

3.9: ETHERS, EPOXIDES AND SULFIDES

learning objectives

- name ethers, epoxides, and sulfides using IUPAC (systematic) and selected common name nomenclature
- draw the structure of ethers, epoxides, and sulfides from IUPAC (systematic) and selected common names

Note: Heterocyclic oxygen compounds are included for the sake of completion. Their nomenclature may or may not be required by the professor and requires additional instruction. Make sure to ask.

ETHERS

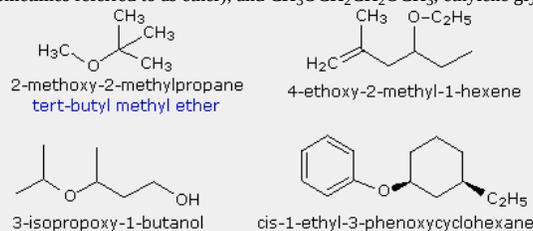
Ethers are compounds having two alkyl or aryl groups bonded to an oxygen atom, as in the formula R^1-O-R^2 . The ether functional group does not have a characteristic IUPAC nomenclature suffix, so it is necessary to designate it as a substituent. To do so the common alkoxy substituents are given names derived from their alkyl component (below):

Alkyl Group	Name	Alkoxy Group	Name
CH_3-	Methyl	CH_3O-	Methoxy
CH_3CH_2-	Ethyl	CH_3CH_2O-	Ethoxy
$(CH_3)_2CH-$	Isopropyl	$(CH_3)_2CHO-$	Isopropoxy
$(CH_3)_3C-$	tert-Butyl	$(CH_3)_3CO-$	tert-Butoxy
C_6H_5-	Phenyl	C_6H_5O-	Phenoxy

The smaller, shorter alkyl group becomes the alkoxy substituent. The larger, longer alkyl group side becomes the alkane base name. Each alkyl group on each side of the oxygen is numbered separately. The numbering priority is given to the carbon closest to the oxygen. The alkoxy side (shorter side) has an "-oxy" ending with its corresponding alkyl group. For example, $CH_3CH_2CH_2CH_2CH_2-O-CH_2CH_2CH_3$ is 1-propoxypentane. If there is cis or trans stereochemistry, the same rule still applies.

Example

Examples are: $CH_3CH_2OCH_2CH_3$, diethyl ether (sometimes referred to as ether), and $CH_3OCH_2CH_2OCH_3$, ethylene glycol dimethyl ether (glyme).



COMMON NAMES

Simple ethers are given common names in which the alkyl groups bonded to the oxygen are named in alphabetical order followed by the word "ether". The top left example shows the common name in blue under the IUPAC name. Many simple ethers are symmetrical, in that the two alkyl substituents are the same. These are named as "dialkyl ethers". If we read the word "ether", the author is most likely communicating the compound $CH_3CH_2OCH_2CH_3$, ethoxyethane (diethyl ether), but we do not know with certainty - another example of the importance of accurate nomenclature.

EPOXIDES

An **epoxide** is a cyclic ether with three ring atoms. These rings approximately define an equilateral triangle, which makes it highly strained. The strained ring makes epoxides more reactive than other ethers. Simple epoxides are named from the parent compound ethylene oxide or oxirane, such as in *chloromethyloxirane*. As a functional group, epoxides feature the *epoxy* prefix, such as in the compound *1,2-epoxycycloheptane*, which can also be called *cycloheptene epoxide*, or simply *cycloheptene oxide*.



A generic epoxide.



The chemical structure of the epoxide glycidol, a common chemical intermediate

A polymer formed by reacting epoxide units is called a *polyepoxide* or an *epoxy*. Epoxy resins are used as adhesives and structural materials. Polymerization of an epoxide gives a polyether, for example ethylene oxide polymerizes to give polyethylene glycol, also known as polyethylene oxide.

SULFIDES (THIOETHERS)

A thioether is a functional group in organosulfur chemistry with the connectivity C-S-C as shown below. Like many other sulfur-containing compounds, volatile thioethers have foul odors.[1] A thioether is similar to an ether except that it contains a sulfur atom in place of the oxygen. The grouping of oxygen and sulfur in the periodic table suggests that the chemical properties of ethers and thioethers are somewhat similar.



General structure of a thioether with the blue marked functional group.

NOMENCLATURE

Thioethers are sometimes called sulfides, especially in the older literature and this term remains in use for the names of specific thioethers. The two organic substituents are indicated by the prefixes. $(\text{CH}_3)_2\text{S}$ is called **dimethylsulfide**. Some thioethers are named by modifying the common name for the corresponding ether. For example, $\text{C}_6\text{H}_5\text{SCH}_3$ is methyl phenyl sulfide, but is more commonly called thioanisole, since its structure is related to that for **anisole**, $\text{C}_6\text{H}_5\text{OCH}_3$.

STRUCTURE AND PROPERTIES

Thioether is an angular functional group, the C-S-C angle approaching 90° . The C-S bonds are about 180 pm.

Thioethers are characterized by their strong odors, which are similar to thiol odor. This odor limits the applications of volatile thioethers. In terms of their physical properties they resemble ethers but are less volatile, higher melting, and less hydrophilic. These properties follow from the polarizability of the divalent sulfur center, which is greater than that for oxygen in ethers.

HETEROCYCLES WITH OXYGEN

In cyclic ethers (heterocycles), one or more carbons are replaced with oxygen. Often, it's called heteroatoms, when carbon is replaced by an oxygen or any atom other than carbon or hydrogen. In this case, the stem is called the oxacycloalkane, where the prefix "oxa-" is an indicator of the replacement of the carbon by an oxygen in the ring. These compounds are numbered starting at the oxygen and continues around the ring. For example,



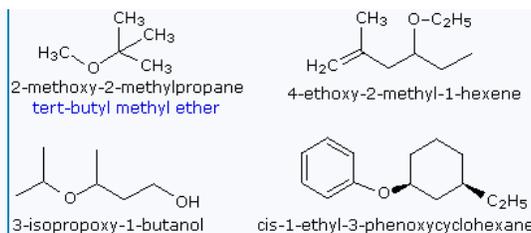
If a substituent is an alcohol, the alcohol has higher priority. However, if a substituent is a halide, ether has higher priority. If there is both an alcohol group and a halide, alcohol has higher priority. The numbering begins with the end that is closest to the higher priority substituent. There are ethers that contain multiple ether groups that are called **cyclic polyethers** or **crown ethers**. These are also named using the IUPAC system.

THIOPHENES

Thiophenes are a special class of thioether-containing heterocyclic compounds. Because of their **aromatic** character, they are non-nucleophilic. The nonbonding electrons on sulfur are **delocalized** into the π -system. As a consequence, thiophene exhibits few properties expected for a thioether - thiophene is non-nucleophilic at sulfur and, in fact, is sweet-smelling. Upon **hydrogenation**, thiophene gives tetrahydrothiophene, $\text{C}_4\text{H}_8\text{S}$, which indeed does behave as a typical thioether.

Example

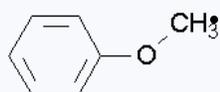
Examples of ethers include $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$, diethyl ether (sometimes referred to as ether), and $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_3$, ethylene glycol dimethyl ether (glyme).



COMMON NAMES

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- **anisole** (try naming anisole by the other two conventions).



oxirane or 1,2-epoxyethane, ethylene oxide, dimethylene oxide, oxacyclopropane,



• **furan** (this compound is aromatic)

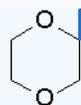


tetrahydrofuran



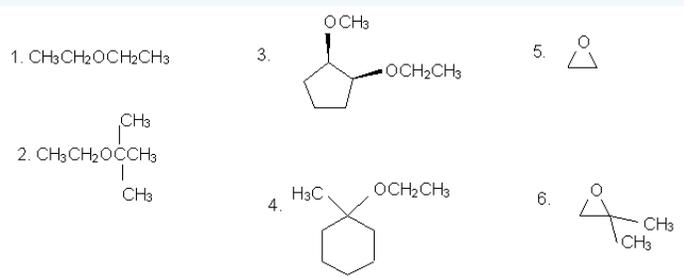
oxacyclopentane, 1,4-epoxybutane, tetramethylene oxide,

dioxane or 1,4-dioxacyclohexane



Exercise

Give the IUPAC and common name (if possible) for each compound respectively.



Answer

1. ethoxyethane; diethyl ether
2. 2-ethoxy-2-methyl-propane; ethyl t-butyl ether (ethyl tert-butyl ether)
3. cis-1-ethoxy-2-methoxycyclopentane; no common name possible
4. 1-ethoxy-1-methylcyclohexane; no common name possible
5. 1,2-epoxyethane; ethylene oxide or dimethylene oxide or oxacyclopropane or oxirane
6. 2,2-dimethyloxirane

CONTRIBUTORS AND ATTRIBUTIONS

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