

4.6: CYCLIC ETHERS - EPOXIDES

OBJECTIVES

After completing this section, you should be able to

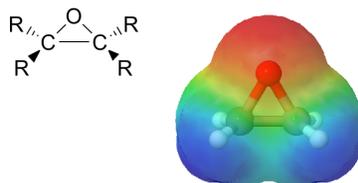
- write an equation to describe the industrial preparation of ethylene oxide.
- list two important industrial uses of ethylene oxide.
- write an equation to describe the normal laboratory preparation of an epoxide.
- identify the epoxide produced from the reaction of a given alkene with a peroxyacid.
- identify the alkene, the reagent, or both, needed to prepare a given epoxide.
- write an equation to describe the preparation of an epoxide from an alkene via a halohydrin.

KEY TERMS

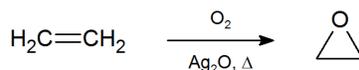
Make certain that you can define, and use in context, the key term below.

- epoxide (oxirane)

Epoxides (also known as **oxiranes**) are three-membered ring structures in which one of the vertices is an oxygen and the other two are carbons. Epoxides behave differently than other ethers due to the strain created by the three-membered ring.

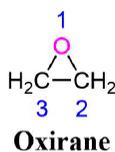


The most important and simplest epoxide is ethylene oxide which is prepared on an industrial scale by catalytic oxidation of ethylene by air. Ethylene oxide is used as an important chemical feedstock in the manufacturing of ethylene glycol, which is used as antifreeze, liquid coolant and solvent. In turn, ethylene glycol is used in the production of polyester and polyethylene terephthalate (PET) the raw material for plastic bottles.

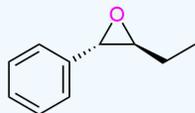


NOMENCLATURE OF EPOXIDES

The name ethylene oxide is not systematic but common. Epoxides are systematically named as an oxirane ring system much like the other cyclic ethers discussed in [Section 18.1](#). The oxygen is numbered in the 1 position.



EXAMPLE 4.6.1



trans-2-Ethyl-3-phenyloxirane



cis-2,3-Dimethyloxirane

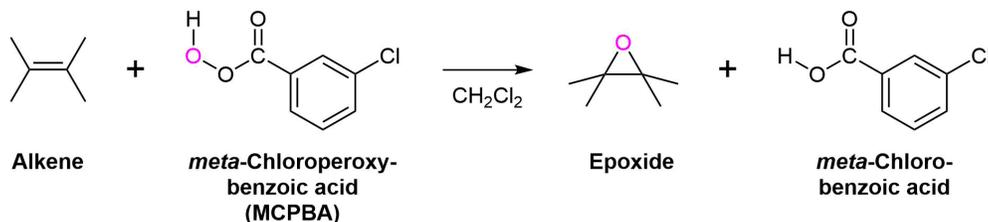


2,2-Dimethyloxirane

SYNTHESIS OF EPOXIDES

As discussed in [Section 8-7](#), epoxides are typically prepared by the reaction of an alkene and a peroxydicarboxylic acid (RCO_3H), such as *meta*-chloroperbenzoic acid (MCPBA). The peroxydicarboxylic acid has the unique property of having an electropositive oxygen atom on the CO_3H group. The reaction is initiated by the electrophilic oxygen atom reacting with the nucleophilic carbon-carbon double bond. The mechanism involves a concerted reaction with a four-part, circular transition state. The result is that the originally electropositive oxygen atom ends up in the oxacyclopropane ring and the CO_3H group becomes CO_2H .

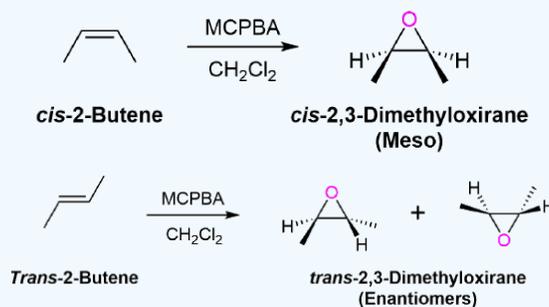
General Reaction



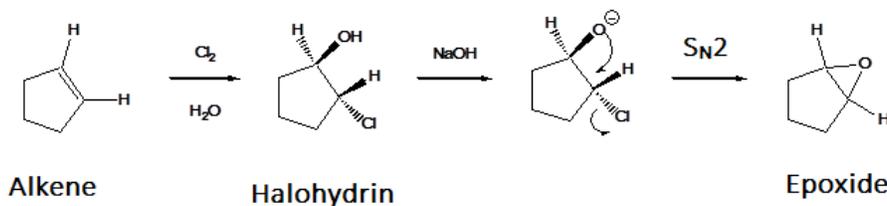
Stereochemical Consideration

The oxygen addition to the alkene is a *syn* addition and is stereospecific. The substituents of a *cis*-alkene will appear in the *cis* configuration on the epoxide ring. Likewise, substituents of a *trans*-alkene will appear in the *trans* configuration on the epoxide ring. During this reaction the sp^2 hybridized carbons of the alkene are converted to sp^3 hybridized carbons in the epoxide. Thus, there is the possibility of two new chiral carbons forming in the epoxide product. In most cases, epoxidation of an alkene will produce a mixture of enantiomers in the product, due to the electrophilic oxygen being able to attack from above or below the plane of the alkene. One major exception is the epoxidation of symmetrical *cis*-alkene which produces a meso compound product.

EXAMPLE 4.6.2



Treatment of an alkene with X_2 & H_2O creates a halohydrin ([Section 8-3](#)). When a halohydrin is treated with a base the alcohol is deprotonated to form an alkoxide. This causes an intramolecular Williamson ether synthesis to produce an epoxide along with the elimination of HX . Note, that this reaction generally forms a mixture of enantiomeric products unless a meso compound is produced.

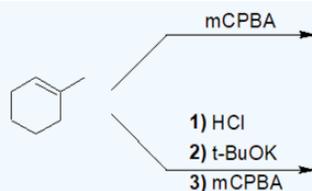


EXERCISE 4.6.1

1) What reagents would you use to perform the following transformation?



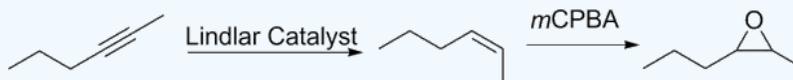
2) Predict the products of the following reactions:



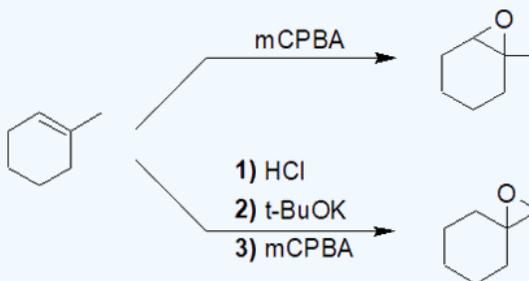
3) Predict the product of the following reaction. Be sure to include proper stereochemistry.

Answer

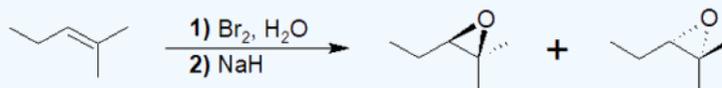
1) Lindlar's catalyst reduces alkynes to cis/Z alkenes. This stereochemistry is retained after epoxidation.



2)



3)



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