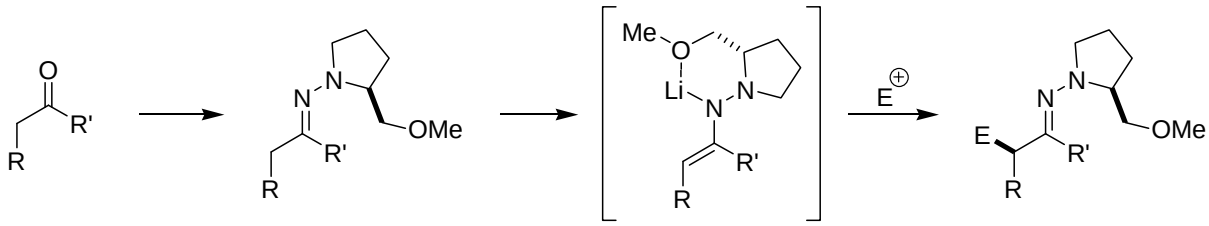
Lecture “Modern Synthetic Methods”

Take-home messages from Week 6

2.3.2 Alkylation of enolates derived from aldehydes or ketones

Enders’ alkylation: - Transformation of the carbonyl group into a chiral hydrazone

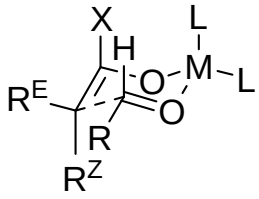
- Chiral hydrazine auxiliary prepared from L-proline
- Auxiliary cleaved off either oxidatively or hydrolytically



2.4. The Aldol Reaction

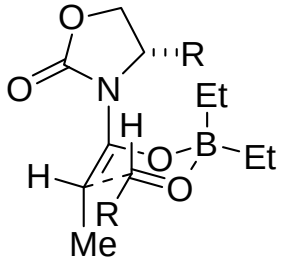
Need to control:	1) Enolate geometry	- same solutions as in enolate alkylation
	2) Enolate site attack	- “ “ “ “
	3) Carbonyl site attack	- solved by Zimmermann-Traxler TS

Zimmermann-Traxler transition state:



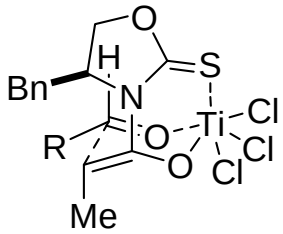
- Enolate metal also activates carbonyl in a cyclic array
- Aldehyde is placed with *H* being pseudo-axial
- (*E*)-Enolates give *anti*-aldol products
- (*Z*)-Enolates give *syn*-aldol products

Evans aldol reaction:



- Use of boron enolates: six-membered ring contracts, leading to better selectivity
- Boron has only 4 coordination sites, therefore no chelate to oxazolidinone: dipole repulsion

Crimmings aldol reaction:



- Titanium enolate allows for additional coordination
- Thiooxazolidinones work better