Chemistry 121(01) Winter 2009

Introduction to Organic Chemistry and Biochemistry
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TR 9::00 - !0:00 am & 1:00-2:00 pm.

December 19, Test 1 (Chapters 12-14)
January 2 Test 1 (Chapters 15-16)
February 6 (Chapters 17-19)
February 27, (Chapters 20-22)
March 2, 2009, Make Up Exam:
Bring Scantron Sheet 882-E

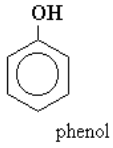
Chapter 14: Alcohols, Phenols and Ethers

Sections 14.1-4.21

Chapter 14: Alcohols, Phenols, and Ethers

Chapter 5. Alcohols, Phenols, and Ethers

Functional groups:
alcohol: R-O-H
phenols: Ar-OH
ether: R-O-R'
thiol: R-S-H



phenol

Alkyl, R = CH_3 Mehtyl etc.

Phenyl, Ar = C_6H_5

Nomenclature of compounds containing functional groups

The IUPAC system deals with functional groups two different ways.

Modification of the hydrocarbon name to indicate the presence of a functional group.

alcohol, -OH use -ol ending.

ether: CH_3CH_2-O-CH_3 use methoxy methoxy ethane

thiol: R-S-H use -thiol ending.

Alcohol example

C - C - C - C - O - H

Base contains 4 carbon
- alkane name is butane
- remove -e and add -ol

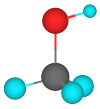
alcohol name - butanol

OH is on the first carbon so - 1-butanol

Alcohols - Structure

The functional group of an alcohol is an -OH group bonded to an sp^3 hybridized carbon

- bond angles about the hydroxyl oxygen atom are approximately 109.5°



Oxygen is also sp^3 hybridized

- two sp^3 hybrid orbitals form sigma bonds to carbon and hydrogen
- the remaining two sp^3 hybrid orbitals each contain an unshared pair of electrons

Alcohols - Nomenclature

IUPAC names

- the parent chain is the longest chain that contains the -OH group
- number the parent chain in the direction that gives the -OH group the lower number
- change the suffix -e to -ol

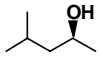
Common names

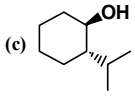
- name the alkyl group bonded to oxygen followed by the word alcohol

Alcohols - Nomenclature

Problem: Write the IUPAC name of each alcohol

(a) $CH_3(CH_2)_6CH_2OH$

(b) 

(c) 

Alcohols - Nomenclature

Compounds containing

- two -OH groups are named as diols,
- three -OH groups are named as triols, etc.

1,2-Ethanediol
(Ethylene glycol)

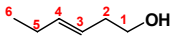
1,2-Propanediol
(Propylene glycol)

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

Alcohols - Nomenclature

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

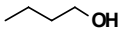
Alcohols - Nomenclature

Examples:

Ethanol
(Ethyl alcohol)

1-Propanol
(Propyl alcohol)

2-Propanol
(Isopropyl alcohol)

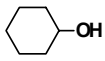


1-Butanol
(Butyl alcohol)

2-Butanol
(*sec*-Butyl alcohol)

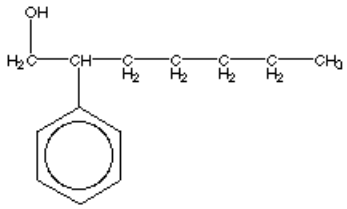
2-Methyl-1-propanol
(Isobutyl alcohol)

2-Methyl-2-propanol
(*tert*-Butyl alcohol)



Cyclohexanol
(Cyclohexyl alcohol)

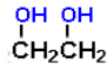
Name the alcohol



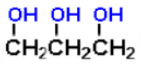
Common names

Ethyl alcohol CH_3CH_2-OH

ethylene glycol



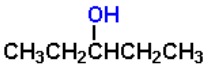
glycerol



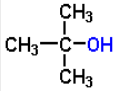
Classification of alcohols

Primary $CH_3CH_2CH_2CH_2-OH$

Secondary

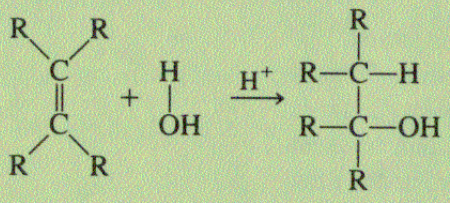


Tertiary.

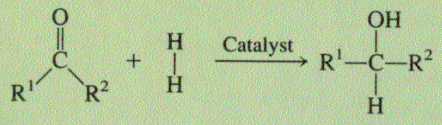


SUMMARY OF REACTIONS

Preparation of alcohols by hydration of alkenes:

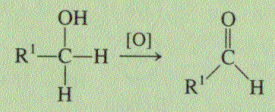


Preparation of alcohols by reduction of an aldehyde or ketone:



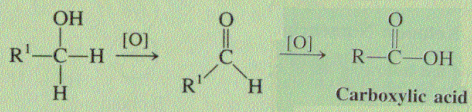
Aldehyde or ketone Water Alcohol

Oxidation of a primary alcohol:



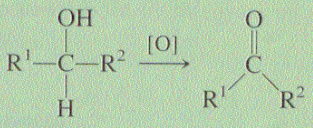
1° Alcohol An aldehyde

Oxidation of a primary alcohol:



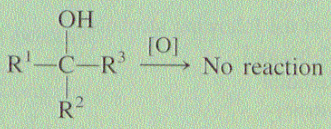
1° Alcohol An aldehyde

Oxidation of a secondary alcohol:



2° Alcohol A ketone

Oxidation of a tertiary alcohol:

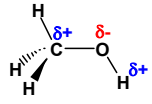


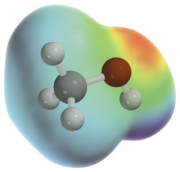
3° Alcohol

Physical Properties

Alcohols are polar compounds

- both the C-O and O-H bonds are polar covalent





Hydrogen Bonding

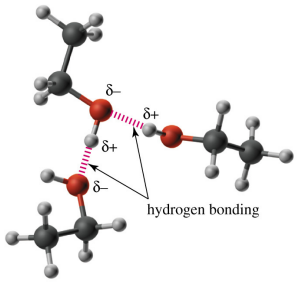
Alcohols associate in the liquid state by hydrogen bonding

Hydrogen bonding: the attractive force between a partial positive charge on hydrogen and a partial negative charge on a nearby oxygen, nitrogen, or fluorine atom

- the strength of hydrogen bonding in alcohols is approximately 2 to 5 kcal/mol
- hydrogen bonds are considerably weaker than covalent bonds (for example, 110 kcal/mol for an O-H bond)
- nonetheless, hydrogen bonding can have a significant effect on physical properties

Hydrogen Bonding

- Figure 8.3 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).



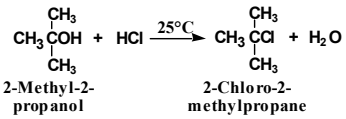
Boiling Points

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

Structural Formula	Name	Molecular Weight (g/mol)	Boiling Point (°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
$CH_3CH_2CH_2CH_2CH_2OH$	1-pentanol	88	138	2.3 g/100 g
$HOCH_2CH_2CH_2CH_2OH$	1,4-butanediol	90	230	infinite
$CH_3CH_2CH_2CH_2CH_2CH_3$	hexane	86	69	insoluble

Conversion of ROH to RX

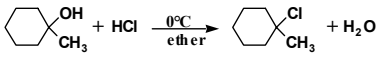
- water-soluble 3° alcohols react very rapidly with HCl, HBr, and HI



- low-molecular-weight 1° and 2° alcohols are unreactive under these conditions

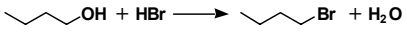
Conversion of ROH to RX

- water-insoluble 3° alcohols react by bubbling gaseous HCl through a solution of the alcohol dissolved in diethyl ether or THF



1-Methyl-cyclohexanol → 1-Chloro-1-methyl cyclohexane

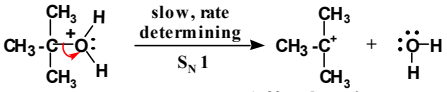
- 1° and 2° alcohols require concentrated HBr and HI to form alkyl bromides and iodides



1-Butanol → 1-Bromobutane (Butyl bromide)

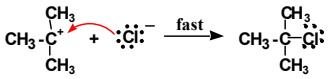
Reaction of a 3° ROH with HX

- Step 2: loss of H_2O from the oxonium ion gives a 3° carbocation intermediate



An oxonium ion → A 3° carbocation intermediate

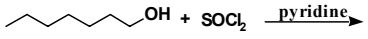
- Step 3: reaction with halide ion completes the reaction



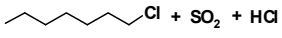
2-Chloro-2-methylpropane (*tert*-Butyl chloride)

Reaction with $SOCl_2$

Thionyl chloride, $SOCl_2$, is the most widely used reagent for conversion of alcohols to alkyl chlorides



1-Heptanol + Thionyl chloride



1-Chloroheptane

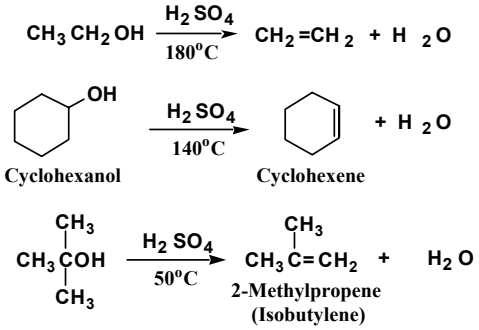
Dehydration of Alcohols

An alcohol can be converted to an alkene by elimination of H and OH from adjacent carbons (a β-elimination)

- 1° alcohols must be heated at high temperature in the presence of an acid catalyst, such as H_2SO_4 or H_3PO_4
- 2° alcohols undergo dehydration at somewhat lower temperatures
- 3° alcohols often require temperatures only at or slightly above room temperature

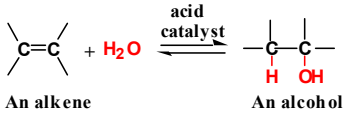
Dehydration of Alcohols

- examples:



Hydration-Dehydration

Acid-catalyzed hydration of an alkene and dehydration of an alcohol are competing processes

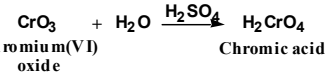


- large amounts of water favor alcohol formation
- scarcity of water or experimental conditions where water is removed favor alkene formation

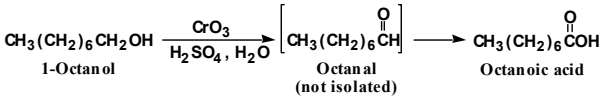
Oxidation of Alcohols

Oxidation of a 1° alcohol gives an aldehyde or a carboxylic acid, depending on the oxidizing agent and experimental conditions

- the most common oxidizing agent is chromic acid

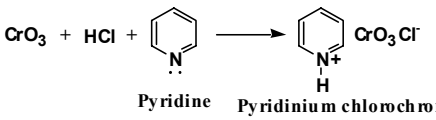


- chromic acid oxidation of 1-octanol gives octanoic acid

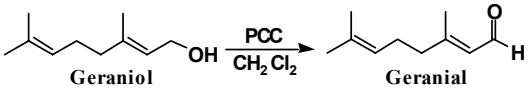


Oxidation of Alcohols

- to oxidize a 1° alcohol to an aldehyde, use PCC



- PCC oxidation of geraniol gives geranial



Tertiary alcohols are not oxidized by either of these reagents; they are resistant to oxidation

Acidity of Alcohols

- pK_a values for several low-molecular-weight alcohols

Compound	Structural Formula	pK_a	
hydrogen chloride	HCl	-7	Stronger acid
acetic acid	CH_3COOH	4.8	
methanol	CH_3OH	15.5	
water	H_2O	15.7	
ethanol	CH_3CH_2OH	15.9	
2-propanol	$(CH_3)_2CHOH$	17	
2-methyl-2-propanol	$(CH_3)_3COH$	18	Weaker acid

*Also given for comparison are pK_a values for water, acetic acid, and hydrogen chloride.

Reaction with Active Metals

Alcohols react with Li, Na, K, and other active metals to liberate hydrogen gas and form metal alkoxides

- Na is oxidized to Na^+ and H^+ is reduced to H_2

$$2\,CH_3CH_2OH + 2\,Na \longrightarrow 2\,CH_3CH_2O^-Na^+ + H_2$$

Sodium ethoxide

- alkoxides are somewhat stronger bases that OH^-
- alkoxides can be used as nucleophiles in nucleophilic substitution reactions
- they can also be used as bases in β-elimination reactions

Conversion of ROH to RX

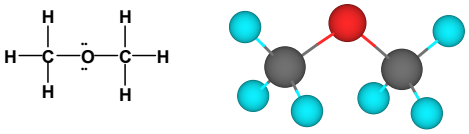
Conversion of an alcohol to an alkyl halide involves substitution of halogen for -OH at a saturated carbon

- the most common reagents for this purpose are the halogen acids, HX, and thionyl chloride, $SOCl_2$

Ethers - Structure

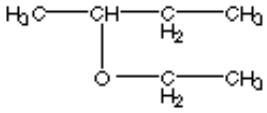
The functional group of an ether is an oxygen atom bonded to two carbon atoms

- oxygen is sp^3 hybridized with bond angles of approximately 109.5°
- in dimethyl ether, the C-O-C bond angle is 110.3°



Naming Ethers

2-propoxybutane



2-methoxyphenol
ethoxycyclopropane
isopropyl propyl ether
methyl phenyl ether

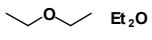
Ethers - Nomenclature

IUPAC

- the longest carbon chain is the parent alkane
- name the -OR group as an alkoxy substituent

Common names:

- name the groups bonded to oxygen followed by the word ether



Et$_2$O

Ethoxyethane
(Diethyl ether)

2-Methoxy-2-methylpropane
(methyl *tert*-butyl ether, MTBE)

trans-2-Ethoxycyclohexanol

Ethers - Nomenclature

Although cyclic ethers have IUPAC names, their common names are more widely used

Ethylene oxide

Tetrahydrofuran, THF

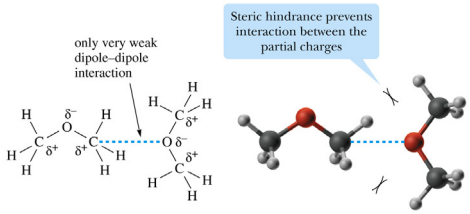
Tetrahydropyran

1,4-Dioxane

Ethers - Physical Properties

Ethers are polar molecules

- each C-O bond is polar covalent
- however, only weak attractive forces exist between ether molecules



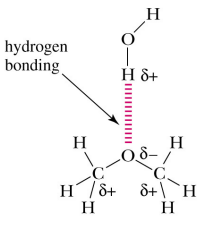
Ethers - Physical Properties

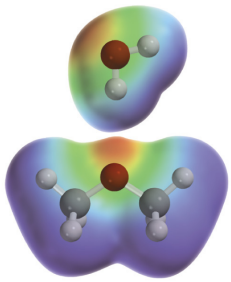
- boiling points are lower than those of alcohols

Structural Formula	Name	Molecular Weight	Boiling Point (°C)	Solubility in Water
CH_3CH_2OH	ethanol	46	78	infinite
CH_3OCH_3	dimethyl ether	46	-24	7.8 g/100 g
$CH_3CH_2CH_2CH_2OH$	1-butanol	74	117	7.4 g/100 g
$CH_3CH_2OCH_2CH_3$	diethyl ether	74	35	8 g/100 g
$CH_3CH_2CH_2CH_2CH_2OH$	1-pentanol	88	138	2.3 g/100 g
$HOCH_2CH_2CH_2CH_2OH$	1,4-butanediol	90	230	infinite
$CH_3CH_2CH_2CH_2OCH_3$	butyl methyl ether	88	71	slight
$CH_3OCH_2CH_2OCH_3$	ethylene glycol dimethyl ether	90	84	infinite

Ethers - Physical Properties

- ethers are hydrogen bond donors





Ethers - Physical Properties

- the effect of hydrogen bonding is illustrated by comparing the boiling points of ethanol and dimethyl ether

CH_3CH_2OH	CH_3OCH_3
Ethanol	Dimethyl ether
bp 78°C	bp -24°C

Reactions of Ethers

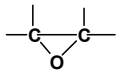
Ethers resemble hydrocarbons in their resistance to chemical reaction

- they do not react with strong oxidizing agents such as chromic acid, H_2CrO_4
- they are not affected by most acids and bases at moderate temperatures

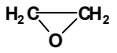
Because of their good solvent properties and general inertness to chemical reaction, ethers are excellent solvents in which to carry out organic reactions

Epoxides

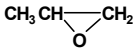
Epoxide: a cyclic ether in which oxygen is one atom of a three-membered ring



Functional group of an epoxide

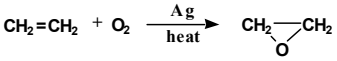


Ethylene oxide



Propylene oxide

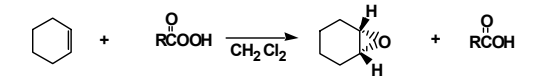
- ethylene oxide is synthesized from ethylene and O_2



Ethylene — Ethylene oxide

Epoxides

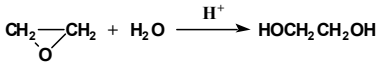
- other epoxides are synthesized from an alkene and a peroxycarboxylic acid, RCO_3H



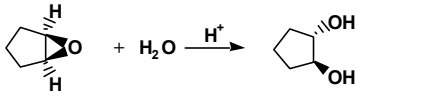
Cyclohexene — A peroxy-carboxylic acid — 1,2-Epoxycyclohexane (Cyclohexene oxide) — A carboxylic acid

Reactions of Epoxides

- ethers are generally unreactive to aqueous acid
- epoxides, however, react readily because of the angle strain in the three-membered ring
- reaction of an epoxide with aqueous acid gives a glycol



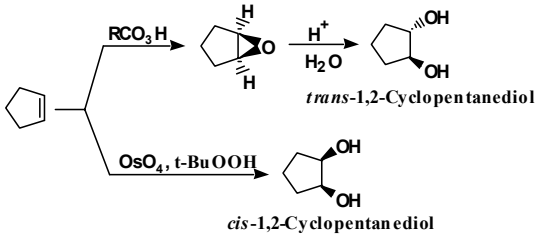
Ethylene oxide — 1,2-Ethanediol (Ethylene glycol)



1,2-Epoxycyclopentane (Cyclopentene oxide) — *trans*-1,2-Cyclopentanediol

A Cycloalkene to a Glycol

- both cis and trans glycols can be prepared

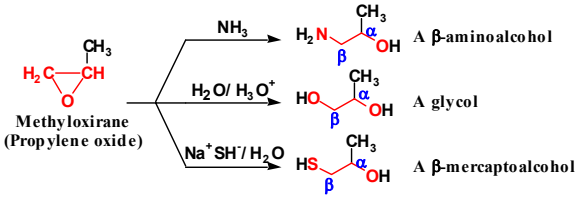


trans-1,2-Cyclopentanediol

cis-1,2-Cyclopentanediol

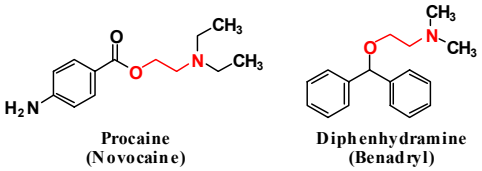
Other Epoxide Ring Openings

- the value of epoxides lies in the number of nucleophiles that will bring about ring opening, and the combinations of functional groups that can be synthesized from them



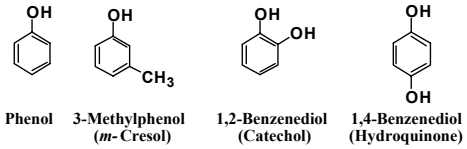
Epoxides as Building Blocks

- following are structural formulas for two common drugs, each synthesized in part from ethylene oxide



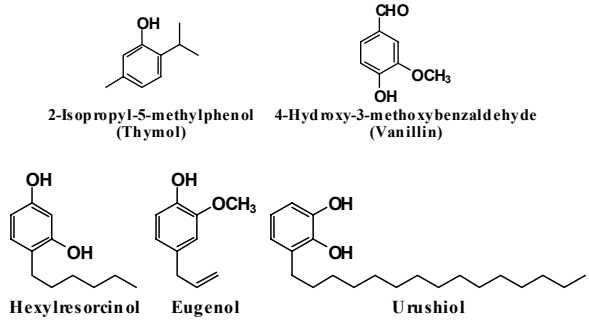
Phenols

The functional group of a phenol is an -OH group bonded to a benzene ring



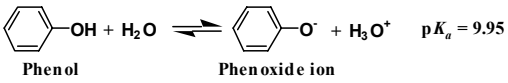
Phenols

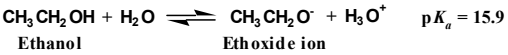
- some phenols



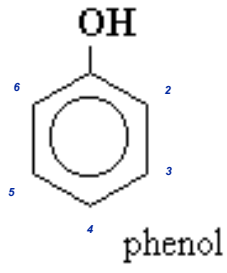
Acidity of Phenols

Phenols are significantly more acidic than alcohols

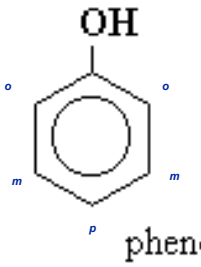




Naming Phenols

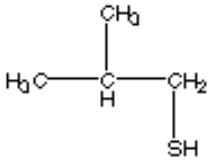


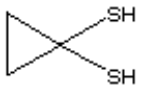
phenol



phenol

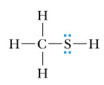
Naming thiols





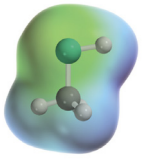
Thiols - Structure

The functional group of a thiol is an -SH (sulfhydryl) group bonded to an *sp*^{3} hybridized carbon



(a)

(b)



Methanethiol. The electronegativities of carbon and sulfur are virtually identical (2.5 each), while sulfur is slightly more electronegative than hydrogen (2.5 versus 2.1). The electron density model shows some slight partial positive charge on hydrogen of the S—H group and some slight partial negative charge on sulfur.

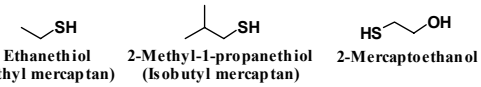
Thiols - Nomenclature

IUPAC names:

- the parent chain is the longest chain containing the -SH group
- add -thiol to the name of the parent chain

Common names:

- name the alkyl group bonded to sulfur followed by the word mercaptan
- alternatively, indicate the -SH by the prefix mercapto

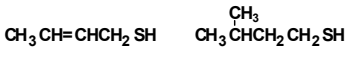


Ethanethiol (Ethyl mercaptan) | 2-Methyl-1-propanethiol (Isobutyl mercaptan) | 2-Mercaptoethanol

Thiols - Physical Properties

Low-molecular-weight thiols have a STENCH

Present in the scent of skunks:



2-Butene-1-thiol | 3-Methyl-1-butanethiol (Isobutyl mercaptan)

Natural gas odorants:

2-Methyl-2-propanethiol (*tert*-Butyl mercaptan) | 2-Propanethiol (Isopropyl mercaptan)

Thiols - Physical Properties

The difference in electronegativity between S and H is 2.5 - 2.1 = 0.4

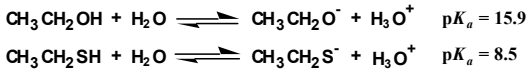
Because of their low polarity, thiols

- show little association by hydrogen bonding
- have lower boiling points and are less soluble in water than alcohols of comparable MW

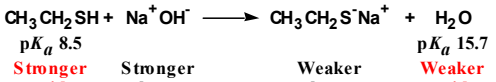
Thiol	Boiling Point (°C)	Alcohol	Boiling Point (°C)
methanethiol	6	methanol	65
ethanethiol	35	ethanol	78
1-butanethiol	98	1-butanol	117

Acidity of Thiols

Thiols are stronger acids than alcohols



Thiols react with strong bases to form salts

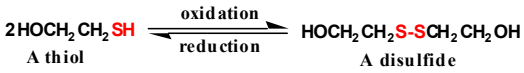


Stronger acid | Stronger base | Weaker base | Weaker acid

Oxidation of Thiols

thiols are oxidized by a variety of oxidizing agents, including O_2, to disulfides

disulfides, in turn, are easily reduced to thiols by several reagents



A thiol — A disulfide

- this easy interconversion between thiols and disulfides is very important in protein chemistry