Fundamentals of Organic Chemistry

CHEM 109

For Students of Health Colleges

Credit hrs.: (2+1)

King Saud University

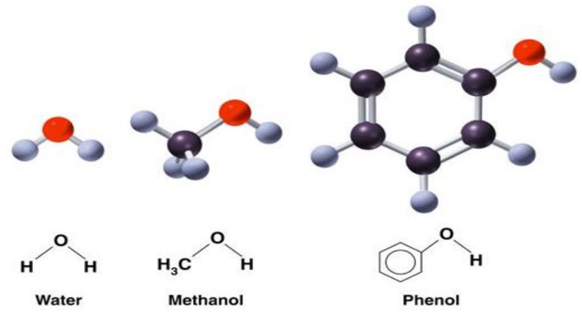
College of Science, Chemistry Department

CHAPTER 4. ALCOHOLS, PHENOLS AND ETHERS

Alcohols, Phenols and Ethers

- **Alcohols, phenols and ethers** may be viewed as organic *derivatives of water*.
- **Alcohols** **and** **phenols** have a common functional group, *the hydroxyl group, -OH*.

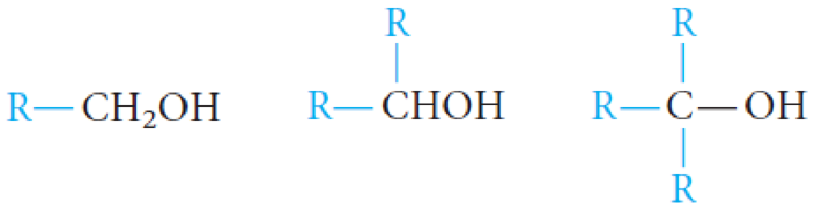
H-O-H	R-O-H	Ar-O-H	R-O-R	R-O-Ar	Ar-O-Ar
Water	Alcohol	Phenol		Ether	



- **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.

Classification of Alcohols and Ethers

- **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.



primary (1°) secondary (2°) tertiary (3°)

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

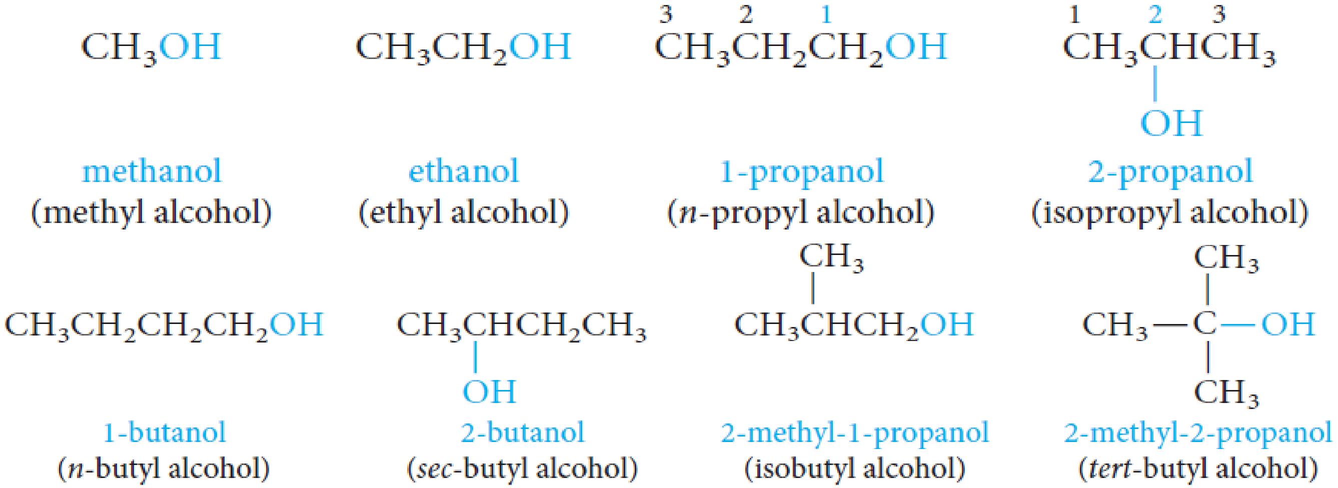
- **Ethers are classified as**
  - **Symmetrical ethers;**

    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 Alcohols

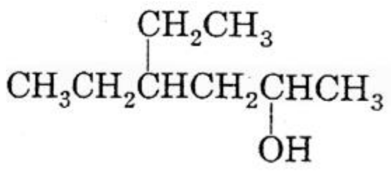
- The **common names** for the simplest alcohols consist of alkyl group attached to the hydroxyl function followed by the word alcohol: Alkyl *alcohol* .
- In the **IUPAC system**, alcohols are named according to the following rules.
  1. Select the longest continuous carbon chain that *contains the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



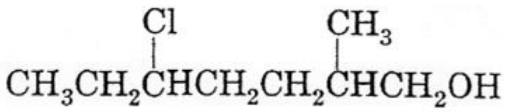
Nomenclature of Alcohols

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.

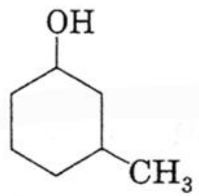


4-Ethyl-2-hexanol
(*not* 3-Ethyl-5-hexanol)

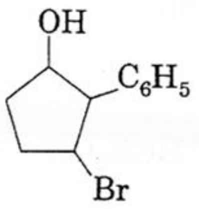


5-Chloro-2-methyl-1-heptanol
(*not* 3-Chloro-6-methyl-7-heptanol)

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)

Nomenclature of Alcohols

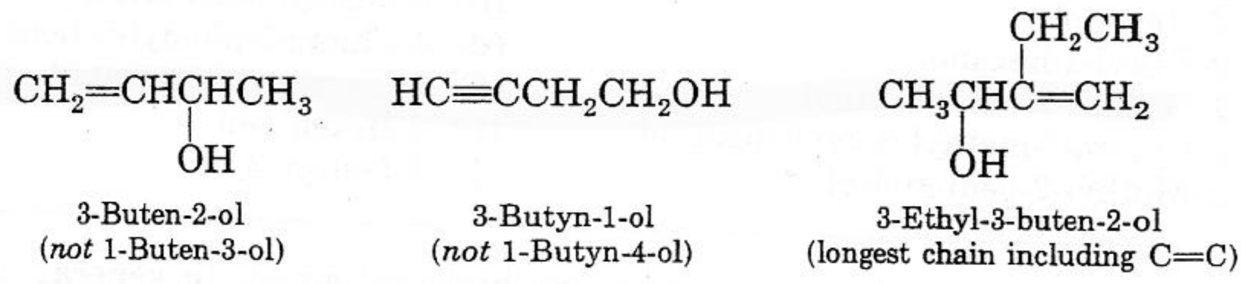
4. With Unsaturated Alcohols; If a molecule contains both an -OH group and a C=C or C-C triple bond, the -OH group takes preference before the double or triple bonds in getting the lower number.

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.

$CH_2{=}CHCH_2OH$

2-propen-1-ol

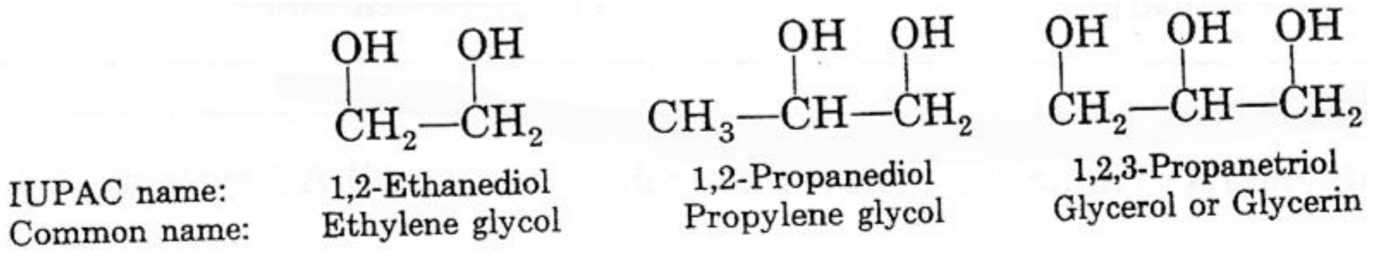
(allyl alcohol)

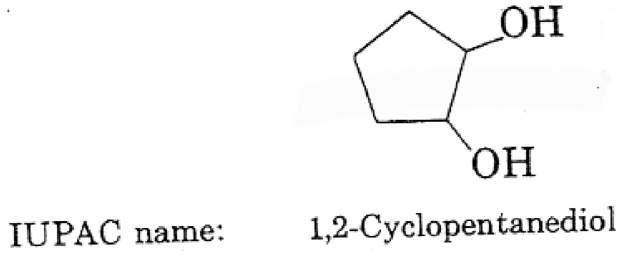


Nomenclature of Alcohols

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.

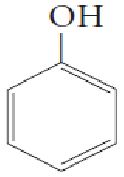




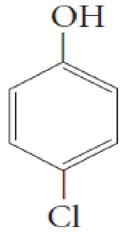
- *Ethylene glycol is used as the "permanent" antifreeze in automobile radiators and as a raw material in the manufacture of Dacron.*
- *Ethylene glycol is completely miscible with water.*
- *Glycerol is a syrupy, colorless, water-soluble, high-boiling liquid with a distinctly sweet taste. Its soothing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

Nomenclature of Phenols

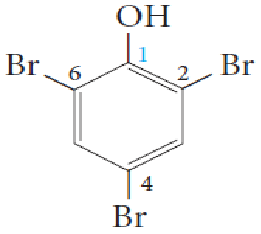
- **Phenols** are usually named as derivatives of the parent compounds.



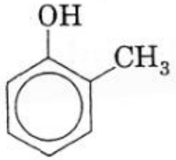
phenol



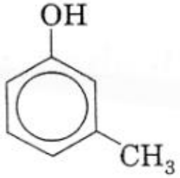
p-chlorophenol



2,4,6-tribromophenol



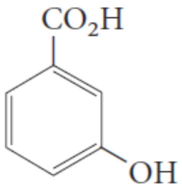
o-Cresol



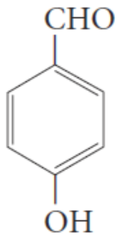
m-Cresol

p-Cresol

- 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**.

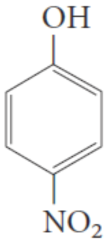


m-hydroxy benzoic acid



p-hydroxybenzaldehyde

but

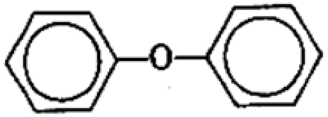
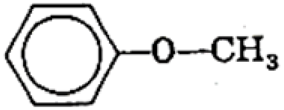


p-nitrophenol
(*not* *p*-hydroxynitrobenzene)

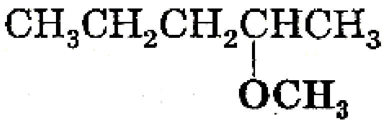
Nomenclature of Ethers

- ## Common Names

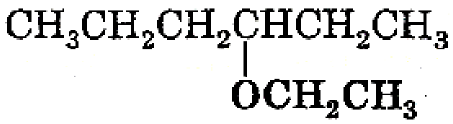
Ethers are usually named by giving the name of each alkyl or aryl group, in alphabetical order, followed by the word *ether*.

Methyl ether	CH_3—O—CH_3	Ethyl methyl ether	CH_3—O—CH_2CH_3
Ethyl ether	CH_3CH_2—O—CH_2CH_3	Ethyl-*n*-propyl ether	CH_3CH_2—O—$CH_2CH_2CH_3$
Vinyl ether	CH_2=CH—O—CH=CH_2	*t*-Butyl methyl ether	$(CH_3)_3C$—O—CH_3
Phenyl ether		Methyl phenyl ether (anisole)	

- ## 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 Alcohols and Ethers

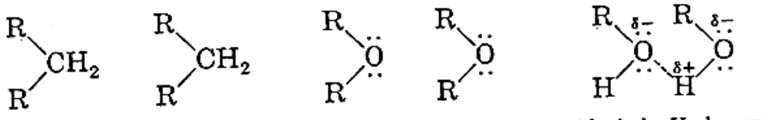
Physical State

- *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 (bps) than alcohols with an equal number of carbon atoms.*
- Ether has nearly the same b.p. as the corresponding hydrocarbon in which a $-CH_2-$ 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

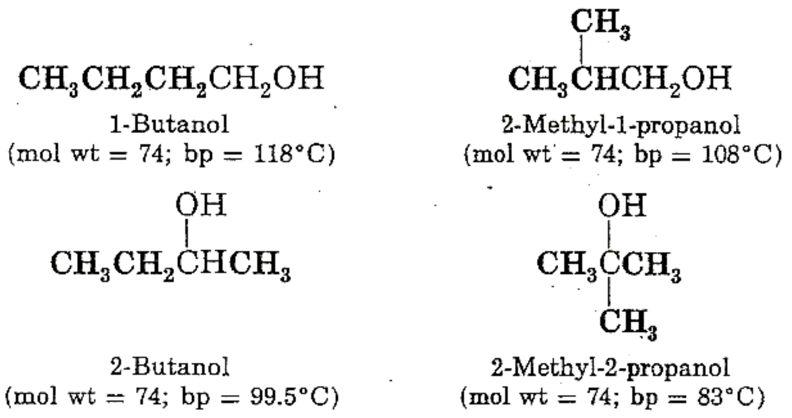
Alcohols: Hydrogen bonding between molecules; high boiling points

Compound	Formula	bp	mol wt	Water solubility (g/100 mL, 20°C)
1-butanol	$CH_3CH_2CH_2CH_2OH$	118°C	74	7.9
diethyl ether	$CH_3CH_2—O—CH_2CH_3$	35°C	74	7.5
pentane	$CH_3CH_2—CH_2—CH_2CH_3$	36°C	72	0.03

Physical Properties of Alcohols 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.*



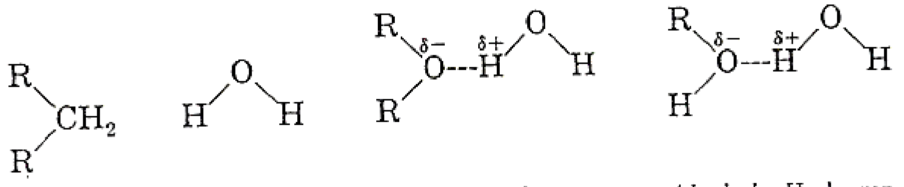
- Phenol and most other phenols have high boiling points.

Physical Properties of Alcohols 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_2O At 20 °C
$CH_3CH_2CH_3$	propane	44	−42	insoluble
CH_3OCH_3	methyl ether	46	−24	soluble
CH_3CH_2OH	ethanol	46	78	soluble
$CH_3CH_2CH_2CH_3$	*n*-butane	58	−0.5	insoluble
$CH_3CH_2OCH_3$	ethyl methyl ether	60	8	soluble
$CH_3CH_2CH_2OH$	1-propanol	60	97	soluble
$CH_3(CH_2)_3CH_3$	*n*-pentane	72	35	insoluble
$CH_3CH_2OCH_2CH_3$	ethyl ether	74	36	7.5 g/100 g
$CH_3(CH_2)_2CH_2OH$	1-butanol	74	118	7.9 g/100 g
$CH_3(CH_2)_5CH_3$	*n*-heptane	100	98	insoluble
$CH_3(CH_2)_2O(CH_2)_2CH_3$	*n*-propyl ether	102	91	0.2 g/100 g
$CH_3(CH_2)_4CH_2OH$	1-hexanol	102	157	0.6 g/100 g

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

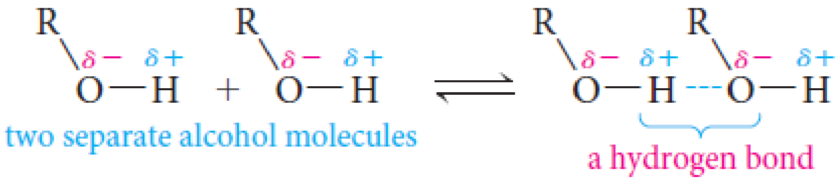
Hydrogen Bonding in Alcohols and Ethers

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

	CH_3CH_2OH	CH_3OCH_3	$CH_3CH_2CH_3$
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.

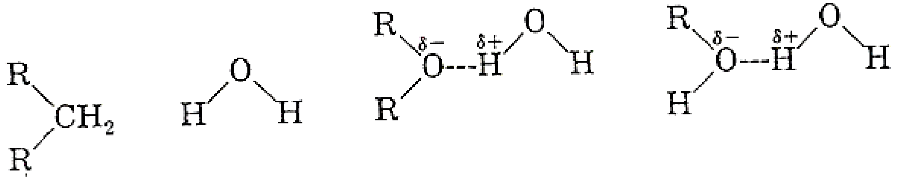


Two or more alcohol molecules thus become loosely bonded to one another through hydrogen bonds.

- 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.

Hydrogen Bonding in Alcohols and Ethers

- The lower molecular-weight alcohols and ethers can form H-bond with water molecules.
- This accounts for the complete miscibility of the lower alcohols and ethers with water.



Alkanes: No hydrogen bonding with water; insoluble

Ethers: Hydrogen bonding with water; soluble

Alcohols: Hydrogen bonding with water; soluble

- 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_2O g/100 g at 20°C
methanol	CH_3OH	65	completely miscible
ethanol	CH_3CH_2OH	78.5	completely miscible
1-propanol	$CH_3CH_2CH_2OH$	97	completely miscible
1-butanol	$CH_3CH_2CH_2CH_2OH$	117.7	7.9
1-pentanol	$CH_3CH_2CH_2CH_2CH_2OH$	137.9	2.7
1-hexanol	$CH_3CH_2CH_2CH_2CH_2CH_2OH$	155.8	0.59

The Acidity of Alcohols and Phenols

- **Like water, alcohols and phenols are weak acids.**

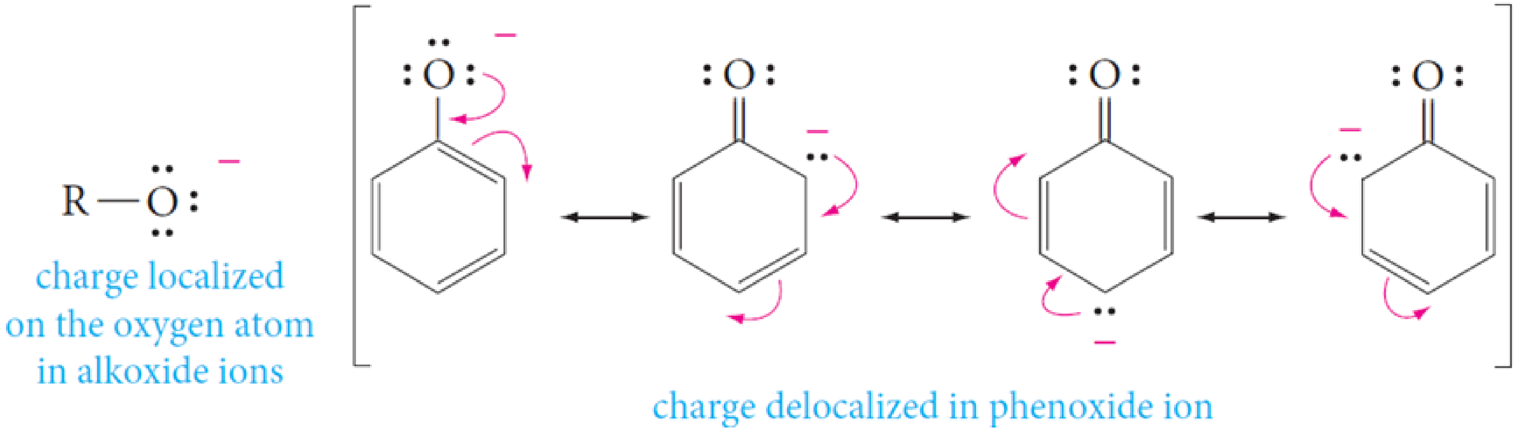
The hydroxyl group can act as a proton donor, and dissociation occurs in a manner similar to that for water

$$\underset{\text{Alcohol as acid}}{RO{-}H} + Base \longrightarrow \underset{\text{Alkoxide ion (conjugate base of alcohol)}}{RO:^-} + Base{-}H$$

$$\underset{\text{Phenol as acid}}{ArO{-}H} + Base \longrightarrow \underset{\text{Phenoxide ion (conjugate base of phenol)}}{ArO:^-} + Base{-}H$$

The Acidity of Alcohols and Phenols

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

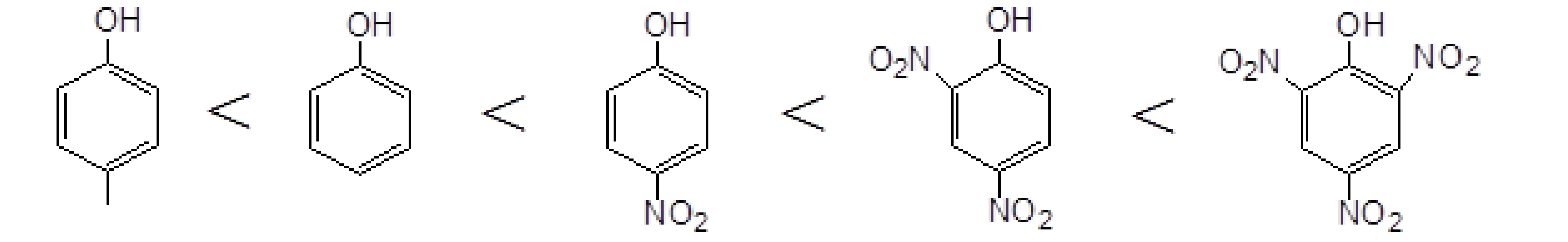


The negative charge of an alkoxide ion is concentrated on the oxygen atom, but the negative charge on a phenoxide ion can be delocalized to the ortho and para ring positions through resonance.

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.



4-Methylphenol (*p*-Cresol) < Phenol < 4-Nitrophenol < 2,4-Dinitrophenol < 2,4,6-Trinitrophenol (Picric acid)

Methoxyethanol < Ethanol < Chloroethanol < Trichloroethanol

The Acidity of Alcohols and Phenols

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

$$2\,R\ddot{\underset{\cdot\cdot}{O}}{-}H + 2\,K \longrightarrow 2\,R\ddot{\underset{\cdot\cdot}{O}}{:}^{-}\ K^{+} + H_2$$

alcohol — potassium alkoxide

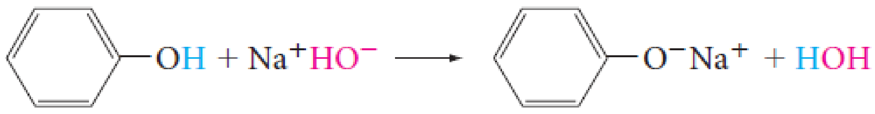
- Treatment of alcohols with sodium hydroxide <u>does not convert</u> them to their alkoxides.

  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 <u>converts</u> them to phenoxide ions.

$$ROH + Na^{+}HO^{-} \not\rightleftharpoons RO^{-}Na^{+} + H_2O$$



phenol — sodium phenoxide

Preparation of Alcohols

1. Hydration of Alkenes

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

$$RCH{=}CHR + H{-}OH \xrightleftharpoons{H^+} \underset{\substack{| \quad | \\ H \quad OH}}{RCHCHR}$$

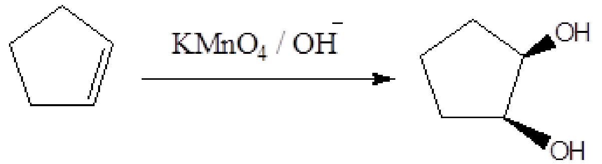
b. The addition follows *Markovnikov's rule*.

$$\underset{\text{Propene}}{CH_3CH{=}CH_2} + H{-}OH \xrightleftharpoons{H^+} \underset{\substack{\text{2-Propanol} \\ \text{(major product)}}}{CH_3\overset{\substack{OH \\ |}}{C}HCH_3}$$

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

2. Oxidation of Cycloalkenes

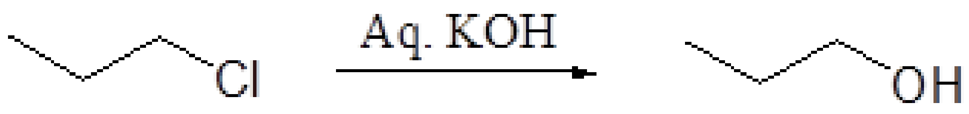
Alkenes react with alkaline potassium permanganate to form glycols.



Cyclopentene → *cis*-Cyclopentane-1,2-diol

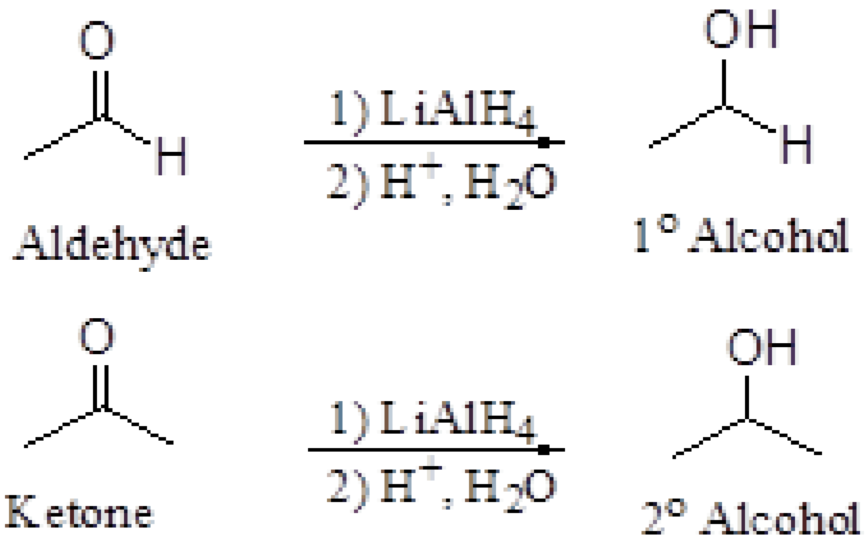
Preparation of Alcohols

- *Nucleophilic Substitution of Alkyl Halide*



- *Reduction of Ketones, and Aldehydes*

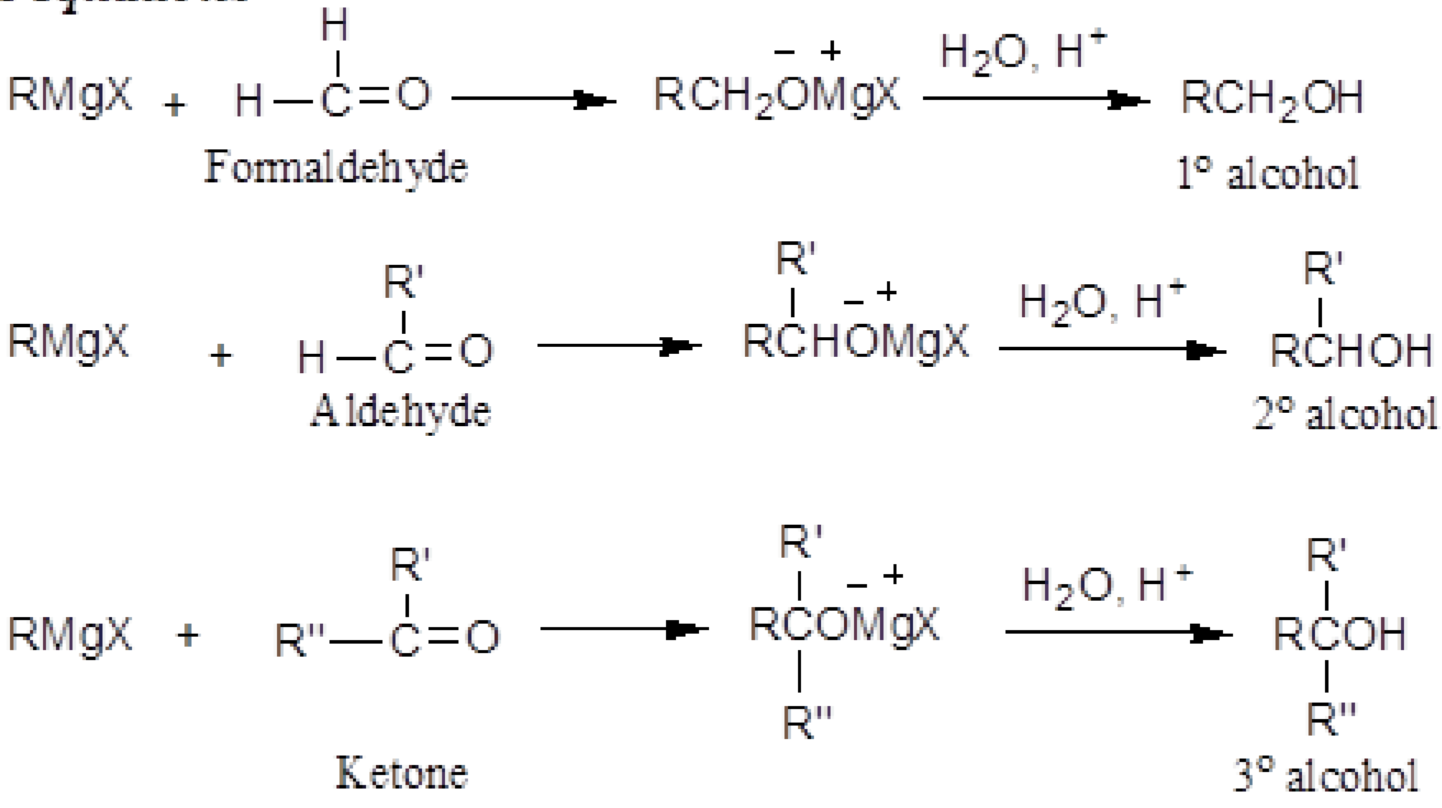
Aldehydes and ketones are easily reduced to primary and secondary alcohols, respectively.



Preparation of Alcohols

- *Addition of Grignard's Reagent to Aldehydes and Ketones*

General equations



Preparation of Phenols

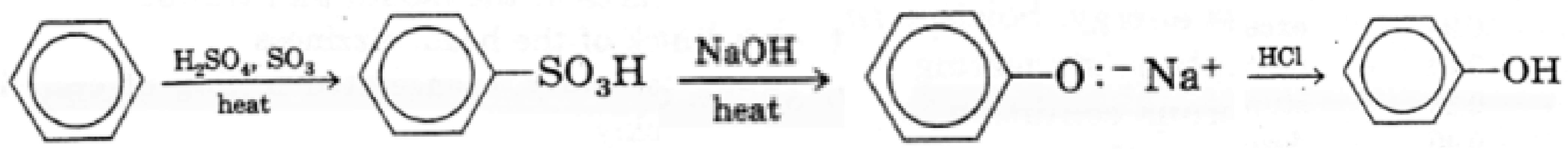
○ *The Alkali Fusion of Sulfonates*

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.



Preparation of Ethers

1) Dehydration of Alcohols

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

$$R{-}OH + H{-}OR \xrightarrow[\text{heat}]{H^+} R{-}O{-}R + H_2O$$

- **Example;**

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

$$\underset{\text{ethanol}}{CH_3CH_2OH + HOCH_2CH_3} \xrightarrow[140^\circ C]{H_2SO_4} \underset{\text{diethyl ether}}{CH_3CH_2OCH_2CH_3} + H_2O$$

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

$$\underset{\text{Ethyl alcohol}}{\underset{H\quad OH}{CH_2CH_2}} \xrightarrow[180^\circ C]{H_2SO_4} \underset{\text{Ethylene}}{CH_2{=}CH_2} + H_2O$$

Preparation of Ethers

2) Williamson Synthesis

- This method has two steps;

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

$$2\,ROH + 2\,Na \longrightarrow 2\,RO^{-}Na^{+} + H_2$$

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

$$RO^{-}Na^{+} + R'{-}X \longrightarrow ROR' + Na^{+}X^{-}$$

  - 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

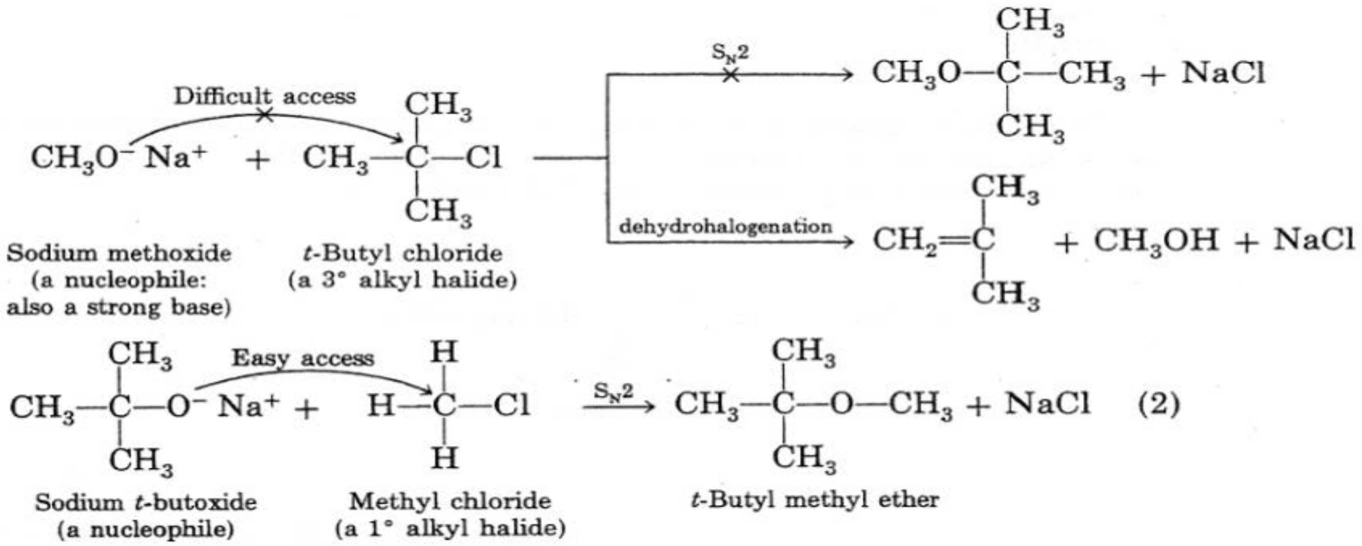
- **Example 1; Preparation of *t*-butyl methyl ether, $(CH_3)_3C\text{-}O\text{-}CH_3$.**
  - **In theory, this could be done by either of two reactions.**

    1. You could react sodium methoxide, $CH_3O^-Na^+$, with *t*-butyl chloride, $(CH_3)_3C\text{-}Cl$.

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

    2. You could react sodium *t*-butoxide, $(CH_3)_3C\text{-}O^-Na^+$, with methyl chloride, CH_3Cl.

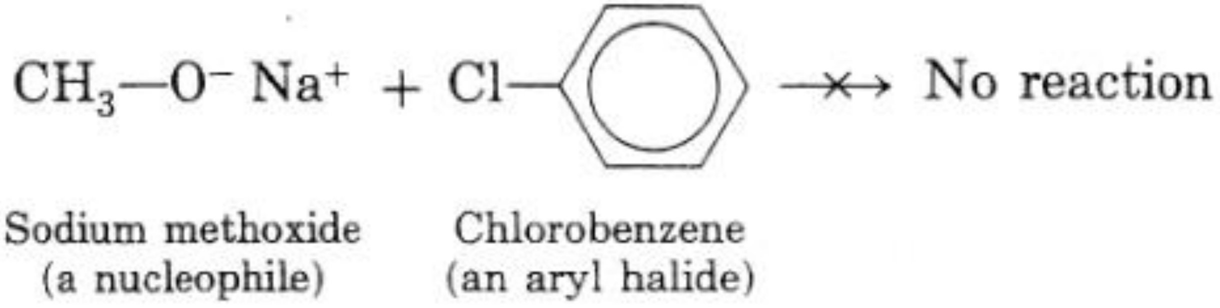
       This route gives the desired ether by substitution.

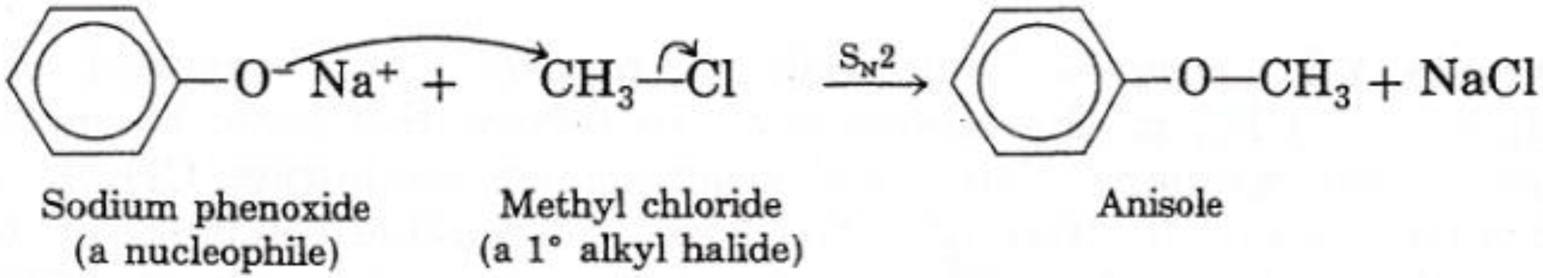


Preparation of Ethers

Example 2; Assume you need to synthesize methyl phenyl ether (anisole), CH_3-O-C_6H_5, by the Williamson method.

- *In theory, you could obtain anisole in either of two ways.*





Reactions of Alcohols, Phenols and Ethers

- **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.
- **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.*

Reactions of Alcohols

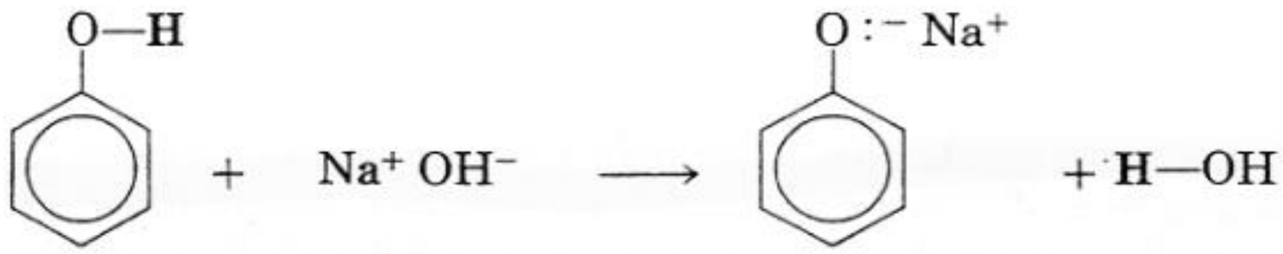
A) Those that involve the breaking of the oxygen-hydrogen bond (CO-H).

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

$$R—OH + Na^+ OH^- \longrightarrow \text{No reaction}$$

$$2\,CH_3O—H + 2\,Na \longrightarrow 2\,CH_3O:^- Na^+ + H_2\uparrow$$

Methanol — Sodium methoxide



Phenol (as an acid) — Sodium hydroxide (a base) — Sodium phenoxide (a salt)

Reactions of Alcohols

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

1) Nucleophilic Substitution Reaction; The Reaction of Alcohols with Hydrogen Halides: Alkyl Halides

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

$$\underset{\text{alcohol}}{R-OH} + H-X \longrightarrow \underset{\text{alkyl halide}}{R-X} + H-OH$$

2) Dehydration of Alcohols: Formation of Alkenes

Alcohols can be dehydrated by heating them with strong acid.

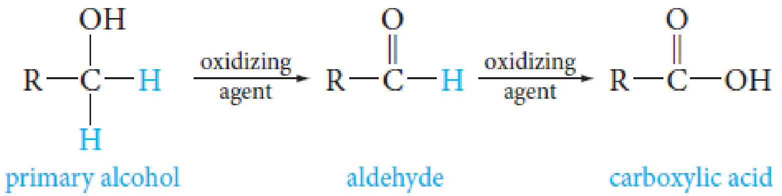
$$\underset{\text{ethanol}}{H-CH_2CH_2-OH} \xrightarrow{H^+,\ 180^\circ C} \underset{\text{ethylene}}{CH_2=CH_2} + H-OH$$

Reactions of Alcohols

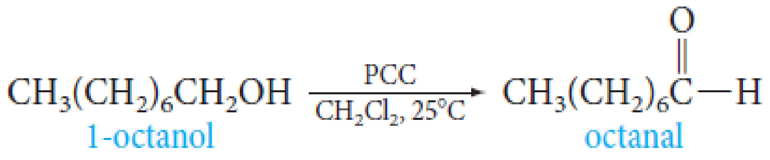
B) Oxidation Reactions

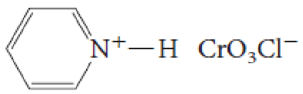
Alcohols with at least one hydrogen attached to the hydroxyl-bearing carbon can be oxidized to carbonyl compounds.

- **Primary alcohols** give aldehydes, which may be further oxidized to carboxylic acids.



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



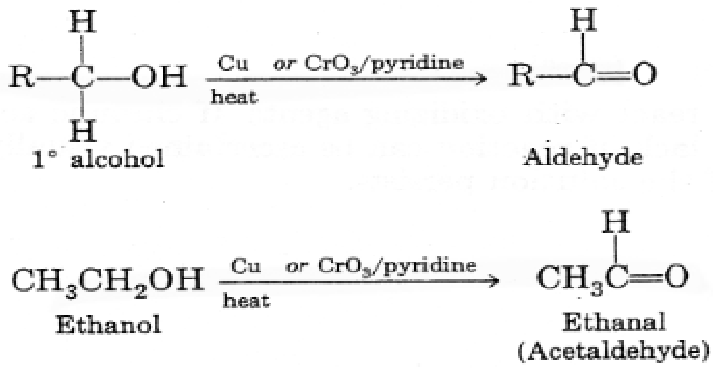


pyridinium chlorochromate (PCC)

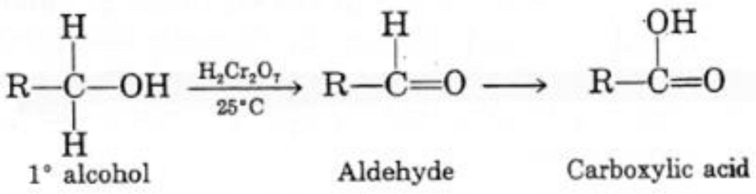
Reactions of Alcohols

B) Oxidation Reactions

- **Primary alcohols** yield aldehydes when treated with *mild oxidizing agents* such as hot metallic copper or CrO_3 in pyridine.



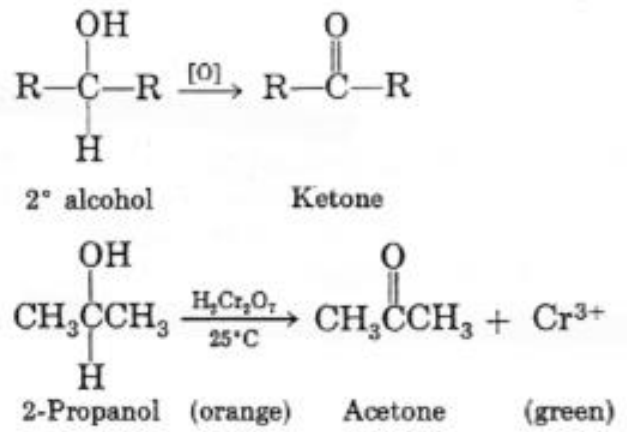
- **Primary alcohols;** when treated with *stronger oxidizing agents*, such as chromic acid, $H_2Cr_2O_7$, or neutral potassium permanganate, $KMnO_4$, the intermediate aldehydes formed initially are oxidized further to carboxylic acids.



Reactions of Alcohols

B) Oxidation Reactions

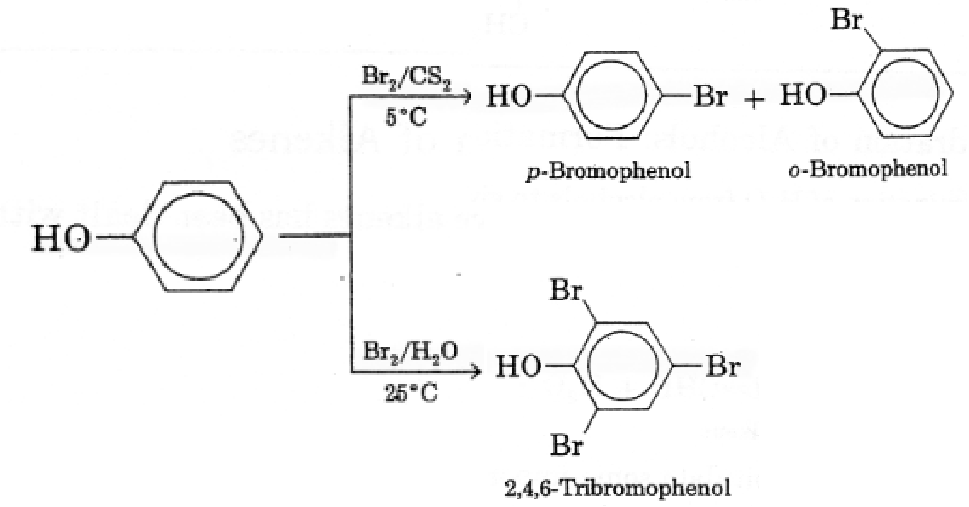
- **Secondary alcohols**, when treated with *any of the oxidizing agents* mentioned previously, yield ketones.



- **Tertiary alcohols**, having no hydrogen atom on hydroxyl-bearing carbon, *do not undergo oxidation*.

Reactions of Phenols

- **Halogenation takes place *without catalyst.***



- **The products depend on the solvent used.**
  - In *aprotic solvents* (solvents that do not release protons) (CCl_4, CS_2)-bromination gives a mixture of o- and *p*-bromophenol.
  - In *protic solvents (solvents that can release protons)* (H_2O)-halogenation gives a trisubstituted phenol is produced.

Reactions of Ethers

○Cleavage of Ethers by Hot Concentrated Acids

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

$$CH_3CH_2{-}\ddot{O}{-}CH_2CH_3 + \underset{(conc)}{HI} \xrightarrow[heat]{} CH_3CH_2OH + CH_3CH_2I$$

➢ 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.

$$R{-}OH + HX \longrightarrow RX + H_2O$$

For example,

$$CH_3CH_2{-}O{-}CH_2CH_3 + \underset{(conc)}{2\,HBr} \xrightarrow[heat]{} 2\,CH_3CH_2Br + H_2O$$