

Chapter 14: Alcohols, Phenols, and Ethers

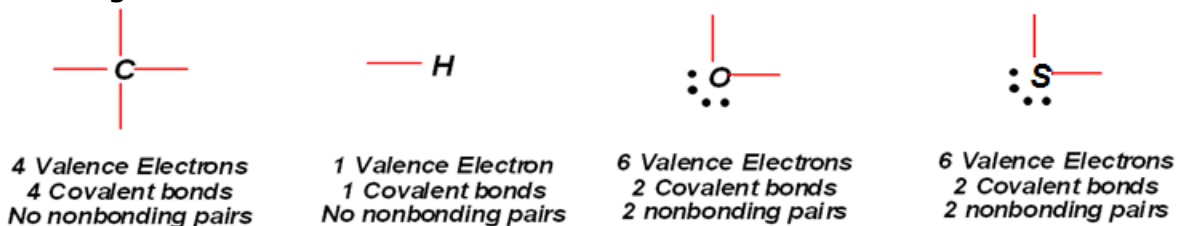
This chapter is the first of three that consider hydrocarbon derivatives with oxygen. This chapter is the first of three that consider hydrocarbon derivatives with oxygen-containing functional groups. Many biochemically important molecules contain carbon atoms bonded to oxygen atoms.

In this chapter we consider hydrocarbon derivatives whose functional groups contain one oxygen atom participating in two single bonds (alcohols, phenols, and ethers). Chapter 15 focuses on derivatives whose functional groups have one oxygen atom participating in a double bond (aldehydes and ketones), and in Chapter 16 we examine functional groups that contain two oxygen atoms, one participating in single bonds and the other in a double bond (carboxylic acids, esters, and other acid derivatives).

14.1 Bonding Characteristics of Oxygen and Sulfur Atoms in Organic Compounds

Oxygen and Sulfur are Group VIA Elements Has 6 valence electrons

- Two lone pairs
- Two bonding pairs, i.e., it can form two covalent bonds
- Two single or one double bond



14.2 Structural Characteristics of Alcohols

-OH functional groups:

Alcohol: **R-O-H**

Phenols: **Ar-OH**

Alcohol: An organic compound in which an —OH group is bonded to a saturated carbon atom.

Saturated carbon atom: A carbon atom that is bonded to four other atoms.

General structure: R-OH (OH is functional group)

- Examples: CH₃OH, C₃H₇OH
- OH in alcohols is not ionic as in NaOH.

14.3 Nomenclature for Alcohols

Common names : Alcohols (C₁-C₄ alkyl groups).

- **Rule 1:** Name all of the carbon atoms of the molecule as a single alkyl group.
 - Example: Methyl (C₁), Ethyl (C₂), propyl (C₃) butyl (C₄)
- **Rule 2:** Add the word alcohol, separating the words with a space.
- Examples

The IUPAC Names:

The **IUPAC system** deals with functional groups two different ways. Modification of the hydrocarbon name to indicate the presence of a functional group.

- OH group takes priority (even over -ene or -yne)
- it must be in the parent chain
- the direction of numbering gives it the lowest possible number to carbon with -OH.
- -ol suffix with number designation
- name other substituents and multiple bonds as usual

alcohol, -OH

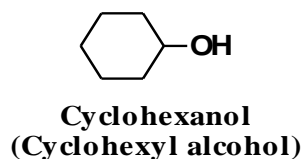
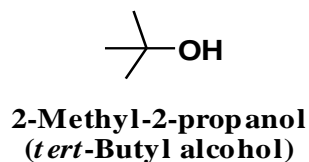
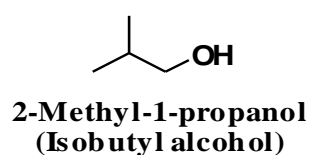
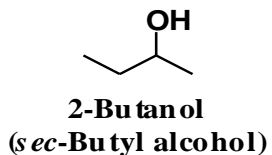
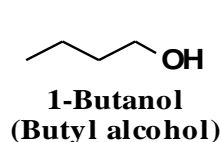
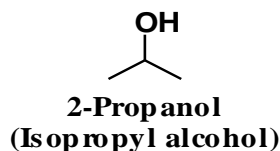
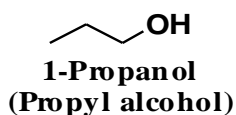
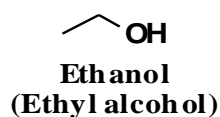
use **-ol** ending.

ether: $\text{CH}_3\text{CH}_2\text{-O-CH}_3$

use **methoxy**

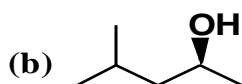
methoxy ethane

Examples:

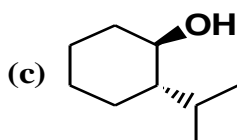


*Common names are in parenthesis

(a) $\text{CH}_3(\text{CH}_2)_6\text{CH}_2\text{OH}$ Octanol



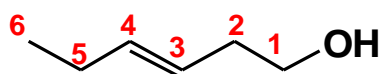
4-methyl-2-pentanol



2-isopropyl cyclohexanol

IUPAC naming of unsaturated alcohols

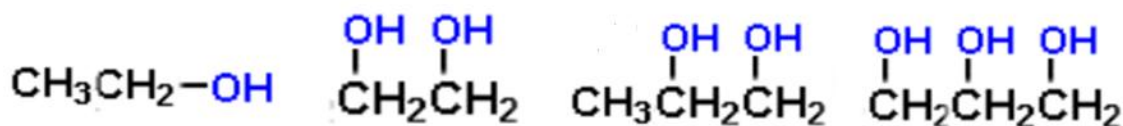
- the double bond is shown by the infix -en-
- the hydroxyl group is shown by the suffix -ol
- number the chain to give OH the lower number



trans-3-hexene-1-ol
(*E*)-3-hexene-1-ol

Alcohol with More than one -OH group

Polyhydroxy alcohols—alcohols that possess more than one hydroxyl group—can be named with only a slight modification of the preceding IUPAC rules. An alcohol in which two hydroxyl groups are present is named as a diol, one containing three hydroxyl groups is named as a triol, and so on. In these names for diols, triols, and so forth, the final -e of the parent alkane name is retained for pronunciation reasons.



1-Ethanol **1,2-Ethanediol** **1,2-Propanediol** **1,2,3-Propanetriol**
(ethyl alcohol) (ethylene glycol) (propylene glycol) (glycerol)

The first two of the preceding compounds have the common names ethylene glycol and propylene glycol. These two alcohols are synthesized,

respectively, from the alkene ethylene and propylene (Section 13.3), hence the common names.

14.4 Isomerism for Alcohols (Constitutional Isomerism)

Isomerism in butanol

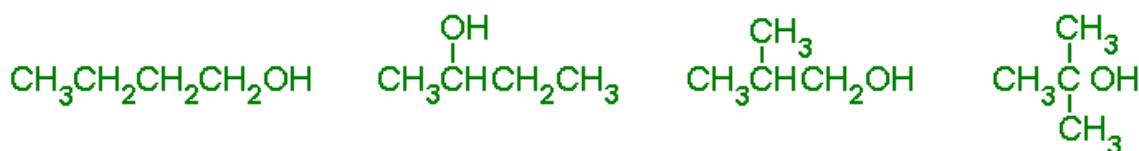
Constitutional isomerism is possible for alcohols containing three or more carbon atoms.

Two types of isomers

Skeletal isomers

Positional isomers

At with alkenes (Section 13.5), both skeletal isomers and **positional isomers** are possible. For monohydroxy saturated alcohols, there are two C3 isomers, four C4, and eight for C5 isomers.



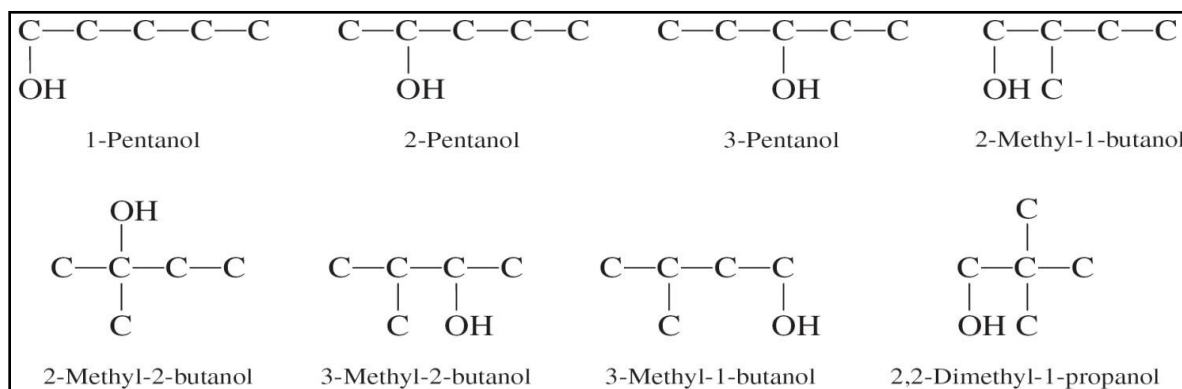
1-butanol

2-butanol

3-methyl-1-propanol

2-methyl-2-propanol

C5 isomers



14.5 Important Commonly Encountered Alcohols

Methyl Alcohol (Methanol)

- Good fuel and used as a solvent in paints
- Commonly called wood alcohol – original method of its preparation was by heating wood at high temperature in the absence of air.
- Currently, nearly all methyl alcohol is produced via the reaction between H_2 and CO .
- Toxic: oxidized by alcohol dehydrogenase in the body to toxic formaldehyde and formic acid – toxic to the eye and can cause blindness and/or optic nerve damage.
 - Treated with ethanol: Ethanol stops oxidation of methanol by competing with alcohol dehydrogenase enzyme.

Ethyl Alcohol (Ethanol)

- Also called grain alcohol as obtained by fermentation of grains like corn, rice and barley.
- Prepared by yeast fermentation of plant sugars by yeast
 - Maximum concentration of ethanol: 18% (yeast enzymes are inactivated at higher concentration of alcohol)
 - Excellent solvent and a fuel
 - Distributed as denatured Alcohol: Toxic substances such as methanol are added to prevent human consumption
 - Oxidized by body to acetaldehyde – toxic and causes hangover effects of alcohol
 - Consumption of alcohol during pregnancy can cause birth defects and fetal alcohol syndrome
 - Also known to cause liver damage, loss of memory and alcoholism (addiction to alcohol)

Isopropyl Alcohol (2-Propanol)

- Isopropyl alcohol is a three-carbon monohydroxy alcohol.
- A 70% isopropyl alcohol in water is marketed as rubbing alcohol (used to combat high body temperature by rubbing on the skin).
- Isopropyl alcohol has a bitter taste.
- Toxicity: Twice that of ethyl alcohol (often induces vomiting and thus doesn't stay down long enough to be fatal).
- In the body it is oxidized to acetone.

Glycerol (1,2,3-Propanetriol)

- Glycerol is a **triol** with three -OH groups attached on three adjacent carbon atoms.
- Clear thick liquid
- Byproduct of fat metabolism
- Used in skin lotions and soaps
- Used in shaving creams due to lubricating properties
- Often called biological antifreeze

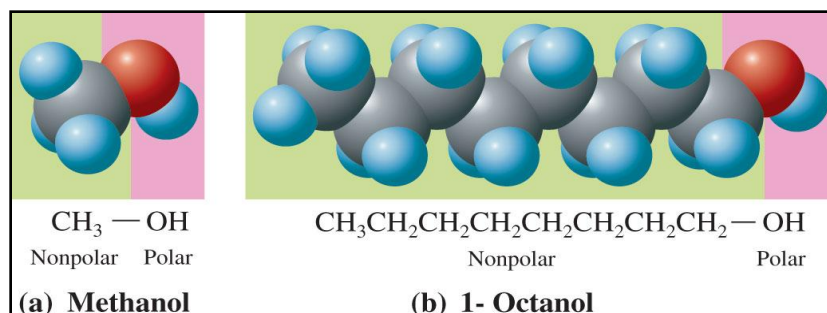
14.6 Physical Properties of Alcohols

Alcohol molecules have both **polar** and **nonpolar** character.

- The hydroxyl group is polar part of the molecule
- The alkyl (R) group is nonpolar part of the molecule

The physical properties depend on which portion of the structure "dominates."

- Length of the nonpolar carbon chain
- Number of polar hydroxyl groups



Space-filling molecular models showing the nonpolar (green) and polar (pink) parts of methanol and 1-octanol.

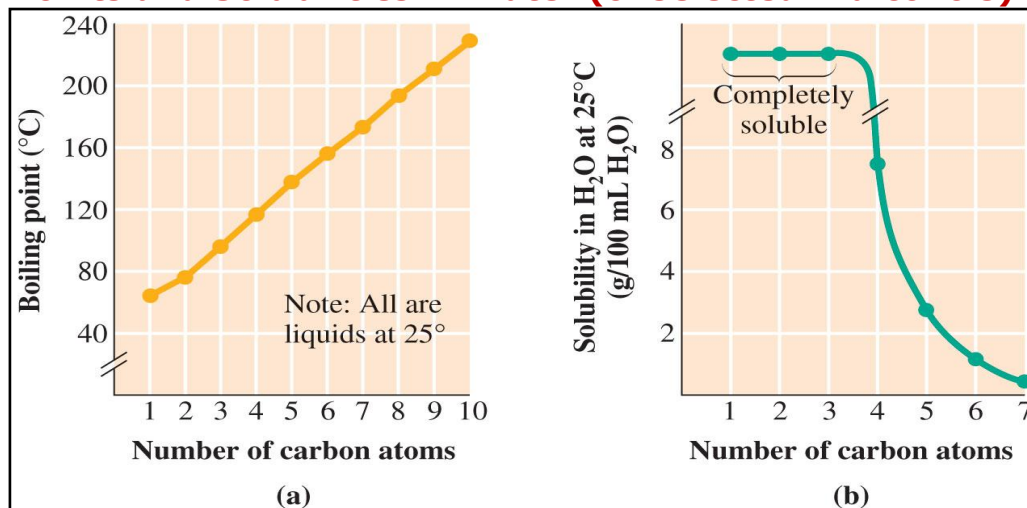
The polar **hydroxyl functional group** dominates the physical properties of methanol. The molecule is completely soluble in water (polar) but only partially so in hexane (nonpolar).

Conversely, the nonpolar portion of 1-octanol dominates its physical properties; it is infinitely soluble in hexane and has limited solubility in water.

Boiling Points and Water Solubilities

- The boiling points of 1-alcohols with an $-\text{OH}$ group on an end carbon increases as the length of the carbon chain increases.
- Small monohydroxy alcohols are soluble in water in all proportions.
- As carbon chain length increases beyond three carbons, solubility in water rapidly decreases

Boiling Points and Solubilities in Water (of selected 1-alcohols)



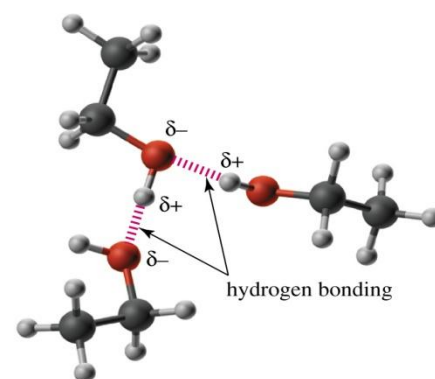
Structural Formula	Name	Molecular Weight (g/mol)	Boiling Point (°C)	Solubility in Water
CH ₃ OH	methanol	32	65	infinite
CH ₃ CH ₃	ethane	30	-89	insoluble
CH ₃ CH ₂ OH	ethanol	46	78	infinite
CH ₃ CH ₂ CH ₃	propane	44	-42	insoluble
CH ₃ CH ₂ CH ₂ OH	1-propanol	60	97	infinite
CH ₃ CH ₂ CH ₂ CH ₃	butane	58	0	insoluble
CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ OH	1-pentanol	88	138	2.3 g/100 g
HOCH ₂ CH ₂ CH ₂ CH ₂ OH	1,4-butanediol	90	230	infinite
CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ CH ₃	hexane	86	69	insoluble

Alcohols and Hydrogen Bonding

The differences in physical properties between alcohols and alkanes

1. Alcohols have higher boiling points than alkanes of similar molecular mass.
2. Alcohols have much higher solubility in water than alkanes of similar molecular mass.

Figure shows the association of ethanol molecules in the liquid state (only two of the three possible hydrogen bonds to the upper oxygen are shown here).



Alcohols have higher boiling points and are more soluble in water than hydrocarbons

14.7 Preparation of Alcohols

14.8 Classification of Alcohols

Alcohols are classified as **primary (1°)**, **secondary (2°)**, or **tertiary (3°)** alcohols

Primary alcohol (1°): Hydroxyl-bearing carbon atom is bonded to only one other carbon atom.

Secondary alcohol (2°): Hydroxyl bearing carbon atom is bonded to two other carbon atoms.

Tertiary alcohol (3°): Hydroxyl-bearing carbon atom is bonded to three other carbon atoms.

Reactions are dependent on the type of alcohol **1°**, **2°**, or **3°**

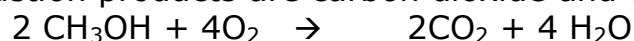
Primary	Secondary	Tertiary
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{-OH}$	$\text{CH}_3\text{CH}_2\overset{\text{OH}}{\underset{ }{\text{CH}}}\text{CH}_2\text{CH}_3$	$\text{CH}_3\text{-}\overset{\text{CH}_3}{\underset{\text{CH}_3}{\underset{ }{\underset{ }{\text{C}}}}\text{-OH}$

14.9 Chemical Reactions of Alcohols

Combustion Reactions

Like other hydrocarbons alcohols are also flammable.

The combustion products are carbon dioxide and water.



Alcohol Dehydration

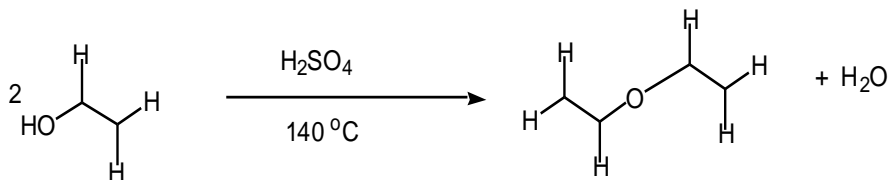
Intramolecular- Alcohol Dehydration

- A dehydration reaction in which the components of water (-H and -OH) are removed from a single reactant
- An alcohol can be converted to an alkene by elimination of H and OH from adjacent carbons (a β -elimination)

Intermolecular- Alcohol Dehydration

In this reaction, two molecules of alcohol combine to form an ether (Condensation reaction)

- Only true for **primary alcohols** and 140°C .

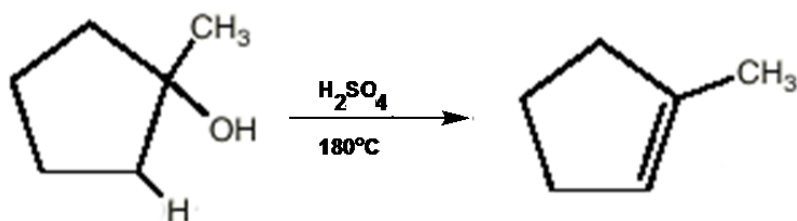


- **Secondary** and **tertiary** alcohols always give alkene.

Dehydration of an alcohol can result in more than one alkene product, because hydrogen loss can occur from either of the neighboring carbon atoms.

Example: Dehydration of 2-butanol produces two alkenes.

Zaitsev's rule (or the opposite of **Markovnikov's rule**) can be used determine the dominant product.



Oxidation of Alcohols

Addition of oxygen or removal of hydrogen

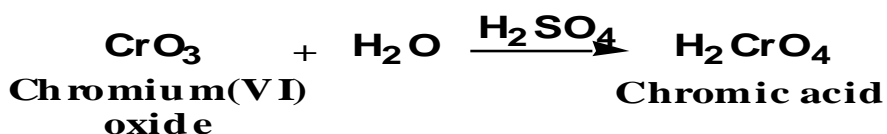
Mild Oxidizing Agents: KMnO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$, H_2CrO_4

Primary and Secondary Alcohols can be oxidized by mild oxidizing agents

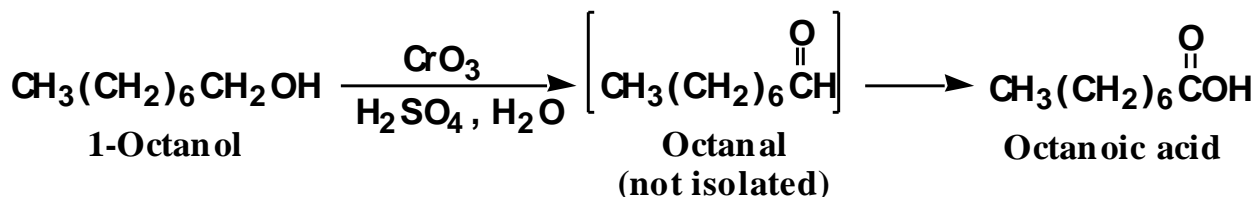
1° alcohol

Oxidation of a **1° alcohol** gives an **aldehyde** and then get oxidized to **carboxylic acid**, depending on the oxidizing agent and experimental conditions

- the most common oxidizing agent is chromic acid

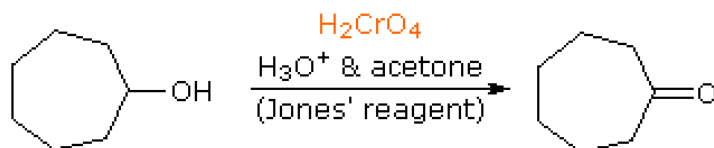
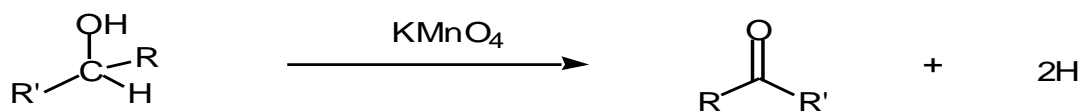


- chromic acid oxidation of 1-octanol gives octanoic acid



2° alcohol

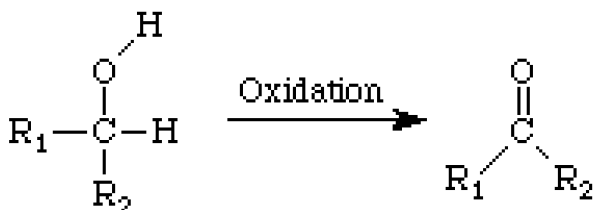
Oxidation of a **2° alcohol** gives an **Ketone** the most common oxidizing agent is chromic acid.



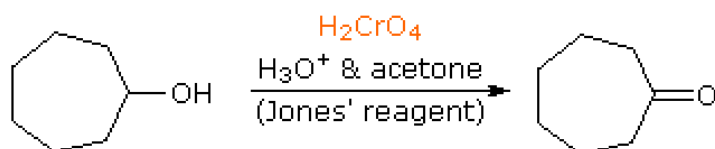
chromic acid oxidation of heptanol gives heptanone.

2° alcohol

Oxidation of a **2° alcohol** gives an **Ketone** the most common oxidizing agent is chromic acid.

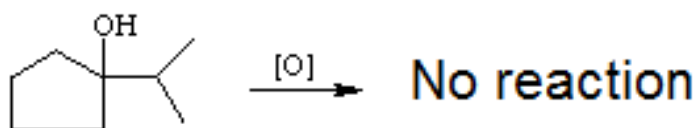


Chromic acid oxidation of heptanol gives heptanone.

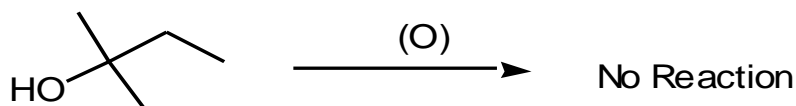
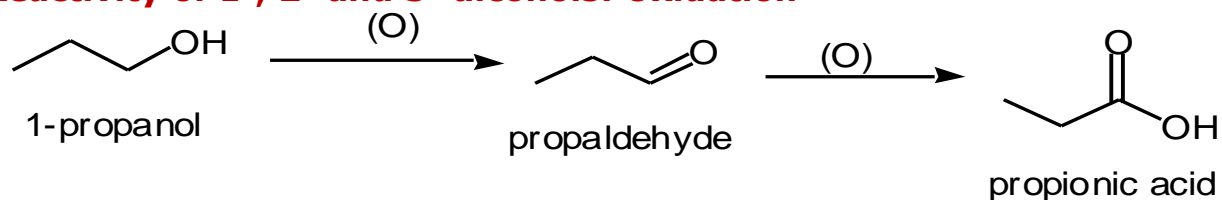


3° alcohol

Oxidation of a **3° alcohol** will not take place there is no hydrogen to be removed from a 3° carbon atom on a 3° alcohol.



Reactivity of 1°, 2° and 3° alcohols: Oxidation

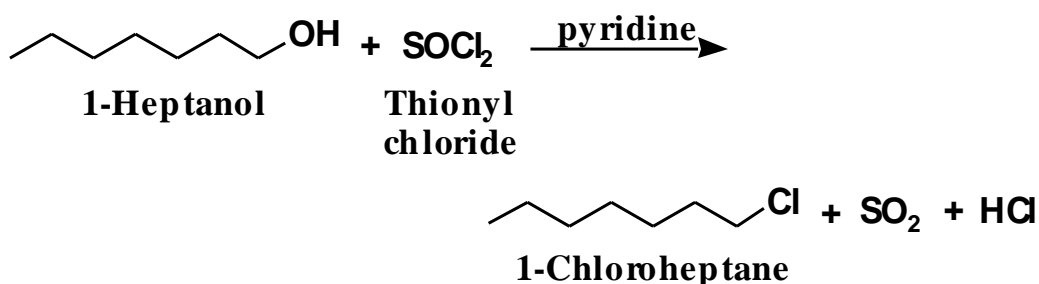
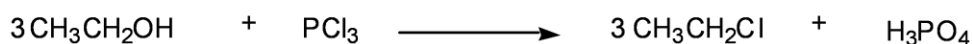
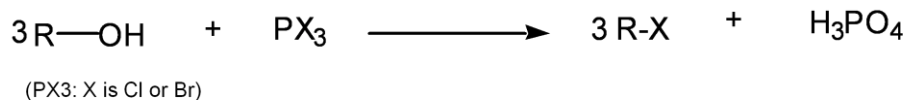
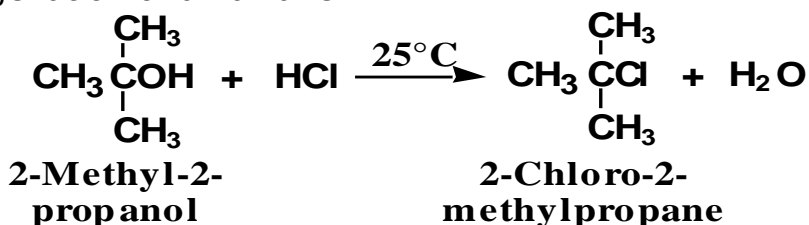


2-methyl-2butanol

Halogenation of Alcohol

Alcohols undergo halogenation reactions. In this reaction a halogen atom is substituted for the hydroxyl group producing an alkyl halide.

Alkyl halide production by this reaction is superior to alkyl halide production through halogenation of an alkane.



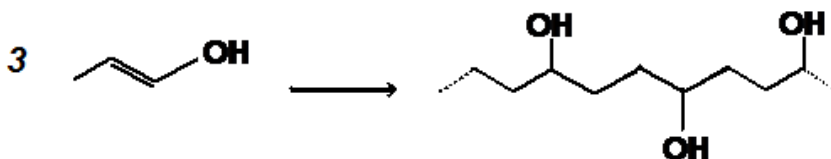
Polymeric Alcohols

Polyvinyl alcohol (PVA)

It is possible to synthesize polymeric alcohols with structures similar to those of substituted polyethylenes.

The simplest polymer is polyvinyl alcohol (PVA)

- PVA is a tough, whitish polymer that can form strong films,
- tubes, and fibers that are highly resistant to hydrocarbon solvents
- Unlike most organic polymers, PVA is water-soluble



14.11 Structural Characteristics of Phenols

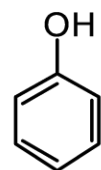
Phenol: An organic compound in which an —OH group is attached to a carbon atom that is part of an aromatic carbon ring system

Aryl group: An aromatic carbon ring system from which one hydrogen atom has been removed.

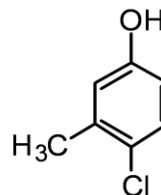
General formula for an aryl alcohol: Ar-OH

Substituted phenols: Aryl group substituted with other groups like CH₃, NO₂, etc.

Phenyl, Ar = C₆H₅



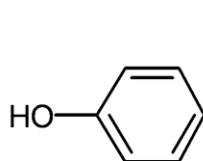
phenol



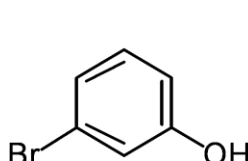
4-chloro-3-methyl phenol
Substituted phenol

14.12 Nomenclature for Phenols

- Phenols: Name "Phenol" is approved by IUPAC
 - Assign the position of the substituent followed by its name and the word phenol
 - Carbon atom with -OH is always number 1 and the other substituents will be assigned minimum possible numbers with reference to hydroxyl carbon

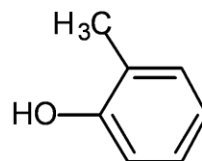


phenol



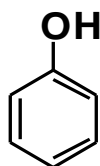
3-bromophenol

m-bromophenol

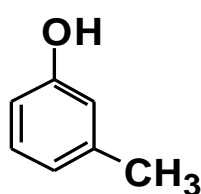


2-methylphenol

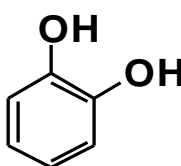
o-methylphenol



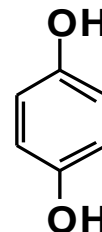
Phenol



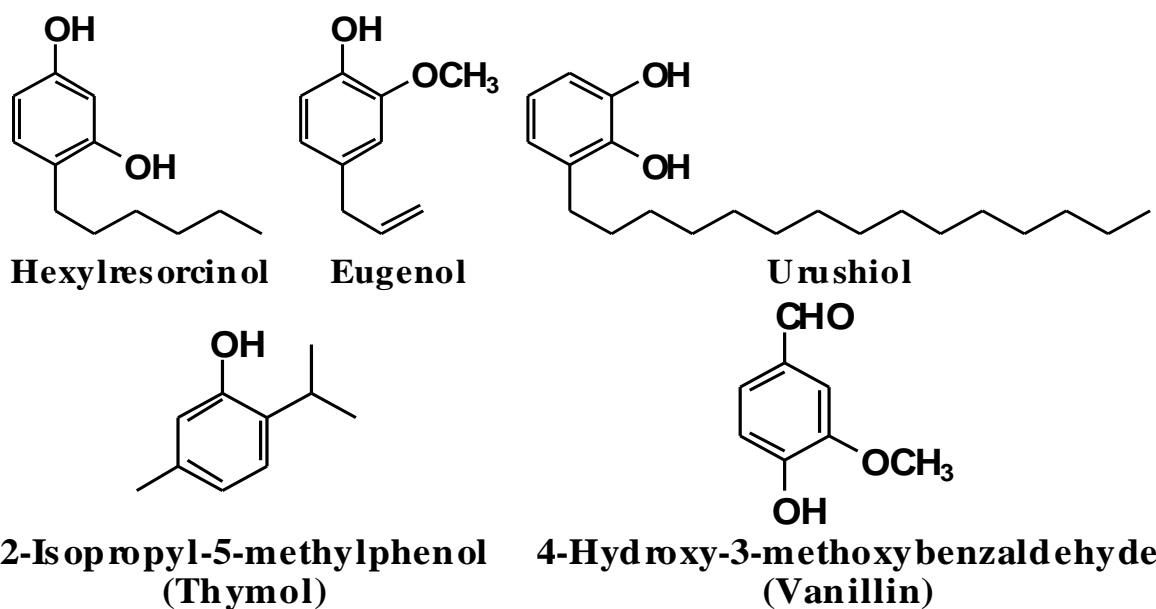
3-Methylphenol
(*m*-Cresol)



1,2-Benzenediol
(Catechol)



1,4-Benzenediol
(Hydroquinone)



14.13 Physical and Chemical Properties of Phenols

Phenols :

- Low-melting solids or oily liquids at room temperature.
- Sparingly soluble in water
- Many phenols have antiseptic and disinfectant properties.
- The simplest phenol: phenol
- A colorless solid with a medicinal odor
- Melting point: 41°C
- More soluble in water than any other phenols

Acidity of Phenols

- Unlike alcohols, phenols are weak acids in solution.
- As acids, phenols have K_a values of about 10^{-10} M.

Phenoxide anions are stabilized by resonance with the aromatic ring
 pK_a of phenol is 10
 (deprotonated by NaOH at pH 10)
 Electron withdrawing groups further stabilize the phenoxide anion
 (especially ortho or para)
 pK_a of p-nitrophenol is 7

Alcohols have pK_a of over 15.
Higher the pK_a of compound is lower the acidity.

Antiseptic properties of phenols

- 4-hexylresorcinol is an ingredient in many mouthwashes and throat lozenges.
- o-phenylphenol and 2-benzyl-4-chlorophenol are the active ingredients in Lysol, a disinfectant.

Antioxidant properties of phenols

Phenols have antioxidant properties: **BHA** (butylated hydroxy anisole) and **BHT** (butylated hydroxy toluene) are used as food preservatives to protect it from air oxidation

Vitamin E is a phenolic antioxidant

A number of phenols found in plants are used as flavoring agents and/or antibacterials.

Vanillin is a phenolic which gives flavor of vanilla

14.15 Structural Characteristics of Ethers

Ethers: Oxygen bonded to two carbon atoms (functional group)

- Have **-O-** functional groups
- General formula: $R-O-R$
- Examples:
 - CH_3-O-CH_3 , $CH_3-O-C_2H_5$
 - Water and ether have similar structure in that two H of water are replaced by R groups in ethers.

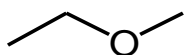
14.16 Nomenclature for Ethers

Common names

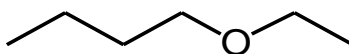
Name the two hydrocarbon groups attached to oxygen atom of the ether and add the word ether

- The hydrocarbon groups are listed in alphabetical order
- When both R groups are same then di is used with the name of R group

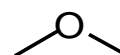
Examples:



ethyl methyl ether



butyl ethyl ether



dimethyl ether

IUPAC Naming

Rule 1: Select the longest carbon chain and use its name as the base name.

Rule 2: Change the "-yl" ending of the other hydrocarbon group to "-oxy" to obtain the alkoxy group name

Examples: methyl becomes methoxy, ethyl becomes ethoxy, etc.

Rule 3: Place the alkoxy name, with a locator number, in front of the base chain name.

Examples:

Isomers of Ethers

Ethers have carbon chains (two alkyl groups) therefore the constitutional isomerism possibilities in ethers depend on:

- The partitioning of carbon atoms between the two alkyl groups, and
- Isomerism possibilities for the individual alkyl groups present.
- Isomerism is not possible for a C₂ or a C₃ ether
- C₄ and C₅ ethers exhibit constitutional isomers.

Functional Group Isomerism

Ethers and alcohols with the same number of carbon atoms and the same degree of saturation have the same molecular formula.

For example: Dimethyl ether, and ethyl alcohol both have the molecular formula C₂H₆O (constitutional isomers).

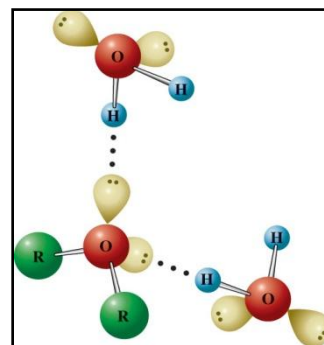
Functional group isomers are constitutional isomers that contain different functional groups.

C₃ ether—alcohol functional group isomerism possibilities are three (see below)

14.18 Physical and Chemical Properties of Ethers

Physical Properties: The boiling points of ethers are similar to those of alkanes of comparable molecular mass and are much lower than those of alcohols of comparable molecular mass.

Ethers more soluble in water than alkanes of similar molar mass because ethers can hydrogen bond



Structural Formula	Name	Molecular Weight	Boiling Point (°C)	Solubility in Water
$\text{CH}_3\text{CH}_2\text{OH}$	ethanol	46	78	infinite
CH_3OCH_3	dimethyl ether	46	-24	7.8 g/100 g
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$	1-butanol	74	117	7.4 g/100 g
$\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$	diethyl ether	74	35	8 g/100 g
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$	1-pentanol	88	138	2.3 g/100 g
$\text{HOCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$	1,4-butanediol	90	230	infinite
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}_3$	butyl methyl ether	88	71	slight
$\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_3$	ethylene glycol dimethyl ether	90	84	infinite

Chemical Properties:

Ethers are Flammable, e.g., Diethyl ether has boiling point of 35°C and therefore a flash-fire hazard.

Ethers react slowly with oxygen from the air to form unstable hydroperoxides and peroxides.

Unreactive towards acids, bases and oxidizing agents (useful for organic reactions)

Like alkanes, ethers also undergo halogenation reactions

Cyclic Ethers

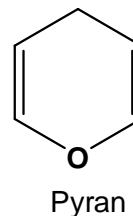
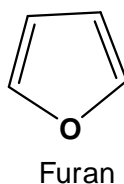
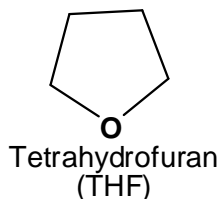
Contain the ether functional groups as part of a ring system (heterocyclic organic compounds).

Heterocyclic organic compound: a cyclic organic compound in which one or more of the carbon atoms in the ring have been replaced with atoms of other elements.

Important cyclic ethers:

THF : Useful as a solvent in that it dissolves many organic compounds and yet is miscible with water.

Polyhydroxy derivatives of the five-membered (**furan**) and six membered (**pyran**) carbohydrates are cyclic ether systems.



14.20 Sulfur Analogs and Alcohols and Ethers

R-SH ---- Thiol

R-S-R ---- Thioether

Lower boiling point than corresponding alcohols due to lack of hydrogen bonding

Strong disagreeable odor
Natural gas odor is due to added thiols

-S- and -SH functional groups:

Thioether: R-S-R'

Thiol: R-S-H

- Thiols are named in the same way as alcohols in the IUPAC system, except that the "-ol" becomes "-thiol."
- The prefix thio- indicates the substitution of a sulfur atom for an oxygen atom.
- As in the case of diols and triols, the "-e" at the end of the alkane name is also retained for thiols.

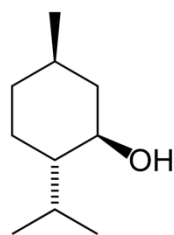
14.21 Sulfur Analogs of Ethers

Thioethers (or sulfides): An organic compound in which a sulfur atom is bonded to two carbon atoms by single bonds.

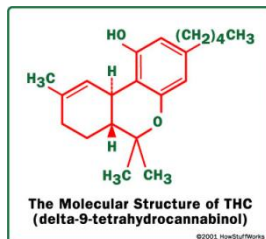
- *General* formula: $R-S-R$.
- Like thiols, thioethers (or sulfides) have strong characteristic odors.
- Thiols are more reactive than their alcohol and ether counterparts. A carbon-sulfur covalent bond is weaker than a carbon-oxygen bond.
- Dimethyl sulfide is a gas at room temperature and ethyl methyl sulfide is a liquid.

Thiols and thioethers exhibit functional group isomerism in the same manner that alcohols and ethers.

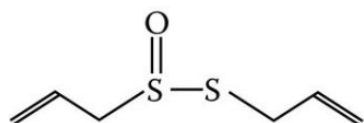
Menthol: A Useful Naturally Occurring Terpene Alcohol; Ethers as General Anesthetics; Marijuana: The Most Commonly Used Illicit Drug; Garlic and Onions: Odiferous Medicinal Plants



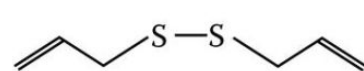
Menthol



Marijuana



Allicin (garlic)



**Diallyl disulfide
(garlic and onions)**

Garlic and Onions