Make up lecture
11/24 - 7pm Tuesday
219 BRL

Reading for next week:
2.4, 4, 5

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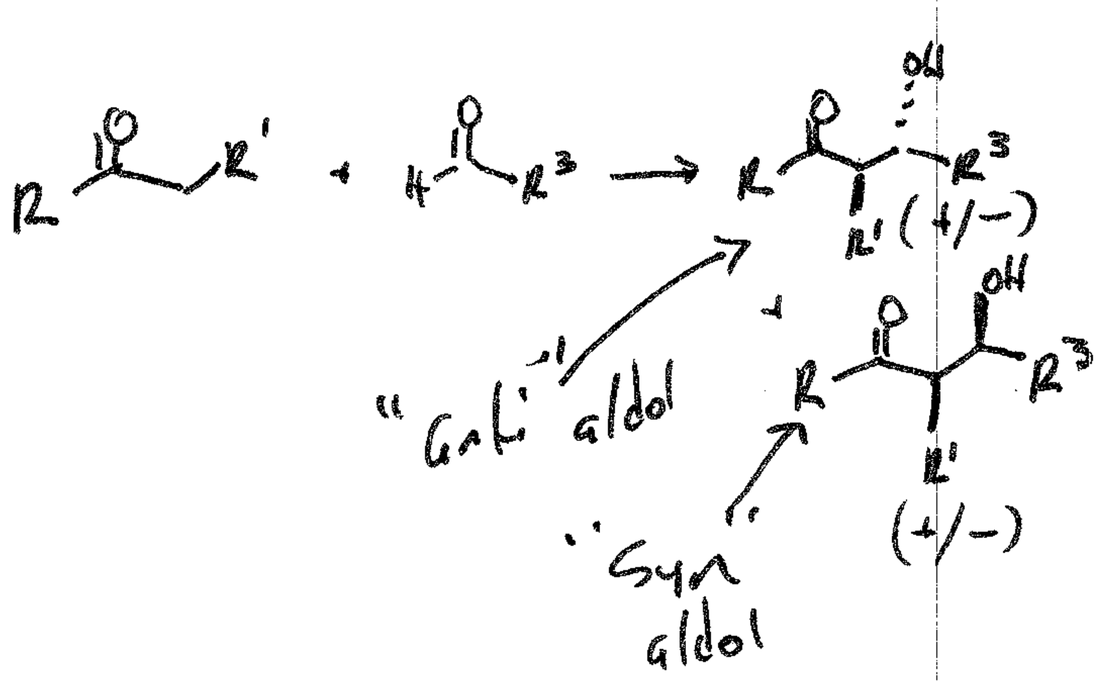
office hours moved next week
Saturday 10AM 10/31/09

Today: Aldol Rxns
Micheal Rxns
Allyl additions to carbonyls

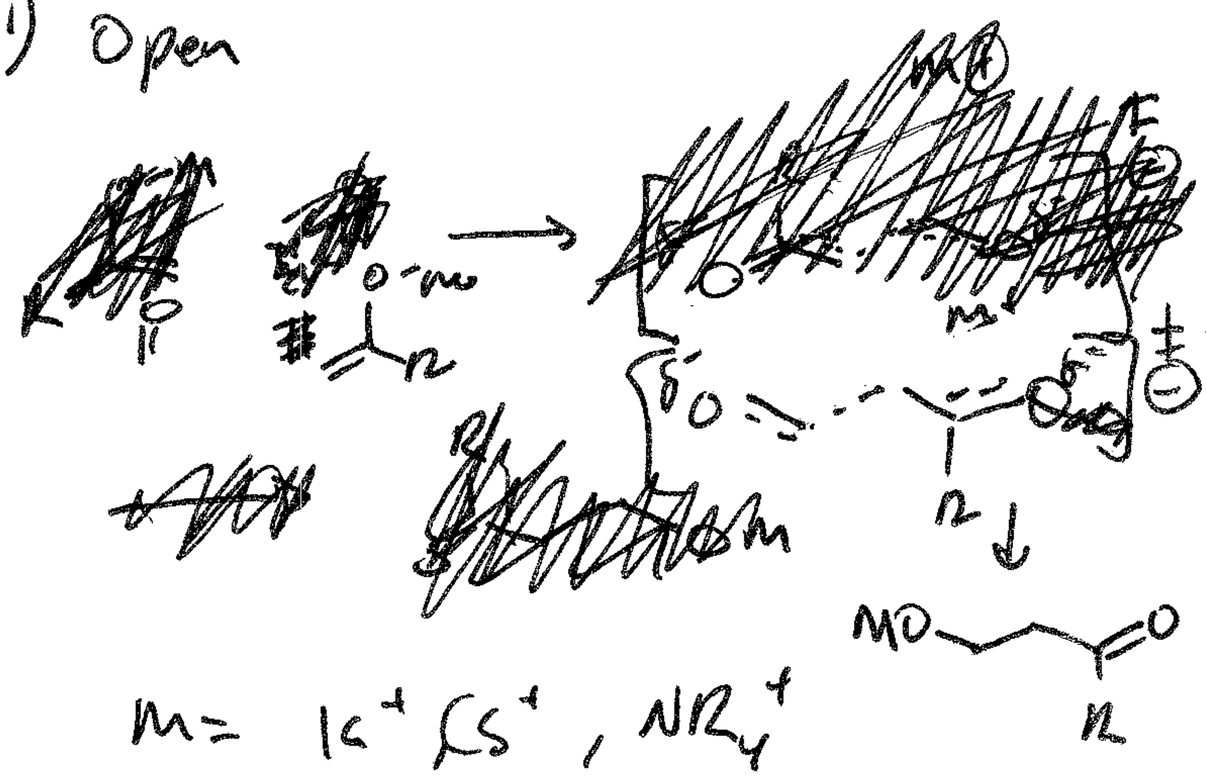
Read about
Claisen & Ireland
(2.3)

Basic Aldol Rxn



Three types of Aldol Rxns

1) Open



typically not used, poor DS.

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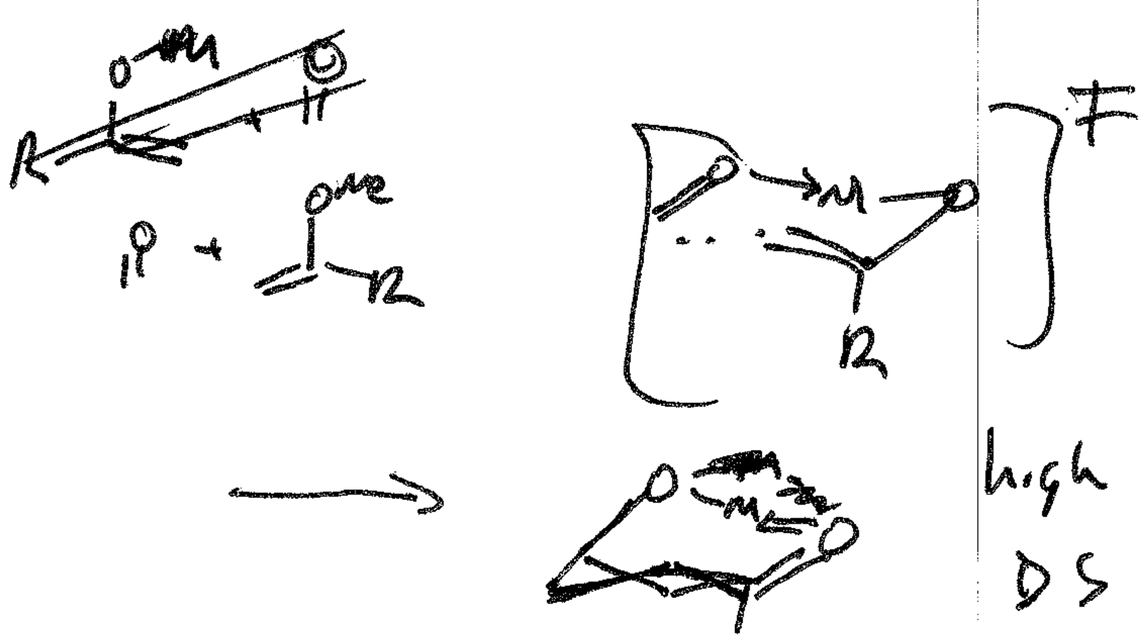
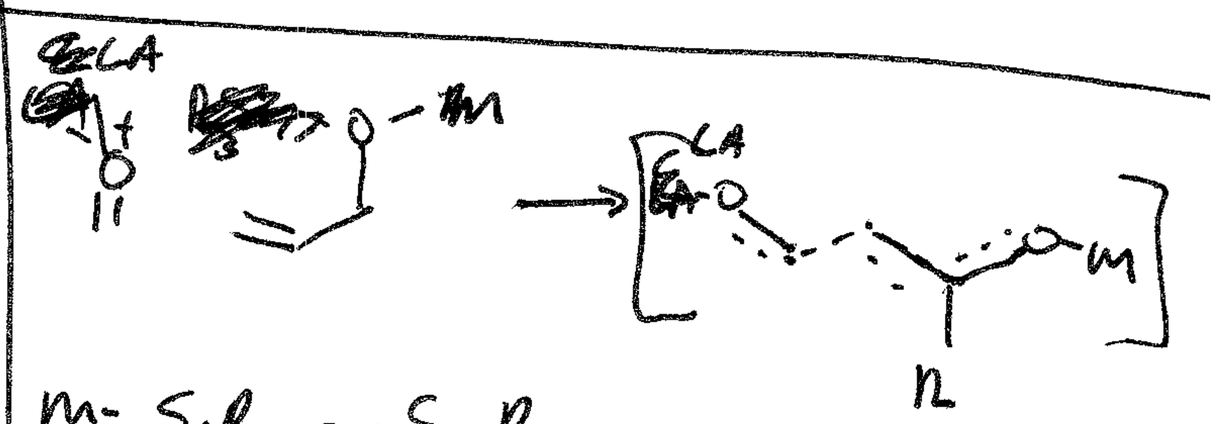
2) closed transition state

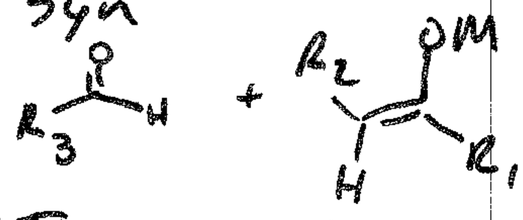


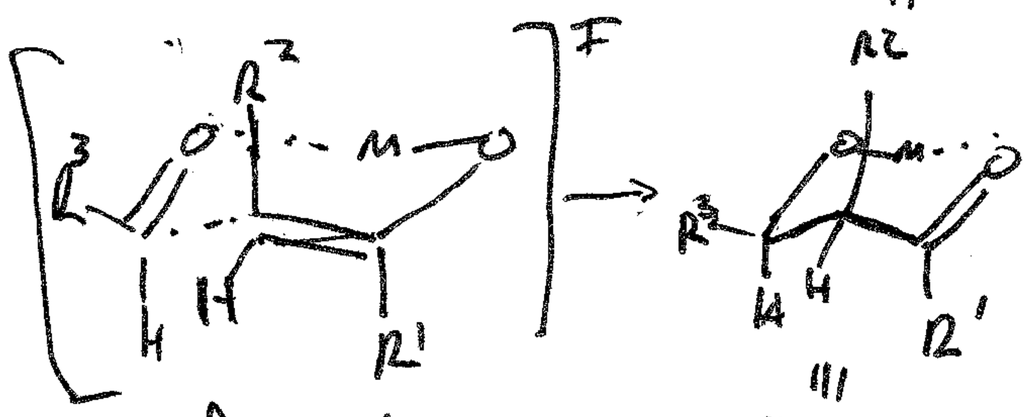


Mukayama Aldol. ~~high~~

Stereoselection in closed T.S

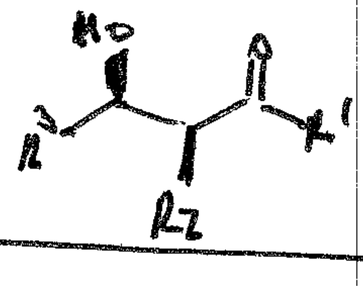
Zenolates ⇒ syn

Consider 

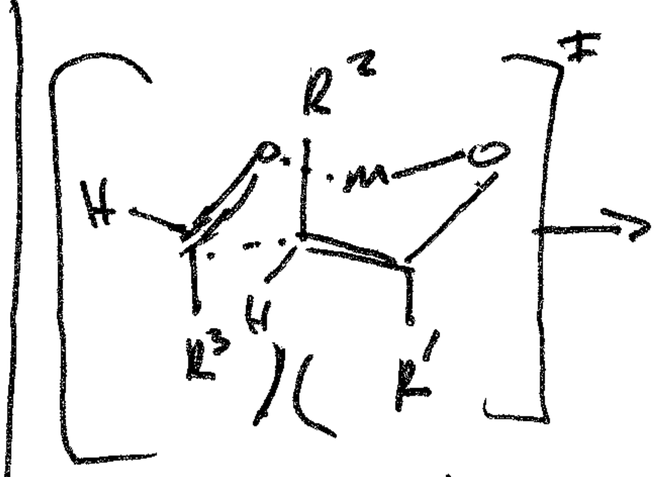


favored

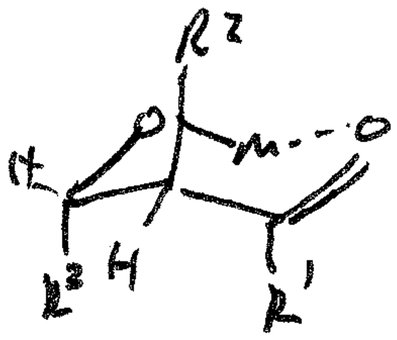
III



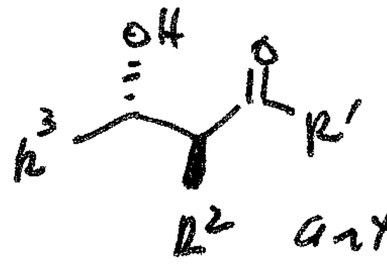
syn



disfavored



III

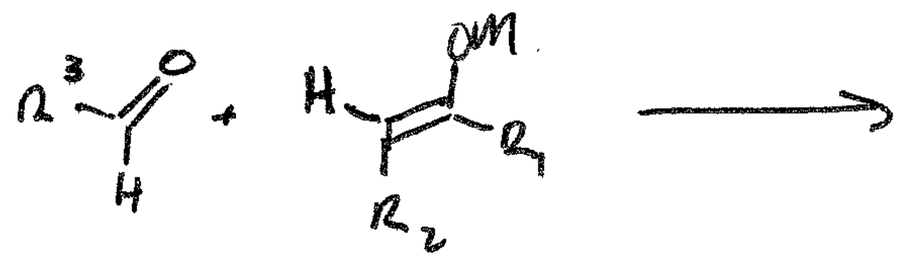


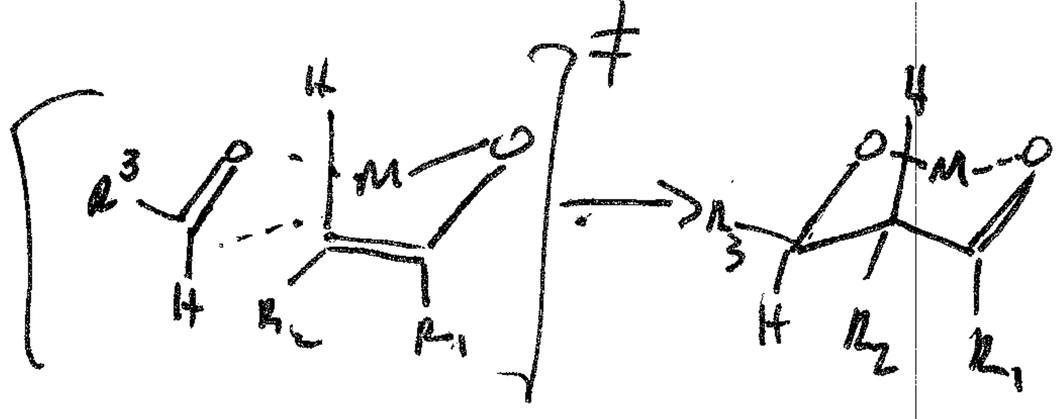
anti

Zimmerman-Traxler model.

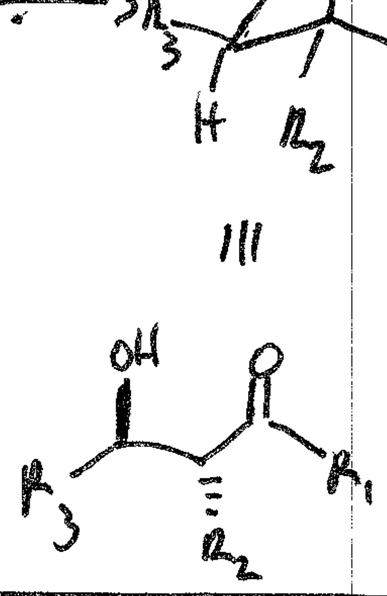
JACS, 1957, 79, 1920

E-enolates ⇒ anti





III

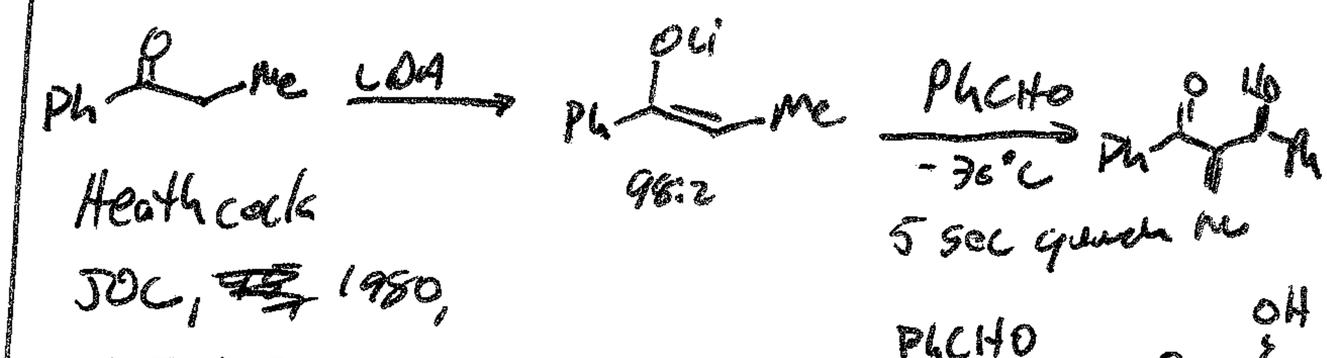


Closed TS Best for short M–O bonds

N	B–O	1.4 Å	) oft used
	Zr–O	1.5 Å	
	Li–O	1.95 Å	) not often used.
	Al–O	1.9 Å	
	Mg–O	2.1 Å	

selectivity ↓ non-selective

Note: Lithium Aldols Also reversible

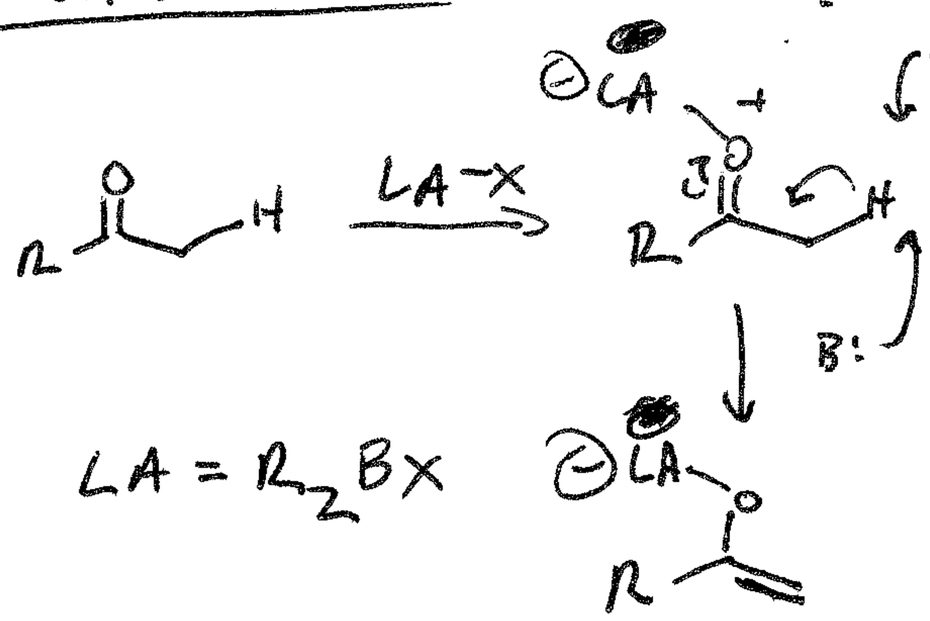


Heathcock

JOC, ~~37~~, 1980, ~~37~~ 45, 1066.

Boron aldols not reversible | 1 min

Boron enolates

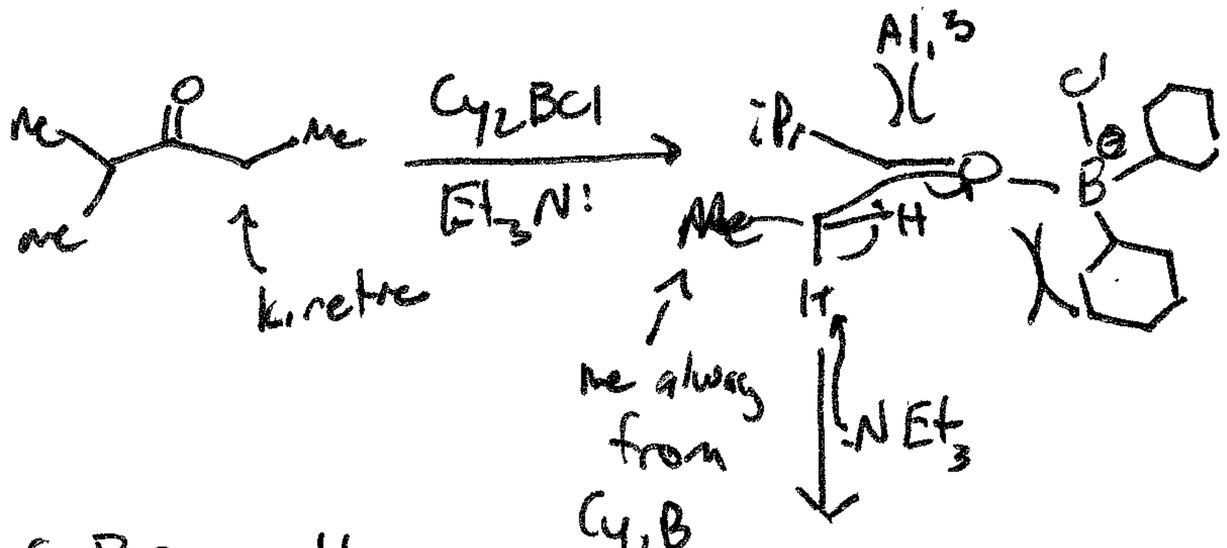


LA = R_2BX

E vs Z ?

Patterson TL, 1992, 33, 7223

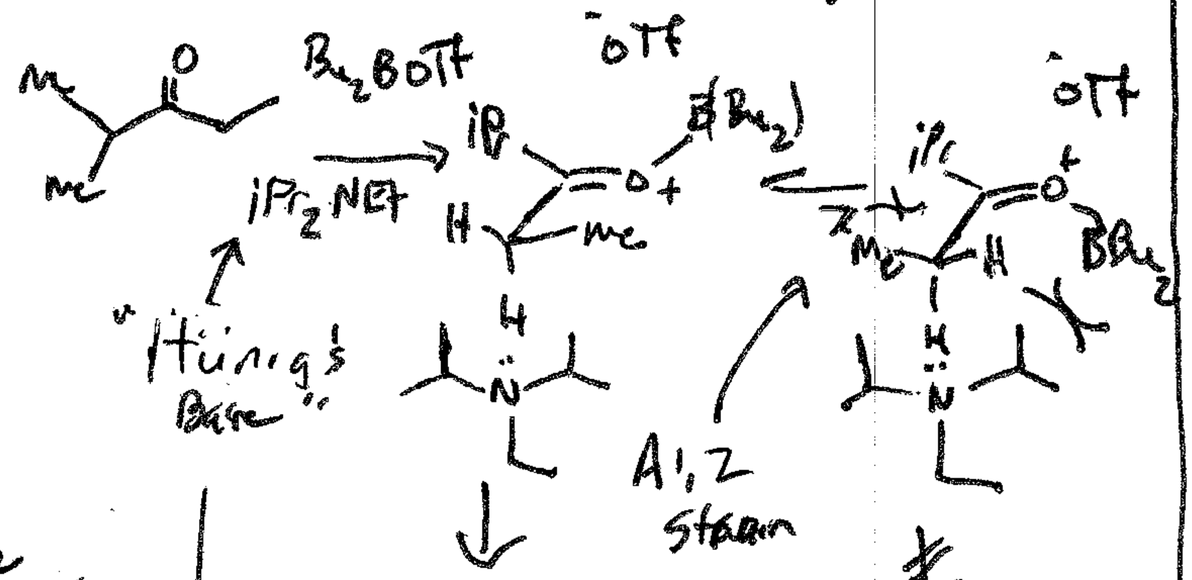
Case 1 Large R_2B-X, Small amine base



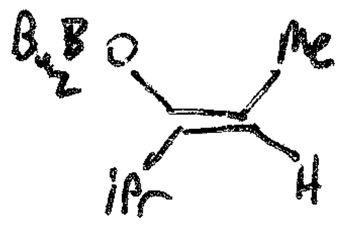
E boron enolate ≡

Et₃NHCl

Case 2 - Small R_2B-X, Large amine base

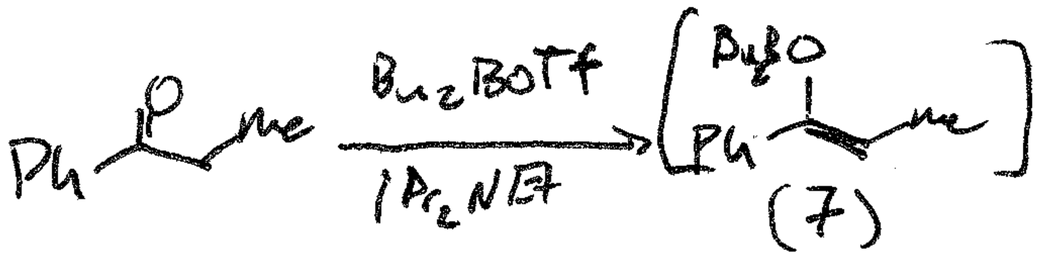


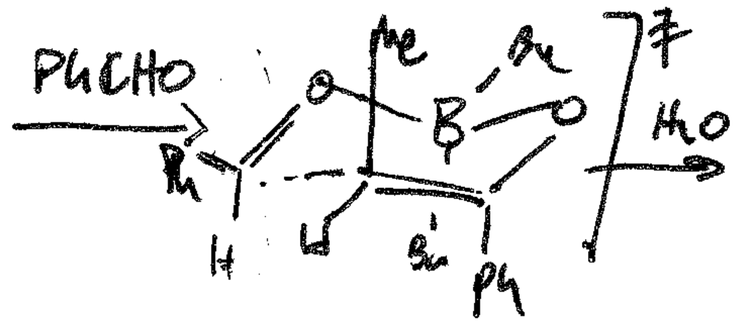
Note OTf is better LG... even smaller!

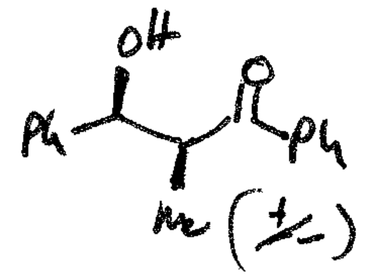


7-Boron enolate

Example





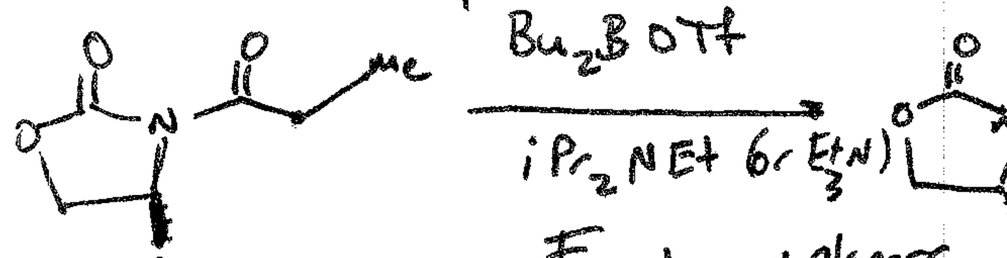


JACS
Evans, V, 1981, 103, 3099

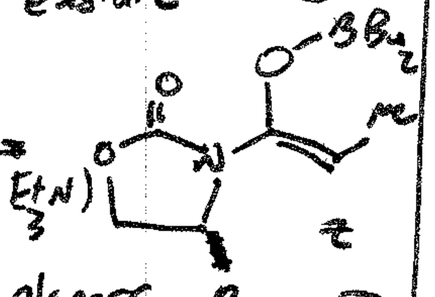
>97:3 syn
82°c

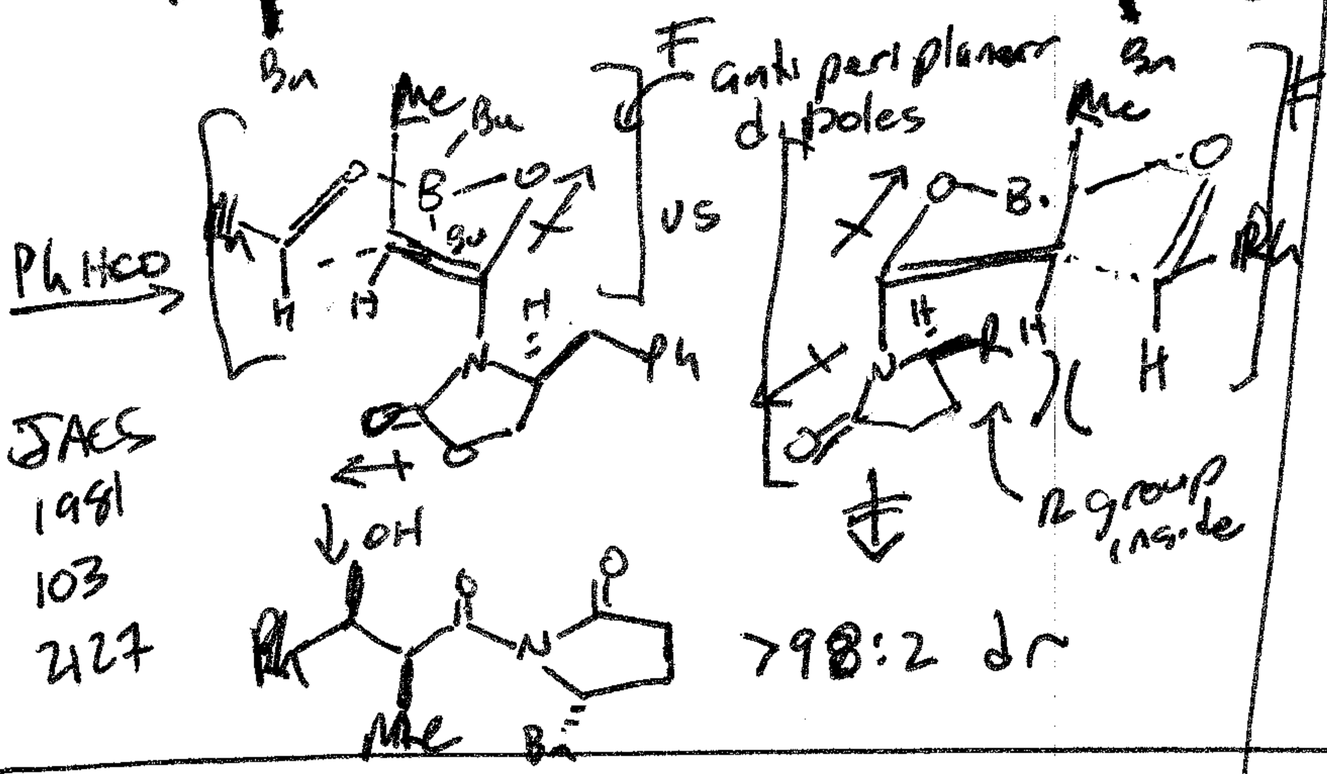
Evans Chiral aux. Aldol rxns

Note both amide & R_2Bx give the enolate



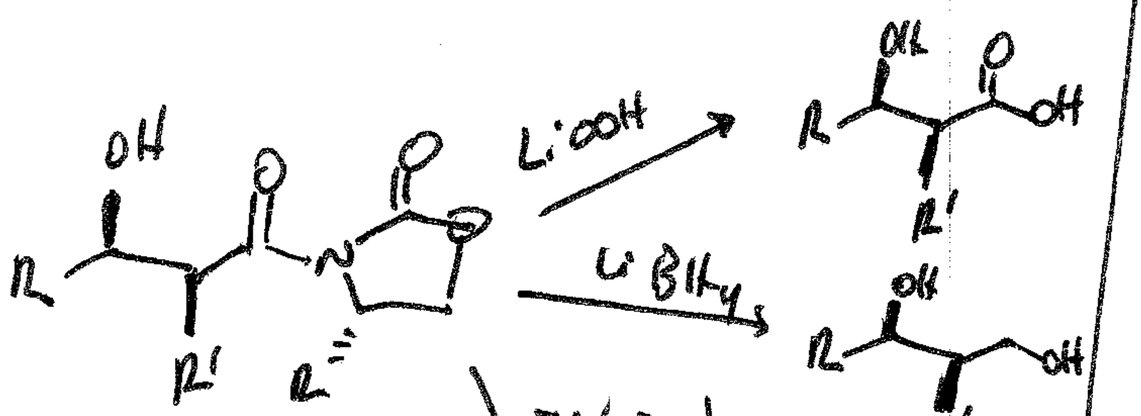
NO chelate!



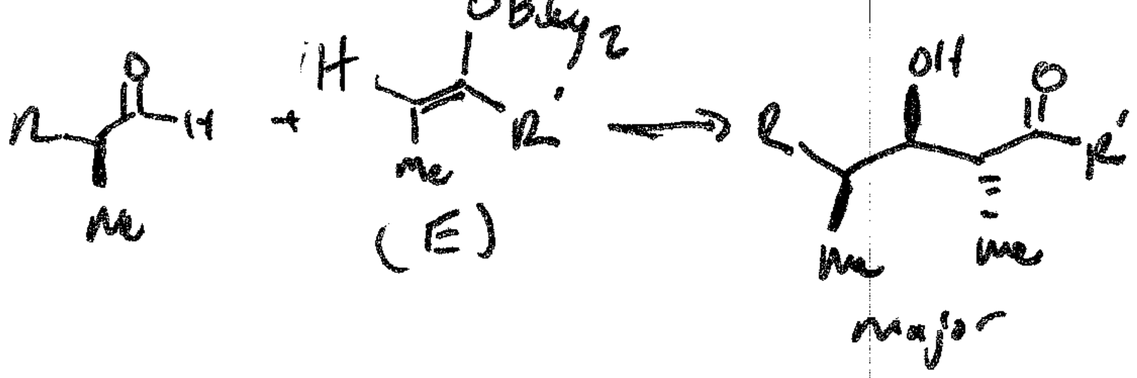


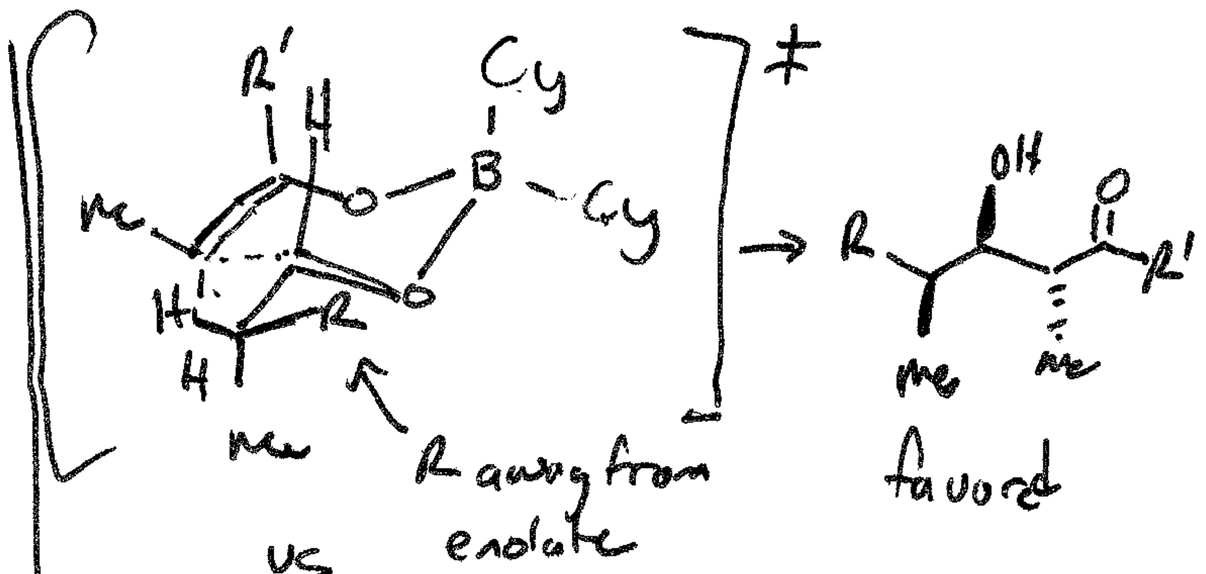
JACS
1981
103
2127

>98:2 dr

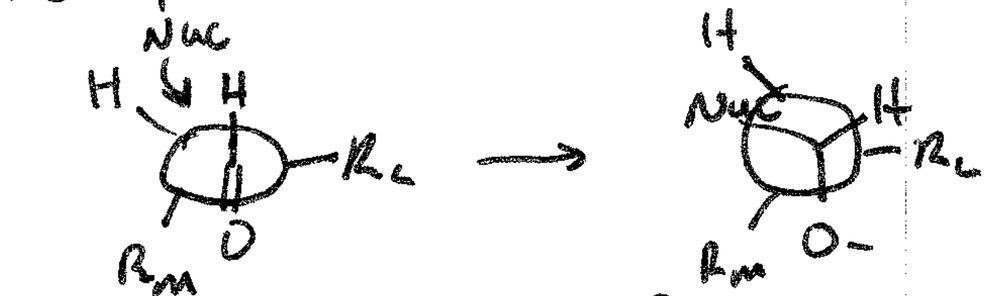


Felkin Control - α-Chiral aldehydes

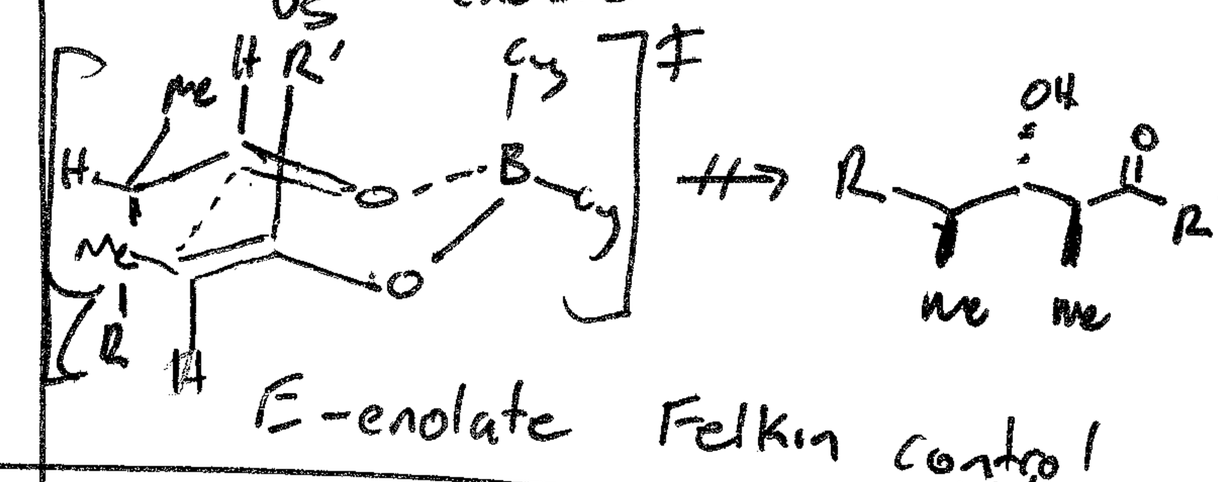


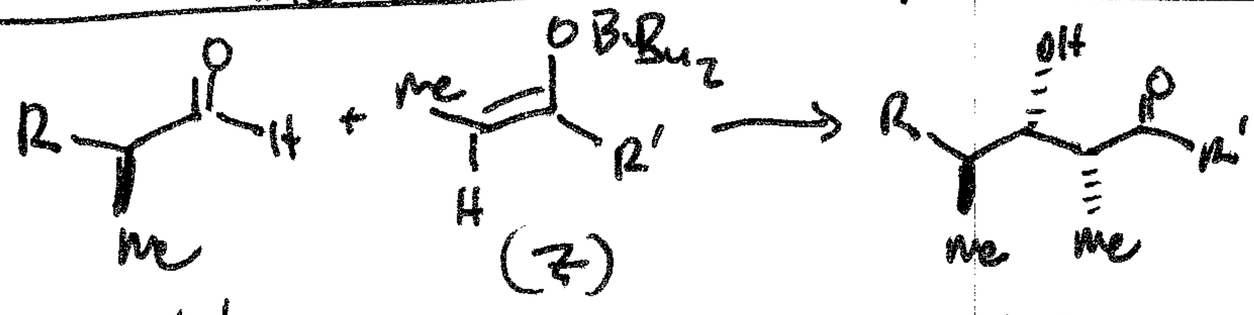


Recall Felkin control

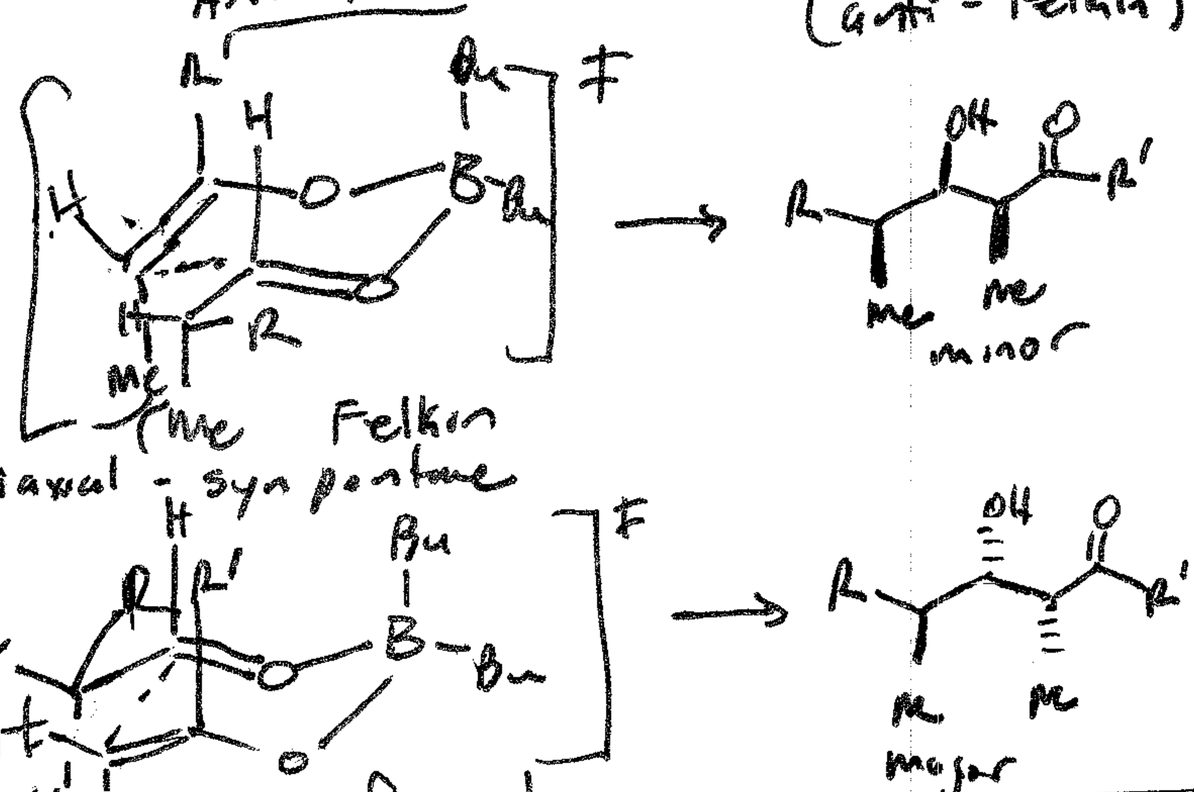


Roush JOC, 1991, 56, 4851

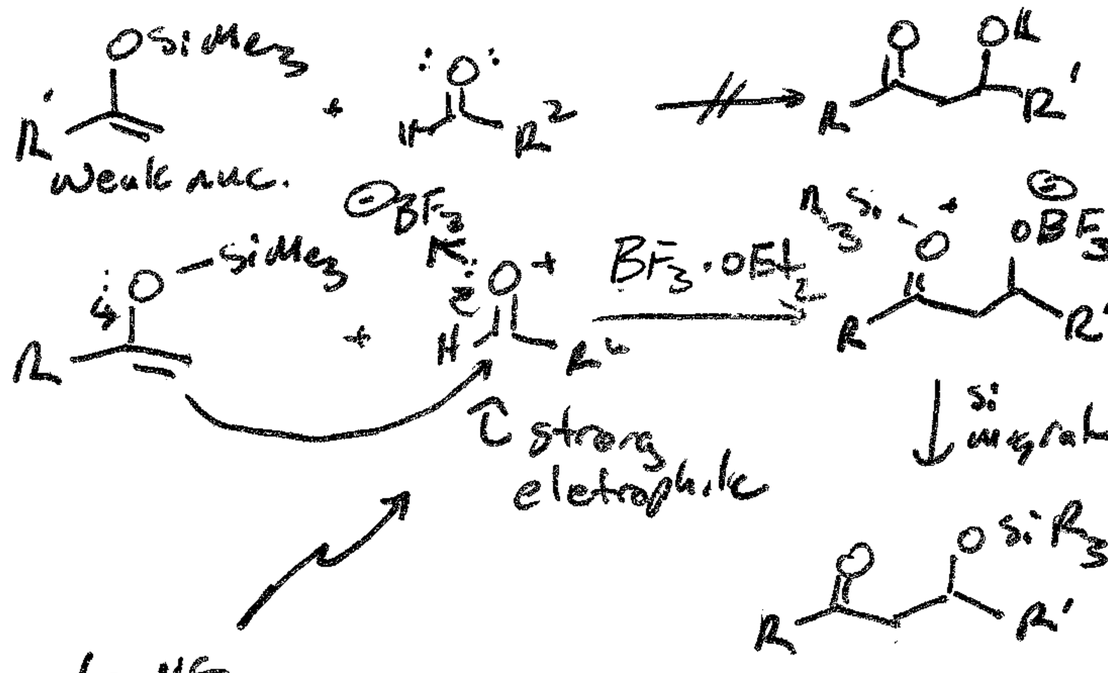




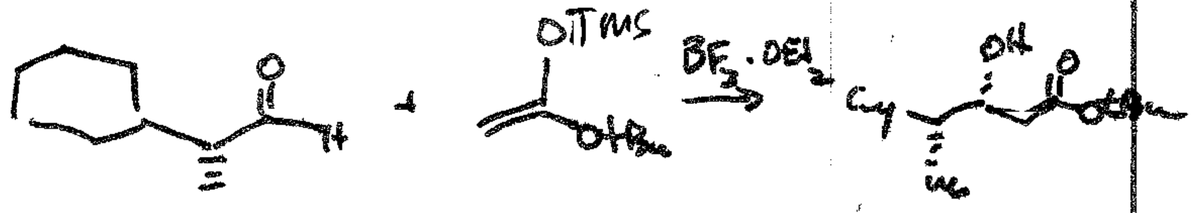
Z enolate Anti Felkin

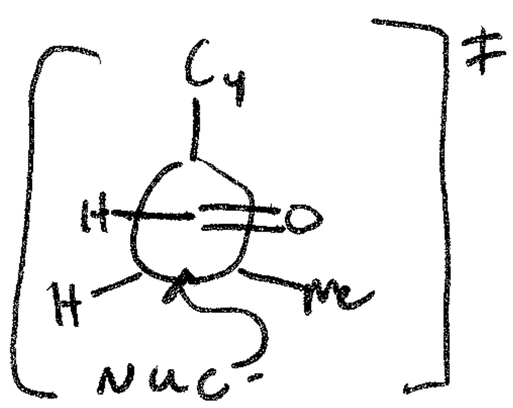


Mukaiyama Aldol

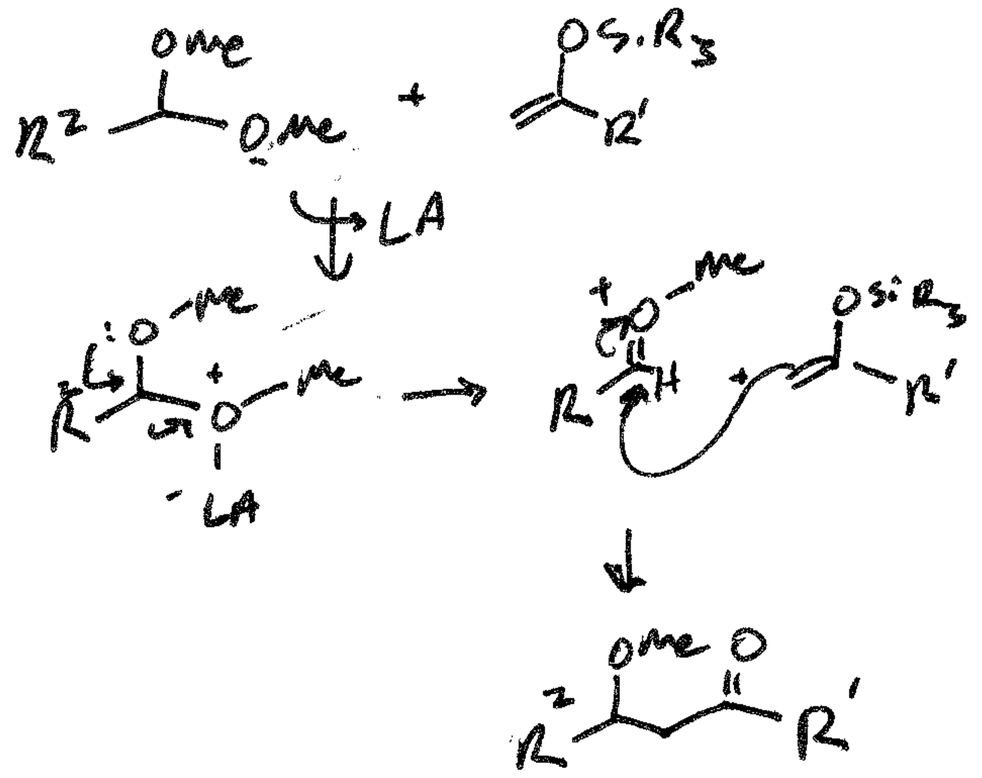


Features 1: Open TS - better Felkin control

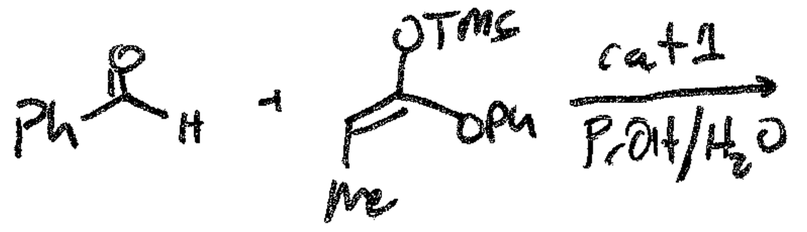


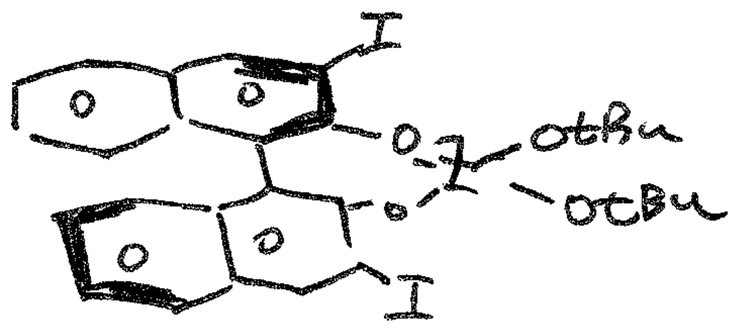


2) Lewis acid activation of ketals



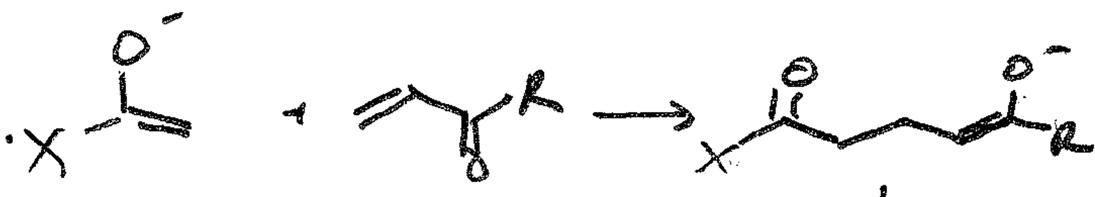
Asy. Mukaiyama Aldol - Many, many examples





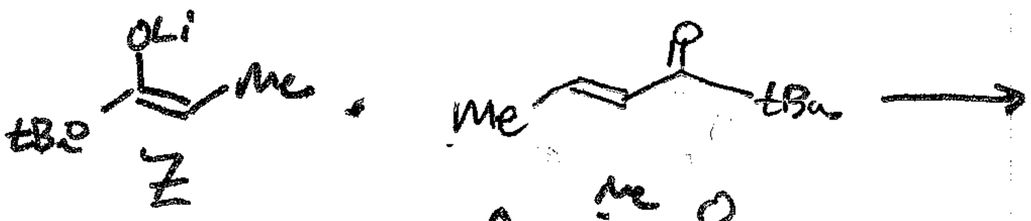
see Carreira 4.4 for review!

Vinylogous Aldol - Michael Rxn (1,4 addition)



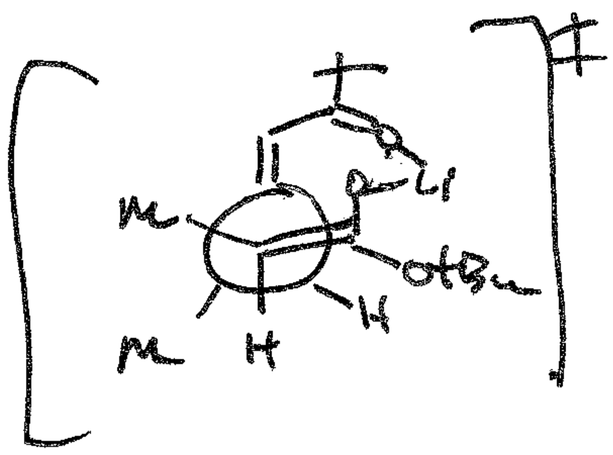
1,5 carbonyls

Michael Rxn can be highly diastereoselective



anti > 95:5

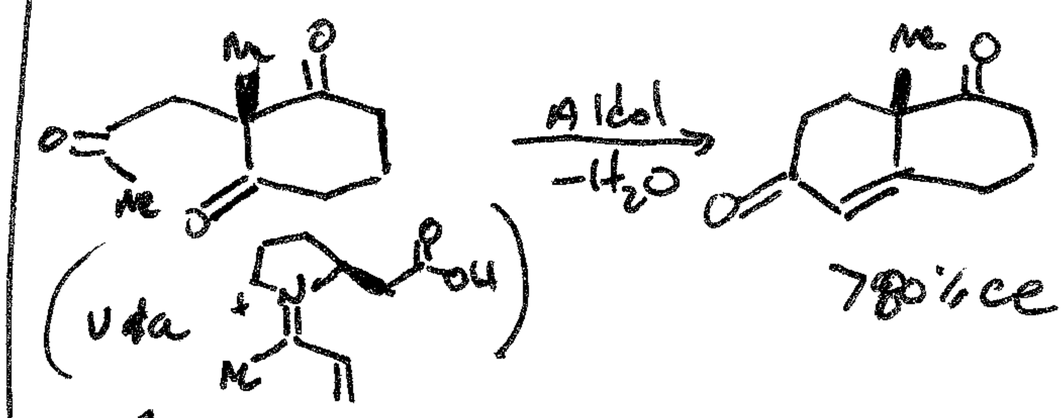
E ⟹ syn but lower selectivity



Heathcock

JOC, 1990, 55, 157

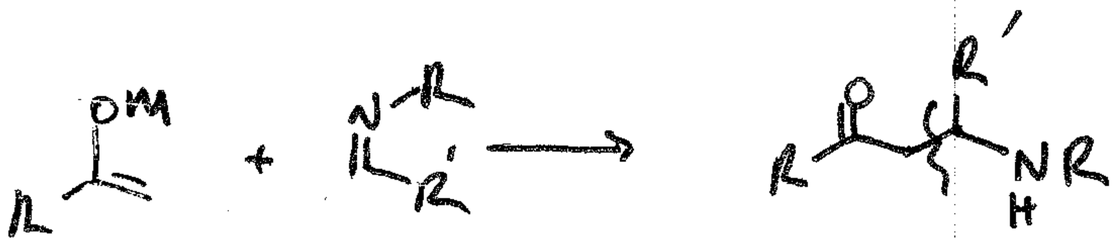
Combined Michael, Aldol



Robinson annulation

Note: general phenomenon. "Organo-catalysis"

Aldols w/ imines ⇒ Mannich Rxn

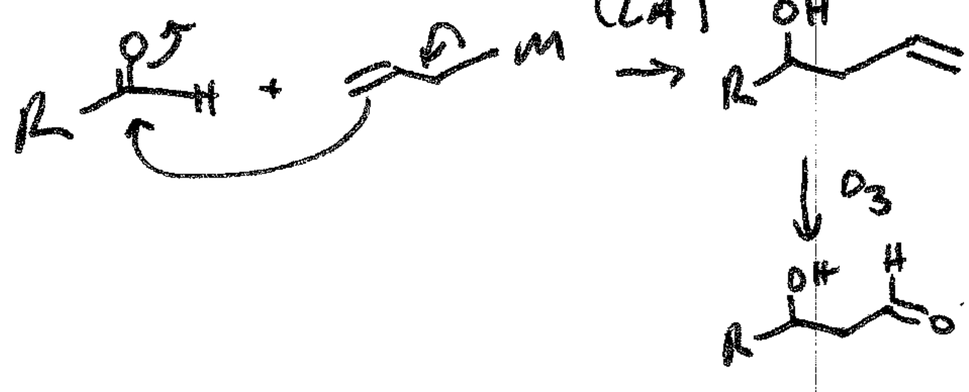


good way to install Nitrogen centers.

imine often generated in situ

from $RNH_2 + HCR_2$

Allyl metaladdition - Alt to Aldol



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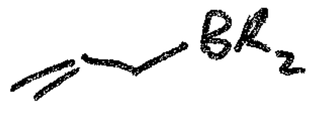
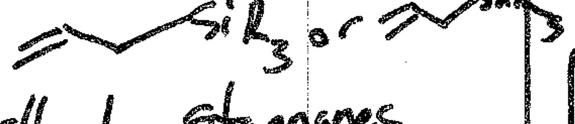
2 types

1)  allyl boranes

2)  allyl stannanes or silanes

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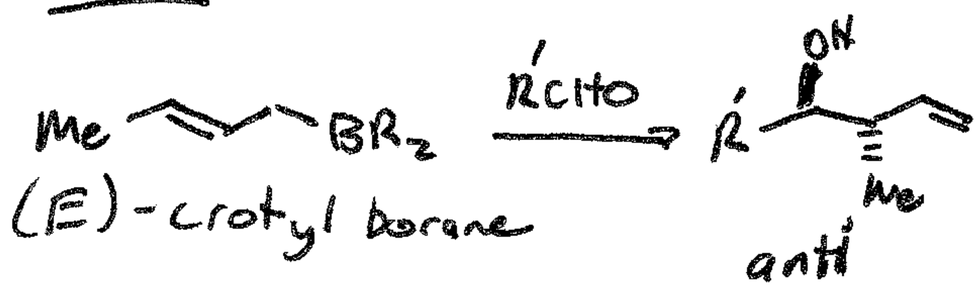
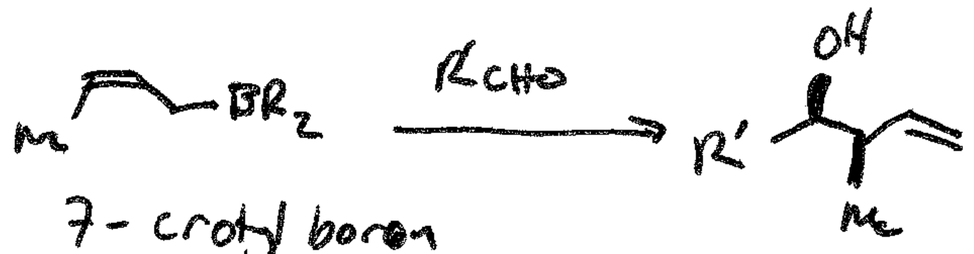
Boron

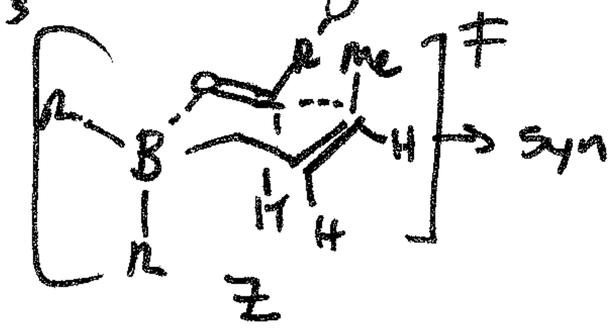


(E)-crotyl borane

anti



7-crotyl boron

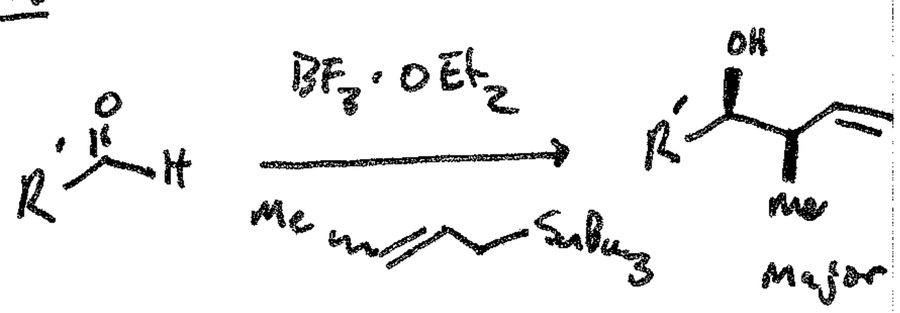


Z

syn

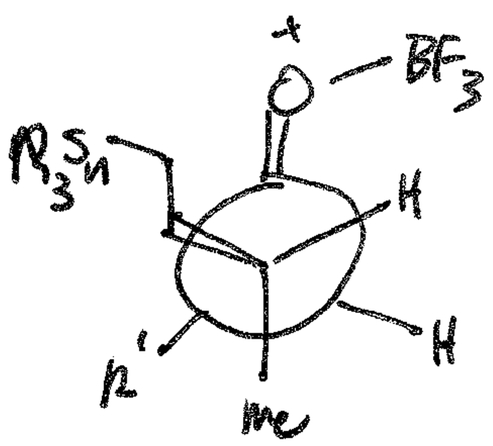
racemic unless R_2B is chiral

Syn



major

4:1 → 50:1



Both E & Z give syn

E gives higher selectivity

Syn - synclinal (C=O & CC gauche)

Keck, JOC, 1994, ~~7885~~ 59, 7889