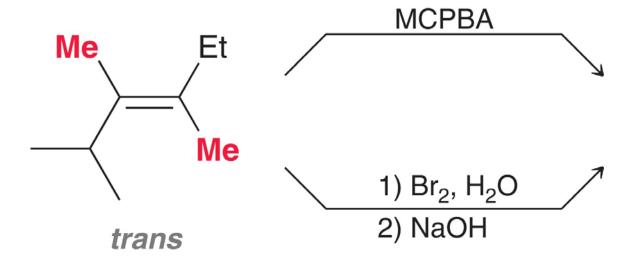
## Chapter 13:Highlights

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**

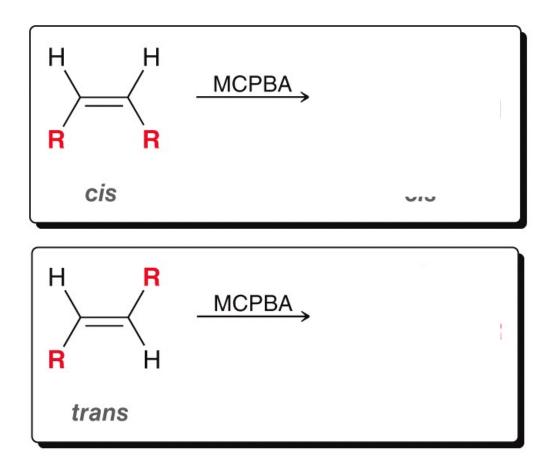
- The epoxidation methods we have discussed so far are NOT enantioselective
- Draw the products



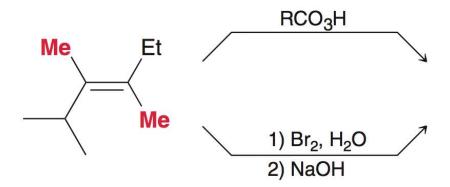
meta-Chlorobenzoic acid

## **Epoxidation**

• Epoxidations of alkenes ARE stereospecific

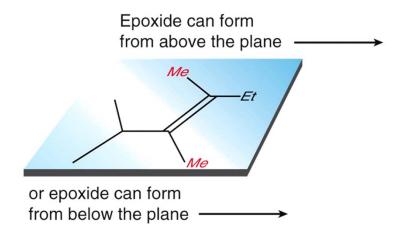


## **Enantioselective Epoxidation**



## **Enantioselective Epoxidation**

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



### **Enantioselective Epoxidation**

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

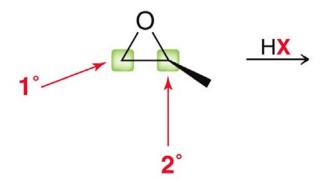
This catalyst will cause an enantioselective epoxidation of an allylic alcohol

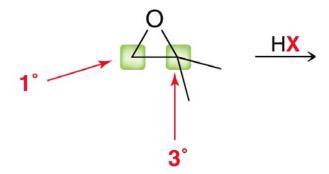
## Acid catalyzed Ring Opening of Epoxides

•

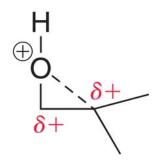
#### Acid catalyzed Ring Opening of Epoxides

Under acidic, conditions, Nu attack still occurs

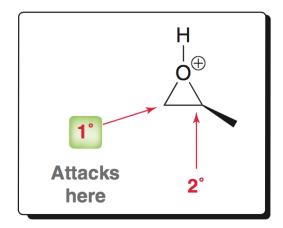




#### Acid catalyzed Ring Opening of Epoxides

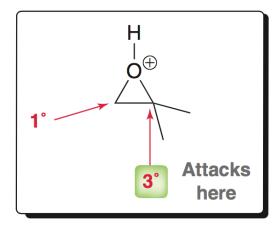


**Primary vs. secondary** 



**Dominant factor** = **steric effect** 

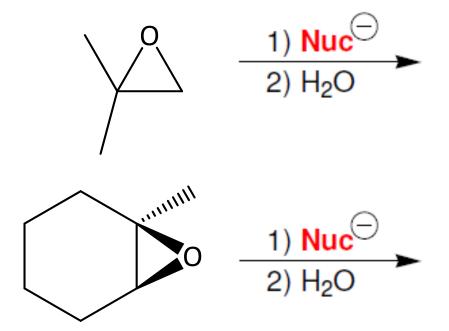
**Primary vs. tertiary** 



**Dominant factor** = <u>electronic effect</u>

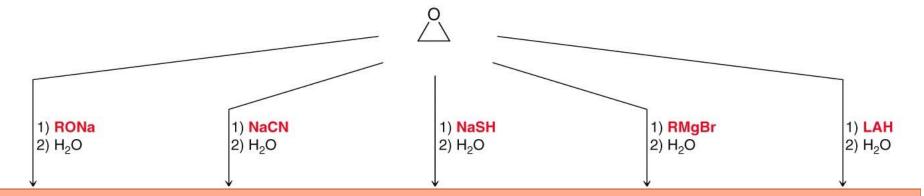
## Basic Ring-opening of Epoxides

Most ethers do not react with neutral or basic nucleophiles



## Basic Ring-opening of Epoxides

 Epoxides can be opened by many other strong nucleophiles as well

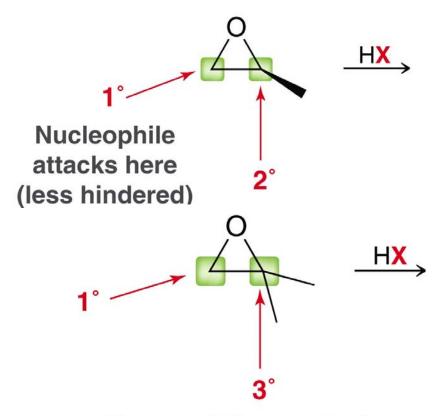


## Basic Ring-opening of Epoxides

Strong nucleophiles react readily with epoxides

## Ring-opening of Epoxides - Regiochemistry

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



Nucleophile attacks here, even though it is more hindered

# Summary: Epoxides

#### Reaction of Epoxide with hydrogen halides.

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

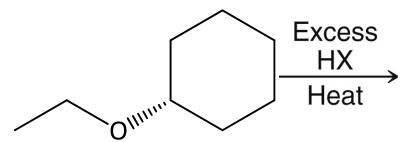
$$\begin{array}{c} H & O \\ H_3C & CH_3 \end{array} \xrightarrow[0^{\circ}C]{} 1 \text{ eq. HBr} \\ \hline \text{o°C} \\ \text{cis 2,3-dimethyloxirane} \end{array}$$

$$H_3C$$
 $CH_3$ 
 $HBr$ 
 $O$ 
 $O$ 
 $O$ 
 $O$ 

trans (2R,3R) 2,3-dimethyloxirane

#### Reactions of Ethers

Predict the products for the following acid-promoted cleavage



#### 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