Massachusetts Institute of Technology Organic Chemistry 5.512

April 7, 2006 Prof. Rick L. Danheiser

Stereocontrolled Conjugate Addition

- ★ Catalytic Asymmetric Conjugate Addition I: Unstabilized Nucleophiles

 Hayashi-Miyaura Rh-Catalyzed Conjugate Addition Reactions

 Cu-Catalyzed Conjugate Addition of Organozinc and Organomagnesium Compounds

 Organocatalytic Conjugate Addition of Activated Aromatic Compounds
- ★ Catalytic Asymmetric Conjugate Addition II: Conjugate Reduction
- ★ Catalytic Asymmetric Conjugate Addition III: Stabilized Nucleophiles Michael Reactions Using Heterobimetallic Catalysts (Shibasaki) Organocatalytic Michael Reactions (Jorgensen)

Cu-Catalyzed Conjugate Addition of Organozinc Compounds

B. Feringa et al. In *Modern Organocopper Chemistry;* Krause, N., Ed.; Wiley-VCH, 2002, pp 224-258

Cu-Catalyzed Conjugate Addition of Organomagnesium Compounds

B. Feringa et al.

Angew. Chem. Int. Ed. 2005, 44, 2752 and J. Am. Chem. Soc. 2004, 126, 12784

Organocatalytic Conjugate Addition of Activated Aromatic Compounds

Reviews: See Berkessel and Gröger

R CHO
$$\begin{array}{c}
R_2^* N H_2^+ C I^- \\
-H_2 O
\end{array}$$

$$\begin{array}{c}
Ph \\
N \\
H
\end{array}$$

$$\begin{array}{c}
R_1 \\
N \\
R_2^*
\end{array}$$

$$\begin{array}{c}
R_2^* N R_2^* \\
R_1 \\
R_2
\end{array}$$

$$\begin{array}{c}
R_2^* N R_2^* \\
R_1 \\
R_2
\end{array}$$

$$\begin{array}{c}
R_2^* N R_2^* \\
R_1 \\
R_2
\end{array}$$

Catalytic Asymmetric Conjugate Reduction

Buchwald Cu-Catalyzed Conjugate Reduction: J. Am. Chem. Soc. 2003, 125, 11,253 and refs cited

MacMillan Organocatalytic Conjugate Reduction: J. Am. Chem. Soc. 2005, 127, 32

Enantioselective Organocatalytic Hydride Reduction (EOHR)

EOHR: Origins of Enantiocontrol with Catalyst 2



