Massachusetts Institute of Technology

Organic Chemistry 5.512

May 2, 2005
Prof. Rick L. Danheiser

Unit 9

Stereocontrolled Hydroboration and Dihydroxylation of Alkenes

- ★ Substrate Control: 1,2-Asymmetric Induction in Hydroboration
- ★ Reagent Controlled Hydroboration
- ★ Substrate Control: 1,2-Asymmetric Induction in Dihydroxylation
- ★ Reagent Controlled Dihydroxylation: Sharpless ADH Reaction

Background Reading

Carey and Sundberg (Part B) 4th Ed. (2001) Chapter 4 pp 226-241 (Hydroboration), Chapter 12 pp 757-762 (Dihydroxylation), and Chapter 12 pp 762-782 (Epoxidation - the next unit)

Review on Hydroboration

"Catalytic Asymmetric Hydroboration: Recent Advances and Applications in Carbon-Carbon Bond-Forming Reactions" Crudden, C. M.; Edwards, D. *Eur. J. Org. Chem.* **2003**, 4695

Reviews on Asymmetric Dihydroxylation and Aminohydroxylation

"Catalytic Asymmetric Dihydroxylation: Discovery and Development" Johnson, R. A.; Sharpless, K. B. In *Catalytic Asymmetric Synthesis*; Ojima, I., Ed.; Wiley-VCH, 2000, pp 357-398

"Recent Advances in Asymmetric Dihydroxylation and Aminohydroxylation" Bolm, C.; Hildebrand, J. P.; Muniz, K. In *Catalytic Asymmetric Synthesis*; Ojima, I., Ed.; Wiley-VCH, 2000, pp 398-428.

Photograph removed
due to copyright reasons.

Photograph removed
due to copyright reasons.

H. C. Brown *K. Barry Sharpless*

Sharpless Asymmetric Dihydroxylation

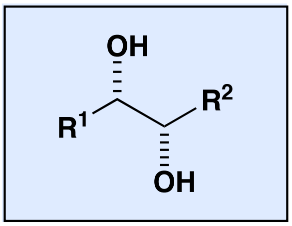
Review on Sharpless ADH

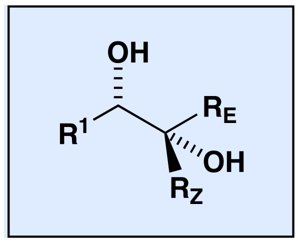
"Catalytic Asymmetric Dihydroxylation" Kolb, H. C.; VanNieuwenhze, M. S.; Sharpless, K. B. *Chem. Rev.* **1994**, *94*, 2483

Organic Syntheses Procedures

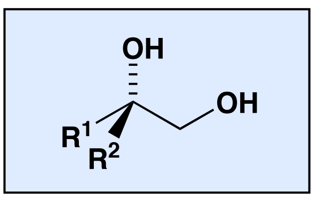
Oi, R.; Sharpless, K. B. *Org. Synth.* Coll. Vol. **9**, 251 and McKee, B. H.; Gilheany, D. G.; Sharpless, K. B. *Org. Synth.* Coll. Vol. **9**, 383

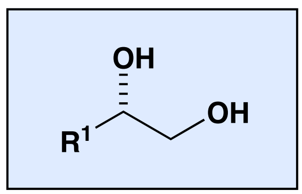
Retrons





Generally very good selectivity for E-disubstituted and trisubstituted alkenes (for either enantiomer)





Borderline to good selectivity for terminal alkenes and 1,1-disubstituted alkenes

AD-mix α $(DHQ)_2PHAL + K_2OsO_2(OH)_4 + K_3Fe(CN)_6$ $81.70/50 g

AD-mix β $(DHQD)_2PHAL + K_2OsO_2(OH)_4 + K_3Fe(CN)_6$

Figures removed due to copyright reasons.