241 Chem

CH-5

Thiols and Sulfides

Learning Objectives

By the end of this chapter the student will Know:

- General formula of Thiols & Sulfides
- Nomenclature of Thiols & Sulfides
- Physical Properties of Thiols & Sulfides
- Preparations of Thiols & Sulfides
- Reactions of Thiols & Sulfides

Structure of Thiols and sulfides

- Thiols, general formula RSH, are the sulphur analogues of alcohols.
- The functional group of a thiol is SH group bonded to an sp^3 hybridized carbon.
- Sulfides or Thioethers, general formula RSR, are the sulphur analogues of ethers .

CH_3SH

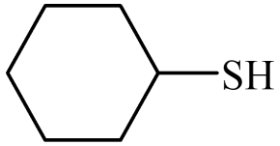
methanethiol
(methyl mercaptan)

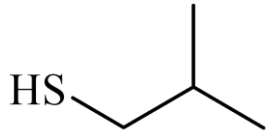
$CH_3CH_2SCH_2CH_3$

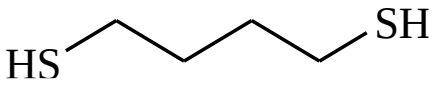
Ethylthioethane
Diethyl sulfide

Nomenclature of Thiols and sulfides

- In the IUPAC system, thiols are named by selecting as the parent alkane the longest chain of carbon atoms that contains the -SH group. To show that the compound is a thiol, retain the final -*e* in the name of the parent alkane and add the suffix -*thiol*.
- The location of the -SH group takes precedence over alkyl groups and halogens in numbering the parent chain.
- In the IUPAC system, -OH takes precedence over -SH in both numbering and naming. In compounds containing these two functional groups, an -SH group is indicated by the IUPAC prefix *mercapto- or sulfanyl-*
- Common names for simple thiols are derived by naming the alkyl group bonded to -SH and adding the word *mercaptan*.
- In the IUPAC system of sulfides, the shorter alkyl group and the sulfur are named as an *alkylthio* group attached to the longer alkane.
- The common names of sulfides are derived in the same way as those of ethers but end in the word *sulfide*.







IUPAC name: 1-butanethiol

Common name: *n*-Butyl mercaptan

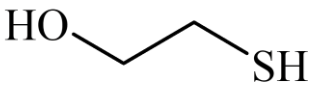
Cyclohexanethiol

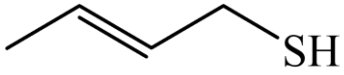
Cyclohexanyl mercaptan

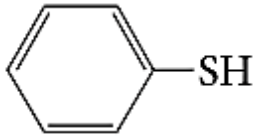
2-Methyl-1-propanethiol

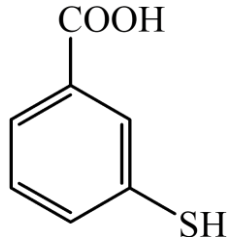
Isopentyl mercaptan

Butane-1,4-dithiol









IUPAC name: 2-Mercaptoethanol

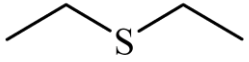
Common name: β-Mercaptoethanol

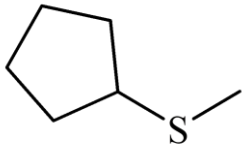
2-Butene-1-thiol

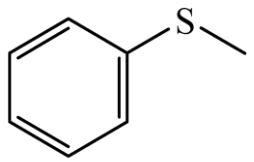
thiophenol

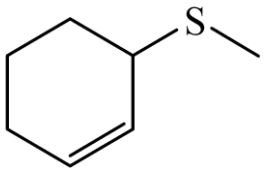
Phenyl mercaptan

3-Mercaptobenzoic acid









IUPAC name: Ethylthioethane

Ethylsulfanylethane

Common name: Diethyl sulfide

(Methylthio)cyclopentane

(Methylsulfanyl)cyclopentane

Cyclopentyl methyl sulfide

Methylthiobenzene

Methylsulfanylbenzene

Methyl Phenyl sulfid

3-Methylthiocyclohexene

3-Methylsulfanylcyclohexene

Physical Properties of thiols

- The S-H bond in thiols is less polar than O-H bond in alcohols, since Sulphur is less electronegative than the oxygen atom. Thus, thiols form much weaker hydrogen bonding than alcohols, and have lower boiling points than analogous alcohols.

	$CH_3CH_2CH_2CH_2OH$	$CH_3CH_2CH_2CH_2SH$
	1-Butanol	1-butanethiol
Boiling point:	117°C	98°C

Acidity and basicity of thiols

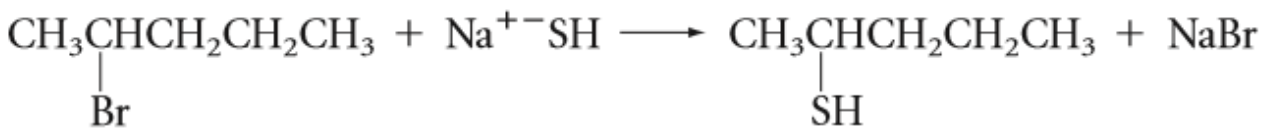
- Thiols are stronger acids (pKa 10) than alcohols (pKa 15).
- Thiolate ions (e.g. $CH_3CH_2S^-$) are stronger nucleophiles than corresponding alkoxides ($CH_3CH_2O^-$). Conversely, thiols are stronger acids than corresponding alcohols.

$$RSH + Na^+OH^- \longrightarrow RS^-Na^+ + HOH$$

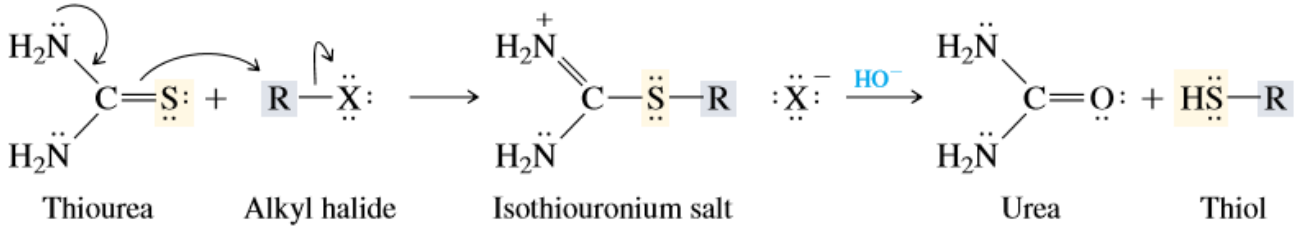
a sodium thiolate

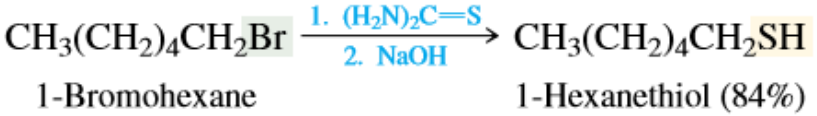
Preparation Of Thiols

1- Nucleophilic substitution reaction of alkyl halides by sodium hydrosulphide (NaSH) {excess of KOH (NaOH) and hydrogen sulfide H_2S}.



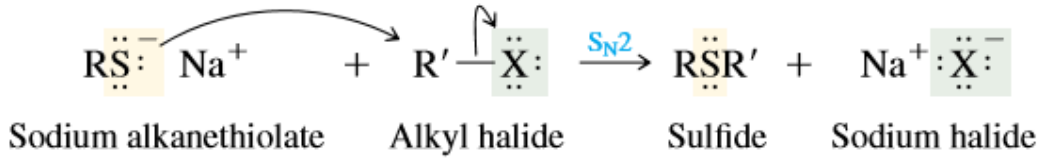
2- Nucleophilic substitution reaction of alkyl halides by thiourea ($NH_2(C{=}S)NH_2$)



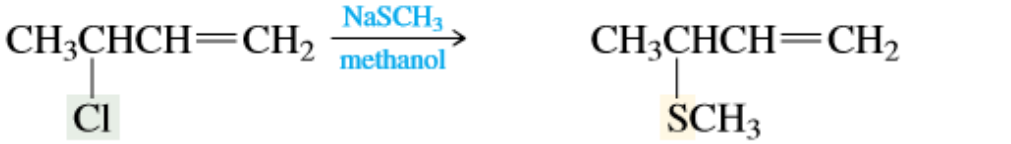


Preparation Of sulfide

1- Substitution reaction of alkyl halides with thiolates to form thioethers (sulfides).



Sodium alkanethiolate | Alkyl halide | Sulfide | Sodium halide



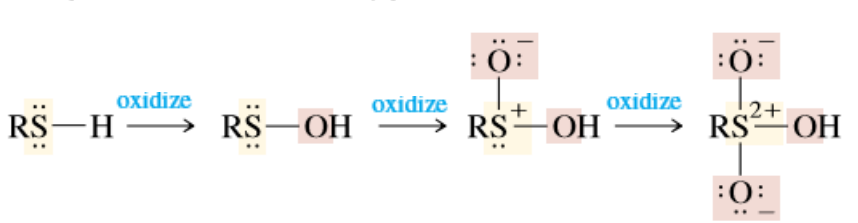
3-Chloro-1-butene

Methyl 1-methylallyl sulfide (62%)

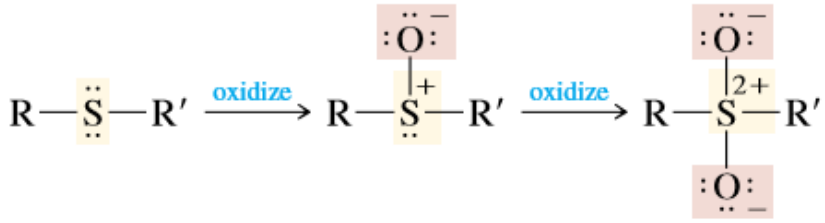
Reactions of thiols and sulfides

1. Oxidation:

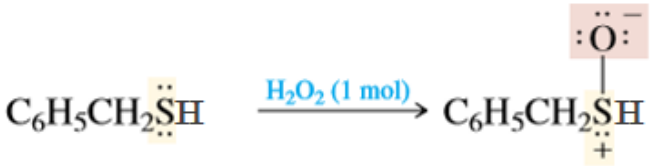
a- Oxidation of thiols to compounds with C=S not occur. Only sulfur is oxidized, not carbon, and compounds containing in various oxidation state are possible by sodium metaperiodate ($NaIO_4$) or Peroxy acid (RCOOOH) or Hydrogen peroxide (H_2O_2).



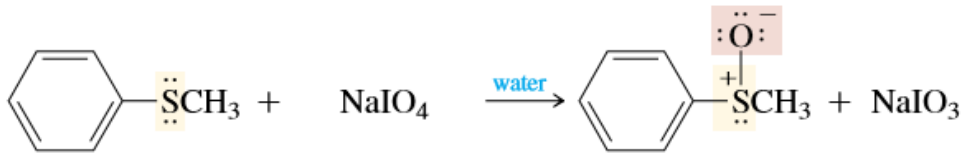
Thiol — Sulfenic acid RSOH — Sulfinic acid RSO_2H — Sulfonic acid RSO_3H



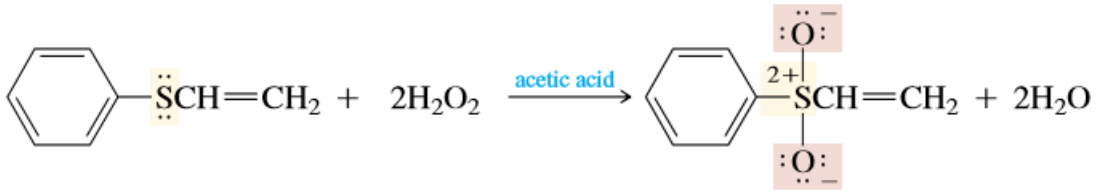
Sulfide — Sulfoxide RSOR` — Sulfone $RSO_2R`$



$C_6H_5CH_2SOH$



$C_6H_5SOCH_3$

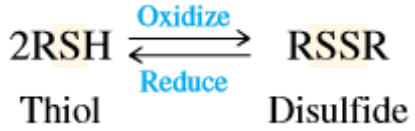


$C_6H_5SO_2CH{=}CH_2$

Reactions of thiols and sulfides

1. Oxidation:

b-The oxidation of thiols to disulfides by iodine (I_2).



2- Alkylation of Sulfides: Sulfonium Salts