Massachusetts Institute of Technology

Organic Chemistry 5.512

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Unit 10

Stereocontrolled Epoxidation

- ★ Substrate Control: 1,2-Asymmetric Induction
- ★ Reagent Control: Sharpless-Katsuki Asymmetric Epoxidation (AE)
- ★ Synthetic Elaboration of AE Products
- ★ Reagent Control: Jacobsen-Katsuki AE
- ★ Reagent Control: Shi AE

Background Reading

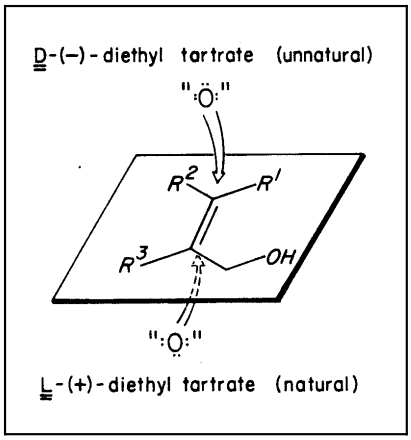
Carey and Sundberg (Part B) 4th Ed. (2001) Chapter 12 pp 762-782 (Epoxidation)

Reviews on Asymmetric Epoxidation

"Catalytic Asymmetric Epoxidation of Allylic Alcohols" Johnson, R. A.; Sharpless, K. B. In *Catalytic Asymmetric Synthesis*; Ojima, I., Ed.; Wiley-VCH, 2000, pp 231-285

"Asymmetric Epoxidation of Unfunctionalized Olefins and Related Reactions" Katsuki, T. In *Catalytic Asymmetric Synthesis*; Ojima, I., Ed.; Wiley-VCH, 2000, pp 287-326.

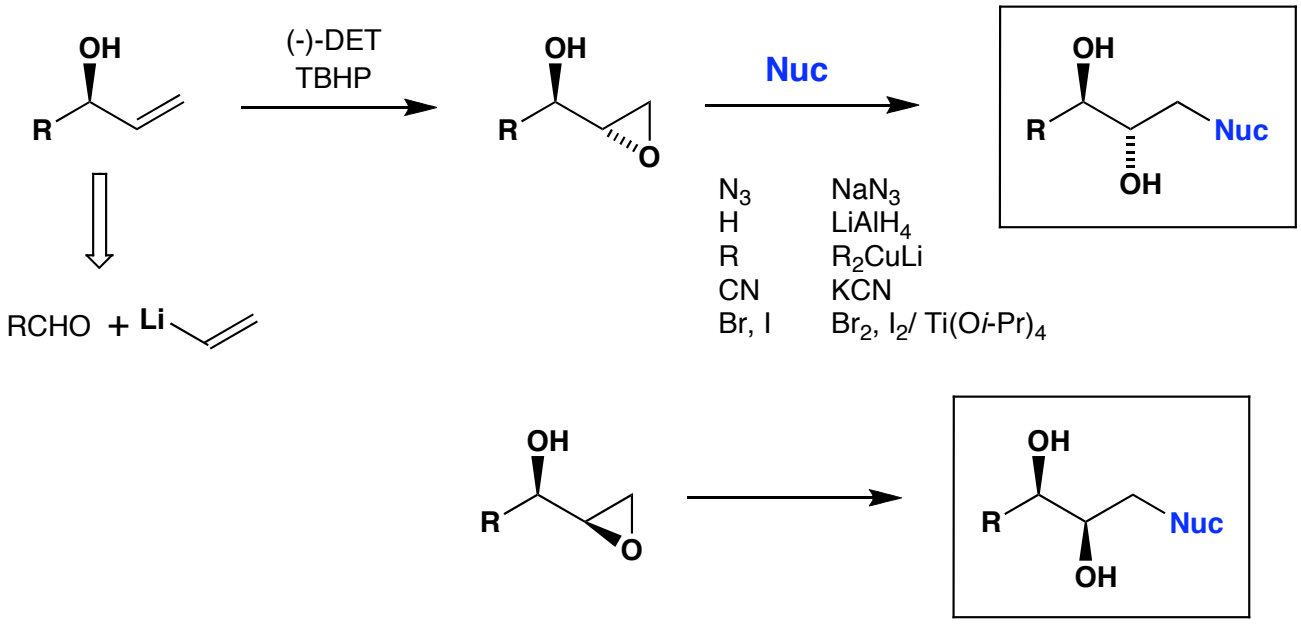
"Asymmetric Epoxidation of Allylic Alcohols: The Katsuki-Sharpless Epoxidation Reaction", Katsuki, T.; Martin, V. S. *Org. Reactions* **1996**, *48*, 1.



★ Synthetic Elaboration of AE Products

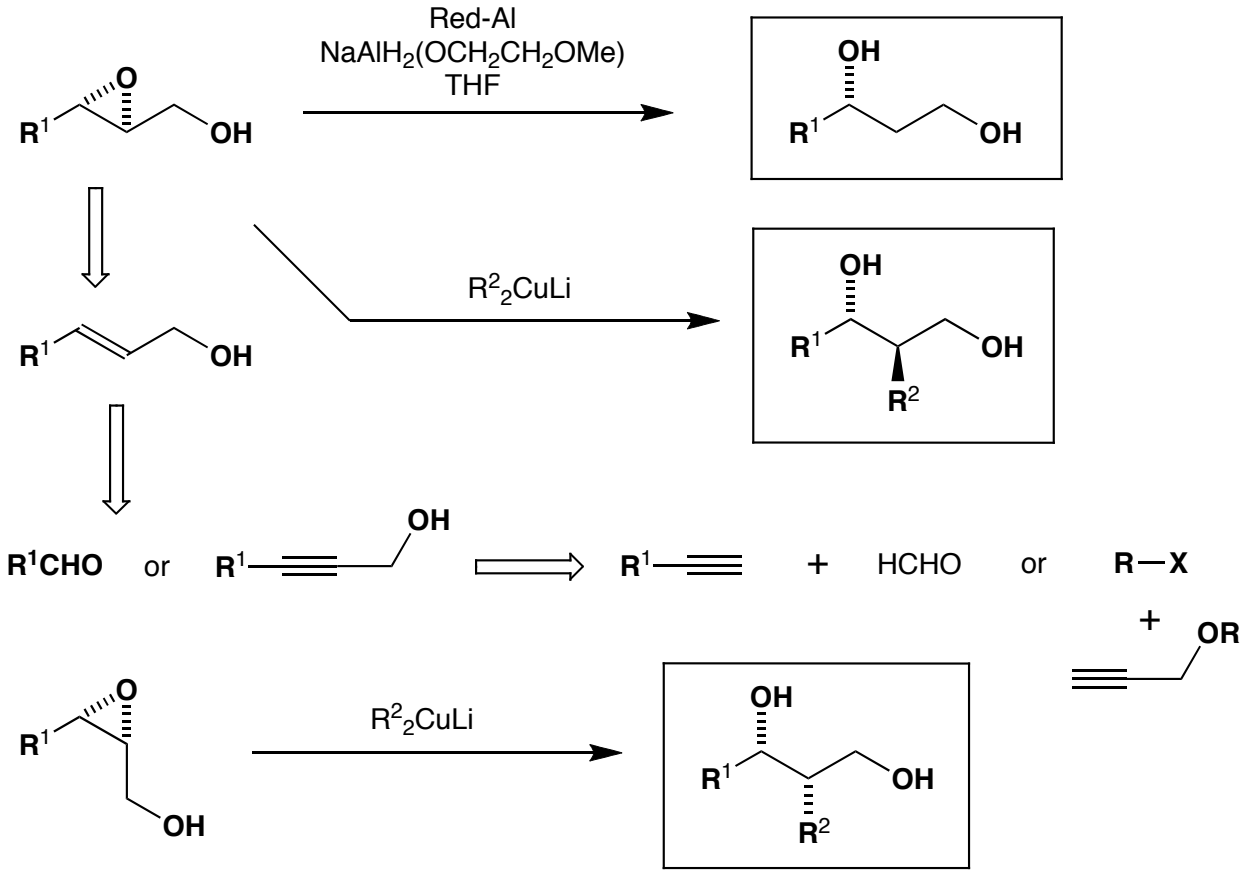
(1) Terminal Epoxides

C-1 Attack ⟶ *2,3-Diols*



(2) 2,3-Epoxy Alcohols

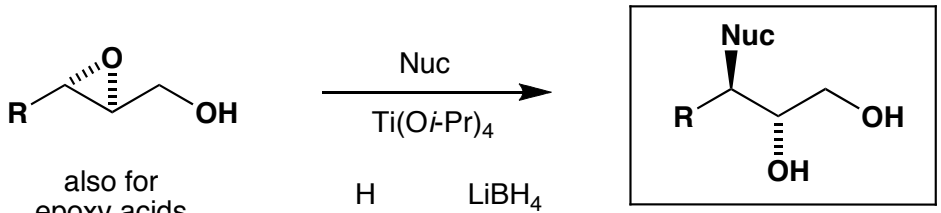
C-2 Attack ⟶ *1,3-Diols*



★ Synthetic Elaboration of AE Products

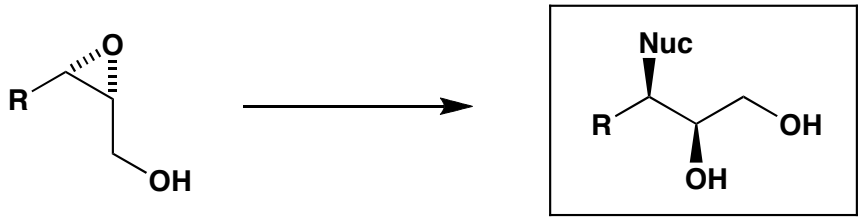
(3) 2,3-Epoxy Alcohols

C-3 Attack ⟶ *1,2-Diols*



also for epoxy acids

H	$LiBH_4$
N_3	Me_3SiN_3
OR	ROH
NR_2	R_2NH
CN	NaCN



(4) 2,3-Epoxy Alcohols

C-1 Attack ⟶ *2,3-Diols*