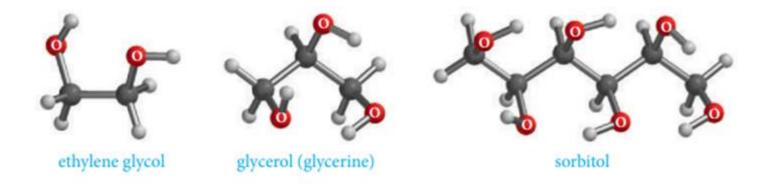
PHA284 Organic Chemistry II

Ankara University
Faculty of Pharmacy
Department of Pharmaceutical Chemistry

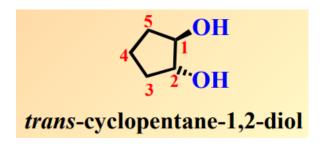
POLYOLS

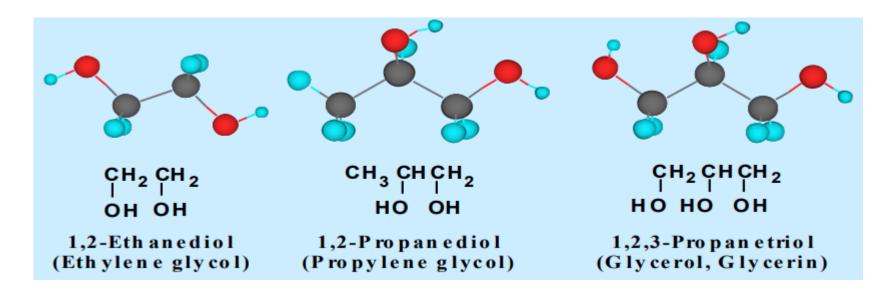
POLYOLS

Compounds with more than one hydroxyl groups are called polyols.



Nomenclature





Physical properties

- Increased viscosity
- Increased boiling points
- Increased solubility in polar solvents
- sweet taste

Preparation of Diols

1) Nucleophilic Substitution Reactions

$$H_2C^-CH_2^-CH_2 \xrightarrow{2KOH} H_2C^-CH_2^-CH_2$$
Br OH OH

Preparation of Diols

2) α -Glycol synthesis

Chemical Properties

Reaction with alkali hydroxides (KOH, NaOH)

Ethers and Epoxides

Ethers and Epoxides

Ethers are compounds that have two organic groups connected to a single oxygen atom.

Epoxides are cyclic, three-membered ring ethers.

The general formula for an ether is R-O-R'

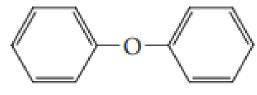
Nomenclature

CH₃CH₂-O-CH₃

ethyl methyl ether

CH₃CH₂-O-CH₂CH₃

diethyl ether (the prefix di- is sometimes omitted)



diphenyl ether

Physical Properties of Ethers

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

*Ethers are less dense than water

*They have lower boiling points (bp's) than alcohols with an equal number of carbon atoms.

Preparation of Ethers

Dehydration of alcohol

$$\begin{array}{c} CH_{3}CH_{2}OH + HOCH_{2}CH_{3} \xrightarrow{H_{2}SO_{4}} CH_{3}CH_{2}OCH_{2}CH_{3} + H_{2}O\\ ethanol & diethyl \ ether \end{array}$$

Preparation of Ethers

Williamson ether synthesis

$$2 \text{ ROH} + 2 \text{ Na} \longrightarrow 2 \text{ RO}^-\text{Na}^+ + \text{H}_2$$

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

Reaction of Ethers

Cleavage of Ethers

$$R - \overset{\cdot \cdot \cdot}{\circ} - R' + H^{+} \xrightarrow{\longleftarrow} R - \overset{\cdot \cdot \cdot}{\circ} - R'$$

$$C_{4}H_{9}-O_{-}C_{4}H_{9} + H_{1} \longrightarrow C_{4}H_{9}I + C_{4}H_{9}OH$$

$$C_{2}H_{5}-O_{-}CH_{3} + H_{1} \longrightarrow C_{2}H_{5}OH + CH_{3}I$$

Reaction of Ethers

Oxidation;

$$R-CH_2-O-CH_2-R'$$
 $\xrightarrow{O_2}$ $R-COOH + R'-COOH$

$$R-O-CH_2-R' \xrightarrow{O_2} R-O-O-CH_2R'$$
Peroxide

Physical properties

- Lower boiling points compared to corresponding alcohols.
- Very slightly soluble in water
- Usually immiscible with water
- Inflammable (small embers)

Epoxides

Epoxides (or oxiranes)

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

Preparation of Epoxides

$$CH_2$$
= $CH_2 + O_2$ $\xrightarrow{\text{silver catalyst}}$ CH_2 — CH_2
 O
ethylene oxide

Reaction of Epoxides

$$\begin{array}{c} \text{CH}_2 - \text{CH}_2 + \text{H} - \text{OH} \xrightarrow{\text{H}^+} \begin{array}{c} \text{CH}_2 - \text{CH}_2 \\ \text{OH} & \text{OH} \end{array}$$
 ethylene oxide ethylene glycol

THIOLS

THIOLS

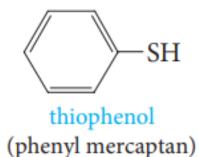
The -SH group, called the sulfhydryl group, is the functional group of thiols. Thiols are named as follows:



CH₃SH

methanethiol (methyl mercaptan) CH₃CH₂CH₂CH₂SH

1-butanethiol (*n*-butyl mercaptan)



Preparation of Thiols

1) Nucleophlic Substitution Reaction

$$R^-X + KSH \longrightarrow R^-SH + KX$$

1) H₂S addition to alkenes;

$$R-CH=CH_2 + HSH \longrightarrow R-CH-CH_2$$

SH H

Chemical Reactions

1) Reaction with sodium:

$$R-SH + Na^{\circ} \longrightarrow R-SNa + 1/2 H_2$$

2) Reaction with aldehydes and ketones:

$$R-C$$
 H
 HSR'
 $R-CH$
 SR'
 $R-CH$
 SR'
 SR'
 SR'

Chemical Properties

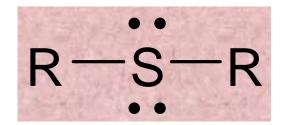
3) Oxidation:

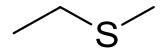
$$R-SH + I_2 + HS-R \longrightarrow R-S-S-R + 2HI$$

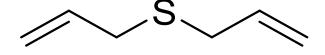
THIOETHERS

THIOETHERS

Thioethers (also called sulfides) are the sulfur analogs of ethers.







ethyl(methyl)sulfane

Diallyl sulfide

Preparation of Thioethers

$$R-X + R'-S^-Na^+ \longrightarrow R-S-R' + NaX$$

Chemical Properties

1) Reaction with alkyl halides;

$$R-\overset{\cdot}{S}-R+R'-X \longrightarrow R-\overset{R}{S}\overset{\cdot}{S}\overset{\cdot}{X}^{\bigcirc}$$

$$R-\overset{\cdot}{S}-R+R'-X \longrightarrow R-\overset{\cdot}{S}\overset{\cdot}{S}$$

$$R'$$
Trialkylsulfonium halide

2) Oxidation;

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