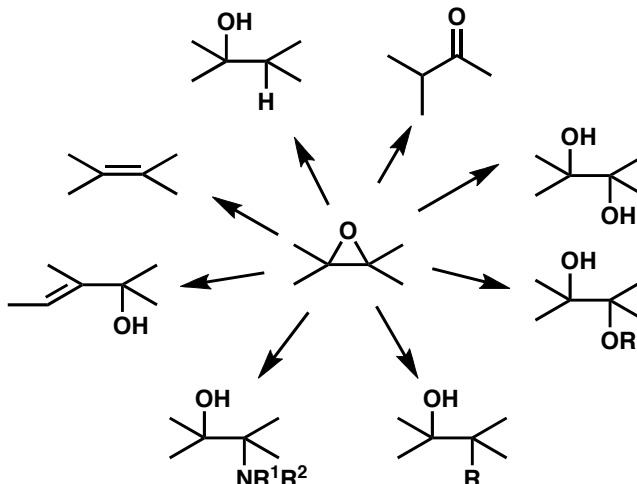


# CHEM 6352 Organic Reactions & Synthesis

## Epoxides: Synthetic Applications

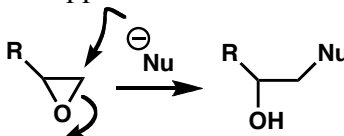
**Introduction:** (Review in *Tet.* **1983**, 39, 2323; *Synth.* **1984**, 629)

Epoxides can be transformed into a variety of products with predictable regio- and stereocontrol.

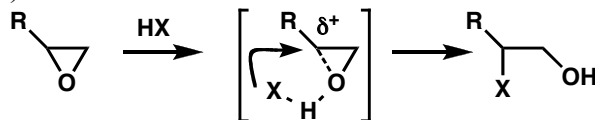


Epoxide opening can be effected under either basic or acidic conditions.

Base: Nucleophile is under Steric Approach control



Acid: Nucleophile (X) is delivered to the site best able to stabilize a carbocation



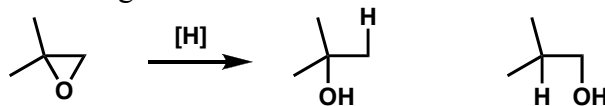
### Opening of Epoxides by External Nucleophiles:

(General Review: *Asymmetric Synthesis* Vol. 5; J.D. Morrison, Academic Press: 1985, pp 216-246)

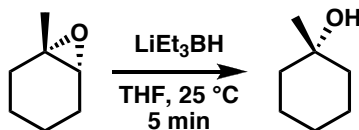
A. Hydride: Reagents Include: H<sub>2</sub>/Cat., LAH, ALH<sub>3</sub>, LiEt<sub>3</sub>BH, Li/NH<sub>3</sub>

--Different Reagents have different selectivity

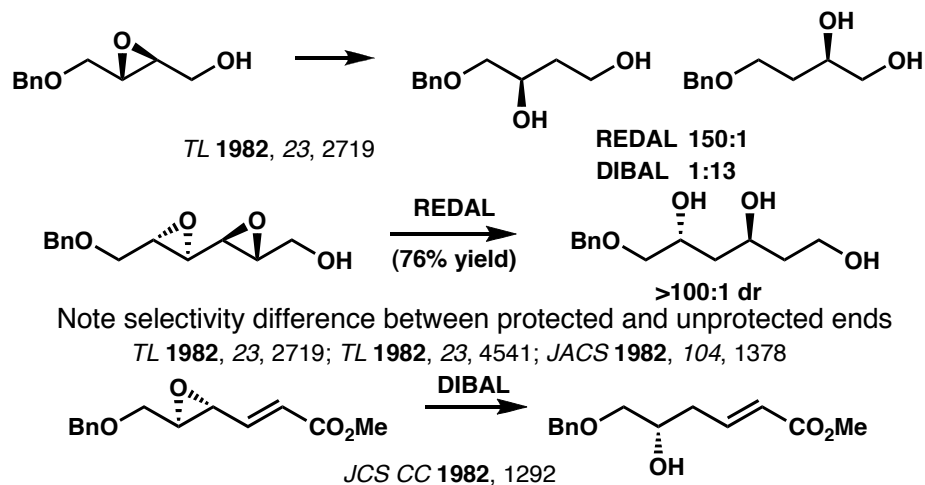
--Different Reagents have varied interactions with other functional groups



LiAlH<sub>4</sub> 98:2  
AlH<sub>3</sub> 5:95

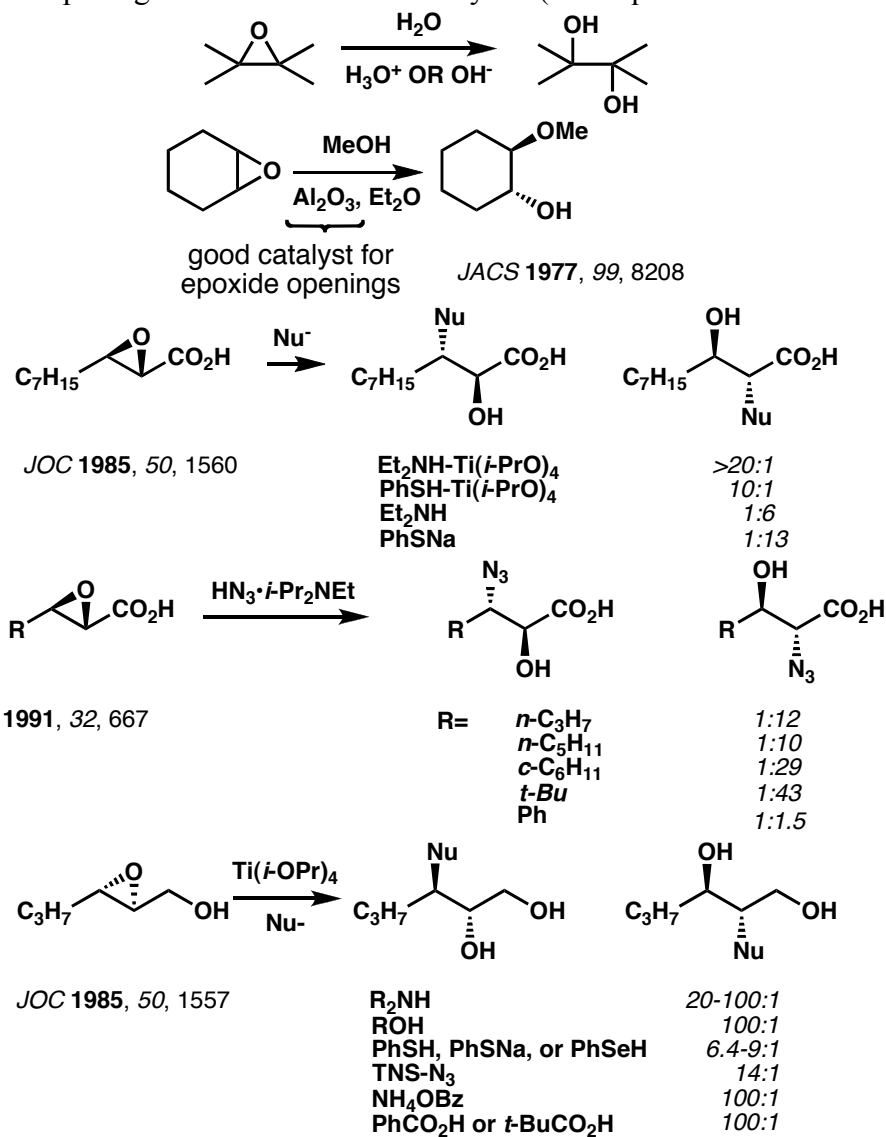


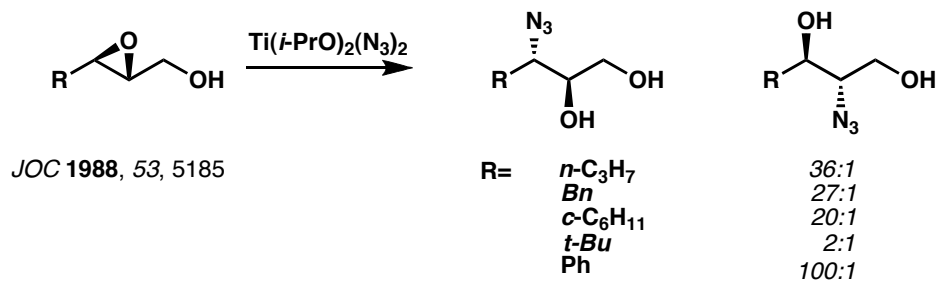
*JACS* **1973**, 95, 8486



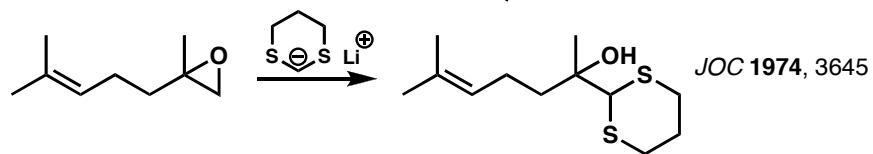
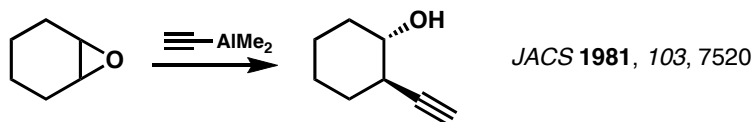
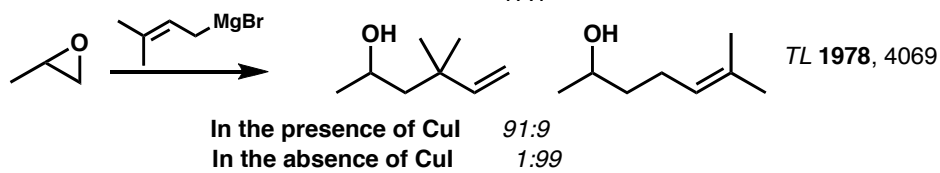
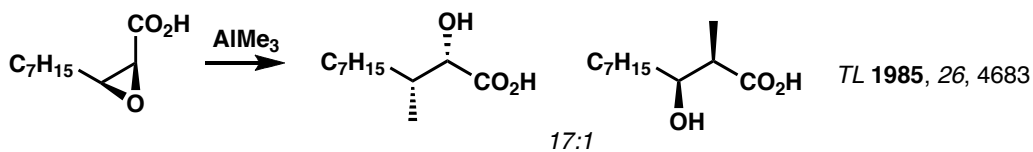
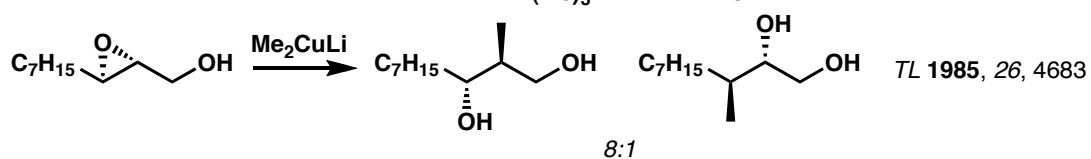
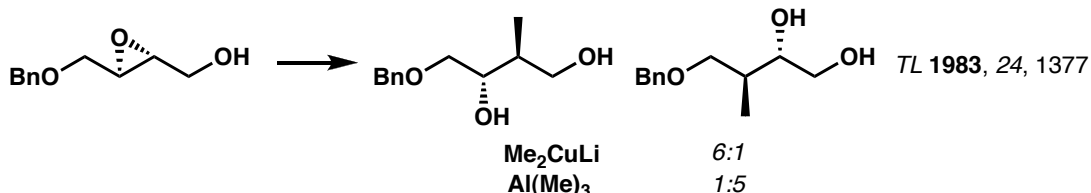
## B. Heteroatom (O, N, S):

Opening can be acid or base catalyzed (best aqueous acid is HClO<sub>4</sub>)



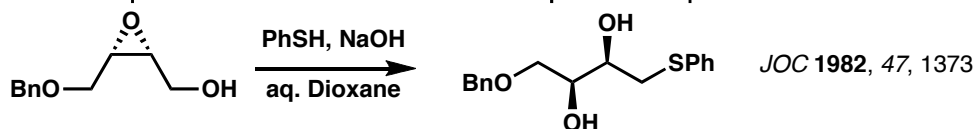
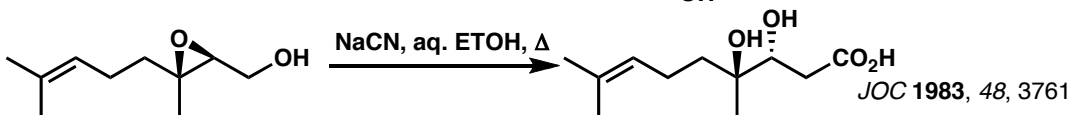
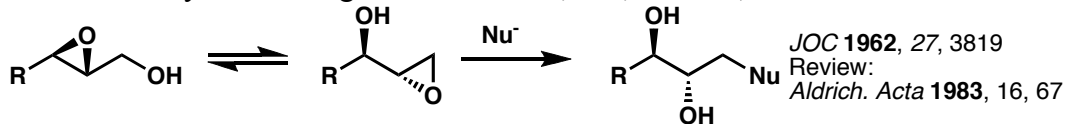


### C. Carbon

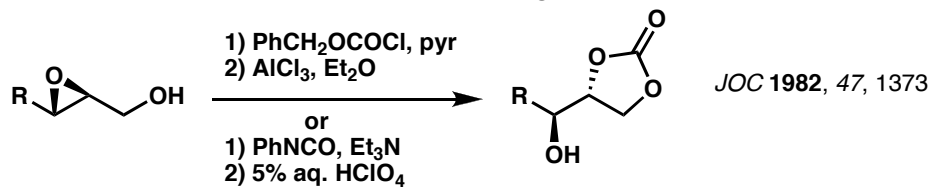
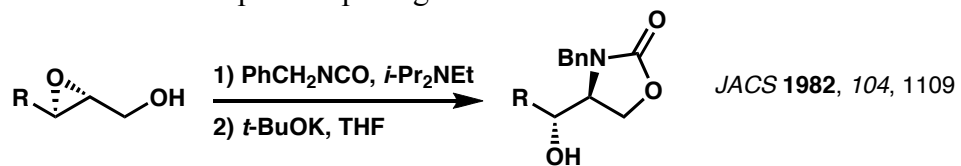


### D. Opening of 2,3-Epoxy Alcohols

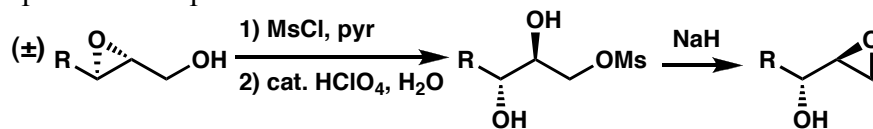
Payne Rearrangement: Nu=HO<sup>-</sup>, RS<sup>-</sup>, RR'NH, N<sub>3</sub><sup>-</sup>



### E. Internal Nucleophilic Opening



### F. Epoxide Transposition



*Aldrich. Acta* **1983**, *16*, 67