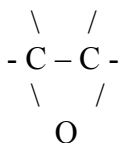


Cyclic Ethers

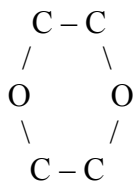
I. Crown ethers are cyclic ethers containing 4-7 oxygen atoms. The most important is 18 crown 6 (18 atoms in the ring, 6 of which are oxygen). Crown ethers are important because they have the ability to trap a cation in its center. The relationship is known as host-guest relationship.

Epoxides – most important 3 membered ring

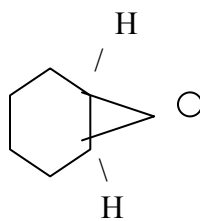
II.



Ethylene oxide
Oxirane



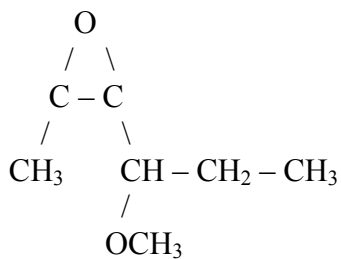
1,4 dioxane



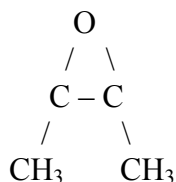
cyclohexene oxide

Cyclohexene oxide obtained from cyclohexene, note the retaining of the ene.

Cyclic Ethers



cis 2,3 epoxy-4-methoxyhexane

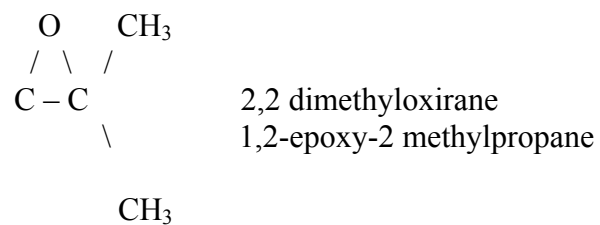
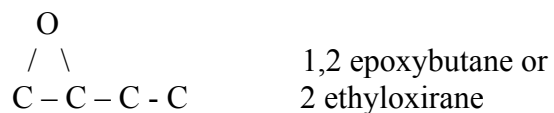


cis 2,3-dimethyl oxirane

cis 2,3-dimethylethylene oxide

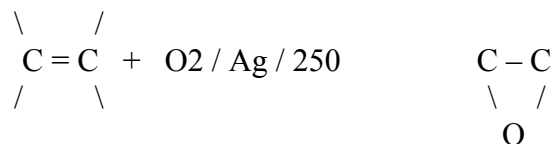
Or cis 2,3-epoxy butane using same numbering system as alkane

Where we use oxirane, we start the numbering from oxygen as 1.



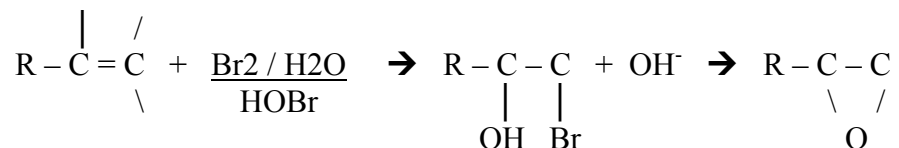
Preparation

1. From alkene

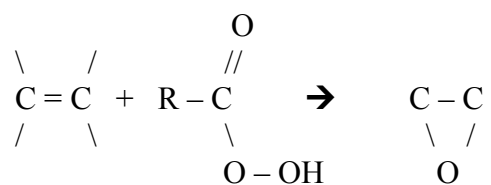


Most important use is to prepare antifreeze.

2. From alkene by forming halohydrins



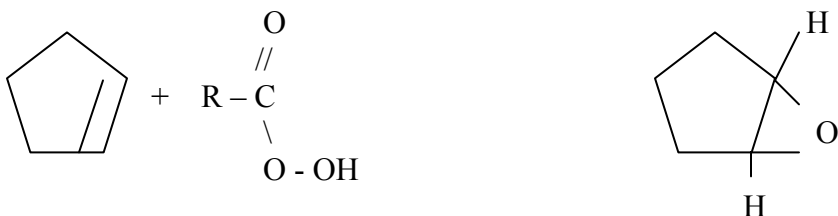
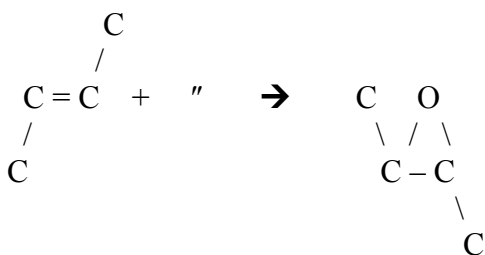
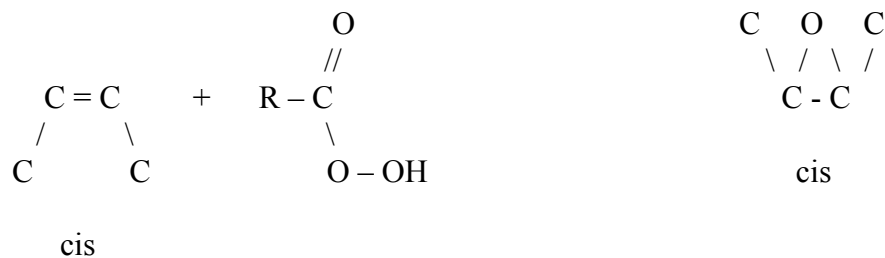
3. Peroxidation of an alkene using peroxyacetic acid or peroxybenzoic acid.



Peroxyacids are unstable and may be unsafe.

Cyclic Ether

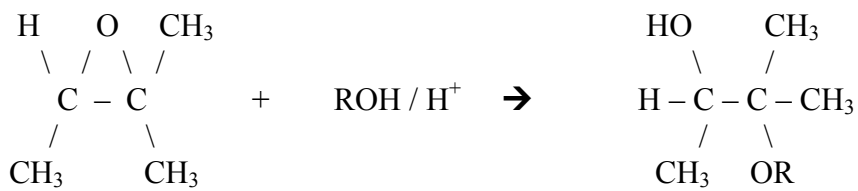
The reaction of alkenes with peroxy acids are stereospecific, e.g.



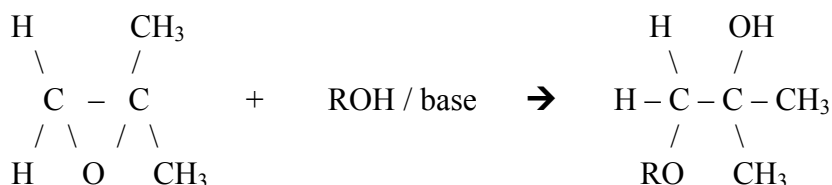
Reactions of Cyclic Ethers

Epoxides react very readily because ring is easy to open due to strain, if the groups on either side are equivalent one product is produced, if not 2 products are expected depending on the pH.

Under acidic conditions, the major product is formed by the reaction of the nucleophile at the more sterically hindered ring C atom of the epoxide.

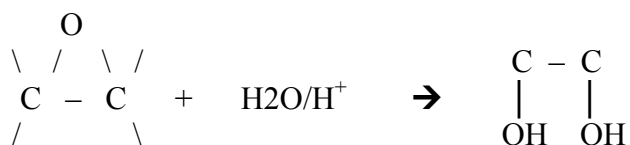


Under basic conditions, the major product is formed by reaction of the nucleophile at the less sterically hindered C atom of the epoxide.

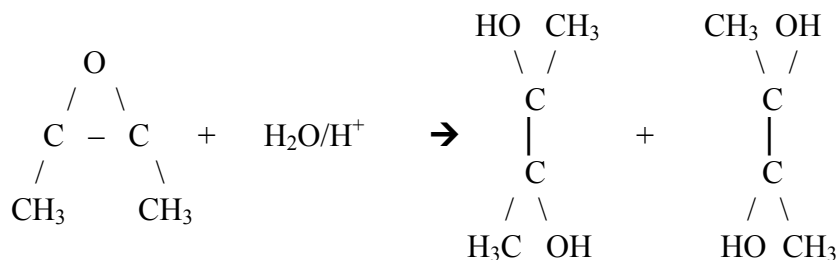


Notice the configuration at the reaction site is inverted in both acid and base catalyzed ring opening of epoxide.

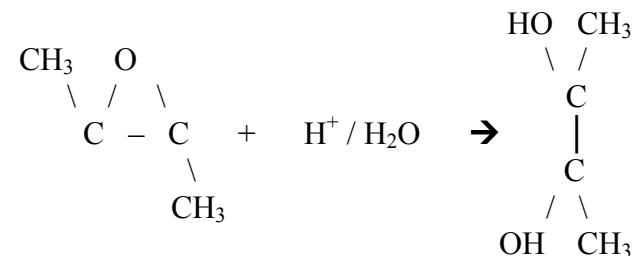
Acid catalyzed cleavage with water given a 1,2 diol



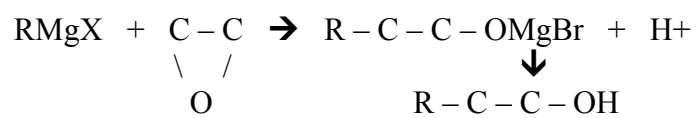
If we have cis 2,3-dimethyloxirane we get 2 enantiomers



If we have trans 2,3-dimethyloxirane, we get meso product.



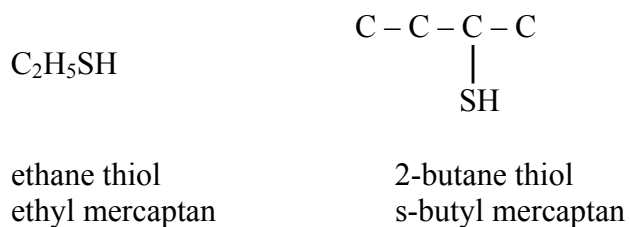
Ether with Grignard reagent mostly used to prepare primary alcohols using ethylene oxide.



Larger epoxides result in rearrangement, hence not practical.

Thio compounds – when O is replaced by S

Thioalcohols or mercaptan (mercury seizing)



Thioether

