

Chapter 13:Highlights

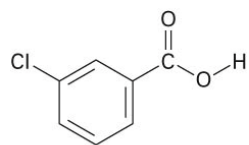
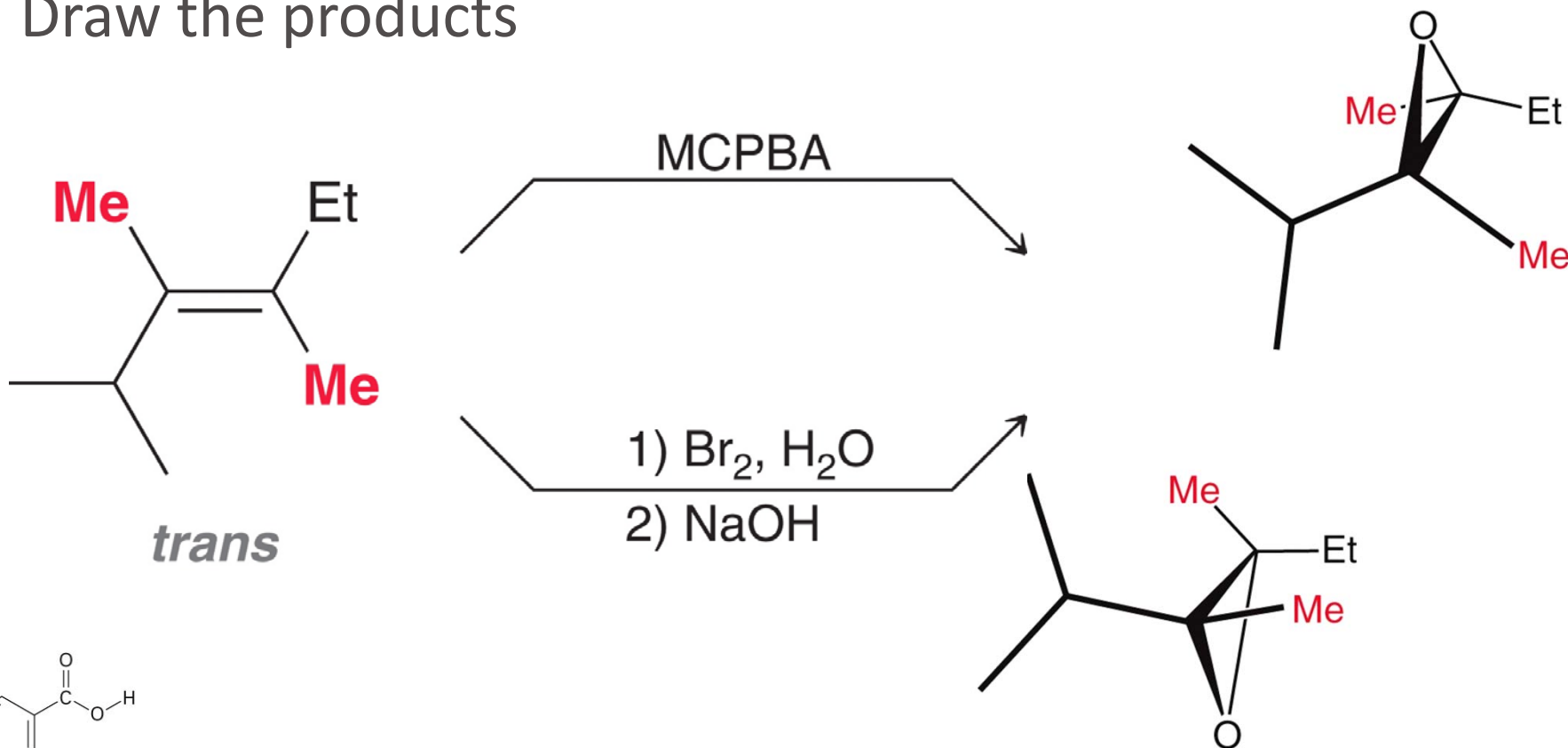
Today –Chapter 13 End! (Ch. 13.8-13.12)

A lot of this is 13.8-13.10....

We will not cover nomenclature of epoxides, thiols, or sulfides.

Epoxidation

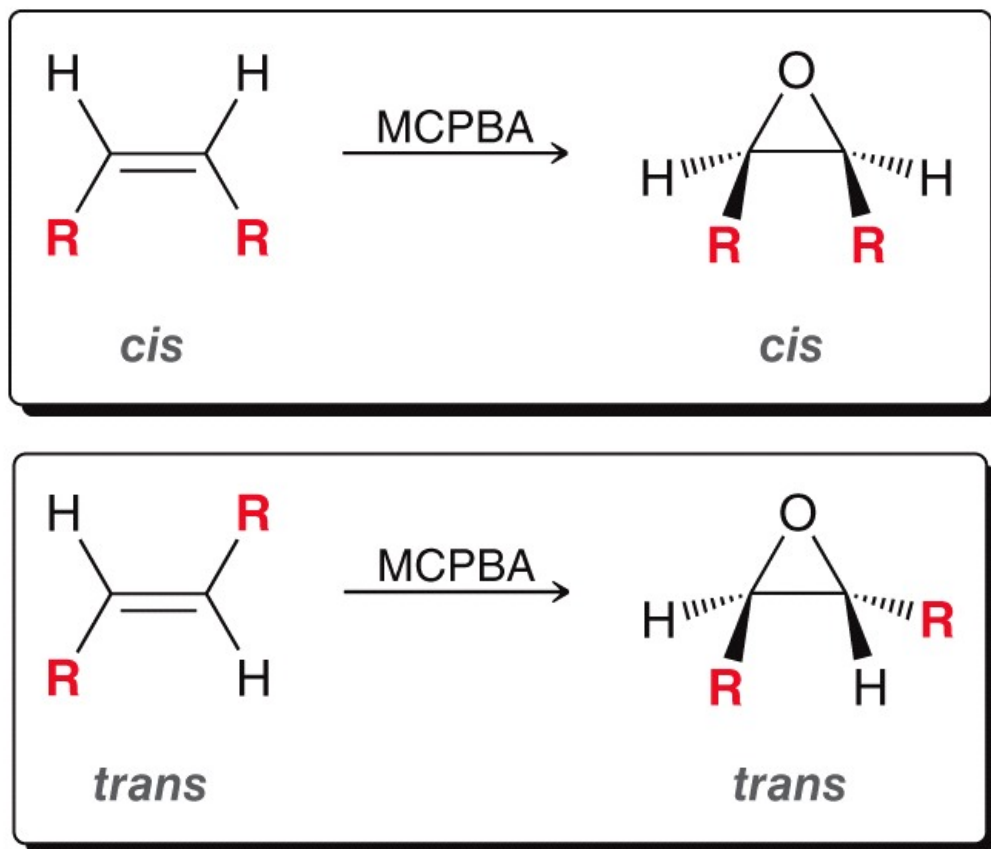
- The epoxidation methods we have discussed so far are NOT enantioselective
- Draw the products



meta-Chloro-
benzoic acid

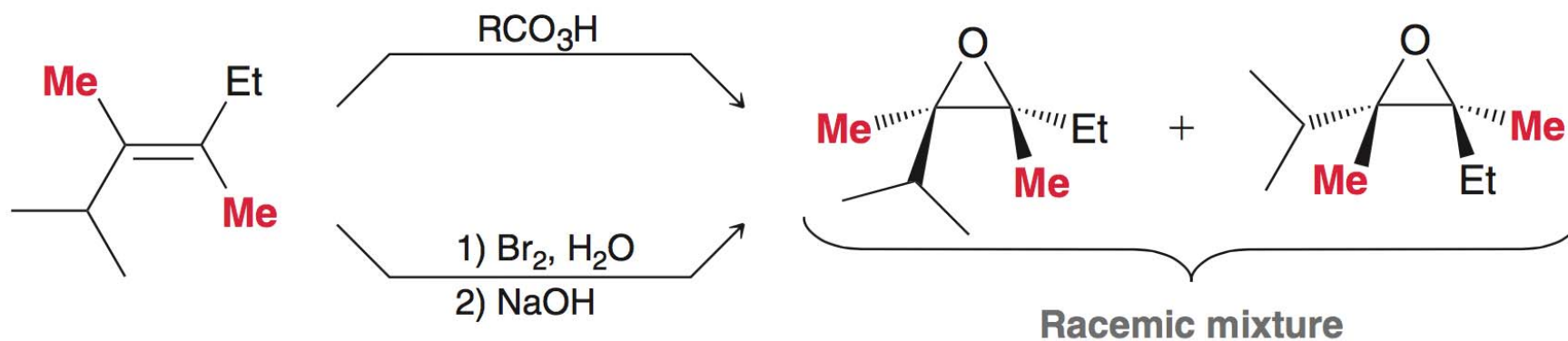
Epoxidation

- Epoxidations of alkenes ARE **stereospecific**



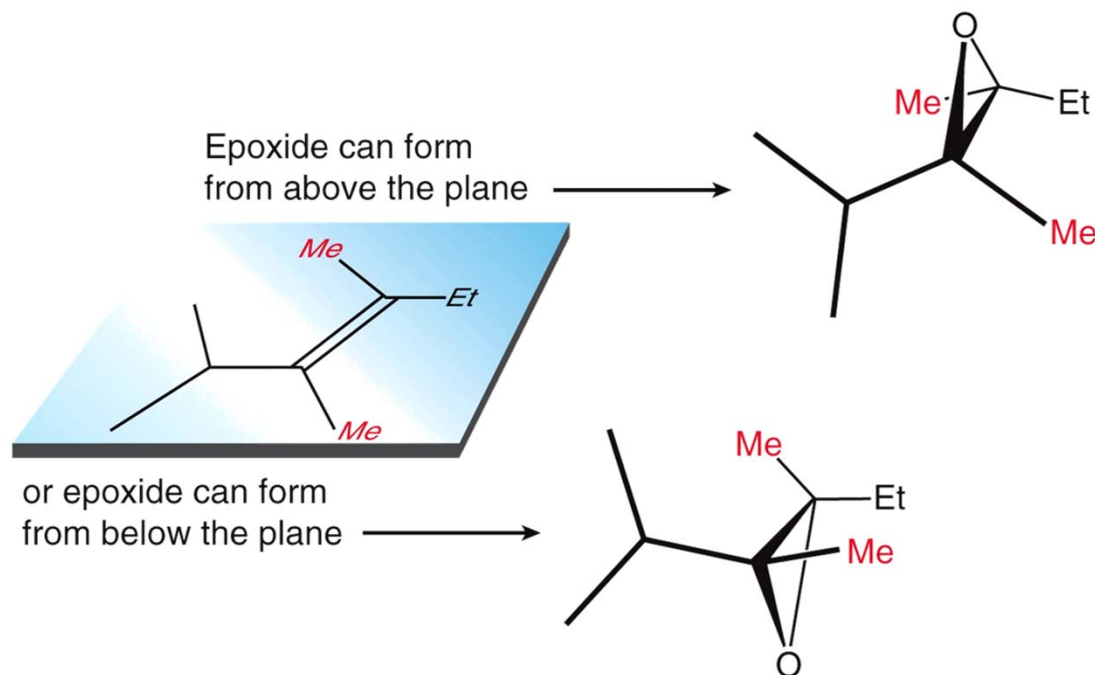
Enantioselective Epoxidation

- The epoxidation methods we have discussed so far are NOT enantioselective
- Epoxidation of an achiral alkene produces a racemic mixture



Enantioselective Epoxidation

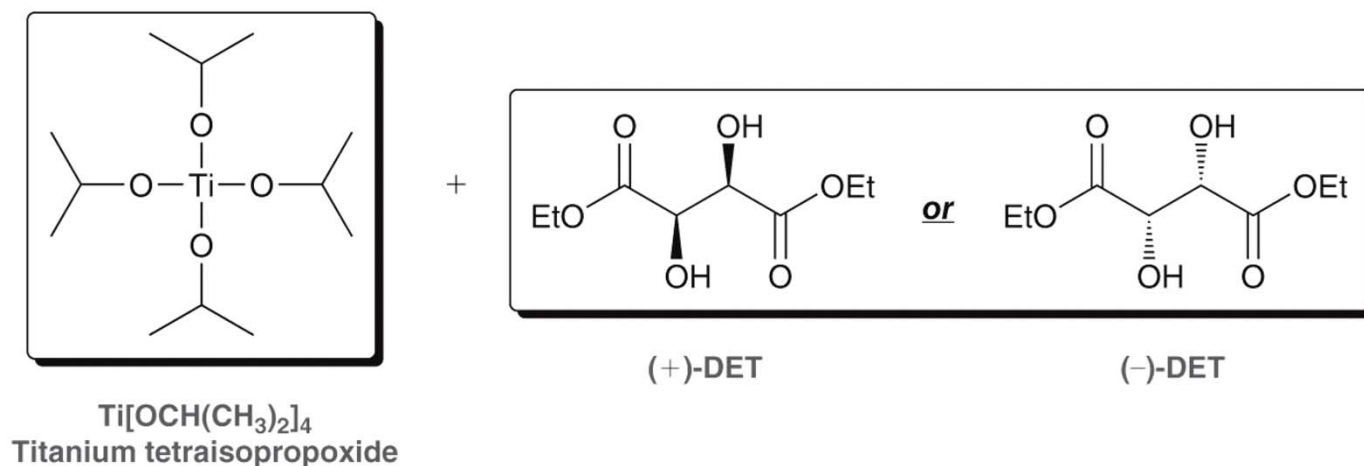
- The epoxidation forms a racemic mixture because the alkene can react on either face



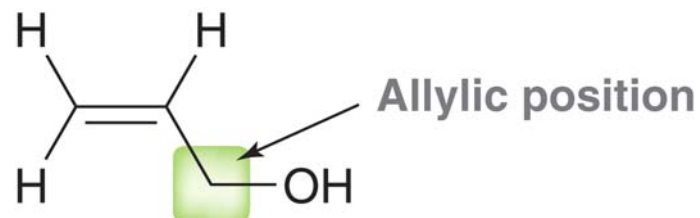
- To selectively react with one face of the alkene, a **chiral catalyst** would have to be used

Enantioselective Epoxidation

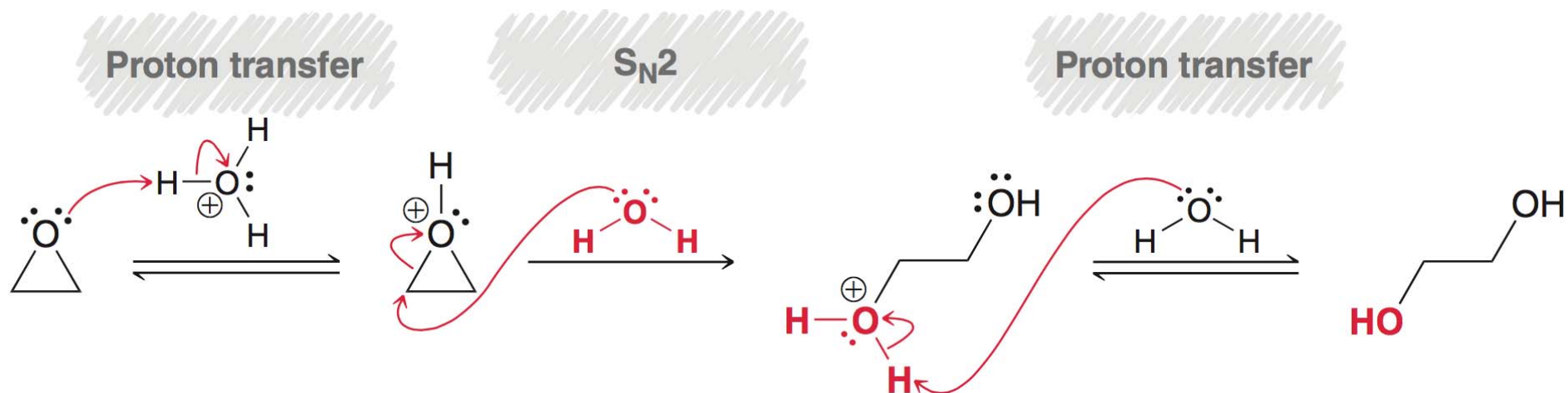
- The Sharpless catalyst is a chiral complex of titanium tetrakisopropoxide and diethyl tartrate.



- This catalyst will cause an enantioselective epoxidation of an allylic alcohol

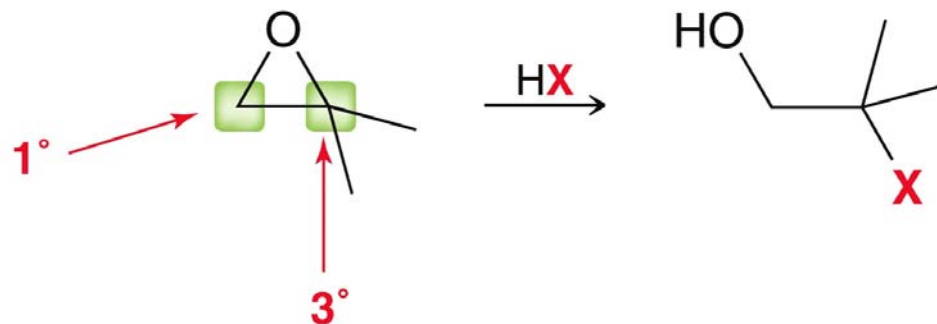
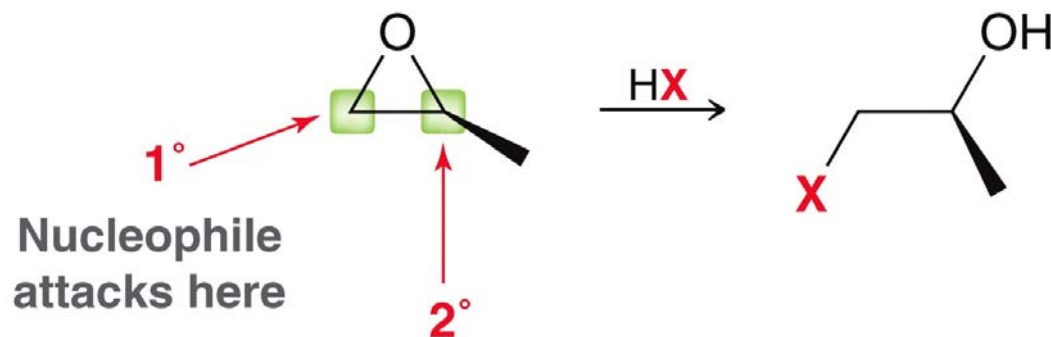


Acid catalyzed Ring Opening of Epoxides



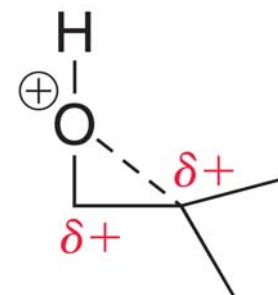
Acid catalyzed Ring Opening of Epoxides

- Under acidic conditions, Nu attack still occurs

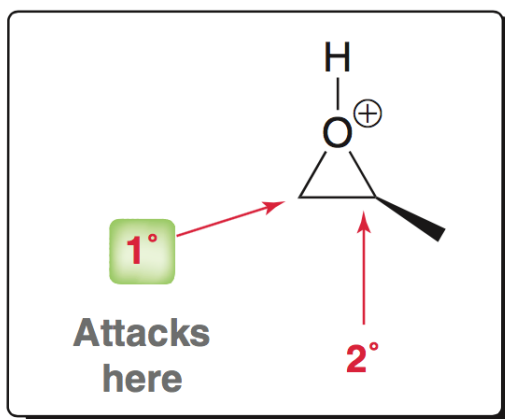


Acid catalyzed Ring Opening of Epoxides

- Since the epoxide is cationic under acidic conditions, electronic effects result in the C-O bond to a 3° carbon to be much weaker
- But, if a 3° carbon is not present, then steric effects dominate

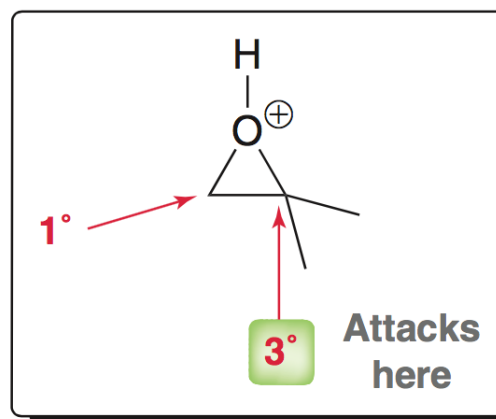


Primary vs. secondary



Dominant factor = steric effect

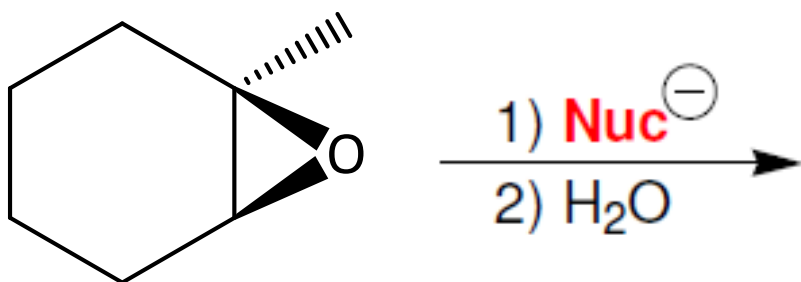
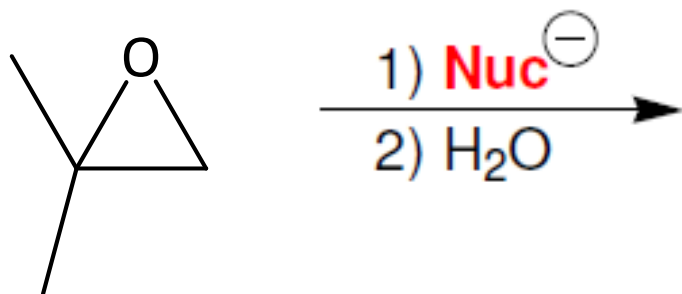
Primary vs. tertiary



Dominant factor = electronic effect

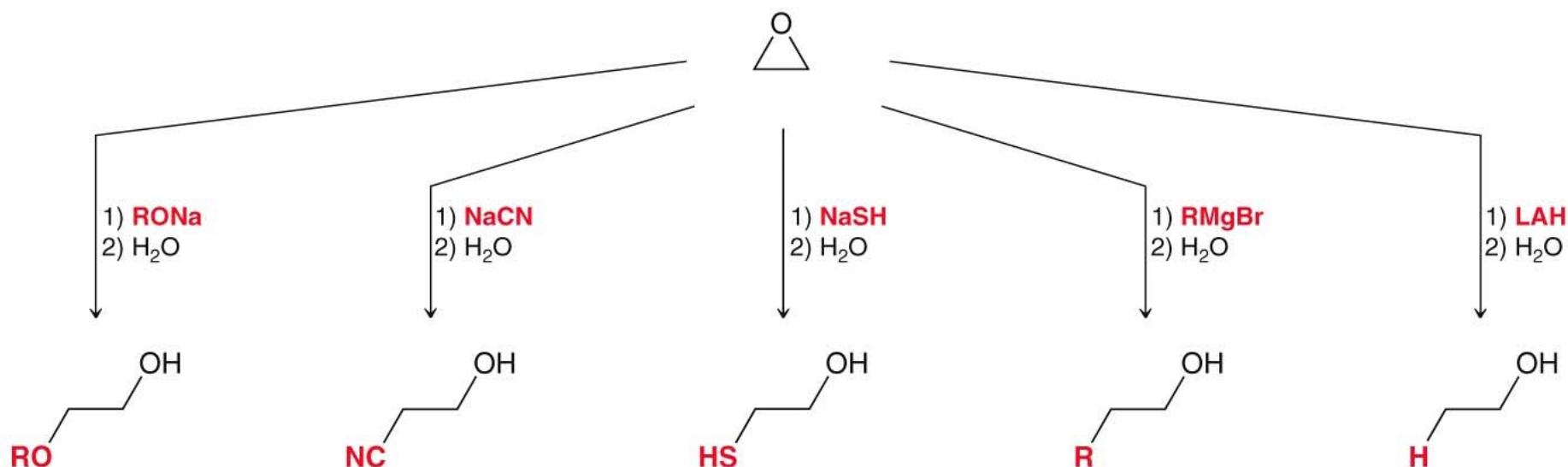
Basic Ring-opening of Epoxides

- Most ethers do not react with neutral or basic nucleophiles \rightarrow RO- is a poor leaving group.
- Epoxides are an exception. The relief of ring strain provides a driving force to open the ether.
- Pay attention to regio- and stereoselectivity.



Basic Ring-opening of Epoxides

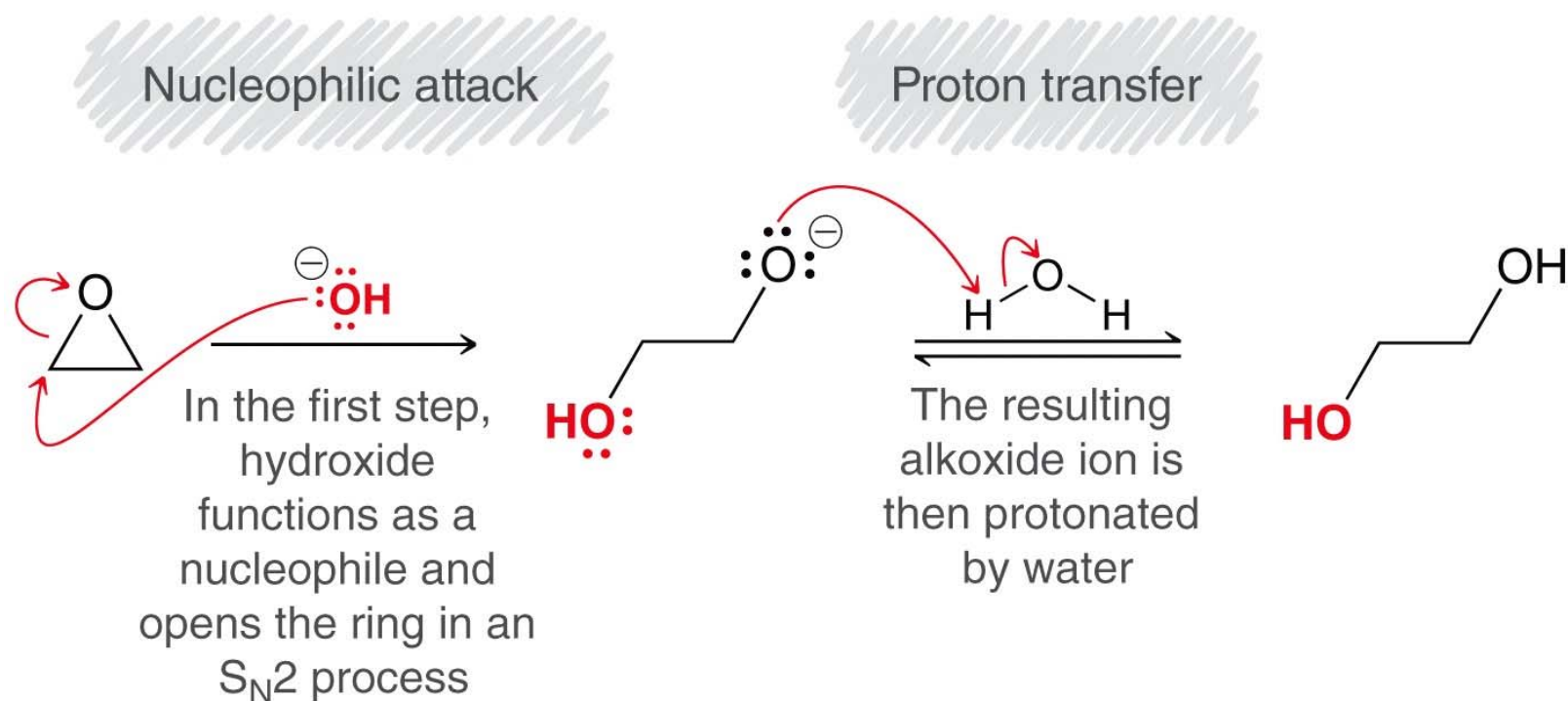
- Epoxides can be opened by many other strong nucleophiles as well



- Both regioselectivity and stereoselectivity must be considered

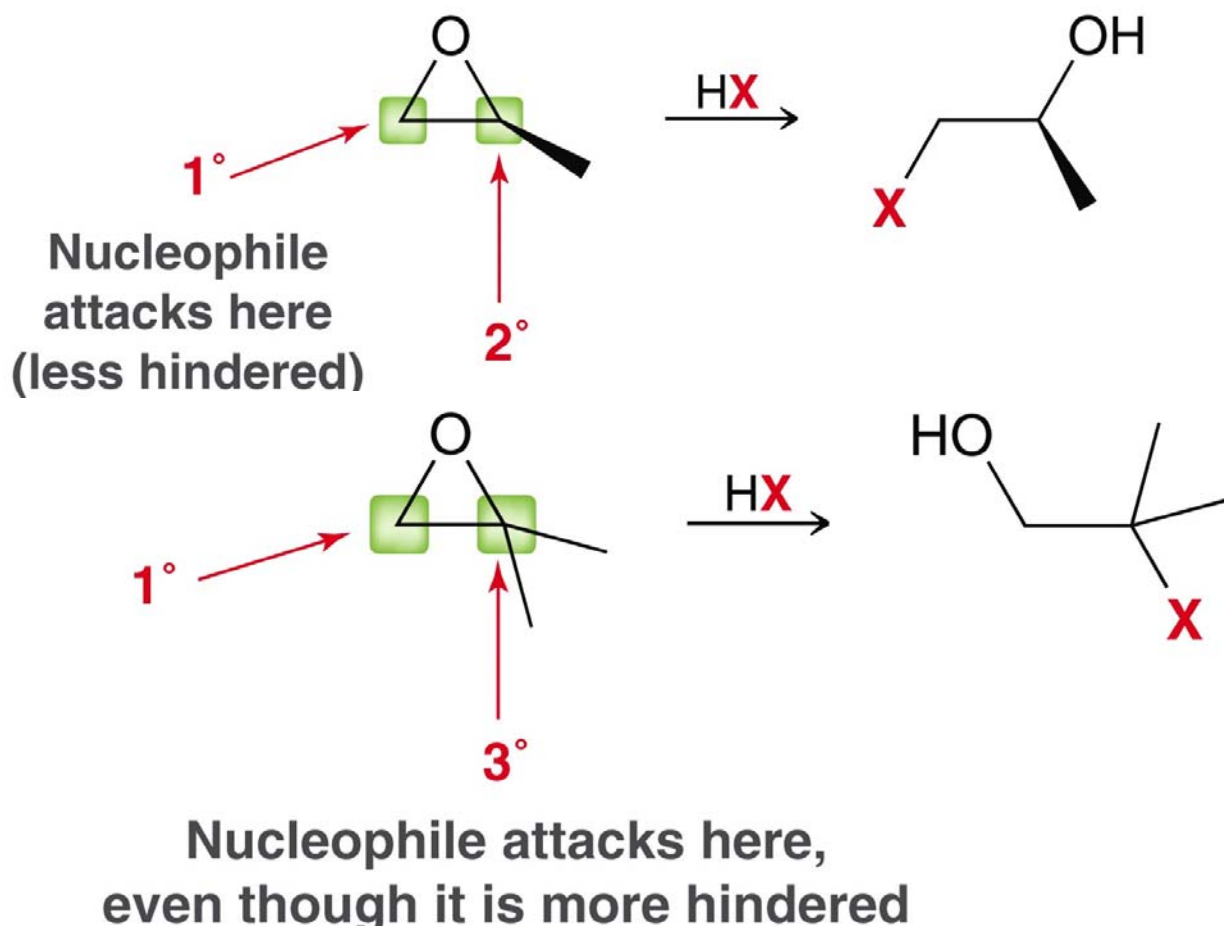
Basic Ring-opening of Epoxides

- Strong nucleophiles react readily with epoxides



Ring-opening of Epoxides - Regiochemistry

- Under Nucleophilic Conditions.... We have to Consider both steric and electronic effects (induction).

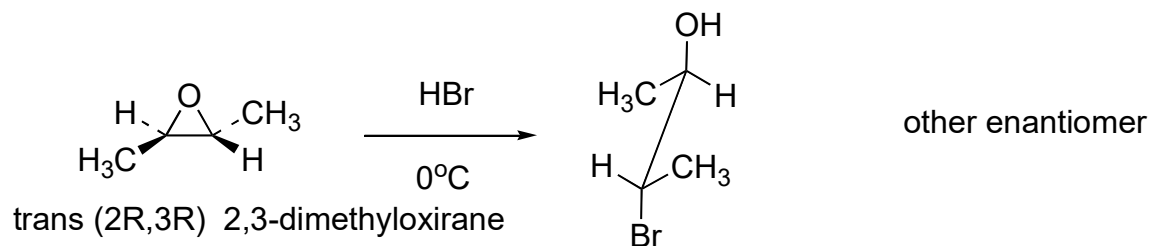
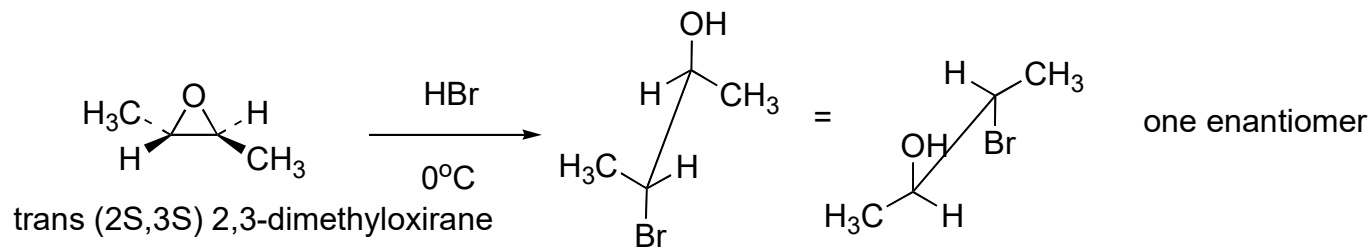
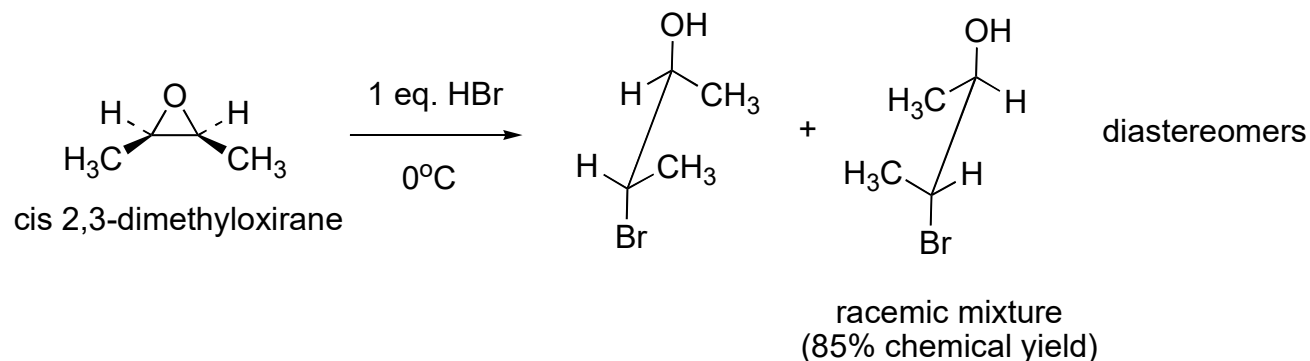


Summary: Epoxides

- 1) Although ethers are normally inert, ring strain in epoxides makes them more reactive.
- 2) Ring opening occurs in both regioselective and stereospecific manners.
- 3) For anionic nucleophiles or **basic** conditions, follow S_N2 rules:
- 4) Acid catalysis changes regiochemistry – by changing the Mechanism – goes through more stable carbocation –like intermediate WHEN YOU have a tertiary CARBON

Reaction of Epoxide with hydrogen halides.

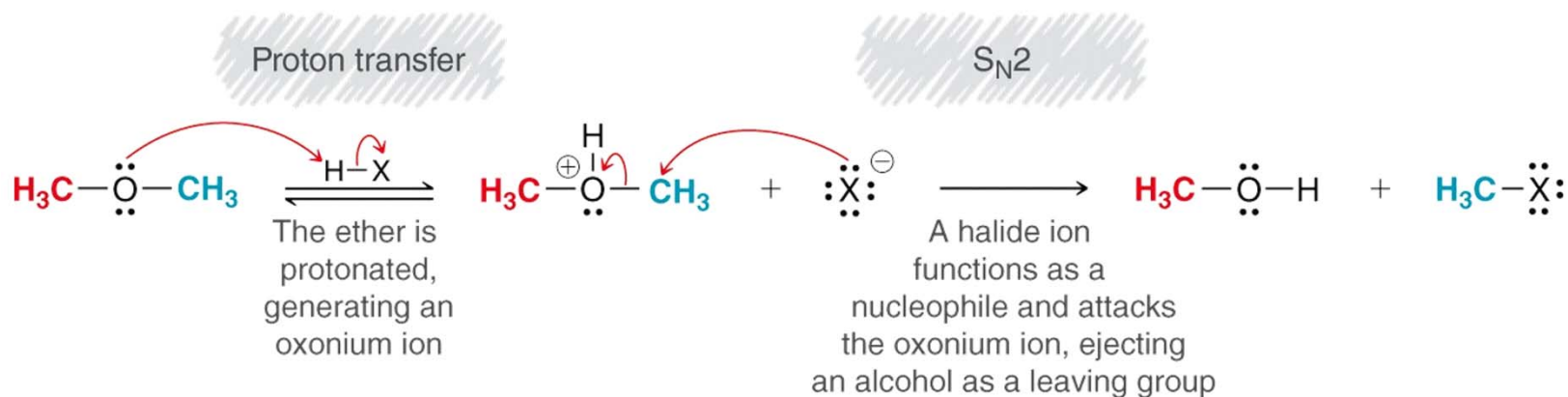
Epoxides are also cleaved by dilute solutions of HX. Here trans halohydrins are produced.



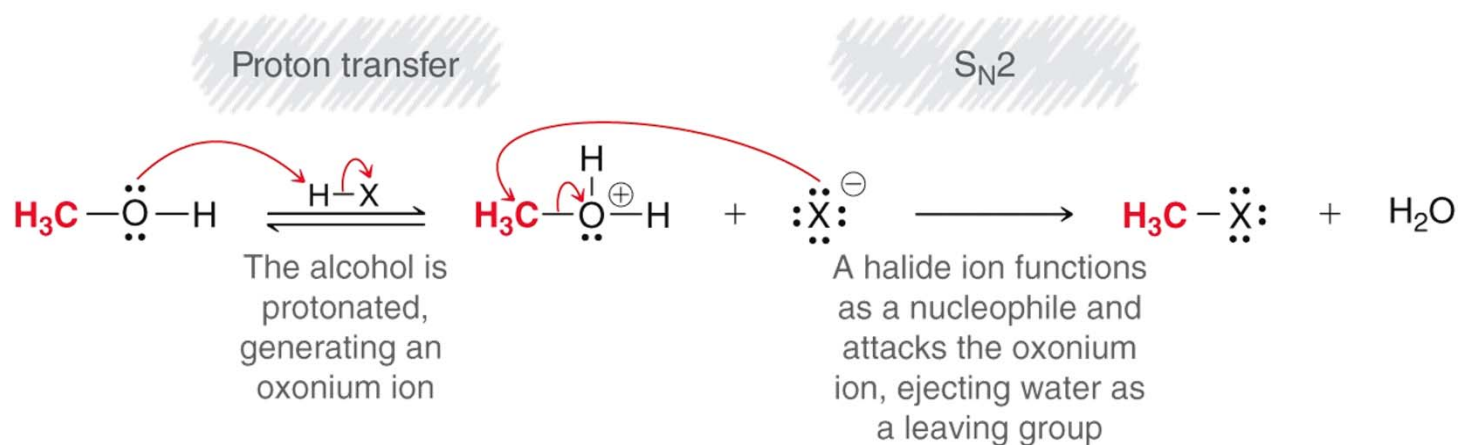
Reactions of Ethers

- Ethers can undergo acid-promoted cleavage

FORMATION OF FIRST ALKYL HALIDE



FORMATION OF SECOND ALKYL HALIDE



For Next Time....

Suggested Homework Problems

Chapter 13 #1, 5, 10, *18, 26, 29, 37, 38, 44, ***51**

Chapter 11 #7, 9, 11, 12, 18, 21, 30