Chemistry 110

Bettelheim, Brown, Campbell & Farrell

Eighth Edition

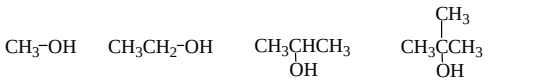
Introduction to General,

Organic and Biochemistry

Chapter 14

Alcohols, Ethers and Thiols

Alcohols have a Hydroxyl Group, -OH, bonded to tetrahedral carbon.



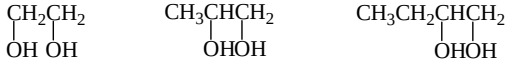
CH_3OH	CH_3CH_2OH	CH_3CHCH_3 (OH)	$CH_3C(CH_3)_2$ (OH)
methanol	ethanol	2-propanol	2-methyl-2-propanol
methyl alcohol	ethyl alcohol	isopropyl alcohol	*tert*-butyl alcohol

IUPAC Names: **Parent Alkane - *e* + *ol***

Common Names: **R-group then "alcohol"**

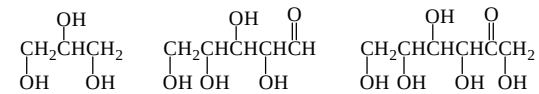
Alcohols are classified as primary, secondary and tertiary – determined by the carbon to which the hydroxyl is attached.

Alcohols bearing more than one hydroxyl group: Diols, Triols & Polyols



CH_2CH_2 (OH OH)	CH_3CHCH_2 (OHOH)	$CH_3CH_2CHCH_2$ (OHOH)
1,2-ethandiol ethylene glycol	1,2-propandiol propylene glycol	1,2-butandiol butylene glycol

Diols with hydroxyls on adjacent carbons are called glycols.

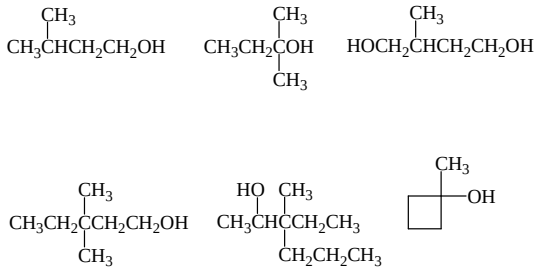


CH_2CHCH_2 (OH OH OH)	$CH_2CHCHCHCH$ (OH OH OH O)	$CH_2CHCHCHCCH_2$ (OH OH OH O OH)
1,2,3-propantriol glycerol (glycerin)	"aldopentose" "sugars"	"ketohexose"

IUPAC Naming of Alcohols

- **The *longest continuous chain* of carbons bearing the hydroxyl, –OH, group is the Parent Alkan*ol* (PA).**
- **Number the chain from the direction giving the –OH the lower number. Place the number, separated by hyphens, in front of the Parent Alkanol. When more than one –OH exists, locate each with a locator number ending the PA with *diol, triol, tetraol, etc.***
- **Construct the name by locating the other substituent groups along the PA and listing them alphabetically, again using *di, tri, etc.* for identical groups. Always separating numbers from numbers with commas, and from words with hyphens.**

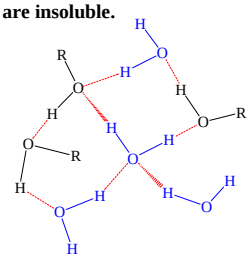
Name these Alcohols using IUPAC



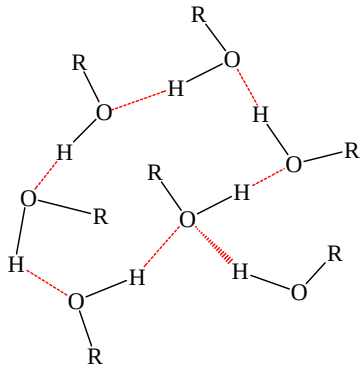
Physical Properties of Alcohols

Alcohols are polar, hydrogen bond with water, and each other, have higher boiling points than alkanes of similar molecular weight and are soluble in water if the substituent group part is not too large and non-polar. C_1-C_7 = miscible to slightly soluble, C_8 and higher are insoluble.

Alcohols have a pKa similar to water, aqueous solutions are not acidic or basic, the pH is not altered.



Hydrogen Bonds – Pure Alcohols



Physical Properties of Alcohols

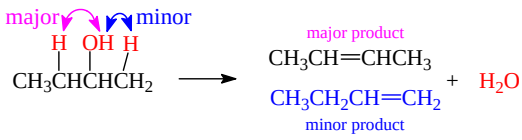
Boiling points of alcohols increase as molecular weight increases and are higher than alkanes of similar Molecular weight.

Structural Formula	Name	Molecular Weight	bp (°C)	Solubility in Water
CH_3OH	methanol	32	65	infinite
CH_3CH_3	ethane	30	-89	insoluble
CH_3CH_2OH	ethanol	46	78	infinite
$CH_3CH_2CH_3$	propane	44	-42	insoluble
$CH_3CH_2CH_2OH$	1-propanol	60	97	infinite
$CH_3CH_2CH_2CH_3$	butane	58	0	insoluble
$CH_3CH_2CH_2CH_2OH$	1-butanol	74	117	8 g/100 g
$CH_3CH_2CH_2CH_2CH_3$	pentane	72	36	insoluble

Reactions of Alcohols

Dehydration:

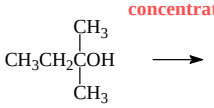
Note! Two carbon atoms involved!

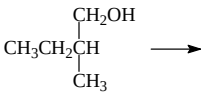


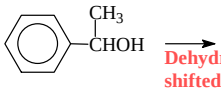
When two alkenes are possible: The one with the most substituents on the double bond is generally favored.

Write the Products of the Reactions Below

Dehydration: **The dehydrating reagents used are commonly concentrated phosphoric or sulfuric acids.**



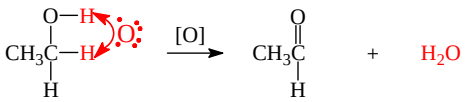




Dehydration/hydration is an equilibrium shifted by the concentration of water!

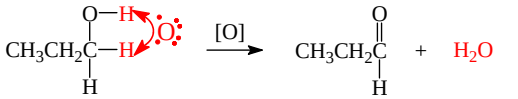
Oxidation of Primary Alcohols

[O] = oxidizing agent, usually K_2CrO_4 and H_2SO_4.



ethanol — ethanal (acetaldehyde)

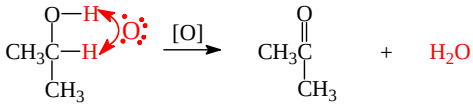
Aldehydes are formed!



propanol — propanal (propionaldehyde)

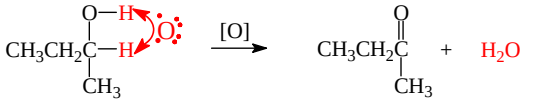
Oxidation of Secondary Alcohols

[O] = oxidizing agent



2-propanol — propanone (acetone)

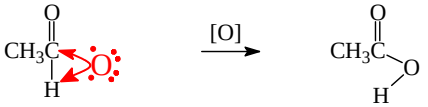
Ketones are formed!



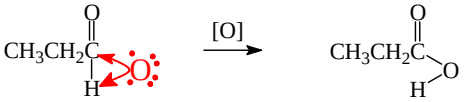
2-butanol — butanone (methyl ethyl ketone)

Further Oxidation of Primary Alcohols

Aldehydes are formed first but oxidize easily to carboxylic acids unless they are distilled out of the reaction mixture as they form!



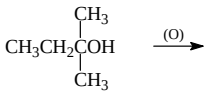
ethanal (acetaldehyde) from ethanol — ethanoic (acetic) acid

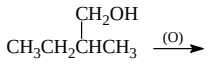


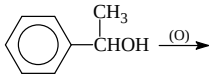
propanal (propionaldehyde) — propanoic (propionic) acid

Ketones and tertiary alcohols resist further oxidation.

Write the Products of the Reactions Below

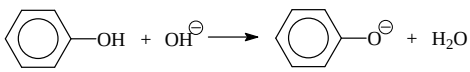






PHENOLS

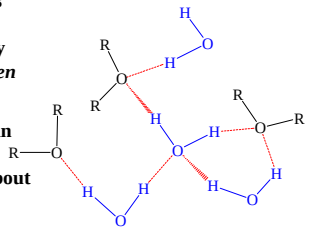
- **Phenols – The *hydroxy* group must be bonded directly to the benzene ring.**
- **Phenols are weakly acidic and ionize in basic solution forming phenoxide anions.**



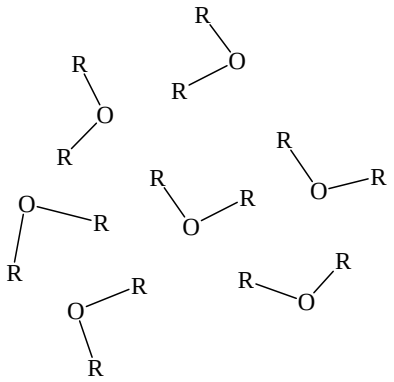
- **Phenols are easily oxidized, the ring itself is attacked and phenols become dark on exposure to air.**

ETHERS

- **Ethers have two non-carbonyl hydrocarbon groups bonded to oxygen.**
- **Ethers are nearly as unreactive as the alkanes.**
- **Ethers are as volatile as alkanes of similar molecular weight. They cannot *donate* a *hydrogen bond* to each other.**
- **Ethers are polar and can *accept* a *hydrogen bond* from water; they are about as soluble in water as isomeric alcohols.**



Hydrogen Bonds – Pure Ethers



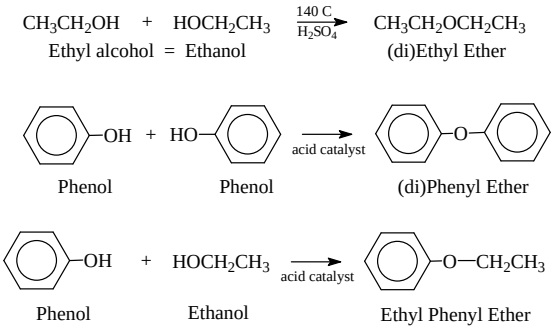
Naming of Ethers

- **Although ethers can be named according to the IUPAC system, chemists almost invariably use common names for low-molecular-weight ethers.**
- **Common names are derived by listing the alkyl groups bonded to oxygen in alphabetical order and adding the word "ether".**
- **Alternatively, name one of the groups on oxygen as an alkoxy group.**

cyclohexyl methyl ether

methoxycyclohexane

Synthesis of Ethers from Alcohols & Phenols



Thioalcohols, Thioethers and Disulfides

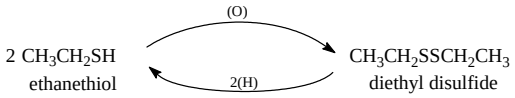
Thioalcohols are also called Mercaptans (capture mercury)

CH_3CH_2SH ethanethiol ethyl mercaptan

$CH_3CH_2SCH_2CH_3$ ethyl thioether

$CH_3CH_2SSCH_2CH_3$ diethyl disulfide

An important reversible biological reaction:



The oxidation of thiols to disulfides and the reduction of disulfides to thiols is important to protein structure. S-H and S—S bonds occur widely in proteins and are easily enzymatically oxidized and reduced.

Naming of Thiols

- **IUPAC names are derived in the same manner as are the names of alcohols, to show that the compound is a thiol, the final -e of the parent alkane is retained and the suffix -thiol added**
- **Common names for simple thiols are derived by naming the alkyl group bonded to the sulfhydryl, -SH, group and adding the word "mercaptan"**

Physical Properties of Thiols

- **Because of the small difference in electronegativity between sulfur and hydrogen (2.5 - 2.1 = 0.4), the S-H bond is nonpolar covalent. Thiols show little association by hydrogen bonding.**
- **Thiols have lower boiling points and are less soluble in water and other polar solvents than alcohols of similar molecular weight.**
- **The most striking property of thiols is their stench! Whether skunks, sewage or rotten eggs the smell is that of one or other kind of thiol.**
- **Thiols are weak acids (pK_a 10), and are comparable in strength to phenols. Thiols react with strong bases such as NaOH to form water-soluble thiolate salts**