

BOOKS

- 1) Organic Chemistry Structure and Function, K. Peter C. Vollhardt, Neil Schore, 6th Edition
- 2) Organic Chemistry, T. W. Graham Solomons, Craig B. Fryhle
- 3) Organic Chemistry: A Short Course, H. Hart, L. E. Craine, D. J. Hart, C. M. Hadad,
- 4) Organic Chemistry: A Brief Course, R. C. Atkins, F.A. Carey

2. ETHERS AND EPOXIDES

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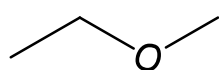
2.4.2.1 Acid-catalyzed Reactions

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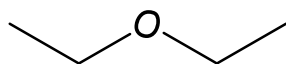
Ethers differ from alcohols in that the oxygen atom of an ether is bonded to two carbon atoms. The hydrocarbon groups may be alkyl, alkenyl, vinyl, alkynyl, or aryl. Ethers have boiling points that are roughly comparable with those of hydrocarbons of the same molecular weight. Ethers, are able to form hydrogen bonds with compounds such as water. Ethers, therefore, have solubility's in water that are similar to those of alcohols of the same molecular weight and that are very different from those of hydrocarbons.

2.1 Nomenclature of Ethers

Simple ethers are frequently given common functional class names. One simply lists (in alphabetical order) both groups that are attached to the oxygen atom and adds the word ether:

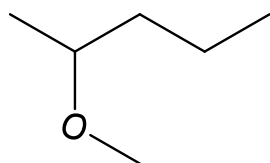


Ethyl methyl ether

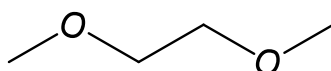


Diethyl ether

IUPAC substitutive names should be used for complicated ethers, however, and for compounds with more than one ether linkage. In this IUPAC style, ethers are named as alkoxyalkanes, alkoxyalkenes, and alkoxyarenes. The RO group is an alkoxy group.

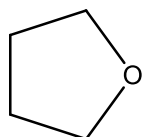


2-Methoxypentane



1,2-Dimethoxyethane

Cyclic ethers can be named in several ways. One simple way is to use replacement nomenclature, in which we relate the cyclic ether to the corresponding hydrocarbon ring system and use the prefix oxa- to indicate that an oxygen atom replaces a CH_2 group.



Oxacyclopentane
(Tetrahydrofuran)

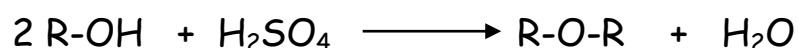


Oxacyclobutane

2.2 Synthesis of Ethers

2.2.1 Ethers by Intermolecular Dehydration of Alcohols

Alcohols can dehydrate to form alkenes. Primary alcohols can also dehydrate to form ethers:



Dehydration to an ether usually takes place at a lower temperature than dehydration to the alkene.

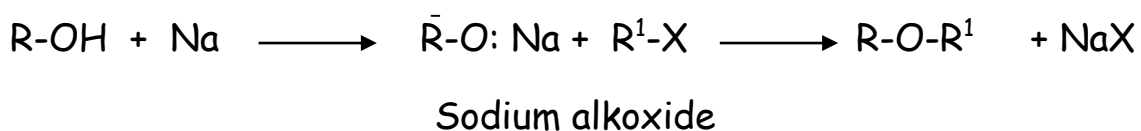
Diethyl ether is made commercially by dehydration of ethanol. Diethyl ether is the predominant product at 140°C ; ethene is the major product at 180°C .

The formation of the ether occurs by an $\text{S}_{\text{N}}2$ mechanism with one molecule of the alcohol acting as the nucleophile and another protonated molecule of the alcohol acting as the substrate. Intermolecular dehydration is not useful for the preparation of

unsymmetrical ethers from primary alcohols because the reaction leads to a mixture of products.

2.2.2 The Williamson Synthesis of Ethers

An important route to unsymmetrical ethers is a nucleophilic substitution reaction known as the Williamson synthesis. The Williamson ether synthesis consists of an S_N2 reaction of a sodium alkoxide with an alkyl halide, alkyl sulfonate, or alkyl sulfate.



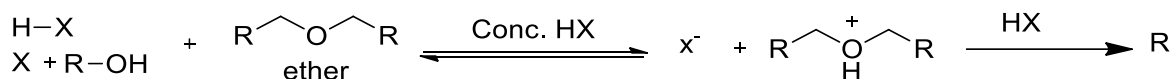
The usual limitations of S_N2 reactions apply here. Best results are obtained when the alkyl halide, sulfonate, or sulfate is primary (or methyl). If the substrate is tertiary, elimination is the exclusive result. Substitution is also favored over elimination at lower temperatures.

2.3 Reactions of Ethers

Dialkyl ethers react with very few reagents other than acids. The only reactive sites that molecules of a dialkyl ether present to another reactive substance are the C-H bonds of the alkyl groups and the -O- group of the ether linkage. Ethers resist attack by nucleophiles and by bases. This lack of reactivity coupled with the ability of ethers to solvate cations (by donating an electron pair from their oxygen atom) makes ethers especially useful as solvents for many reactions.

2.3.1 Reaction of Ethers with Acids

The oxygen of the ether linkage makes ethers basic. Ethers can react with proton donors to form oxonium salts:



X:I, Br

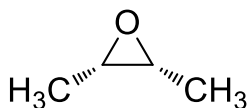
Heating dialkyl ethers with very strong acids (HI, HBr, and H₂SO₄) causes them to undergo reactions in which the carbon-oxygen bond breaks. The mechanism for this reaction begins with formation of an oxonium cation. Then, an S_N2 reaction with a bromide ion acting as the nucleophile produces alcohol and alkyl bromide.

2.4 EPOXIDES

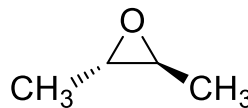
Epoxides are cyclic ethers with three-membered rings. In IUPAC nomenclature epoxides are called oxiranes.



Ethylene oxide
(Oxiran)



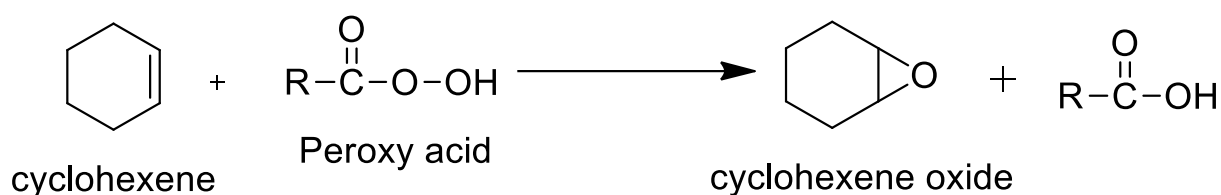
cis-2,3-dimethyloxiran
(cis-2-butene oxide)



trans-2-buteneoxide
(trans-2,3-dimethyloxiran)

2.4.1 Synthesis of Epoxides

Epoxides can be synthesized by the reaction of an alkene with an organic peroxy acid (RCO₃H—sometimes called simply a peracid), a process that is called epoxidation. Meta-chloroperoxybenzoic acid (MCPBA) is one peroxy acid reagent commonly used for epoxidation.



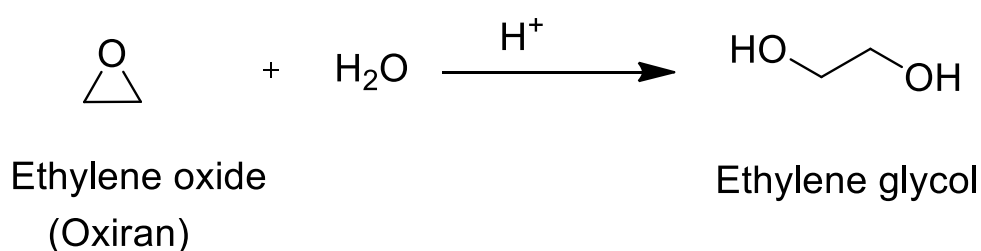
R: CH₃, m-chlorophenyl

2.4.2 Reactions of Epoxides

The highly strained three-membered ring of epoxides makes them much more reactive toward nucleophilic substitution than other ethers.

2.4.2.1 Acid-catalyzed Reactions

Acid catalysis assists epoxide ring opening by providing a better leaving group (an alcohol) at the carbon atom undergoing nucleophilic attack. This catalysis is especially important if the nucleophile is a weak nucleophile such as water or an alcohol. An example is the acid-catalyzed hydrolysis of an epoxide.



2.4.2.2 Base-catalyzed Reactions

Epoxides can also undergo base-catalyzed ring opening. Such reactions do not occur with other ethers, but they are possible with epoxides (because of ring strain), provided that the attacking

nucleophile is also a strong base such as an alkoxide ion or hydroxide ion.

