Category
Organocatalytic Carbocyclizations

Key words
polyene cyclization
cationic polycyclization
organo-SOMO catalysis
thiourea catalysis

Significance: The research groups of MacMillan and Jacobsen have developed examples of organocatalytic carbocyclizations. Rendler and MacMillan employed organo-SOMO catalysis for cyclizations of polyene aldehydes (e.g., 3). Polycycles (e.g., 4) were obtained in good yields and enantioselectivity with 30 mol% of secondary amine catalyst 1. Jacobsen and co-workers developed thiourea catalyst 2 which effects polycyclization of hydroxy lactams (e.g., 5). Polycycles (e.g., 6) were obtained in moderate to good yields and enantiomeric ratios up to 97:3.

Comment: The biosynthesis of complex cyclic terpenes from polyene precursors has inspired the development of biomimetic polyene cyclizations (R. A. Yoder, J. N. Johnston Chem. Rev. 2005, 105, 4730). An enantioselective polyene cyclization induced by Lewis acid assisted chiral Bronsted acid has been developed recently (H. Ishibashi, K. Ishihara, H. Yamamoto J. Am. Chem. Soc. 2004, 126, 11122). The cationic polycyclization reported by Jacobsen is initiated by the formation of a catalyst-bound iminium–chloride ion pair. As the enantioselectivity of the reaction is highly dependent on the size of the arene substituent in 2, stabilizing cation–π-interactions were proposed. Rendler and MacMillan have accomplished radical polycyclization of polyenals using the previously established organo-SOMO catalysis concept.