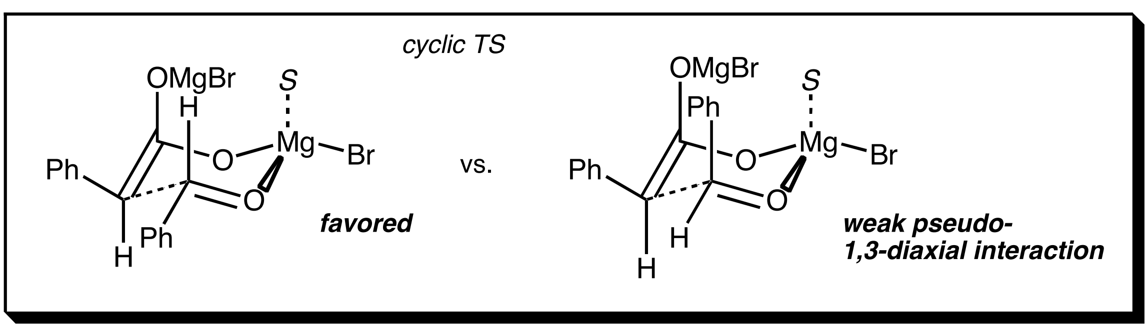
Enolate Chemistry II

The Ivanov Reaction

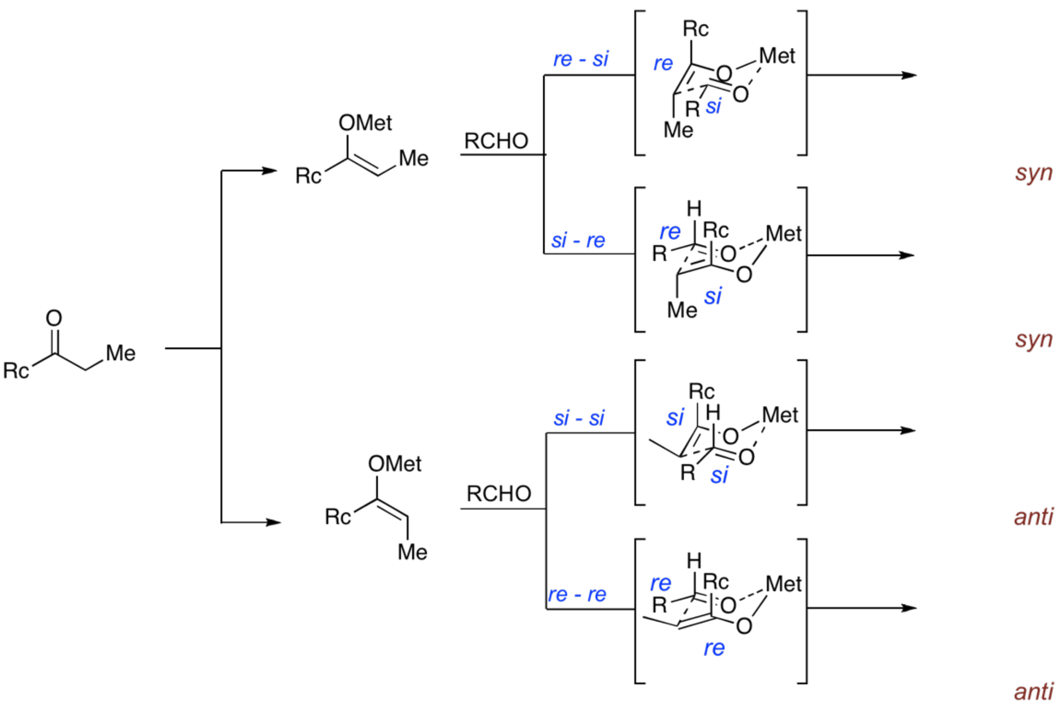
rationalization: **Zimmerman-Traxler**, *JACS* **1957**, *79*, 1920.



To achieve high diastereo- and enantioselectivity, it is necessary to:

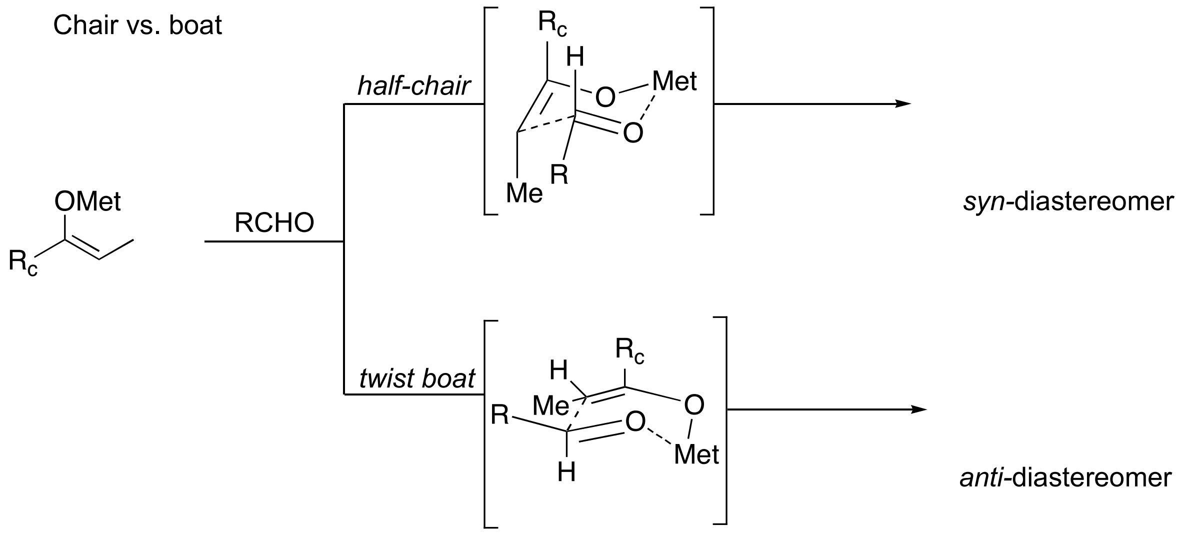
- control the enolization step
- use an auxiliary with a large diastereofacial bias
- control competing transition states, e.g.
    - half-chair vs. twist boat
    - closed vs. open
- use metal-derivatives that have clearly defined coordination geometries.

The stereochemical implications of the Zimmerman-Traxler transition state model for the aldol reaction can be summarized as follows:

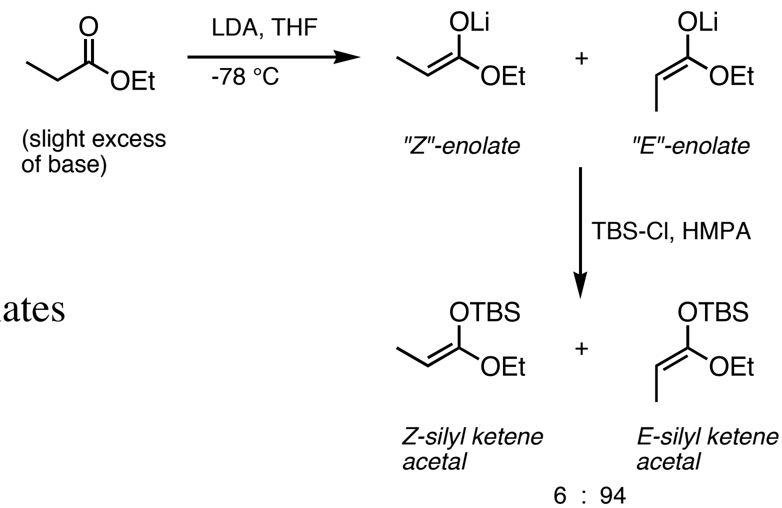


Zimmerman-Traxler transition states represent the most frequently used models, but other possibilities have always to be considered as well:

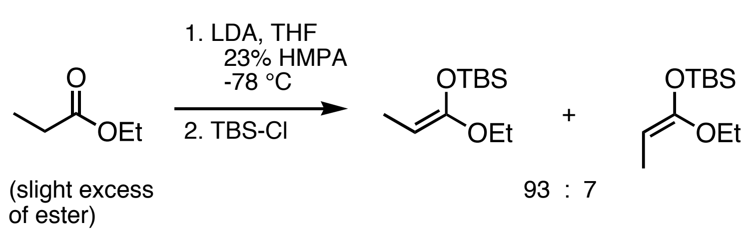
Chair vs. boat



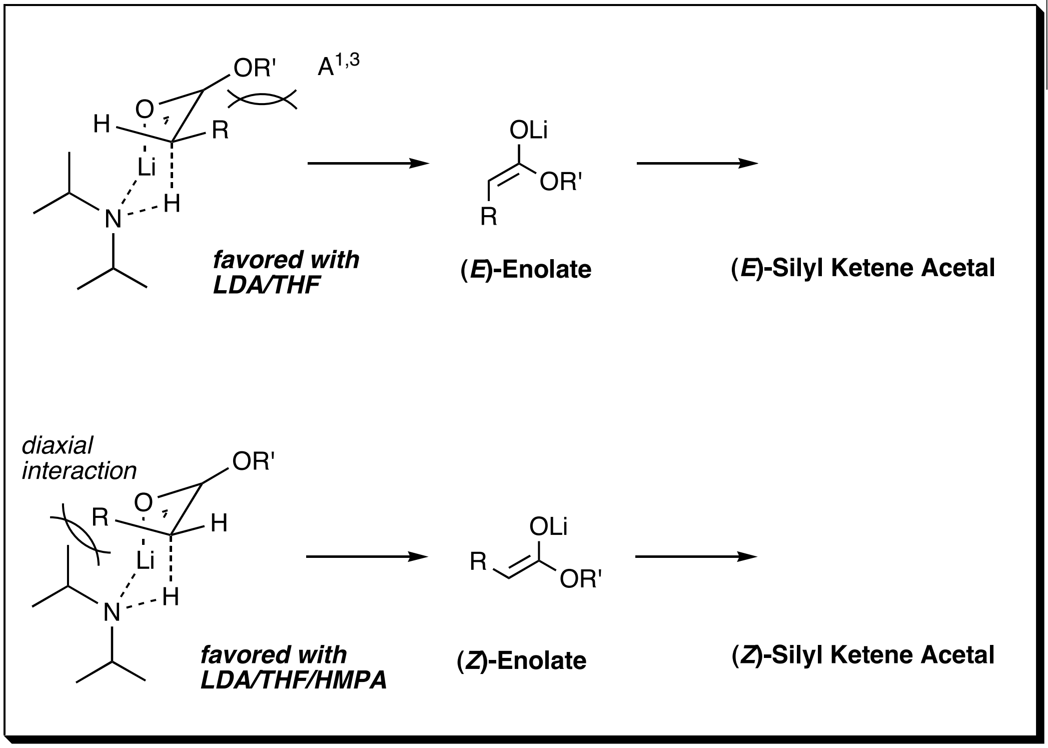
Enolization



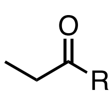
a. Lithium enolates



Transition states for enolization:

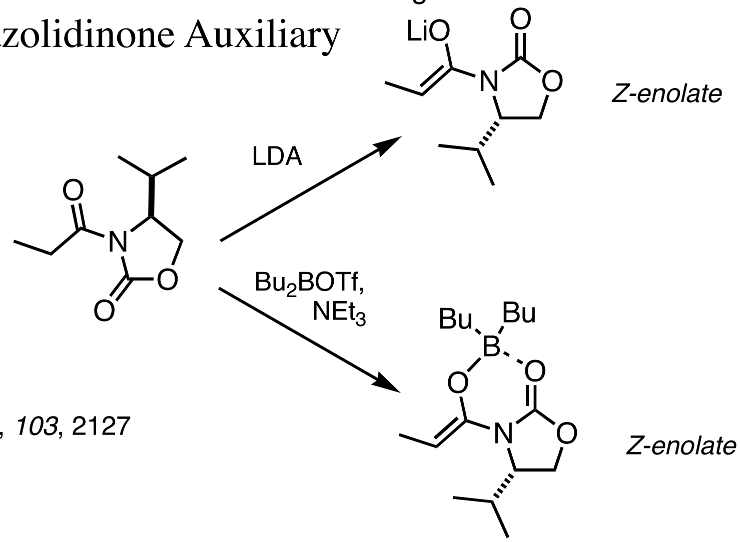


Kinetic ratios for LDA/THF enolization:

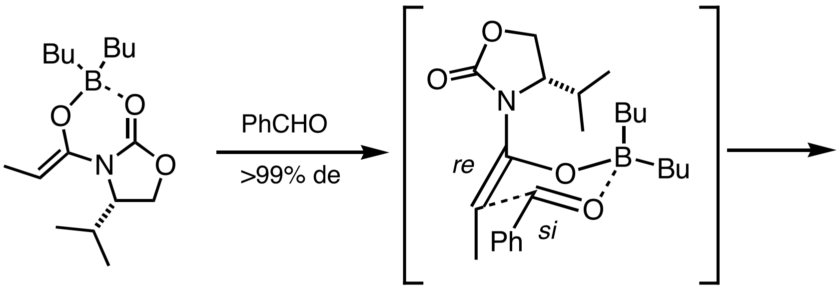


R	*E/Z*	
OMe	95 : 5	
O-*t*-Bu	95 : 5	
Et	50 : 50	
i-Pr	40 : 60	
t-Bu	0 : 100	
Ph	0 : 100	
NEt_2	0 : 100	(cf. Dauben, *JACS* **1985**, *107*, 2264)

Evans' Chiral Oxazolidinone Auxiliary



D. A. Evans, *JACS* **1981**, *103*, 2127



Smith, A. B.; Qiu, Y.; Jones, D. R.; Kobayashi, K. *J. Am. Chem. Soc.* **1995**, *117*, 12011.