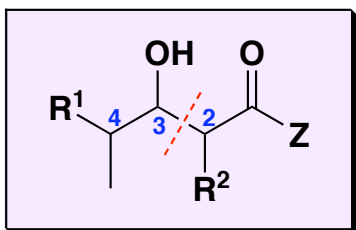


Massachusetts Institute of Technology
Organic Chemistry 5.512

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Prof. Rick L. Danheiser

Unit 6
Stereocontrolled Aldol Reactions

- ★ Overview of the Stereochemistry of the Aldol Reaction and Substrate Control
- ★ Reagent Control: Chiral Auxiliary Strategies
- ★ Reagent Control: Chiral Controller Strategies
- ★ Reagent Control: Chiral Lewis Acid Catalyzed Aldol Reactions



The Aldol Retron

General Review on Recent Advances

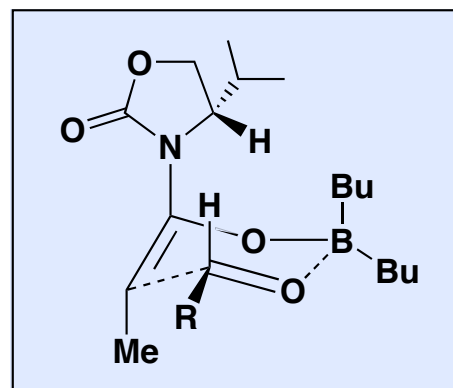
"Current Progress in the Asymmetric Aldol Addition Reaction"
Palomo, C.; Oiarbide, M.; Garcia, J. M.
Chem. Soc. Rev. **2004**, *33*, 65

II. Chiral Auxiliary Strategies

★ 2,3-Syn Aldols

Evans Oxazolidinone
Boron Enolates

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Org. Synth. Coll. Vol. **8**, 339



Review

"Asymmetric Aldol Reactions Using Boron Enolates"
Cowden, C. J.; Paterson, I. *Organic Reactions* **1997**, *51*, 1

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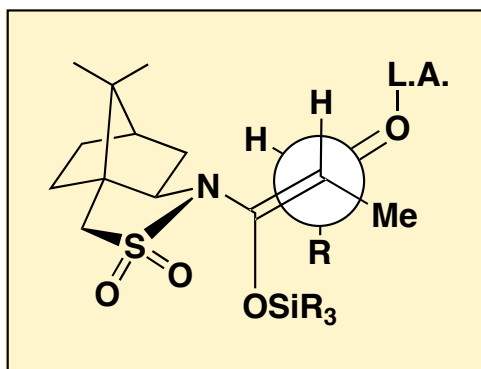
★ 2,3-Anti Aldols

(1) Evans Dones

D. A. Evans et al.
J. Am. Chem. Soc. **2002** 124, 392
and *Org. Lett.* **2002**, 4, 1127

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(2) Oppolzer Sultams



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(3) Masamune Esters

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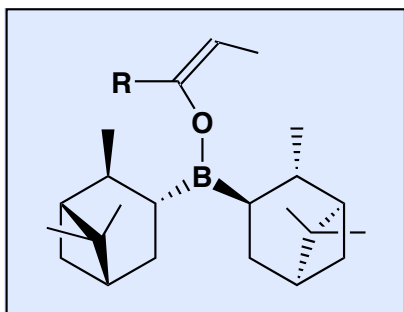
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"Boron-Mediated Aldol Reaction of Carboxylic Esters"
Abiko, A. *Acc. Chem. Res.* **2004**, 37, 387
see also *Org. Synth. Coll. Vol.* **10**, 55 and 343

III. Chiral Controller Strategies

(1) Paterson Boron Enolates



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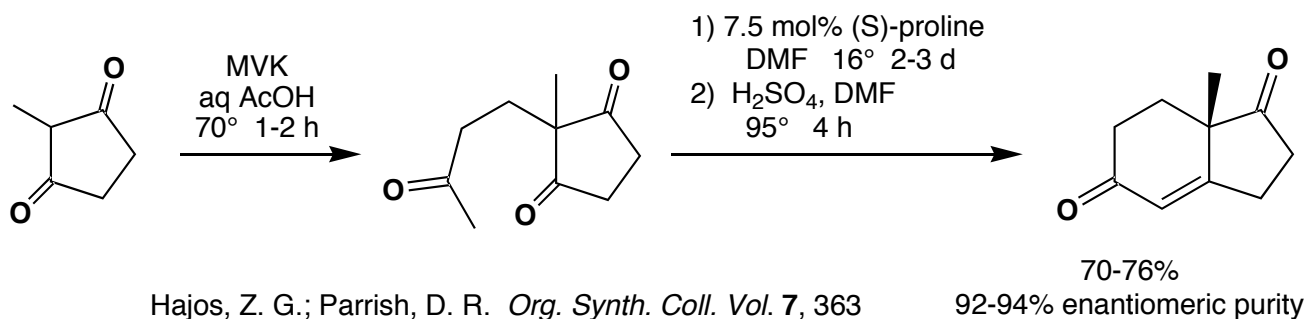
Ian Paterson
Cambridge University

(2) Enamine Aldol Reactions

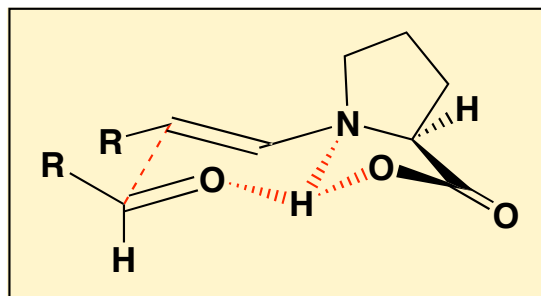
Reviews

- (1) "Proline-Catalyzed Asymmetric Reactions" List, B. *Tetrahedron* **2002**, *58*, 5573
- (2) "Enamine Catalysis Is a Powerful Strategy for the Catalytic Generation and Use of Carbanion Equivalents" List, B. *Acc. Chem. Res.* **2004**, *37*, 548
- (2) "Enamine-Based Organocatalysis with Proline and Diamines" Notz, W.; Tanaka, F.; Barbas, C. F. *Acc. Chem. Res.* **2004**, *37*, 580

Hajos-Parrish-Eder-Sauer-Wiechert Reaction



Figures removed due to copyright reasons.



III. Chiral Lewis Acid Strategies

(1) Carreira Chiral Ti Catalyst

Carreira, E. M.; Singer, R. A.; Lee, W. *J. Am. Chem. Soc.* **1994** *116*, 8837

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(2) Evans Copper BOX and PYBOX Catalysts

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