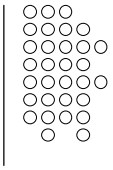
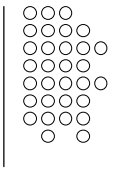
***I. Basic Principles***

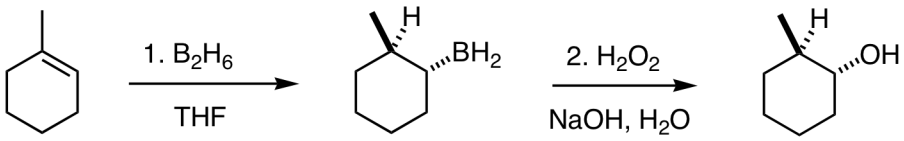
**I-M.** Hydroboration





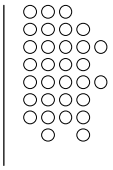
## General Comments on Hydroboration

**Hydroboration** of alkenes proceeds with overall anti-Markovnikov selectivity.
Sources for $BH_3$ (diborane, $BH_3$·THF) or sterically more hindered boranes (9-BBN) add to alkenes to give intermediate organoboranes which can be oxidized with $H_2O_2$ or hydrolyzed with aqueous acid to give alcohols and alkanes, respectively.
The regioselectivity of hydroboration is determined by electronic (polarization of the B-H bond) and steric factors. The more highly hindered the substituents on borane, the higher the regioselectivity in the addition to unsymmetrically substituted alkenes.
The mechanism for hydroboration involves a *syn*-addition across the B-H bond. In the oxidation, the organic residue migrates under retention of configuration.

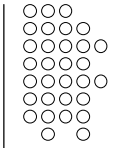



Kobayashi, Y.; Nakayama, Y.; Yoshida, S., "Determination of the stereoisomers of korormicin from eight possible stereoisomers by total synthesis." *Tetrahedron Lett.* **2000**, *41*, 1465-1468. Acetaldehyde oxidizes the hydroboration product. Before coupling, the boronate is converted to the ate complex.

Girard, S.; Robins, R. J.; Villieras, J.; Lebreton, J., "A short and efficient synthesis of unnatural (R)-nicotine." *Tetrahedron Lett.* **2000**, *41*, 9245-9250.

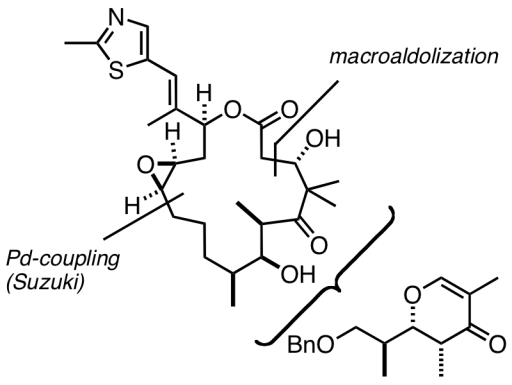


Rh-Catalyzed Hydroboration



Trost, B. M.; Toste, F. D., "A catalytic enantioselective approach to chromans and chromanols. A total synthesis of (-)-calanolides A and B and the vitamin E nucleus." *J. Am. Chem. Soc.* **1998**, *120*, 9074.

## Rh-Catalyzed Hydroboration

Ohmura, T.; Yamamoto, T.; Miyaura, N., "Rhodium- or iridium-catalyzed *trans*-hydroboration of terminal alkynes, giving (Z)-1-alkenylboron compounds." *J. Am. Chem. Soc.* **2000**, *122*, 4990-4991.

Danishefsky's synthesis of epothilone A (*Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2801). Illustrates the renaissance of cycloaddition chemistry and the power of transition metal catalyzed cross-coupling.