Massachusetts Institute of Technology

Organic Chemistry 5.512

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Unit 5

Stereocontrolled 1,2-Addition of Allylmetal Compounds to Carbonyl Groups

- ★ Introduction: Mechanism and Transition States
- ★ Substrate Control: Addition of Achiral Allylmetals to α-Chiral Aldehydes
- ★ Reagent Control: Addition of Chiral Allylmetals to Achiral Aldehydes
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  (with Chiral Lewis Acid Catalysts)
- ★ Addition of Chiral Allylmetals to α-Chiral Aldehydes (Double Asymmetric Synthesis)
- ★ Crotylmetal Additions: 3,4-Stereochemistry (Intrinsic Diastereoselection)
- ★ Crotymetal Additions to α-Chiral Aldehydes

General References

"Allylation of Carbonyls: Methodology and Stereochemistry", Denmark, S. E.; Almstead, N. G. In *Modern Carbonyl Chemistry*; Otera, J., Ed.; Wiley-VCH, 2000, pp 299-402.

"Recent Applications of the Allylation Reaction to the Synthesis of Natural Products", Chemler, S. R.; Roush, W. R. In *Modern Carbonyl Chemistry*; Otera, J., Ed.; Wiley-VCH, 2000, pp 403-490.

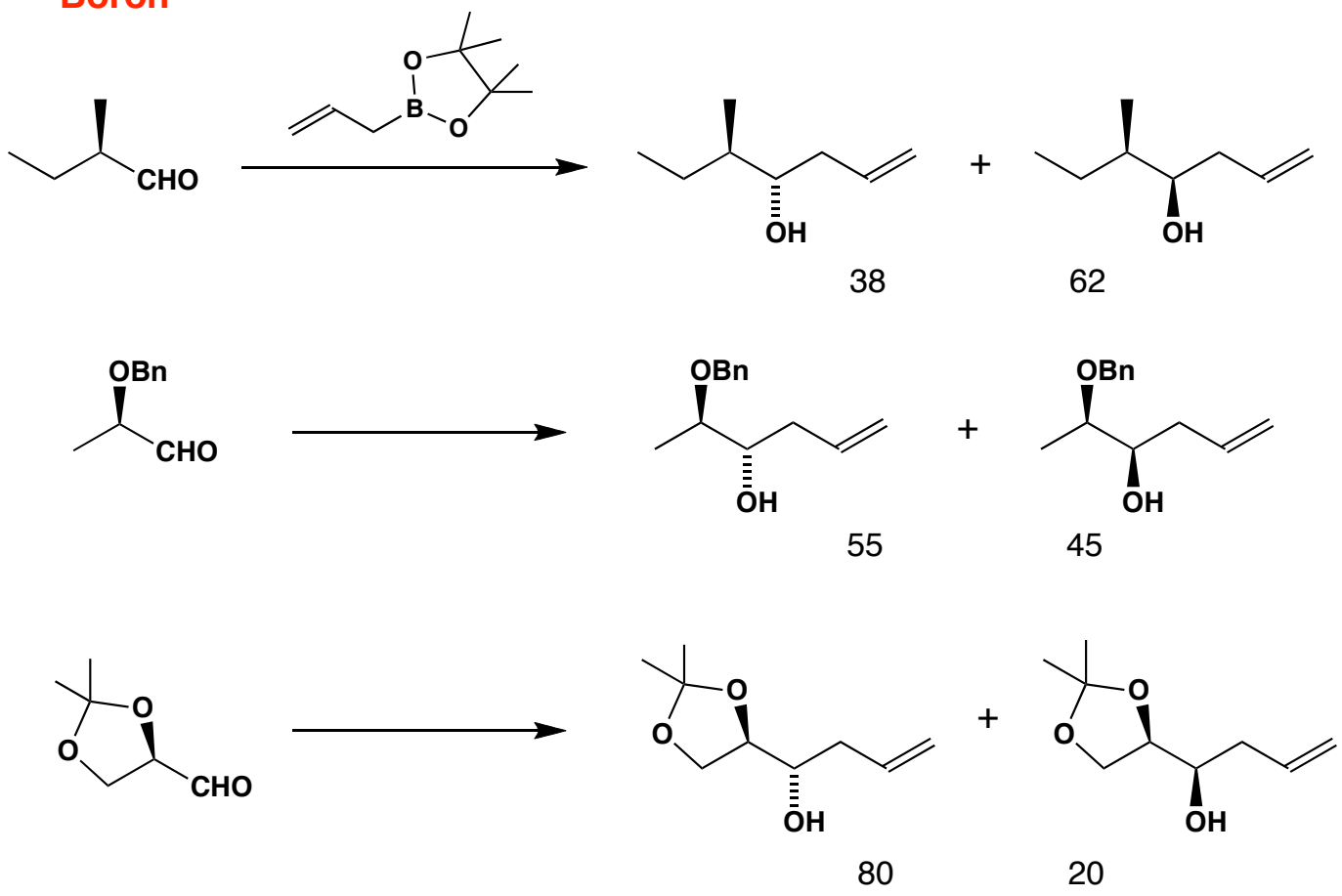
"Catalytic Enantioselective Addition of Allylic Organometallic Reagents to Aldehydes and Ketones", Denmark, S. E.; Fu, J. *Chem. Rev.* **2003**, *103*, 2763-2793.

"Recent Advances in the Activation of Boron and Silicon Reagents for Stereocontrolled Allylation Reactions", Kennedy, J. W. J.; Hall, D. G. *Angew. Chem. Int. Ed.* **2003**, *42*, 4732-4739.

Substrate Control: Addition of Achiral Allylmetals to α–Chiral Aldehydes

Representative Examples

Boron



Tin/Lewis Acid