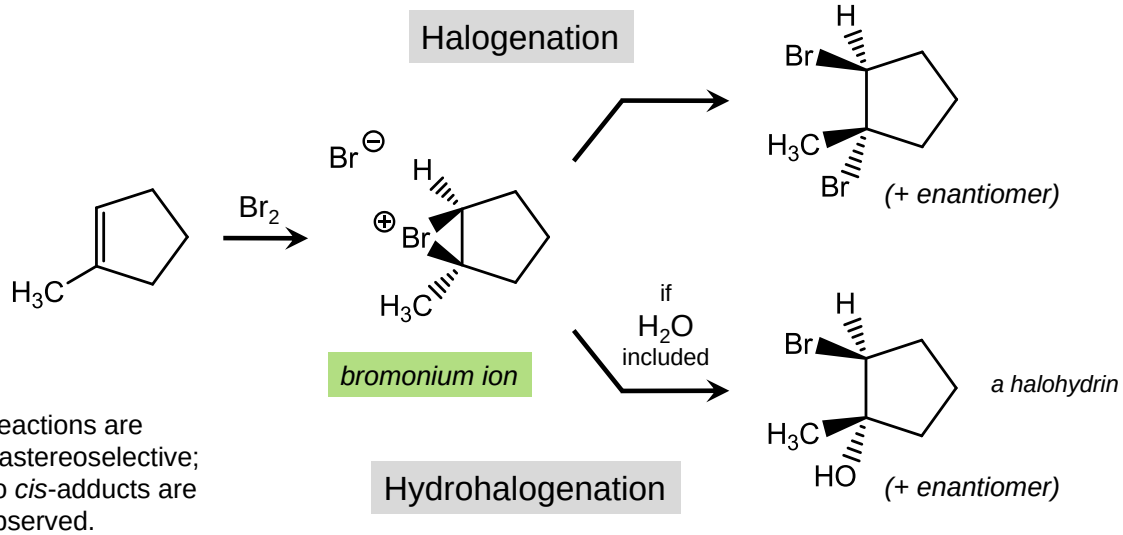
Electrophilic Alkene Halogenation and Hydrohalogenation

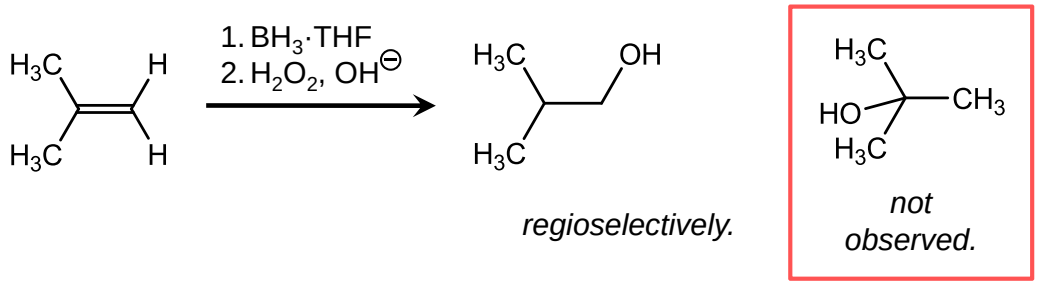
Adds -Br and -Br (or -Br and -OH) *anti* onto double bond, to yield *trans*-products.

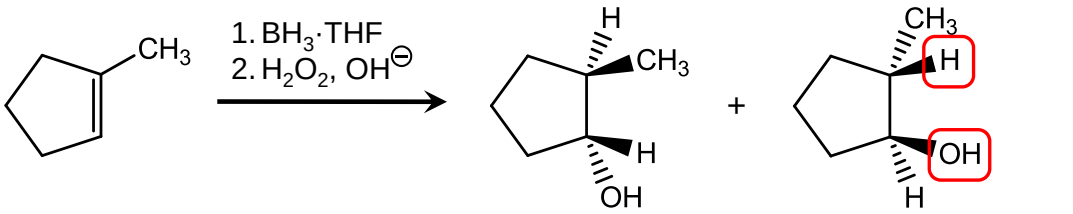


Reactions are diastereoselective; no *cis*-adducts are observed.

Anti-Markovnikov Addition of H_2O via Hydroboration

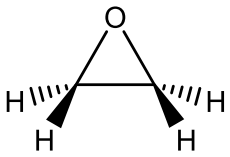
Hydroboration





H & OH add to same face of alkene.

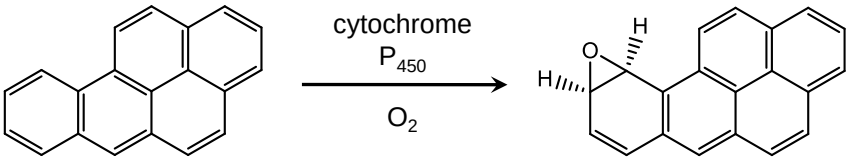
Epoxides



Epoxide: A three-membered ring made of two carbons and one oxygen.

Very reactive towards nucleophiles.

Example from biology:



benzo[a]pyrene

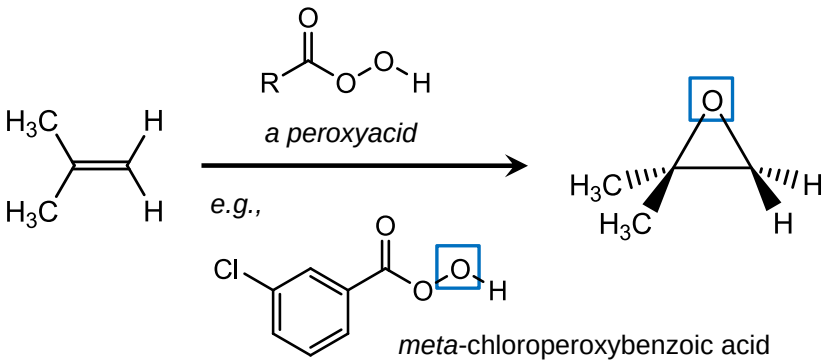
benzo[a]pyrene oxide

a polyaromatic hydrocarbon (PAH)

byproduct of burning tobacco, charring meat

reacts with nucleophiles in DNA to generate DNA "lesions", which can produce cancer-causing mutations

Synthesis of Epoxides

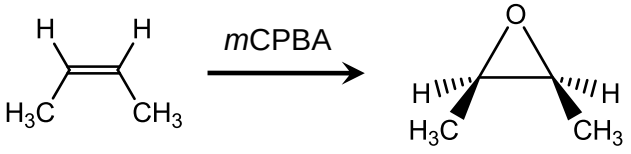


meta-chloroperoxybenzoic acid (*m*CPBA)

Via isotope labeling studies, we know which oxygen from peroxyacid adds.

Stereochemistry of alkene starting material is retained in epoxide product.

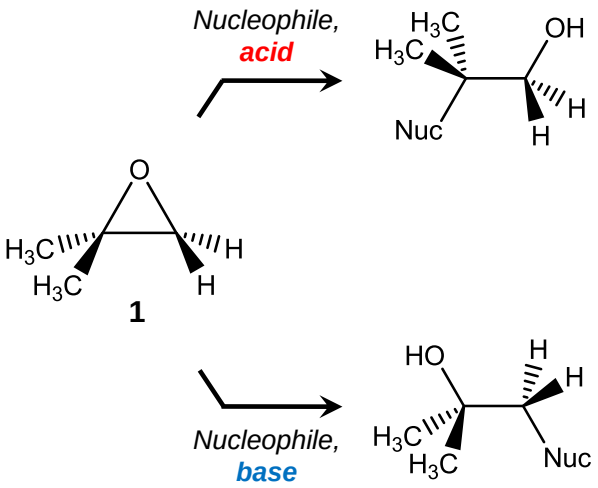
So, a *cis*-alkene…



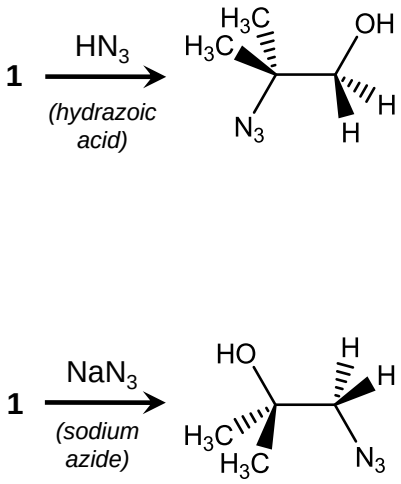
…gives a *cis*-epoxide.

Ring-Opening Reactions of Epoxides

In acid, nucleophile adds to site of most stable carbocation.



Example:



In base, nucleophile adds to least hindered carbon.