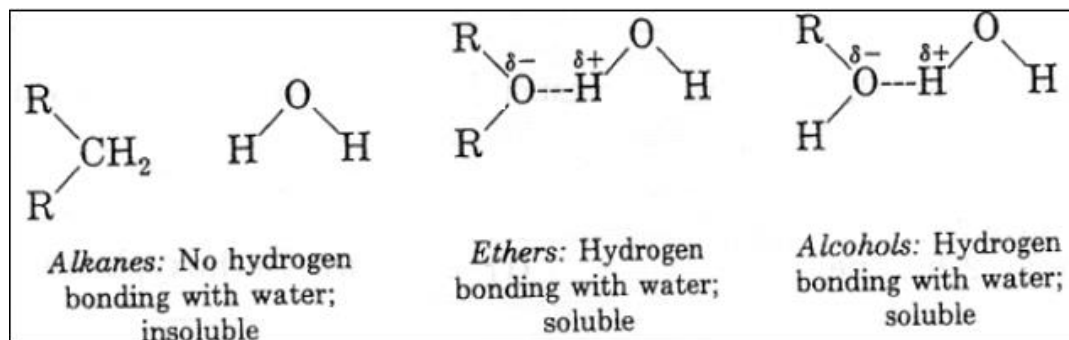
*Alcohols:* Hydrogen bonding between molecules; high boiling points

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

# Physical Properties of Ethers

## Solubility

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

# Preparation of Ethers



- There are **two general methods** for synthesizing ethers.

## 1) Dehydration of alcohols

It is used **commercially** and in the **laboratory** to make certain **symmetrical ethers**.

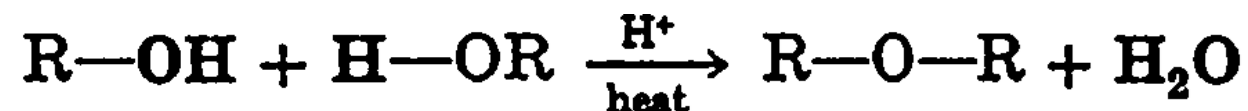
## 2) Williamson synthesis

General **laboratory** method used to prepare all kinds of ethers, **symmetrical** and **unsymmetrical**.

## 1) Dehydration of Alcohols

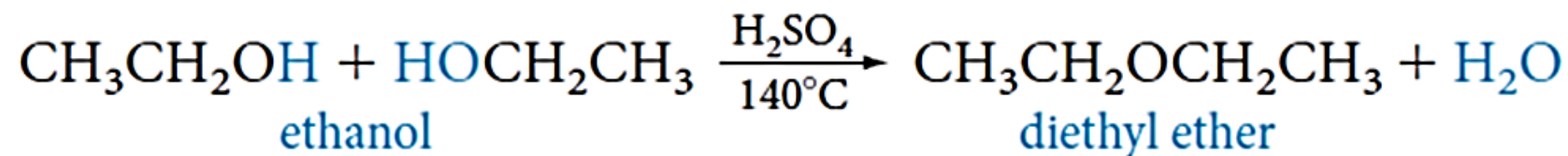
46

It takes place in the presence of acid catalysts ( $\text{H}_2\text{SO}_4$ ,  $\text{H}_3\text{PO}_4$ ) (intermolecular reaction)

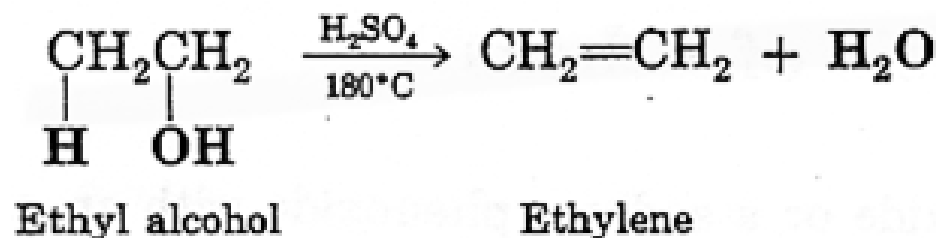


### Example;

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

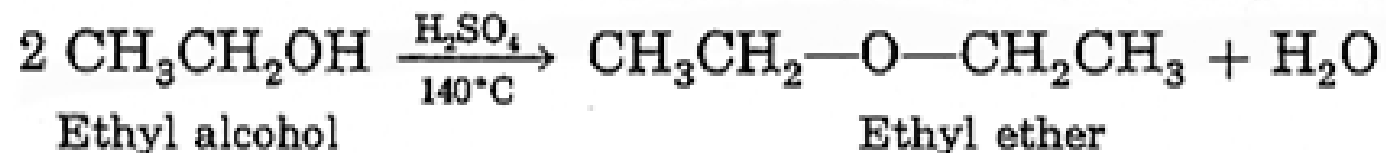


- When ethyl alcohol is dehydrated by **sulfuric acid at 180° C**, the dominant product is **ethylene**.



- **To prepare ethyl ether**

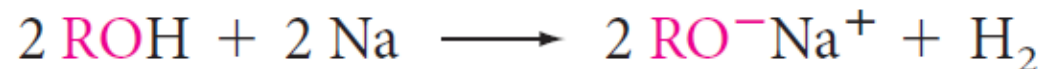
- Dissolve ethyl alcohol in sulfuric acid at ambient temperature.
- Heat the solution to 140°C while adding more alcohol.



## 2) Williamson Synthesis

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- 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.



## 2) Williamson Synthesis

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

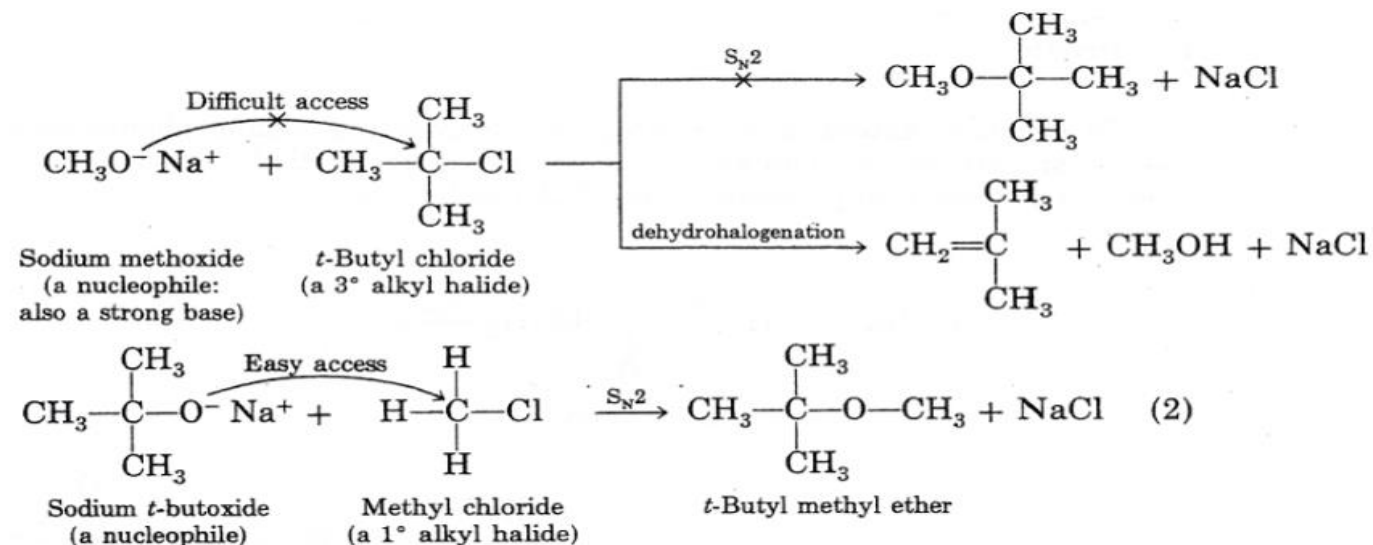
➤ In theory, this could be done by either of two reactions.

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,  $\text{CH}_3\text{Cl}$ .

*This route gives the desired ether by substitution.*

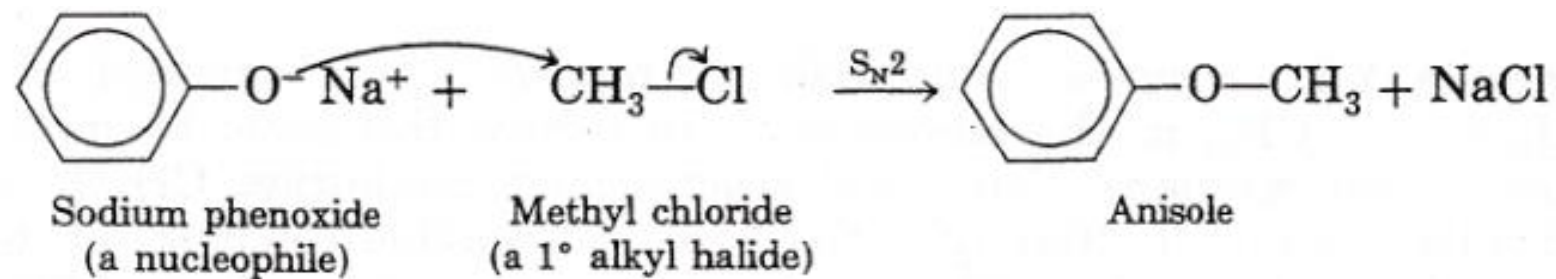
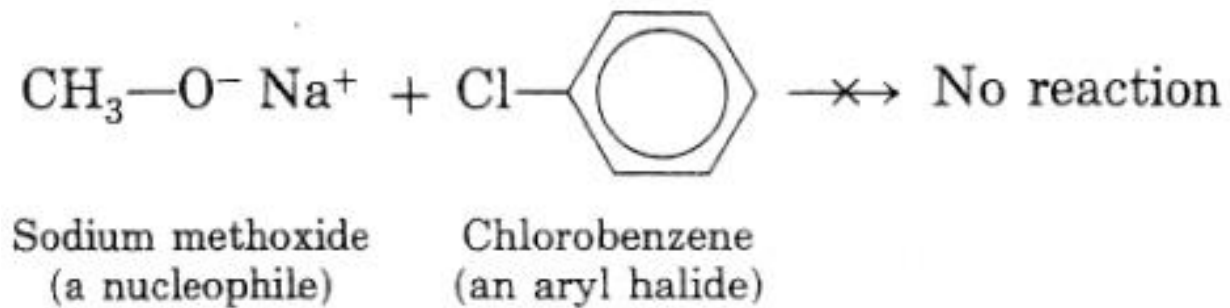


## 2) Williamson Synthesis

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**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.*



# Reactions of Ethers



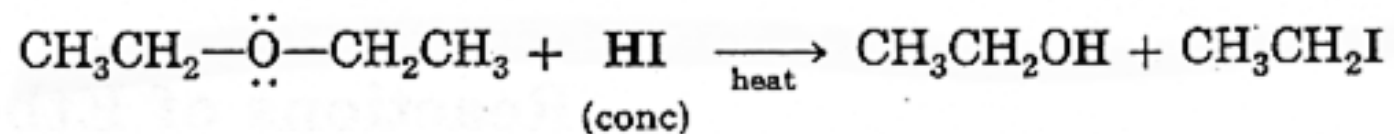
- **Ethers** are quite stable compounds.
- The **ether** linkage does not react with bases, reducing agents, oxidizing agents, or active metals.
- **Ethers** react only under strongly acidic conditions.



## Cleavage of Ethers by Hot Concentrated Acids

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- When **ethers** are heated in concentrated acid solutions, the ether linkage is broken.



- The acids most often used in this reaction are HI, HBr, and HCl.
- If an excess of acid is present, the alcohol initially produced is converted into an alkyl halide by the reaction.



For example,

