14-3 Nomenclature of Ethers

We have been using the common nomenclature of ethers, which is sometimes called the *alkyl alkyl ether* system. The IUPAC system, generally used with more complicated ethers, is sometimes called the *alkoxy alkane* system. Common names are almost always used for simple ethers.

Application: Oxygenated Gasoline

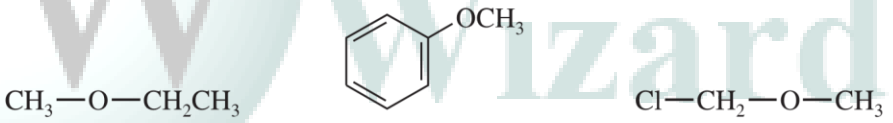
The Clean Air Act of 1990 requires the use of "oxygenated gasoline" in areas with severe air pollution. The preferred "oxygenate" was often MTBE because it blends well with gasoline, lowers the amounts of pollutants in the exhaust, burns well without engine modifications, and has a low toxicity. In 1999, California began a phaseout of MTBE from the gasoline in that state because of concerns that it was polluting groundwater.

14-3A Common Names (Alkyl Alkyl Ether Names)

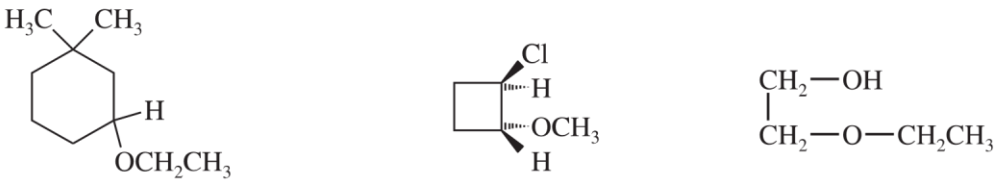
Common names of ethers are formed by naming the two alkyl groups on oxygen and adding the word *ether*. Under the current system, the alkyl groups should be named in alphabetical order, but many people still use the old system, which named the groups in order of increasing complexity. For example, if one of the alkyl groups is methyl and the other is *tert*-butyl, the current common name should be "*tert*-butyl methyl ether," but most chemists use the older common name, "methyl *tert*-butyl ether" (or MTBE). If both groups are methyl, the name is "dimethyl ether." If just one alkyl group is described in the name, it implies the ether is symmetrical, as in "ethyl ether."

14-3B IUPAC Names (Alkoxy Alkane Names)

IUPAC names use the more complex alkyl group as the root name, and the rest of the ether as an **alkoxy group.** For example, cyclohexyl methyl ether is named methoxycyclohexane. This systematic nomenclature is often the only clear way to name complex ethers.



IUPAC name:	methoxyethane	methoxybenzene	chloromethoxymethane
common name:	ethyl methyl ether	methyl phenyl ether, or anisole	chloromethyl methyl ether

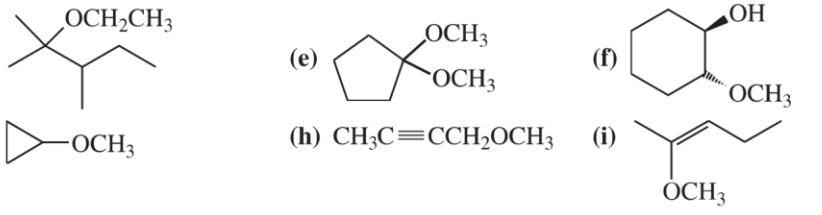


IUPAC name:	3-ethoxy-1,1-dimethylcyclohexane	*trans*-1-chloro-2-methoxycyclobutane	2-ethoxyethanol

PROBLEM 14-4

Give a common name (when possible) and a systematic name for each compound.

(a) $CH_3OCH{=}CH_2$ **(b)** $CH_3CH_2OCH(CH_3)_2$ **(c)** $ClCH_2CH_2OCH_3$



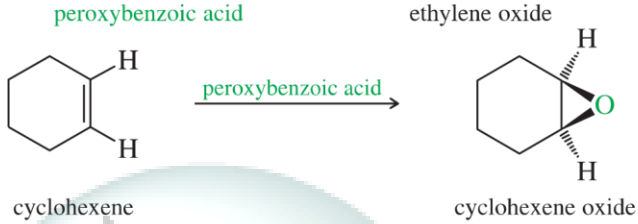
(d) **(e)** **(f)**

(g) **(h)** $CH_3C{\equiv}CCH_2OCH_3$ **(i)**

14-3C Nomenclature of Cyclic Ethers

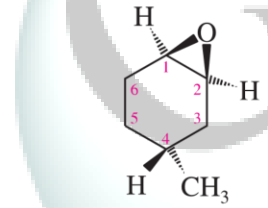
Cyclic ethers are our first examples of **heterocyclic compounds,** containing a ring in which a ring atom is an element other than carbon. This atom, called the **heteroatom,** is numbered 1 in numbering the ring atoms. Heterocyclic ethers are especially important and useful ethers.

Epoxides (Oxiranes) We have already encountered some of the chemistry of epoxides in Section 8-12. **Epoxides** are three-membered cyclic ethers, usually formed by peroxyacid oxidation of the corresponding alkenes. The common name of an epoxide is formed by adding "oxide" to the name of the alkene that is oxidized. The following reactions show the synthesis and common names of two simple epoxides.

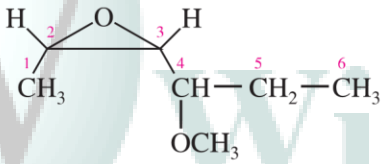


cyclohexene — cyclohexene oxide

One systematic method for naming epoxides is to name the rest of the molecule and use the term "epoxy" as a substituent, giving the numbers of the two carbon atoms bonded to the epoxide oxygen.

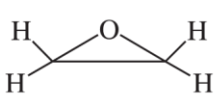


trans-1,2-epoxy-4-methylcyclohexane

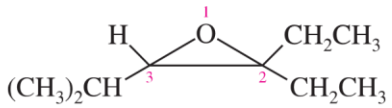


cis-2,3-epoxy-4-methoxyhexane

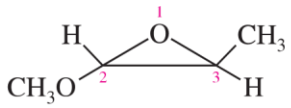
Another systematic method names epoxides as derivatives of the parent compound, ethylene oxide, using "oxirane" as the systematic name for ethylene oxide. In this system, the ring atoms of a heterocyclic compound are numbered starting with the heteroatom and going in the direction to give the lowest substituent numbers. The "epoxy" system names are also listed (in blue) for comparison. Note that the numbering is different for the "epoxy" system names, which number the longest chain rather than the ring.



oxirane
1,2-epoxyethane

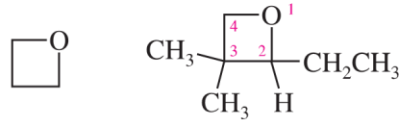


2,2-diethyl-3-isopropyloxirane
3,4-epoxy-4-ethyl-2-methylhexane



trans-2-methoxy-3-methyloxirane
1,2-epoxy-1-methoxypropane

Oxetanes The least common cyclic ethers are the four-membered **oxetanes.** Because these four-membered rings are strained, they are more reactive than larger cyclic ethers and open-chain ethers. They are not as reactive as the highly strained oxiranes (epoxides), however.

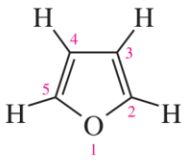


oxetane — 2-ethyl-3,3-dimethyloxetane

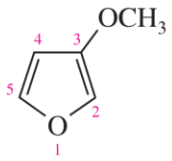
Application: Fumigant

Ethylene oxide has been used as a fumigant for foods, textiles, and soil, and for sterilizing biomedical instruments. It readily diffuses through materials without damaging them. Its antibacterial effect is probably due to its ability to alkylate critical cellular enzymes.

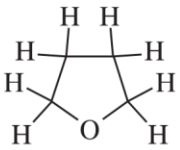
Furans (Oxolanes) The five-membered cyclic ethers are commonly named after an aromatic member of this group, **furan.** We consider the aromaticity of furan and other heterocycles in Chapter 16. The systematic term **oxolane** is also used for a five-membered ring containing an oxygen atom.



furan



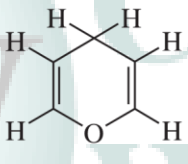
3-methoxyfuran



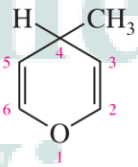
tetrahydrofuran (THF)
(oxolane)

The saturated five-membered cyclic ether resembles furan but has four additional hydrogen atoms. Therefore, it is called *tetrahydrofuran* (THF). One of the most polar ethers, tetrahydrofuran is an excellent nonhydroxylic organic solvent for polar reagents. Grignard reactions sometimes succeed in THF even when they fail in diethyl ether.

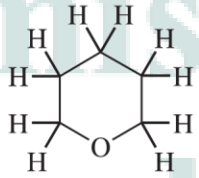
Pyrans (Oxanes) The six-membered cyclic ethers are commonly named as derivatives of **pyran,** an unsaturated ether. The saturated compound has four more hydrogen atoms, so it is called *tetrahydropyran* (THP). The systematic term **oxane** is also used for a six-membered ring containing an oxygen atom.



pyran



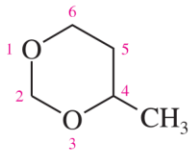
4-methylpyran



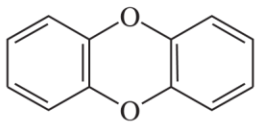
tetrahydropyran (THP)
(oxane)

Dioxanes Heterocyclic ethers with two oxygen atoms in a six-membered ring are called **dioxanes.** The most common form of dioxane is the one with the two oxygen atoms in a 1,4-relationship. 1,4-Dioxane is miscible with water, and it is widely used as a polar solvent for organic reactions.

1,4-dioxane

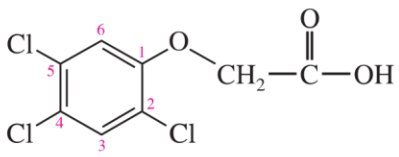


4-methyl-1,3-dioxane

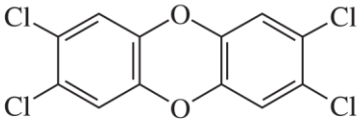


dibenzo-1,4-dioxane (dioxin)

Dioxin is a common name for dibenzo-1,4-dioxane, which is 1,4-dioxane fused with two benzene rings. The name "dioxin" is often used incorrectly in the news media for 2,3,7,8-tetrachlorodibenzodioxin (TCDD), a toxic contaminant in the synthesis of the herbicide called 2,4,5-T or Agent Orange. Surprisingly, TCDD has been in the environment for many millions of years because it is also formed in forest fires. Most dioxins are toxic and carcinogenic (cause cancer) because they associate with DNA and cause a misreading of the genetic code.



2,4,5-trichlorophenoxyacetic acid
(2,4,5-T or Agent Orange)



2,3,7,8-tetrachlorodibenzodioxin
(TCDD, incorrectly "dioxin")

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