108 Chem

Chapter 5

Alcohols and Phenols

Structure of Alcohols and Phenols

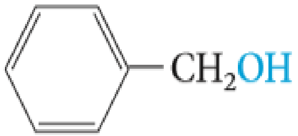
- Alcohols, a class of compounds containing the hydroxyl group (OH)
- Alcohols have a hydroxyl (OH) group bonded to a saturated carbon atom.
    - The alcohol carbon atom may be part of a simple alkyl group, an alkenyl or the carbon atom may be a saturated carbon atom that is attached to a benzene ring:

CH_3OH
methanol
(methyl alcohol)

CH_3CH_2OH
ethanol
(ethyl alcohol)

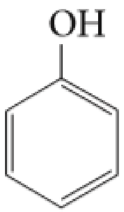
$CH_2{=}CHCH_2OH$
2-propen-1-ol
(allyl alcohol)

$HC{\equiv}C{-}CH_2OH$
2-Propyn-1-ol
(propargyl alcohol)



phenylmethanol
(benzyl alcohol)

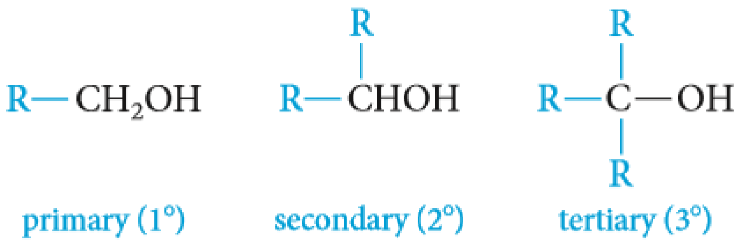
- Phenols are compounds of the general formula ArOH, where Ar is an groups.
- Phenols differ from alcohols in having the OH group attached directly to an benzene ring.
- Phenols is the specific name for hydroxybenzene, and it is the general name for the family of compounds derived from hydroxybenzene.



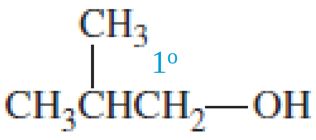
phenol

Classification of Alcohols

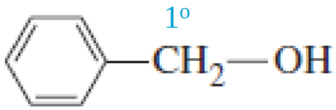
- Alcohols are classified as primary (1º), secondary (2º), or tertiary (3º), depending on whether one, two, or three organic groups are connected to the hydroxyl-bearing carbon atom.
- The carbon atom which connected to the hydroxyl group called carbinol carbon.
- Methyl alcohol, which is not strictly covered by this classification, is usually grouped with the primary alcohols.



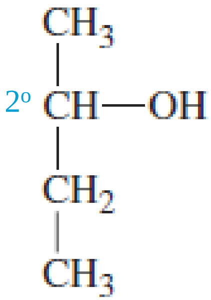
Example:



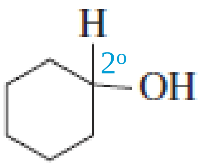
2-methylpropan-1-ol



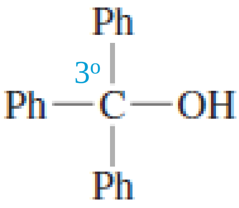
benzyl alcohol



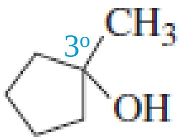
butan-2-ol



cyclohexanol



triphenylmethanol



1-methylcyclopentanol

Type of Alcohols

- Monohydroxyls: containing one hydroxyl group.

$$CH_3CH_2CH_2{-}OH$$

- Dihydroxyls (glycols) : containing two hydroxyl groups.

$$HO{-}CH_2CH_2{-}OH$$

- Polyhydroxyls : containing more than two hydroxyl groups.

$$HO{-}CH_2\underset{\substack{|\\ OH}}{CH}CH_2{-}OH$$

Nomenclature of Alcohols

- Common names derived by naming the *alkyl group* followed by the word *alcohol*.
- The IUPAC system: select the longest carbon chain that contains the -OH group as the parent alkane and numbered from the end closer to OH. change the suffix *-e* of the parent alkane to *-ol*
- use a number to show the location of the OH group.
- If there is a functional group suffix and a substituent, the functional group suffix gets the lowest possible number..
- Cyclic alcohols are named using the prefix *cyclo-*, the carbon bearing the hydroxyl group is assumed to take number 1.
- So the compound containing two hydroxyl groups is named as a *diol* , one containing three hydroxyl groups as a *triol* , and so on.
- Compounds containing OH and C=C groups are often referred to as unsaturated alcohols. choose the chain that include them both even if this is not the longest chain.
- The IUPAC system: the double bond is shown by changing the infix of the parent alkane from *-an-* to *-en-* and the hydroxyl group is shown by changing the suffix of the parent alkene from *-e* to *-ol.*
- Numbers must be used to show the location of both the carbon-carbon double bond and the hydroxyl group.

Nomenclature of Alcohols

CH_3OH

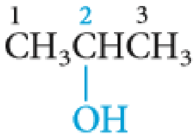
methanol
(methyl alcohol)

CH_3CH_2OH

ethanol
(ethyl alcohol)

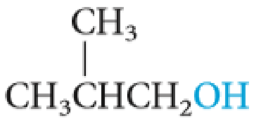
$\overset{3}{C}H_3\overset{2}{C}H_2\overset{1}{C}H_2OH$

1-propanol
(*n*-propyl alcohol)

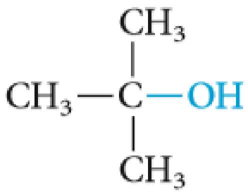


2-propanol
(isopropyl alcohol)

2-butanol
(*sec*-butyl alcohol)

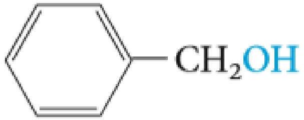


2-methyl-1-propanol
(isobutyl alcohol)

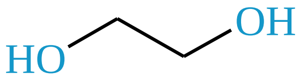


2-methyl-2-propanol
(*tert*-butyl alcohol)

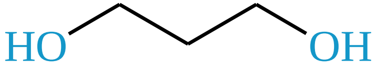
cyclohexanol
(cyclohexyl alcohol)



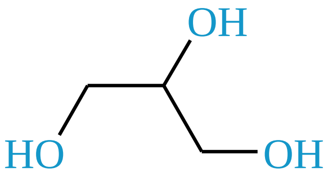
phenylmethanol
(benzyl alcohol)



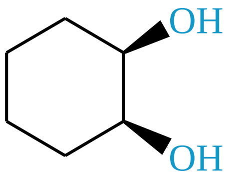
1,2-Ethanediol
(Ethylene glycol)



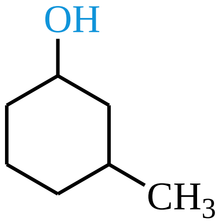
1,3-Propanediol
(Trimethylene glycol)



1,2,3-Propanetriol
(Glycerol or Glycerin)



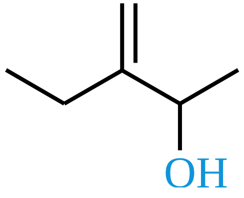
cis-Cyclohexane-1,2-diol



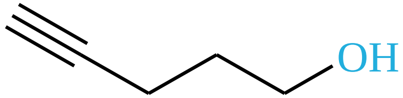
3-Methylcyclohexanol

$CH_2{=}CHCH_2OH$

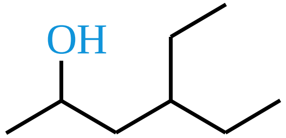
2-propen-1-ol
(allyl alcohol)



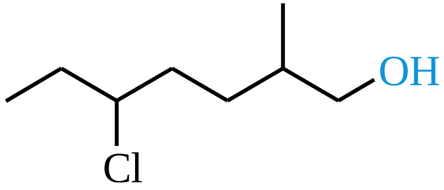
3-Ethyl-3-buten-2-ol



4-Pentyn-1-ol
(*not* 4-Pentyn-1-ol)



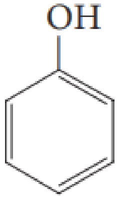
4-Ethyl-2-hexanol



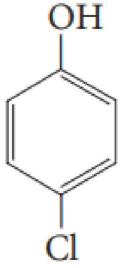
5-Chloro-2-methyl-1-heptanol

Nomenclature of phenols

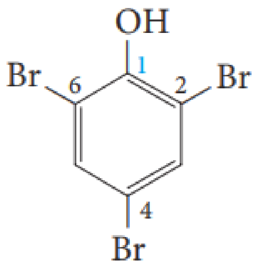
- The simplest member of this class of compounds is named phenol.
- Phenols are usually named as derivatives of the parent compounds.
- Numbering of the ring begins at the hydroxyl-substituted carbon and proceeds in the direction that gives the lower number to the next substituted carbon. Substituents are cited in alphabetical order.



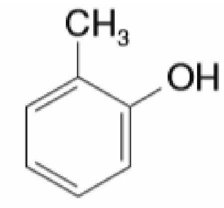
phenol



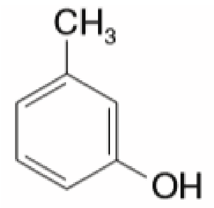
p-Chlorophenol



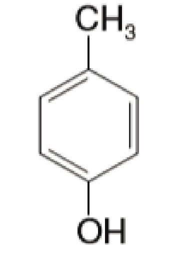
2,4,6-Tribromophenol



2-Methylphenol
(*o*-cresol)

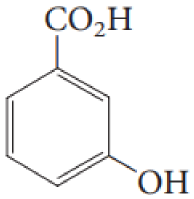


3-Methylphenol
(*m*-cresol)

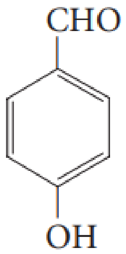


4-Methylphenol
(*p*-cresol)

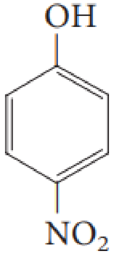
- The hydroxyl group is named as a substituent when it occurs in the same molecule with carboxylic acid, aldehyde, or ketone functionalities, which have priority in naming.



m-Hydroxybenzoic acid



p-Hydroxybenzaldehyde

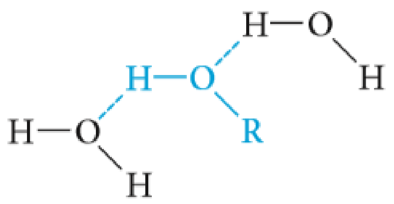


p-Nitrophenol
(*not p*-hydroxynitrobenzene)

Physical Properties of Alcohols

Solubility

- Water and alcohols have similar properties because they all contain hydroxyl groups that can form hydrogen bonds.
- Several of the lower-molecular-weight alcohols as CH_3OH,,,,C_3H_7OH are miscible (soluble in any proportions) with water.
- The solubility decreases as the alkyl group becomes larger.
- The number of hydroxyl groups increases so the solubility increases.

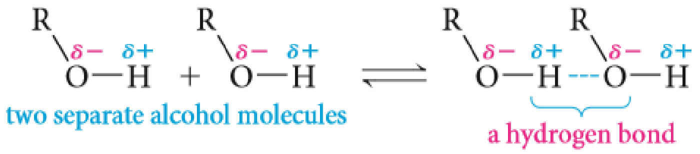


Boiling Points

- The boiling points of alcohols are much higher than those of hydrocarbons with similar molecular weights.

	CH_3CH_2OH	$CH_3CH_2CH_3$
mol wt	46	44
bp	+78.5°C	−42°C

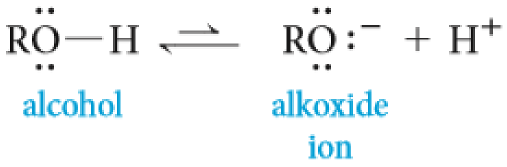
- Alcohol molecules can associate with each other through hydrogen bonding, whereas those of hydrocarbons cannot.



- The boiling point decreases with increase in branching in the alkyl group: 1° alcohol > 2° alcohol > 3° alcohol.
- The boiling points increase with the increase of the number of OH groups .

Physical Properties of Alcohols

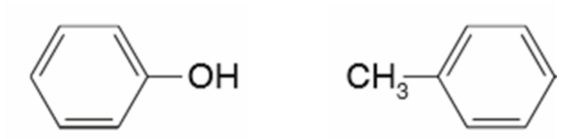
Acidity of Alcohols



- Alcohols can function as both weak acids (proton donors) and weak bases (proton acceptors).
- A strong base can remove the hydroxyl proton to give an alkoxide ion (for example, methoxide ion from methanol, ethoxide ion from ethanol, and so on).
- The order of acidity of various liquid alcohols generally : water > $1^o > 2^o > 3^o$

Physical properties of phenols

- Phenol is a colourless, crystalline
- The presence of hydroxyl groups in phenols means that phenols are like alcohols. For example, they are able to form strong intermolecular hydrogen bonds, and therefore have higher boiling points than hydrocarbons of the same molecular weight.

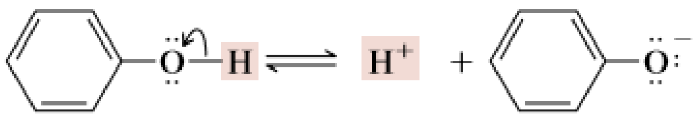


mol wet	94	92
bp	132°C	111°C

- Phenols are also modestly soluble in water because of their ability to form strong hydrogen bonds with water molecules.

Acidity of phenols

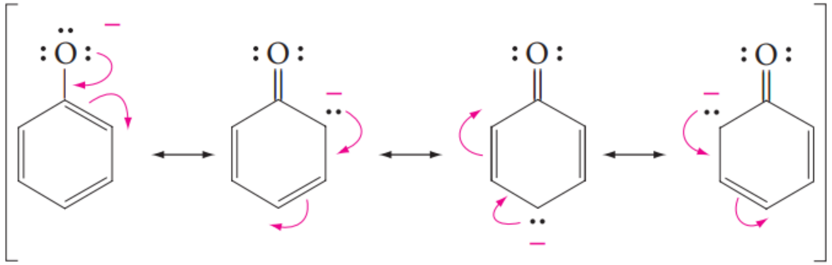
- Like water, alcohols and phenols are weak acids. The hydroxyl group can act as a proton donor, and dissociation occurs in a manner similar to that for water



Phenol　　Phenoxide ion

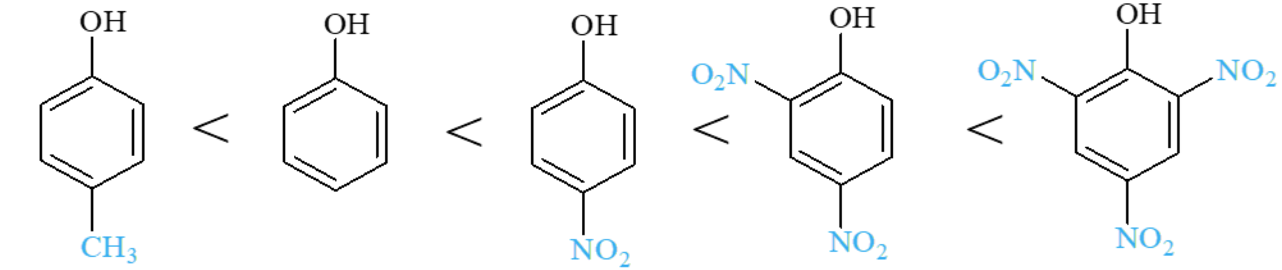
Physical properties of phenols

- Phenols are more acidic than alcohols, and weaker acids than carboxylic acids.
- Phenols are stronger acids than alcohols mainly because the corresponding phenoxide ions are stabilized by resonance.

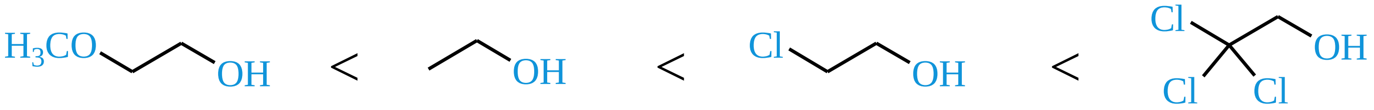


charge delocalized in phenoxide ion

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



4-Methylphenol Phenol 4-Nitrophenol 2,4-Dinitrophenol 2,4,6-Trinitrophenol Picric acid



Methoxyethanol Ethanol Chloroethanol Trichloroethanol

Preparation Of Alcohols

1. Preparation of alcohols via alkenes
    - Addition reaction
    - Oxidation reaction
2. Preparation of alcohols via alkyl halides (Nucleophilic Substitution)
3. Preparation of alcohols via Reduction reaction of:

   Aldehydes, Ketones, Acids and Esters

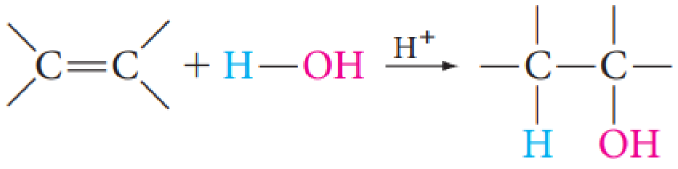
4. Preparation of alcohols via Grignard reagents with:

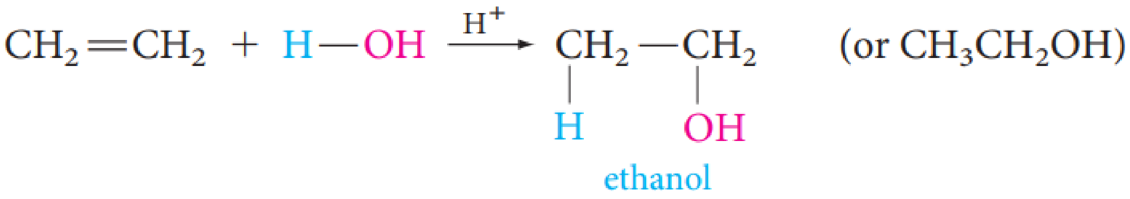
   Aldehydes and Ketones

Preparation Of Alcohols

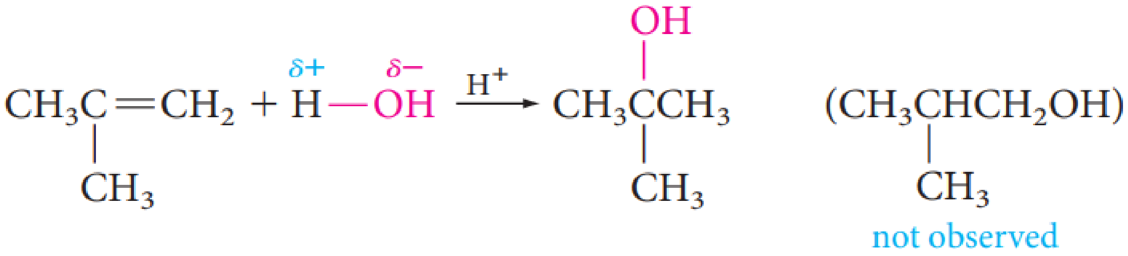
1- Preparation of alcohols via alkenes

a) Acid-Catalyzed Hydration of Alkenes: Addition of water to alkenes





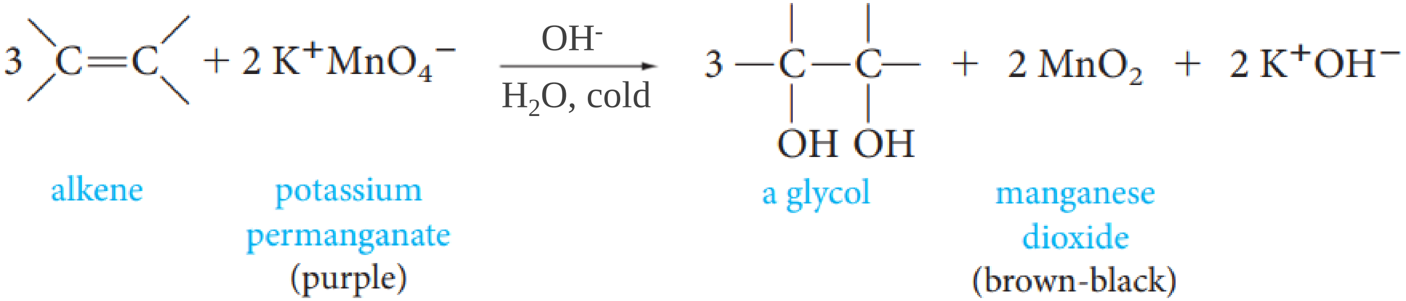
Markovnikov Hydration

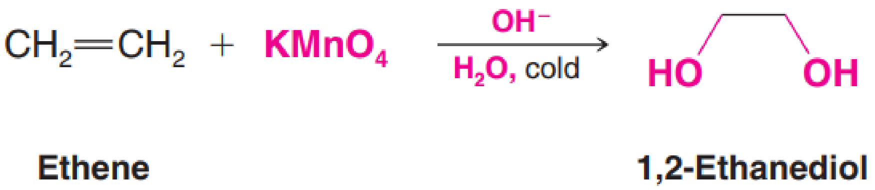


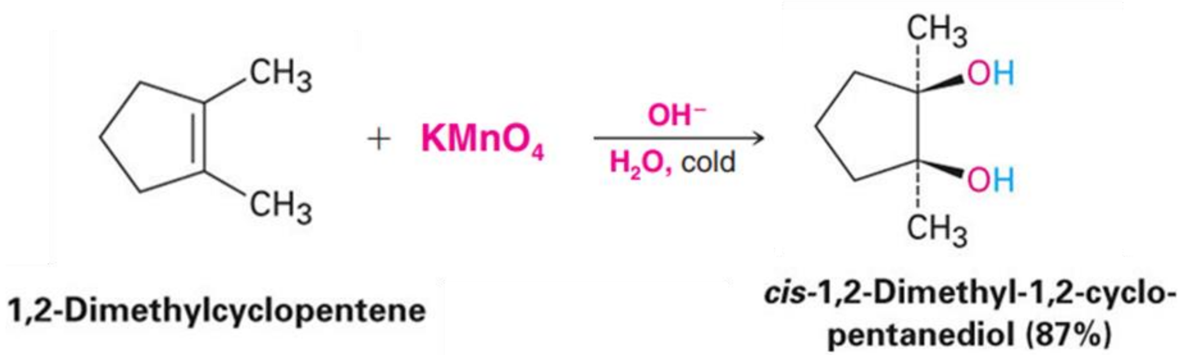
Preparation Of Alcohols

b) Oxidation of alkenes: Synthesis of 1,2-diols

Oxidation of alkenes with Permanganate : syn hydroxylation



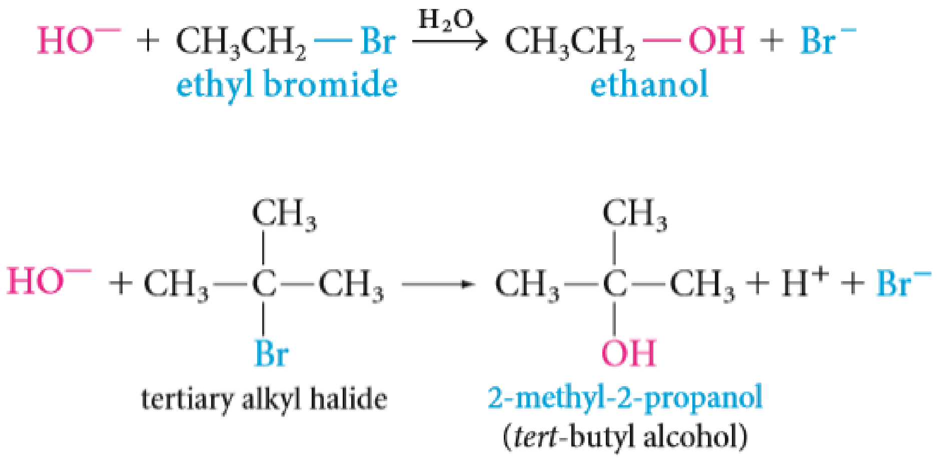




Preparation Of Alcohols

2- Preparation of alcohols via alkyl halides: Hydrolysis of alkyl halides

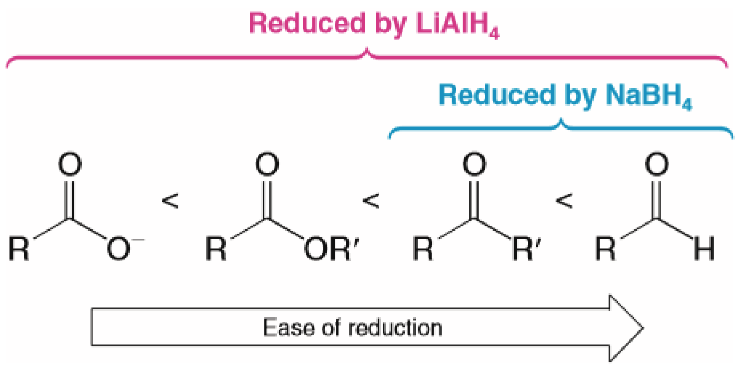
Nucleophilic Substitution Reactions

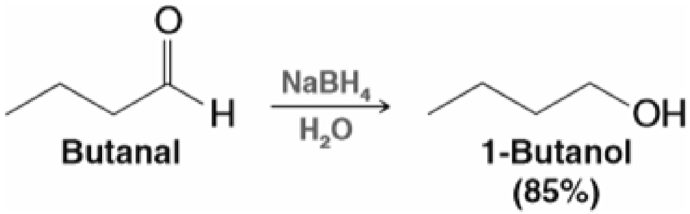


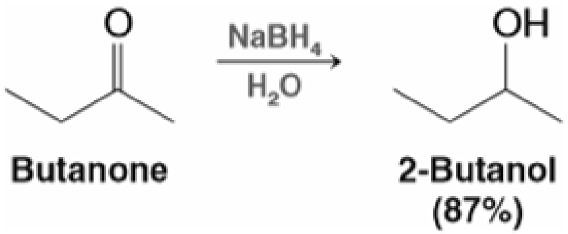
Preparation Of Alcohols

3- Preparation of alcohols via Reduction reaction

- By hydrogenation of the carbon–oxygen double bond.
- sodium borohydride ($NaBH_4$) reduce carbonyl groups (aldehydes, ketones).
- lithium aluminum hydride ($LiAlH_4$) reduce all kind of carbonyl groups.

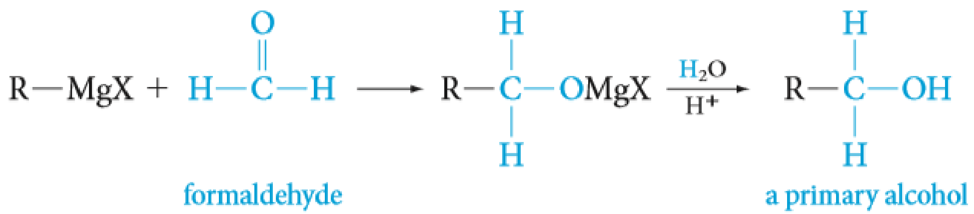




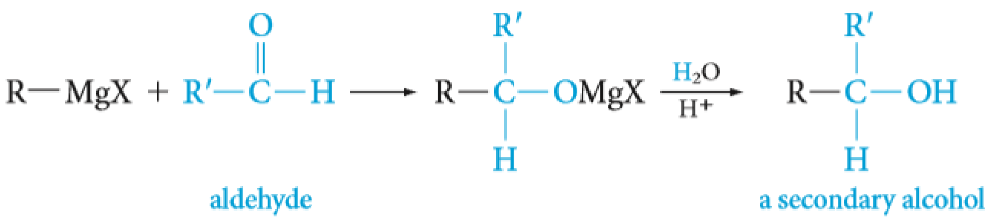


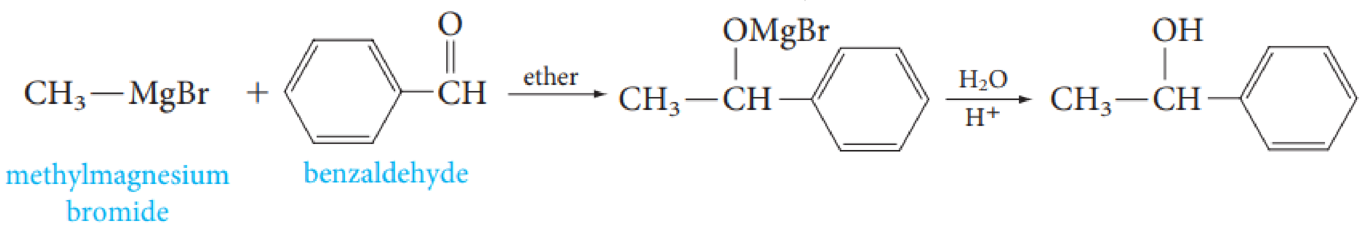
Preparation Of Alcohols

4- Preparation of alcohols via Grignard reagents with Aldehydes and ketones.

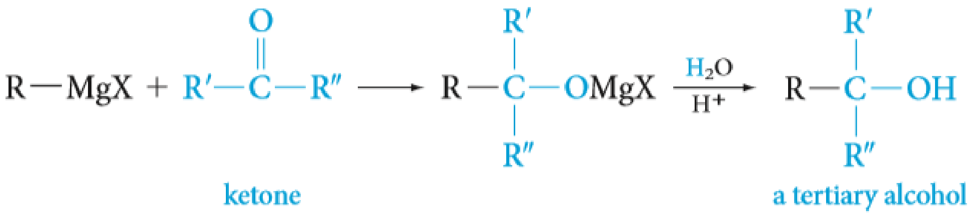


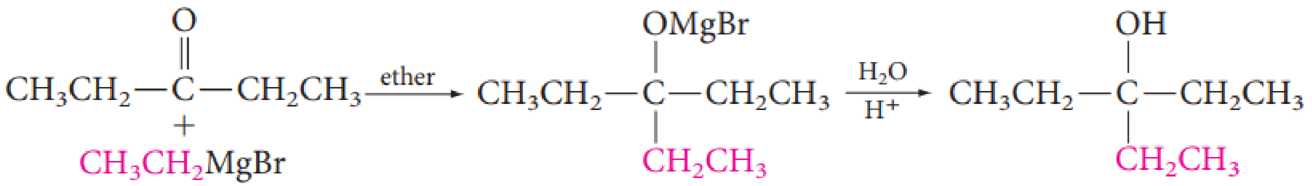
Other aldehydes give secondary alcohols.





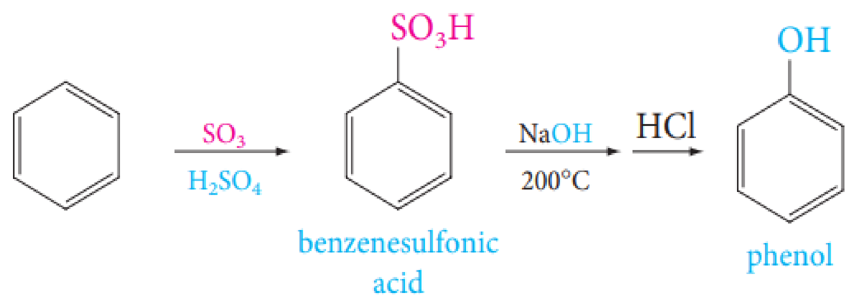
Ketones give tertiary alcohols.





Preparation of Phenols

- Alkali fusion of Benzenesulfonic acid



Reactions Of Alcohols

The reactions of alcohols have mainly to do with the following:

- The hydrogen atom of the hydroxyl group is weakly acidic.
    - Preparation of alkoxides
- The oxygen atom of the hydroxyl group is nucleophilic and weakly basic.
    - Oxidation Reactions
- The hydroxyl group can be converted to a leaving group so as to allow substitution or elimination reactions.
    - Conversion of Alcohols into Alkyl Halides
    - Preparation of alkenes

Reactions Of Alcohols

1- Preparation of alkoxides

They 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

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

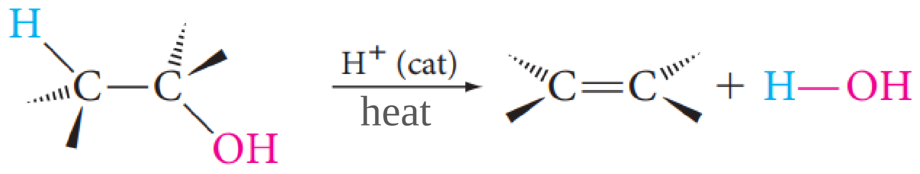
Hint:

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

2- Conversion of Alcohols into Alkyl Halides (S_N1 or S_N2):

$$R{-}OH + H{-}X \xrightarrow{\text{heat, } ZnCl_2} R{-}X + H{-}OH \quad (X = Cl, Br, I)$$

3- Elimination Reaction: Preparation of alkenes (E1 or E2)



$$CH_3CH_2OH \xrightarrow[\text{heat}]{H_2SO_4} CH_2{=}CH_2 + H_2O$$

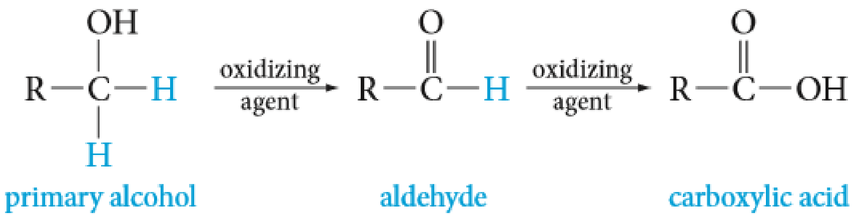
Ethyl alcohol — Ethylene — Water

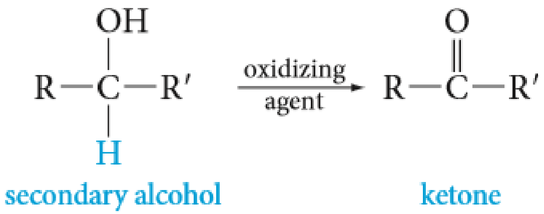
Reactions Of Alcohols

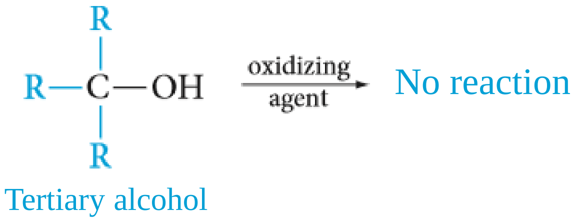
4- Oxidation of Alcohols

Strong oxidizing agent

Potassium permanganate $KMnO_4$,OH^-/ H_3O^+
Chromic oxide CrO_3 / H_2SO_4 (H_2CrO_4 Jones' reagent)

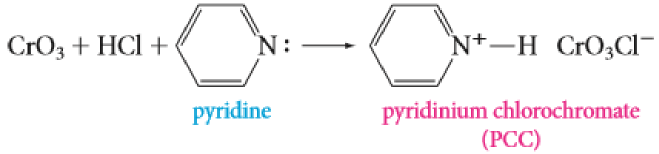


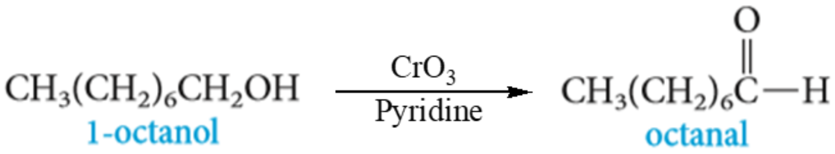


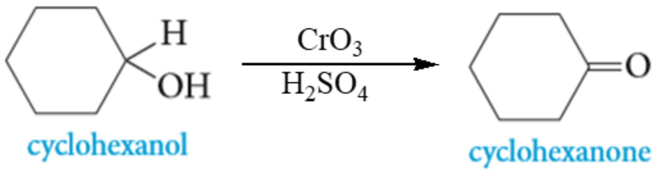


Weak oxidizing agent

Chromic oxide CrO_3 / pyridine
Pyridinium chlorochromate PCC / methylene chloride CH_2Cl_2



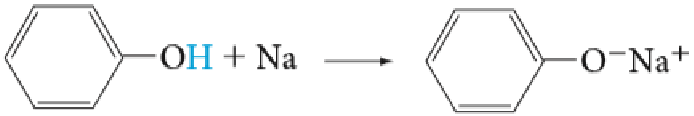




Reactions of phenols

1- Salt formation via strong base or active metal

- With active metals



phenol sodium phenoxide

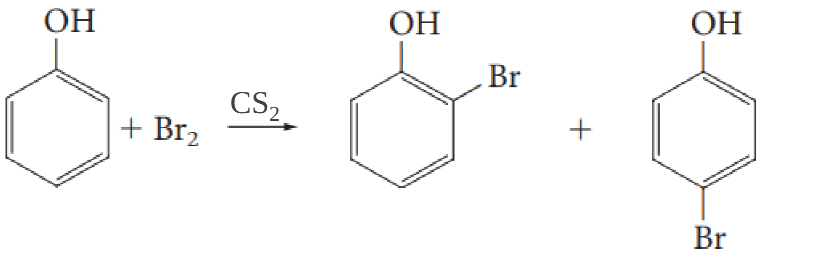
- With bases

phenol sodium phenoxide

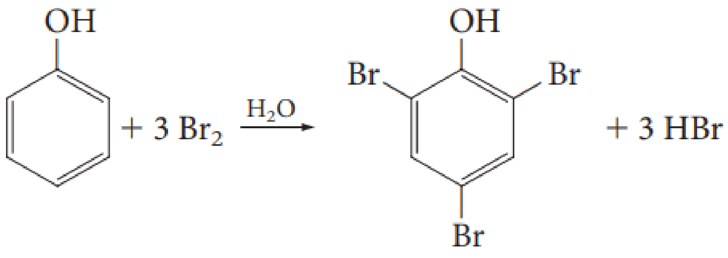
2- Reaction of aromatic nucleus of phenol

The hydroxyl group is a powerful activating group and an ortho - para director in Electrophilic Aromatic Substitutions

Halogenation



phenol *o*-Bromophenol *p*-Bromophenol



phenol 2,4,6-Tribromophenol

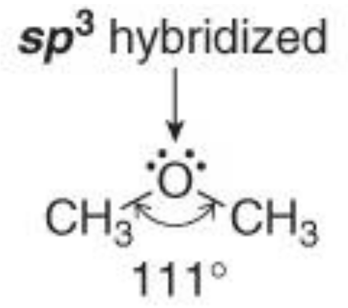
Ethers and Epoxides

Structure of Ethers

- Ethers are organic derivatives of water, where alkyl groups replace both hydrogen atoms. Thus, ethers have two hydrocarbons bonded to an 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.

R—O—R, Ar—O—R, or Ar—O—Ar



- The ether is classified as
  - A symmetrical ether , When the organic groups attached to the oxygen are identical.
  - An unsymmetrical ether , When the organic groups attached to the oxygen are different.

Nomenclature of Ethers

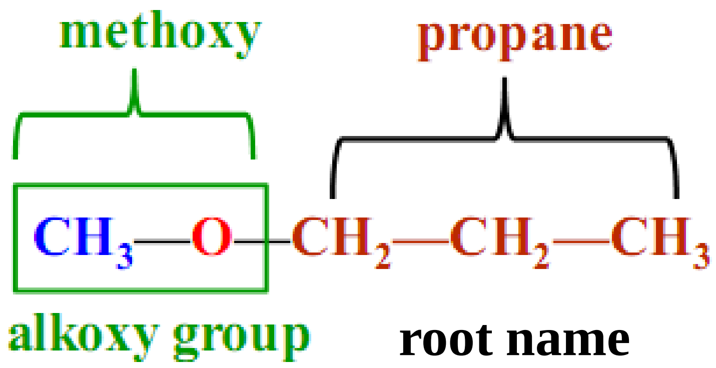
The Common name

The common names of ethers are derived by naming the alkyl groups bonded to the oxygen then listing them in alphabetical order followed by the word "ether".

The IUPAC System

The shorter alkyl group and the oxygen are named as an alkoxy group attached to the longer alkane.

They are named as alkoxyalkanes



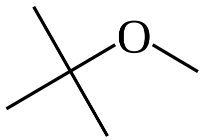
$CH_3CH_2-O-CH_2CH_3$

Common name: Diethyl ether
IUPAC name: Ethoxyethane

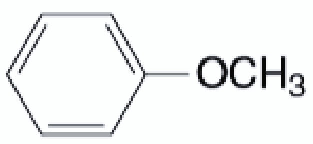
$CH_3CH_2-O-CH_3$

Ethyl methyl ether
Methoxyethane

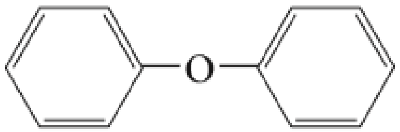
Divinyl ether
Vinyloxyethene



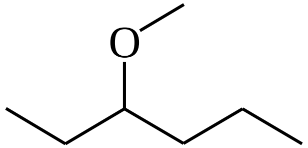
Common name: *tert*-Butyl methyl ether
IUPAC name: 2-Methoxy-2-methylpropane



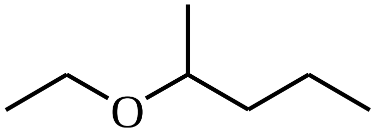
Methyl Phenyl ether (anisole)
Methoxy benzene



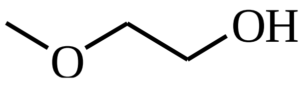
Diphenyl ether
Phenoxybenzene



3-Methoxyhexane



2-Ethoxy-pentane



2-Methoxyethanol

Physical Properties of Ethers

- Ethers are colorless compounds with characteristic, relatively pleasant odors.

Boiling Points:

- They have lower boiling points than alcohols with an equal number of carbon atoms. Because of their structures (no O-H bonds), ether molecules cannot form hydrogen bonds with one another
- An ether has nearly the same boiling point as the corresponding hydrocarbon in which a $-CH_2-$ group replaces the ether's oxygen.

Solubility in water

- Ethers are able to form hydrogen bonds with compounds such as water.
- Ethers have solubilitie in water that are similar to those of alcohols of the same molecular weight and that are very different from those of hydrocarbons.

	$CH_3CH_2OCH_2CH_3$	$CH_3CH_2CH_2CH_2CH_3$	$CH_3CH_2CH_2CH_2OH$
	Diethyl ether	Pentane	1-Butanol
Boiling point:	35°C	36°C	117°C
Solubility in water:	7.5 g/100 mL	Insoluble	9 g/100 mL

Preparation Of Ethers

1. Dehydration of Alcohols

- Intermolecular dehydration of alcohols takes place in the presence of acid catalysts (H_2SO_4, H_3PO_4) under controlled temperature (140 ^{o}C).

$$2\,R{-}OH \xrightarrow[\Delta]{H_2SO_4} R{-}O{-}R + H_2O$$

$$\underset{\text{ethylene}}{CH_2{=}CH_2} \xleftarrow[180^{\circ}C]{H_2SO_4} \underset{\text{ethanol}}{CH_3CH_2OH} \xrightarrow[140^{\circ}C]{H_2SO_4} \underset{\text{diethyl ether}}{CH_3CH_2OCH_2CH_3} + H_2O$$

Preparation Of Ethers

2. The Williamson Synthesis of Ethers

- This method is usually used for preparation of unsymmetrical ethers.

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

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

Nucleophilic Substitution Reaction

- The second step is an nucleophilic substitution reaction, it works best if R′ in the alkyl halide is primary and not well at all if R′ is secondary or tertiary.

$CH_3OCH_2CH_2CH_3$

$$2\,CH_3OH + 2\,Na \longrightarrow 2\,CH_3O^-Na^+ + H_2$$

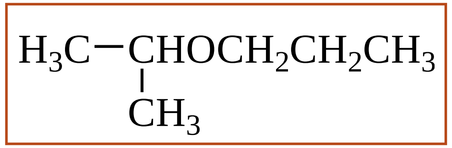
$$CH_3O^-Na^+ + CH_3CH_2CH_2X \longrightarrow CH_3OCH_2CH_2CH_3 + Na^+X^-$$

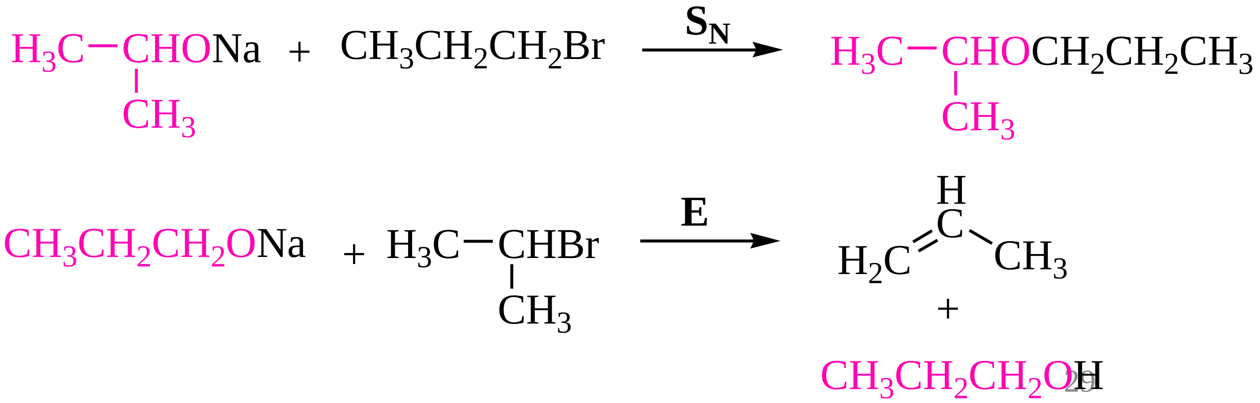
or

$$2\,CH_3CH_2CH_2OH + 2\,Na \longrightarrow 2\,CH_3CH_2CH_2O^-Na^+ + H_2$$

$$CH_3CH_2CH_2O^-Na^+ + CH_3X \longrightarrow CH_3CH_2CH_2OCH_3 + Na^+X^-$$

X is usually Cl, Br, or I.





Reactions Of Ethers

- 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

$$R{-}O{-}R + HX \longrightarrow R{-}X + R{-}OH$$

$$CH_3CH_2OCH_2CH_3 \quad + \quad \text{conc } HI \xrightarrow{\text{heat}} CH_3CH_2OH \quad + \quad CH_3CH_2I$$

- If two or more equivalents of acid:

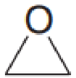
$$CH_3CH_2OCH_2CH_3 \quad + \quad 2 \text{ conc } HBr \xrightarrow{\text{heat}} 2\, CH_3CH_2Br \quad + \quad H_2O$$

Structure of Epoxides

- Epoxides (or oxiranes) are cyclic ethers with a three-membered ring containing one oxygen atom.

Nomenclature of Epoxides

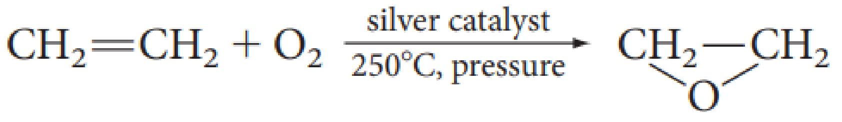
- In IUPAC nomenclature epoxides are called oxiranes.
- The simplest epoxide has the common name ethylene oxide.



Common name:	Ethylene oxide
IUPAC name:	Oxirane

Preparation Of Epoxides

- The most important commercial epoxide is Ethylene Oxide, produced by the silver-catalyzed air oxidation of ethylene.



ethylene oxide