

Ethers, Epoxides, and Sulfides

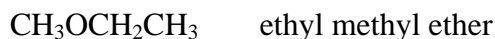
Ethers

Structure: R-O-R

Ethers as solvents: Ethers serve as good solvents for a number of organic reactions. Ethers do not usually react with strong bases, so they are especially good solvents for reactions involving strong bases such as the Grignard reagent.

Common Naming: Name the two alkyl groups bonded to the O in alphabetical order.

Example:



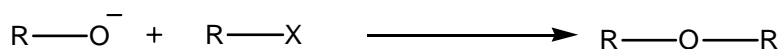
IUPAC Naming: Use the larger alkyl group name as the parent name. Name the rest of the ether as an alkoxy group.

Example:



Making Ethers:

Williamson ether synthesis

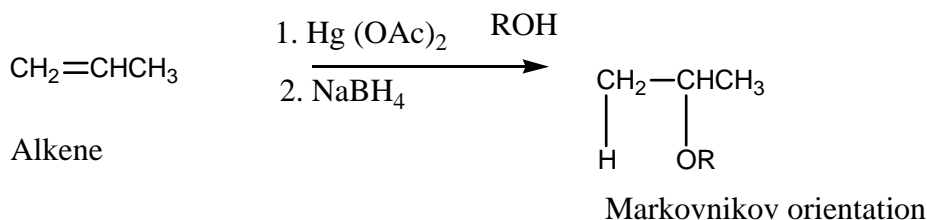


Must be
a primary
alkyl halide,
otherwise an
elimination reaction
will occur.

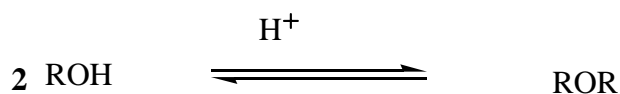
Note: $\text{R}-\text{O}^-$

Can be made from ROH + Na

Alkoxymercuration-demercuration



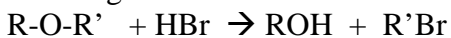
Dehydration of alcohol (2 molecules of alcohol form 1 molecule of ether)



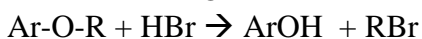
Alcohol must be primary.

Tips regarding the reactions of ethers:

Cleaving with HBr or HI



Or



The alcohol will usually form with the most substituted R group on the ether.
The alkyl halide will usually form with the least substituted R group.

Autooxidation



Occurs by a radical mechanism.

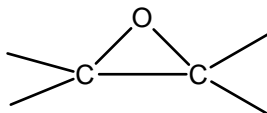
Crown Ethers

Naming: X-crown-Y, where X is the number of atoms (not counting hydrogen) in the ring and Y is the number of oxygen atoms.

Crown ethers solvate metal cations extremely well, forming a compound between the ether and the ionic salt which is soluble in nonpolar solvents.

Epoxydes

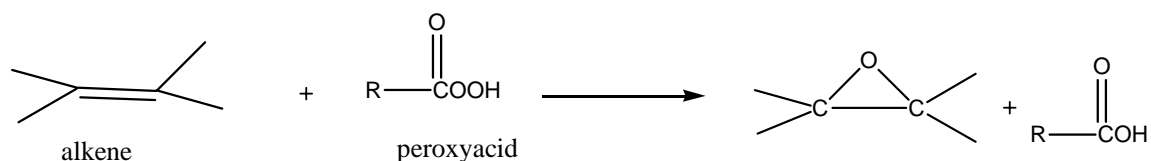
Structure:



Making epoxydes:

Often made from alkenes.

Peroxyacid Epoxidation



meta-chloroperoxybenzoic acid (MCPBA) is a commonly used peroxyacid.

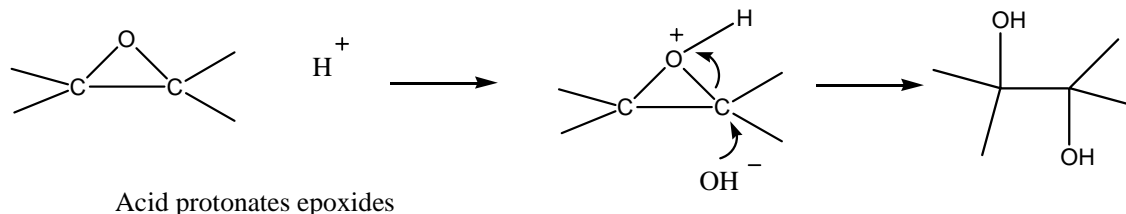
Epoxides can also be formed via an internal SN₂ reaction from halohydrins in the presence of OH⁻. Consult the text for a mechanism of this reaction.

Reactions of Epoxides:

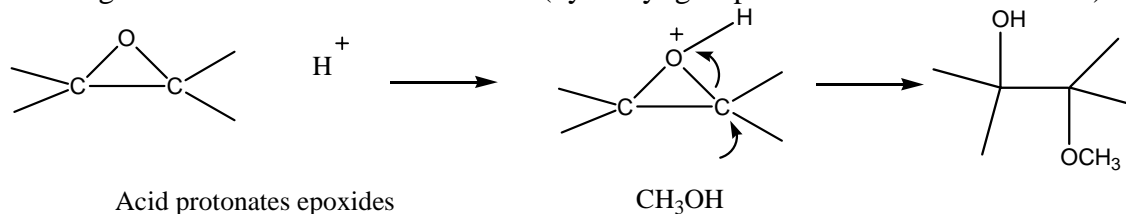
Epoxide ring can be cleaved with water or alcohol under acidic or basic conditions.

Cleaving with water forms a trans diol.

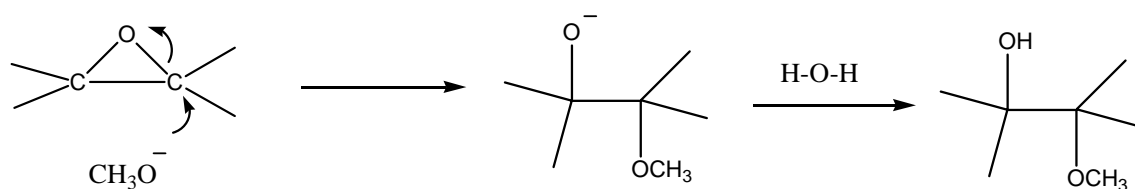
In acidic conditions: The carbon attacked will be the *most substituted*.



Cleaving with alcohol forms a hemiacetal (hydroxyl group and an ether characteristic)



In basic conditions, the carbon attacked will be the *least hindered* because the reaction follows an SN₂ displacement.



Sulfides

Structure: R-S-R

When working on problems involving substitution reactions (SN1 and SN2 types, for example) keep in mind that sulfides are more reactive than ethers. This means that a sulfide is typically a better nucleophile than an ether.

Naming: Name like ethers but replace “ether” with “sulfide” in common name.

Example:

$\text{CH}_3\text{SCH}_2\text{CH}_3$ ethyl methyl sulfide

The IUPAC system uses “alkylthio” in place of “alkoxy.”

Example:

$\text{CH}_3\text{SCH}_2\text{CH}_3$ methylthioethane