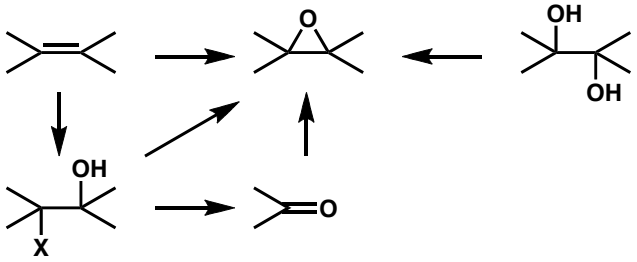
CHEM 6352 Organic Reactions & Synthesis
Epoxides: Preparation

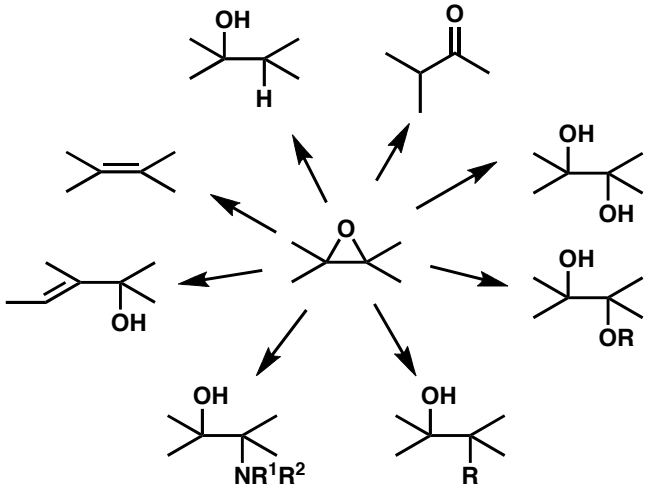
Introduction: (Review in *Tet*. **1983**, *39*, 2323)

A. Epoxides can be prepared from a variety of precursors.



X= Leaving Group (Halogen, OTf, etc.)

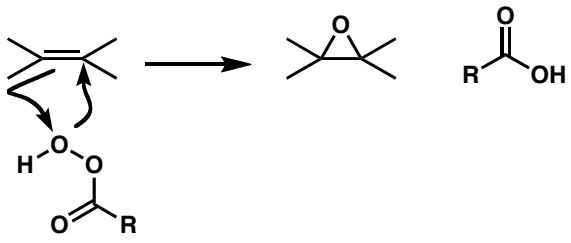
B. Epoxides can be transformed into a variety of products.



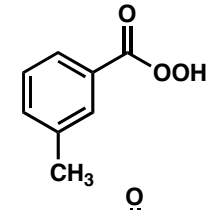
Preparation:

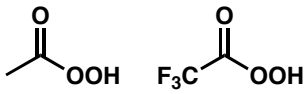
A. Epoxidation of Olefins

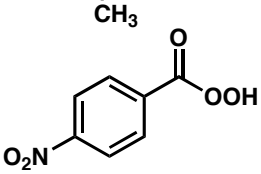
I. Using Organic Peracids – peracids can generally be thought of as electrophilic oxidants.



Common Reagents: m-Chloroperbenzoic acid, peracetic acid, trifluoroperacetic acid, and p-nitroperbenzoic acid.

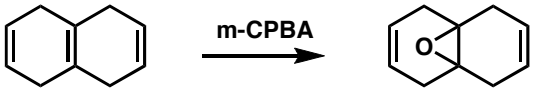




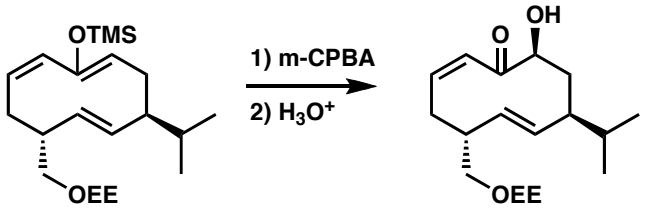


Note: This peracid is used at high temperatures (up to 90 °C) in the presence of a radical scavenger to prevent decomposition

Peracids will generally react with the most nucleophilic olefin:

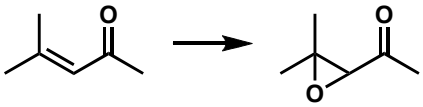


HCA **1960**, *43*, 1546

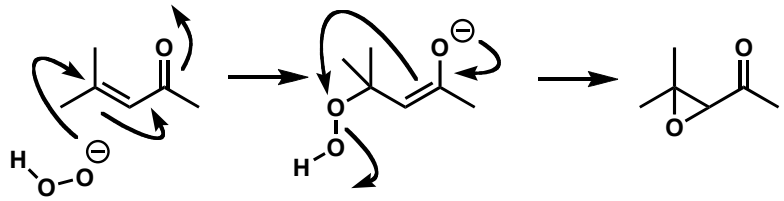


JACS **1979**, *101*, 2493

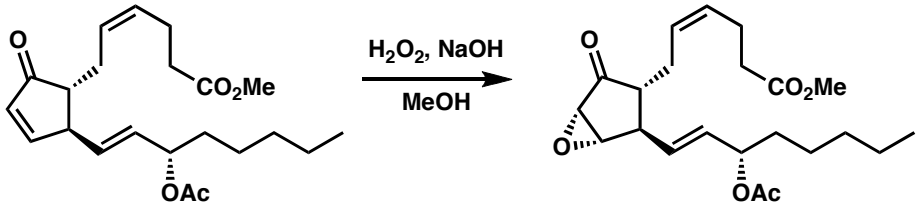
B. Epoxidation of α,ß-unsaturated carbonyl compounds.



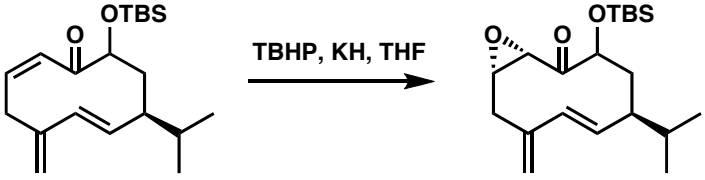
The olefin in an α,ß-unsaturated carbonyl compound is electron poor and requires the use of a nucleophilic form of peroxide. Thus, hydrogen peroxide and *t*-Butyl hydrogen peroxide (TBHP) are often employed in the presence of a base. Mechanism:



Examples:

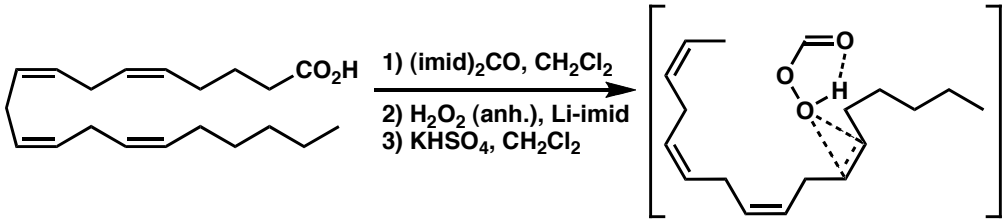


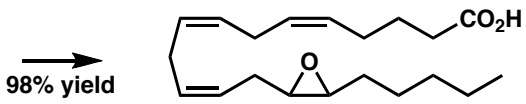
JACS **1973**, *94*, 2123



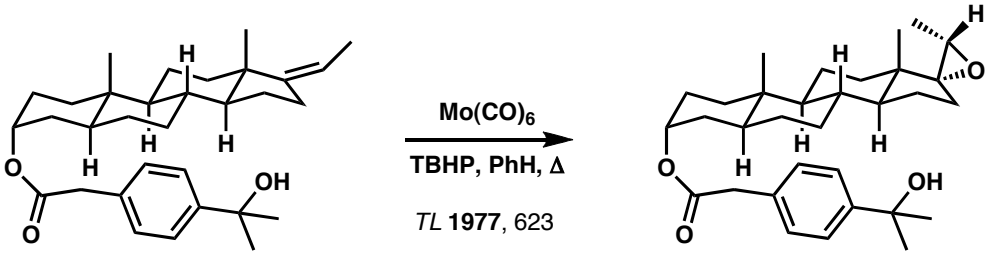
JACS **1979**, *101*, 2493

C. Intramolecular Delivery of Oxygen.



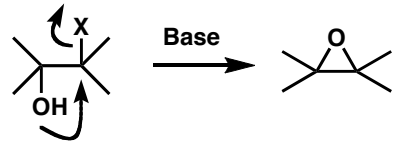


JACS **1979**, *101*, 1586



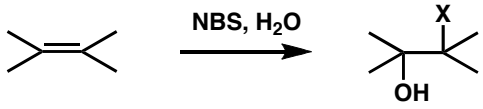
TL **1977**, 623

D. Preparation from Halohydrins

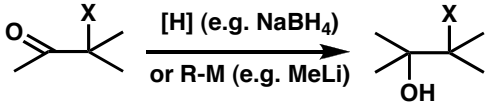


I. Halohydrin Formation

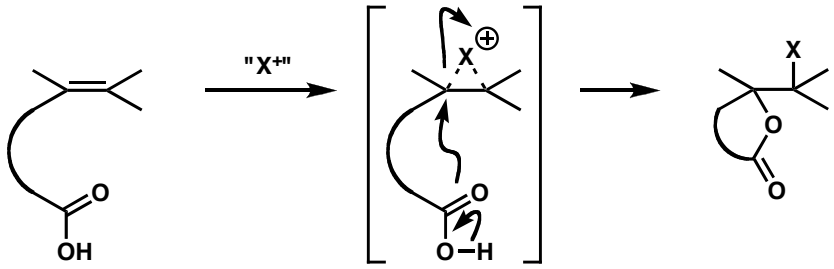
a. From Olefins



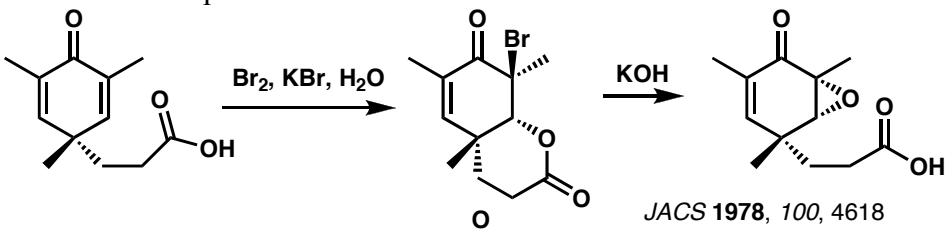
b. From α-haloketones



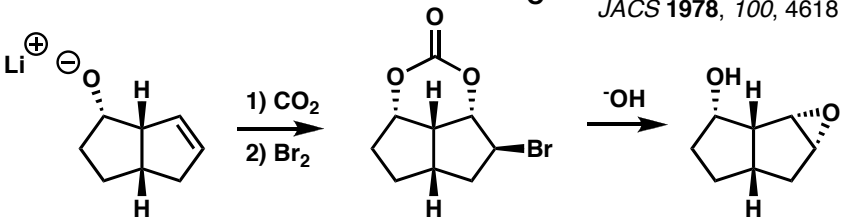
c. Halolactonization Transformations



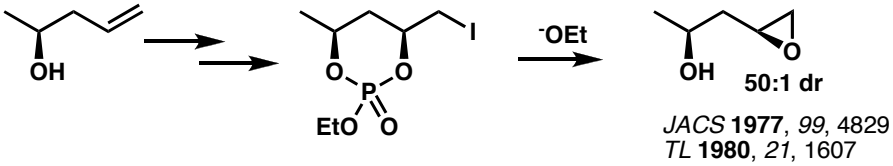
II. Examples:



JACS **1978**, *100*, 4618

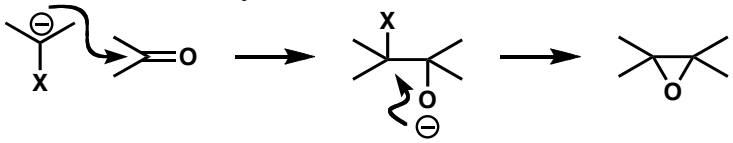


JOC **1981**, *46*, 4808

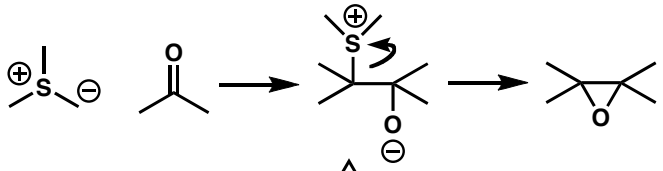


JACS **1977**, *99*, 4829
TL **1980**, *21*, 1607

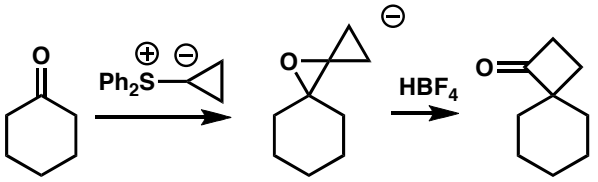
E. Preparation from Carbonyls



I. Sulfur Ylides

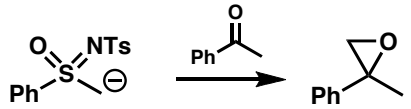


Acc. Chem. Res. **1974**, *7*, 85
Acc. Chem. Res. **1973**, *6*, 341



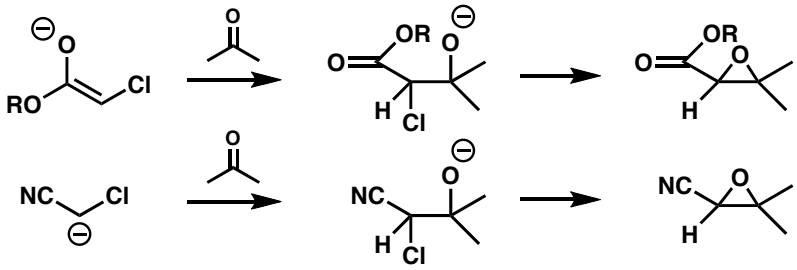
JACS **1973**, *95*, 5311
JACS **1973**, *95*, 5321

II. Sulfoximine Anions

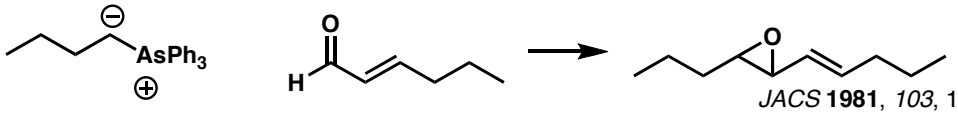


JACS **1970**, *92*, 5753
JOC **1979**, *44*, 2061 & 2065

III. Darzen's Condensation: See Name Reactions!



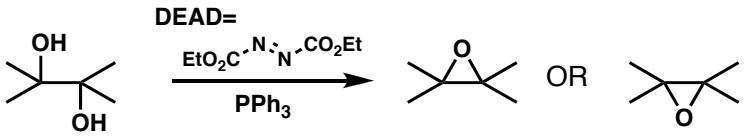
IV. Other Ylides

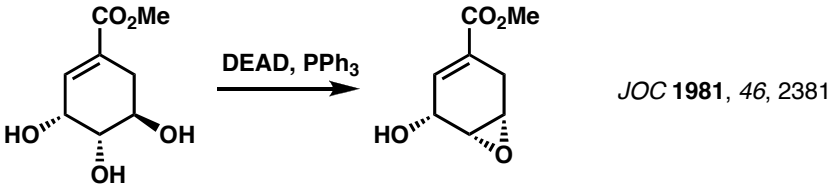


JACS **1981**, *103*, 1283

F. Miscellaneous Preparations of Epoxides

I. From 1,2-diols





JOC **1981**, *46*, 2381