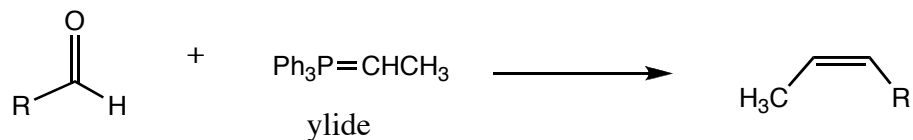
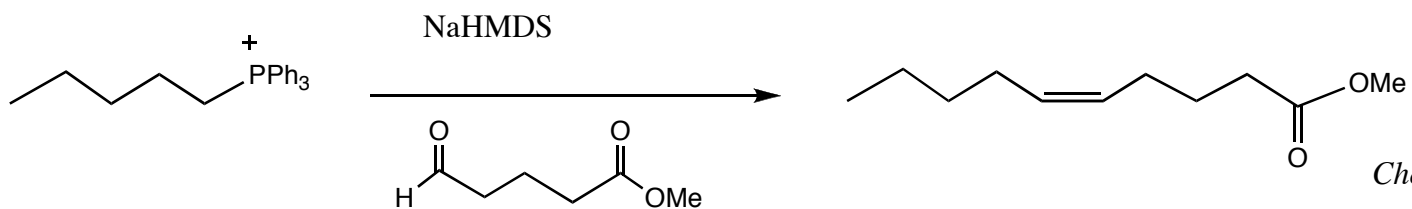
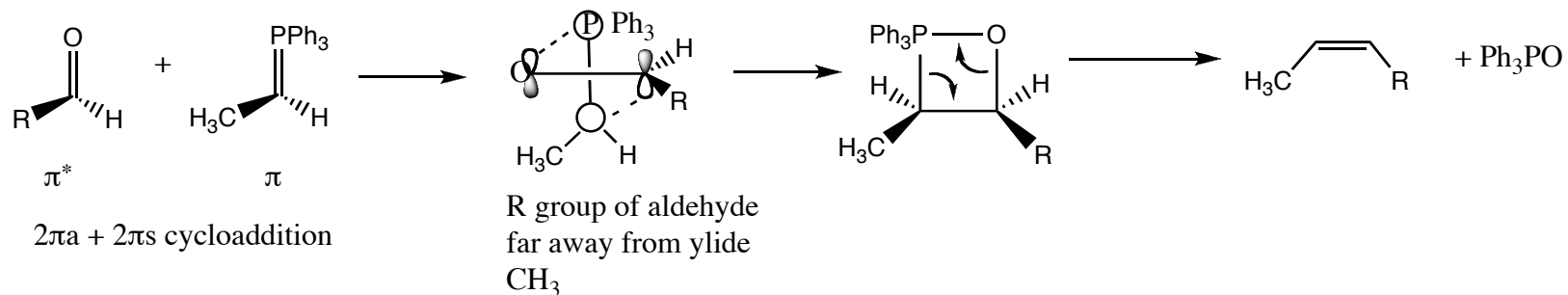


Wittig Reaction - Phosphorous Ylides



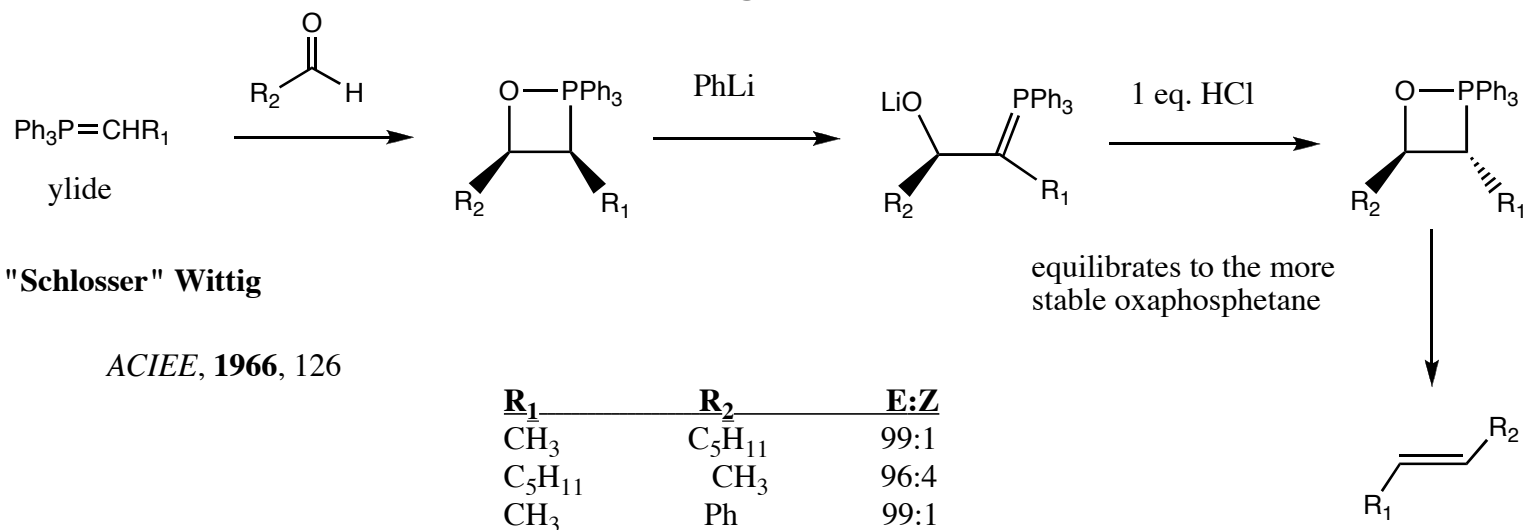
- Stereoselectivity increases as the size of R increases
- *cis*-olefin is derived from non-stabilized ylides

Mechanism: Irreversible [2+2] cycloaddition

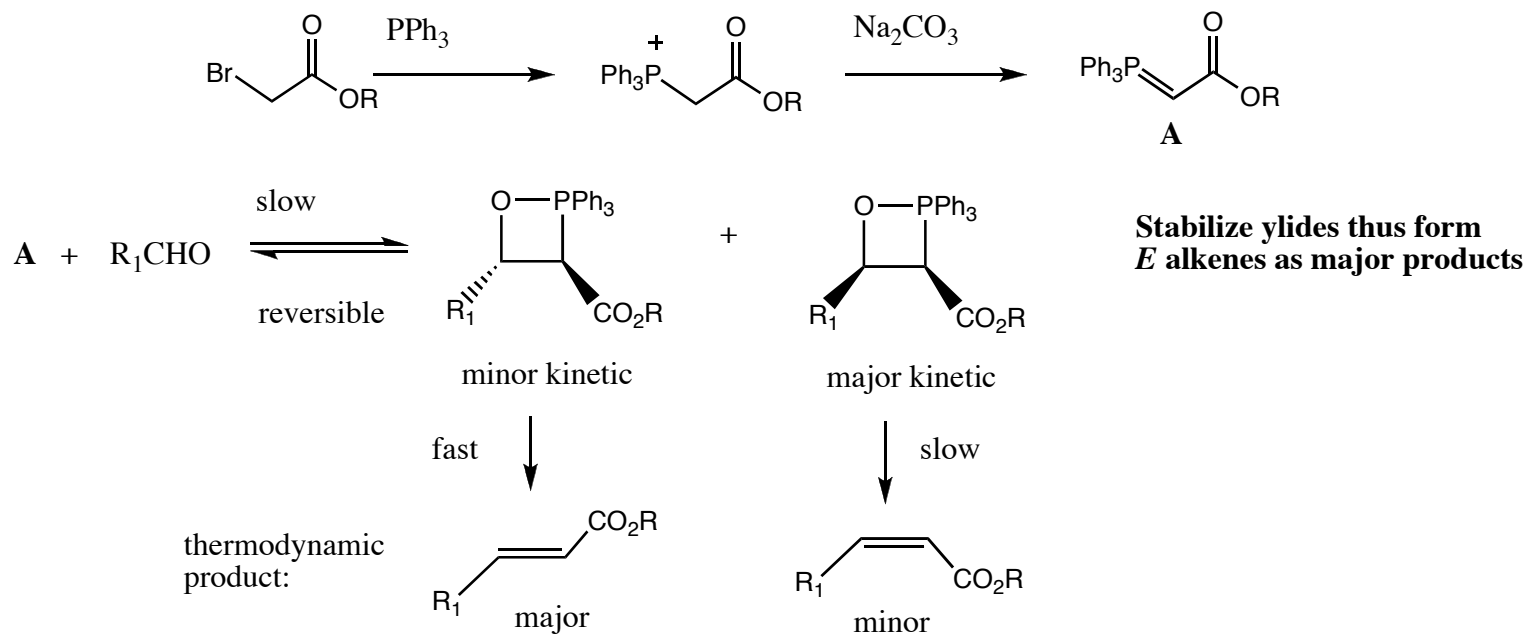


Chem Ber. **1976**, 1694.

E-selective Wittig Reactions



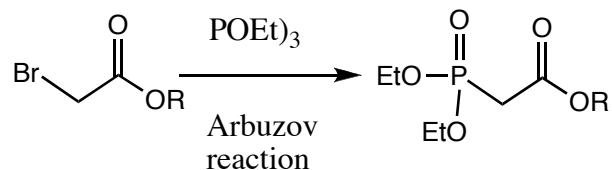
Stabilized Ylides are much less reactive than alkyl ylides; they react with aldehydes, but only slowly with ketones



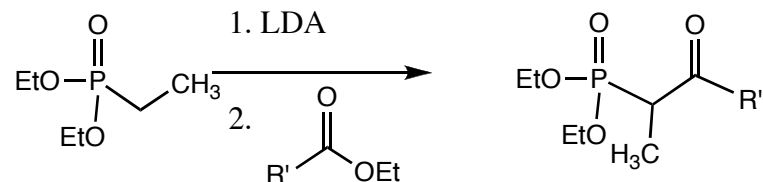
Horner-Wadsworth-Emmons Wittig: *E*-selective

Phosphonate esters are easily deprotonated and are more basic/nucleophilic than stabilized ylides; they react with both ketones and aldehydes

Synthesis:

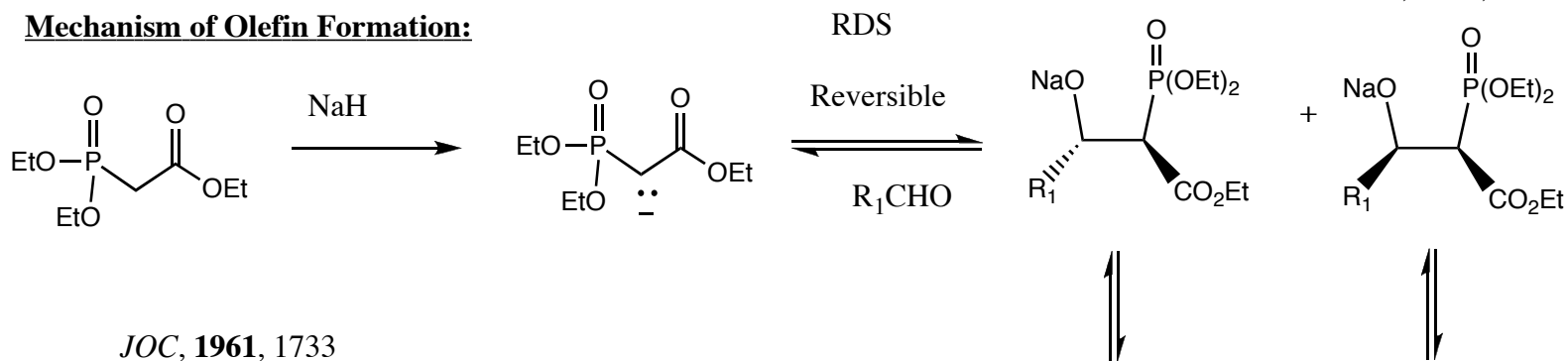


Claisen Condensation:

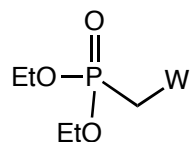


TL, 1976, 2829

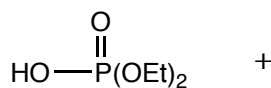
Mechanism of Olefin Formation:



Good for:

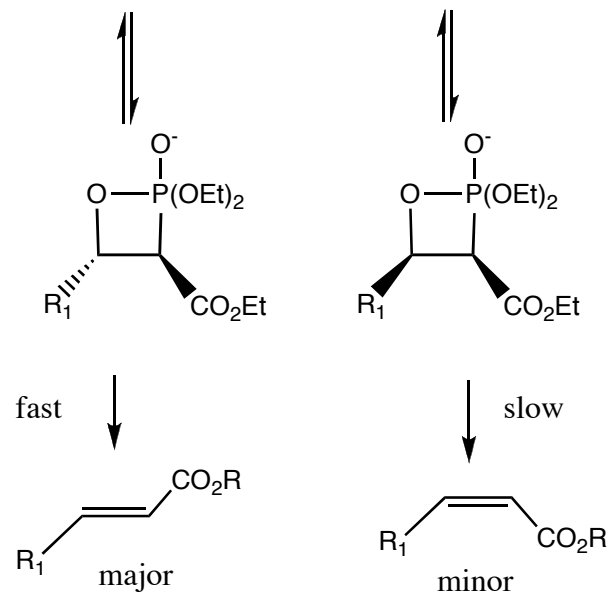


W = CN, CO₂R,
COR, CHO
SO₂Ph, Ph



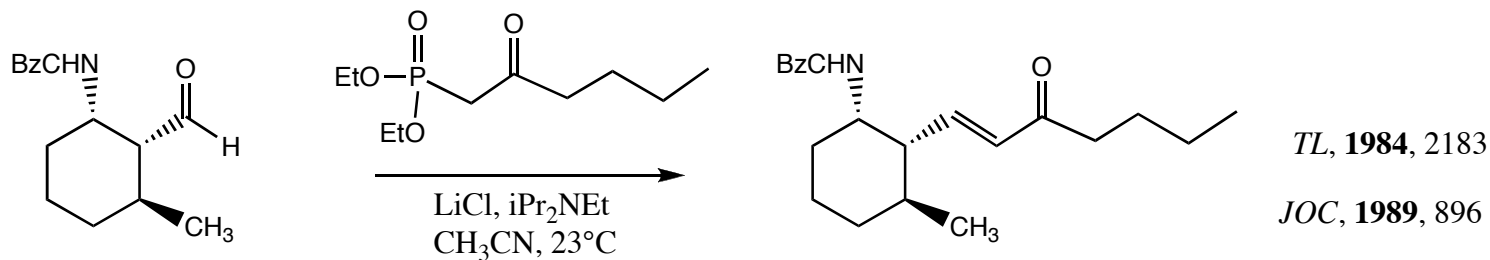
water soluble
phosphate can be
removed in aqueous
workup

thermodynamic
product:

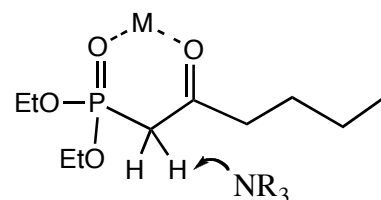


Modifications to the Horner-Emmons Wittig

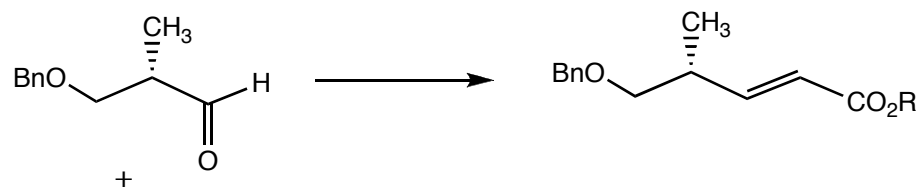
Masamune and Roush: for Base-sensitive substrates, use LiCl/tertiary amine (Et₃N, DBU, iPr₂NEt)



metal ion coordination lowers pK_a further:



Both hindered phosphonates and hindered aldehydes increase *E*-selectivity:



PPh₃=CHCO₂Et

7 : 1 E:Z

(iPrO)₂POCH₂CO₂Et/KOtBu

95:5 E:Z

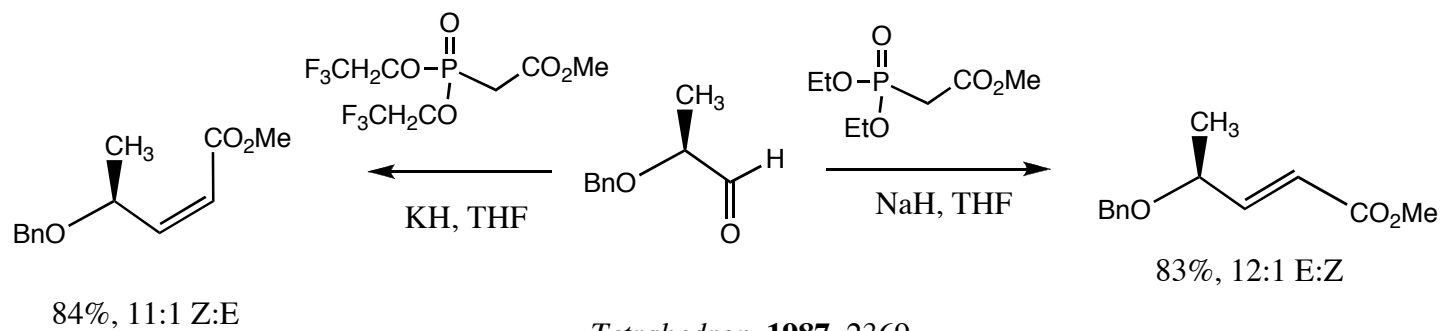
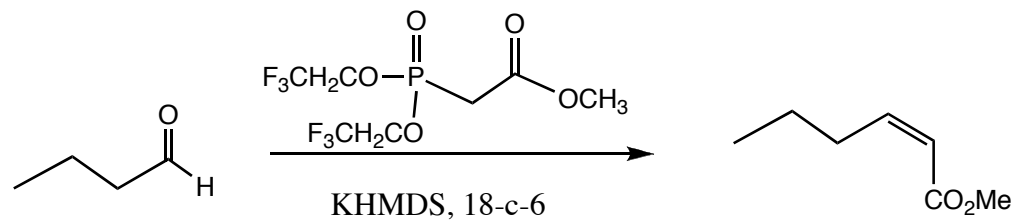
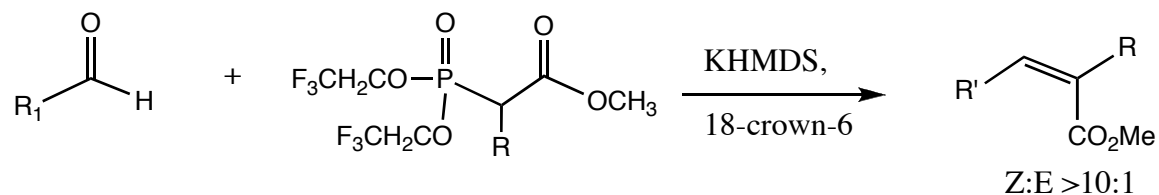
(MeO)₂POCH₂CO₂Me/KOtBu

1:3 E:Z

TL, **1981**, 3873.

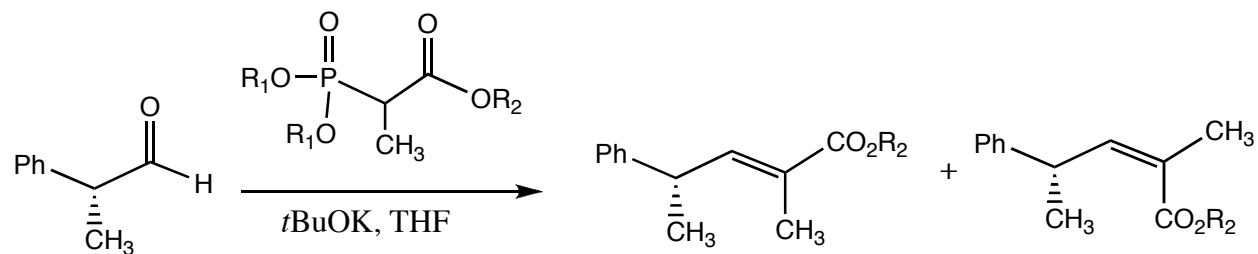
Modifications to the Horner Emmons Wittig, continued

Z-selective olefin synthesis: Still modified phosphonate: *TL*, 1983, 4407

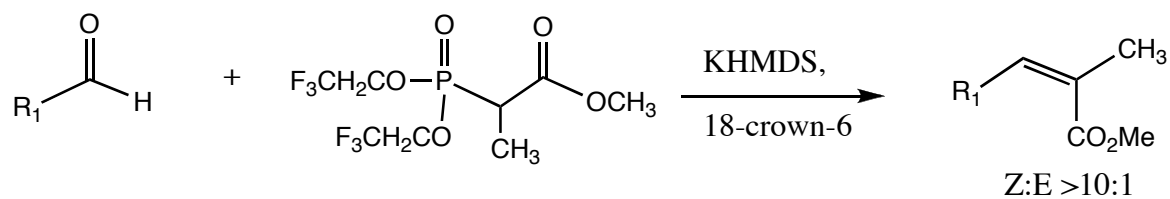


Tetrahedron, 1987, 2369

Trisubstituted Olefins:



R₁	R₂	E:Z
CH ₃	CH ₃	5:95
CH ₃	Et	10:90
Et	Et	40:60
<i>i</i> Pr	Et	90:10
<i>i</i> Pr	<i>i</i> Pr	95:5

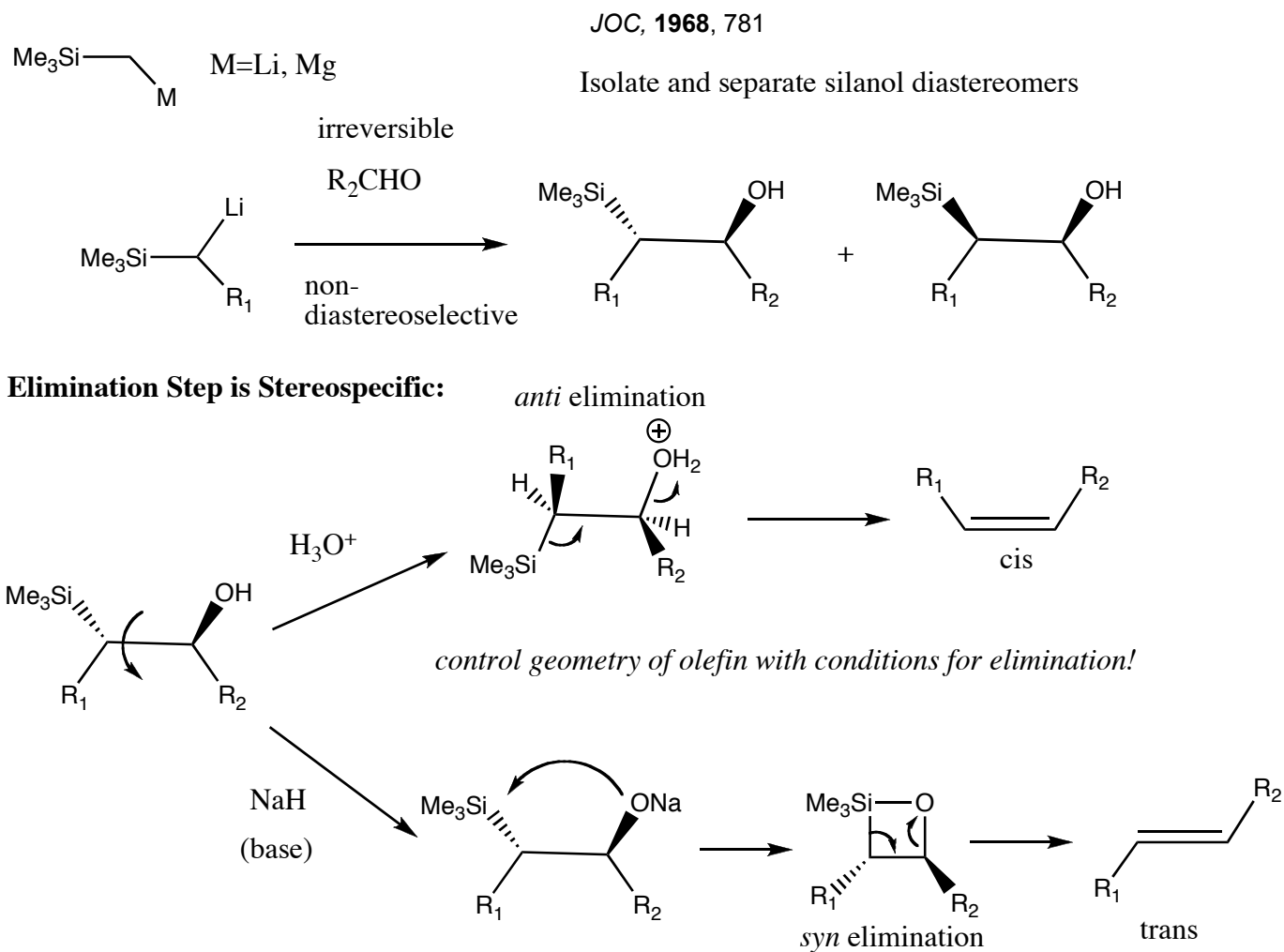


R₁	Z:E
	>50:1
	>50:1
	>50:1

TL, 1983, 4403

Peterson Olefination: An alternative to the Wittig Reaction

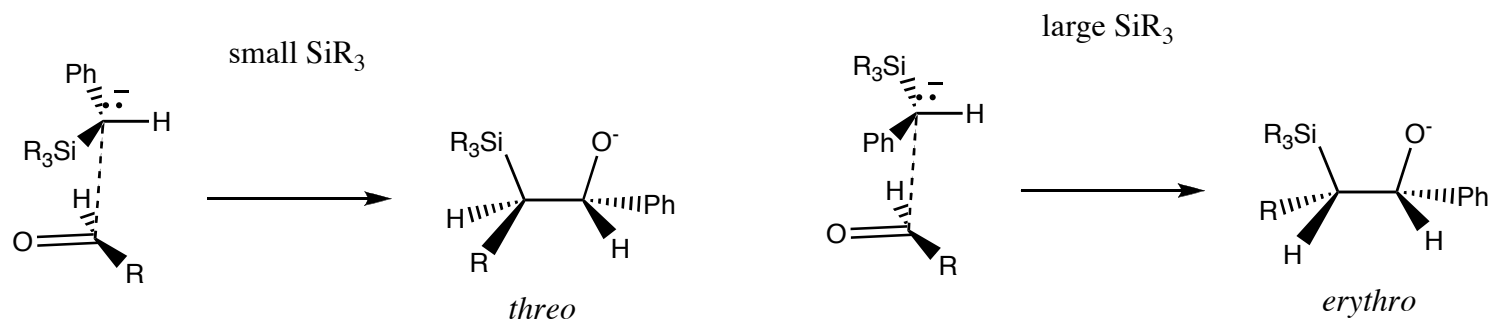
2-step procedure: Addition to aldehyde (non-stereoselective) and silanol elimination (stereospecific)



Stereoselective Additions in the Peterson Olefination:

threo product favored by small SiR₃ (Me₃Si)

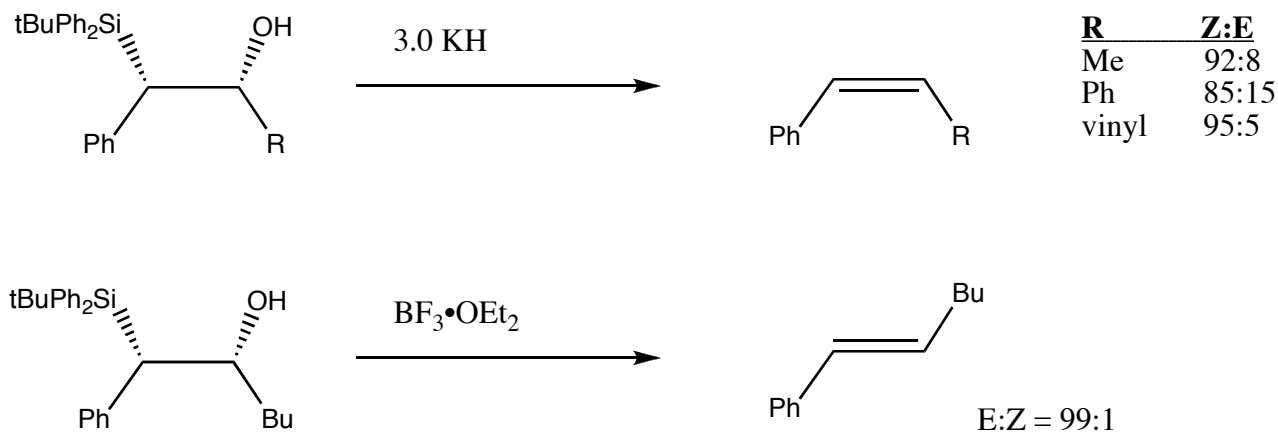
erythro product favored by large SiR₃ (*t*-BuPh₂Si)



maintain an anti relationship between aldehyde R and largest substituent on the silicon reagent

Elimination Step is Stereospecific:

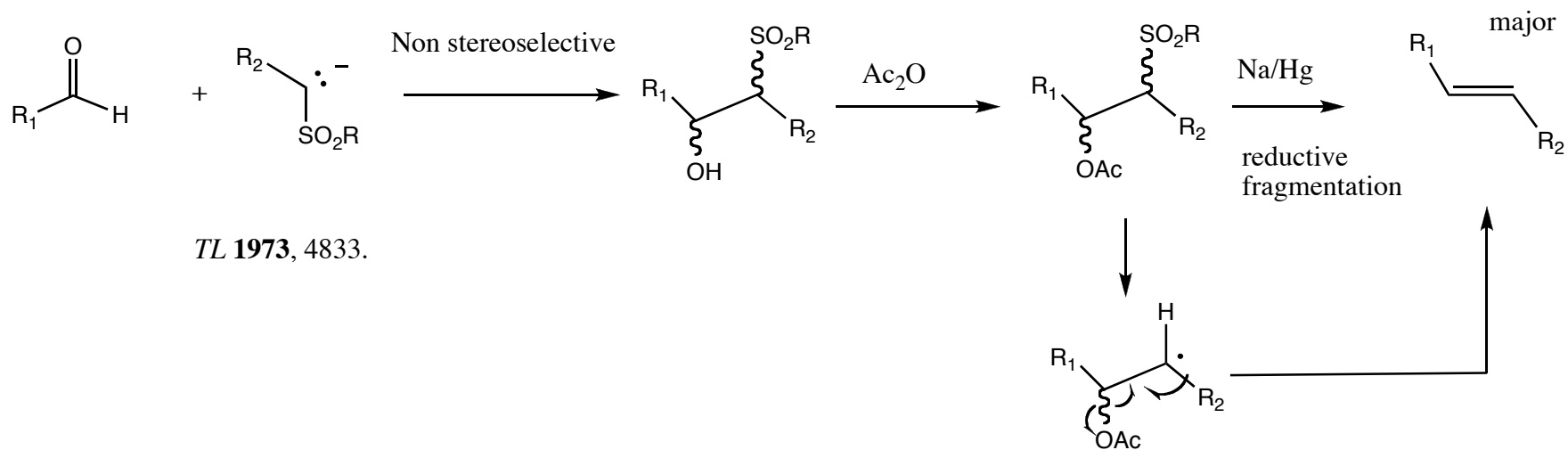
anti elimination



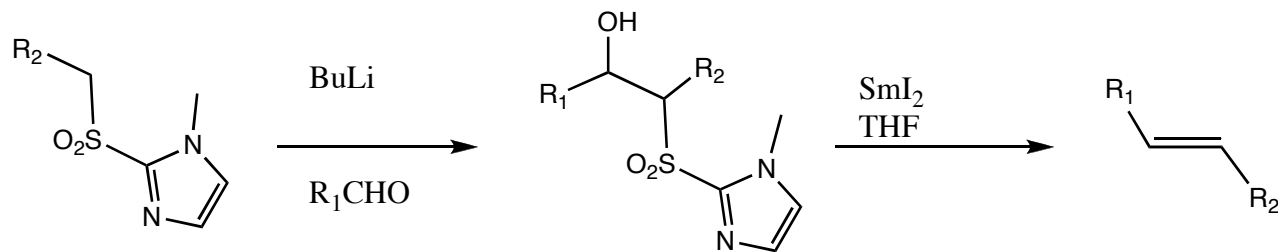
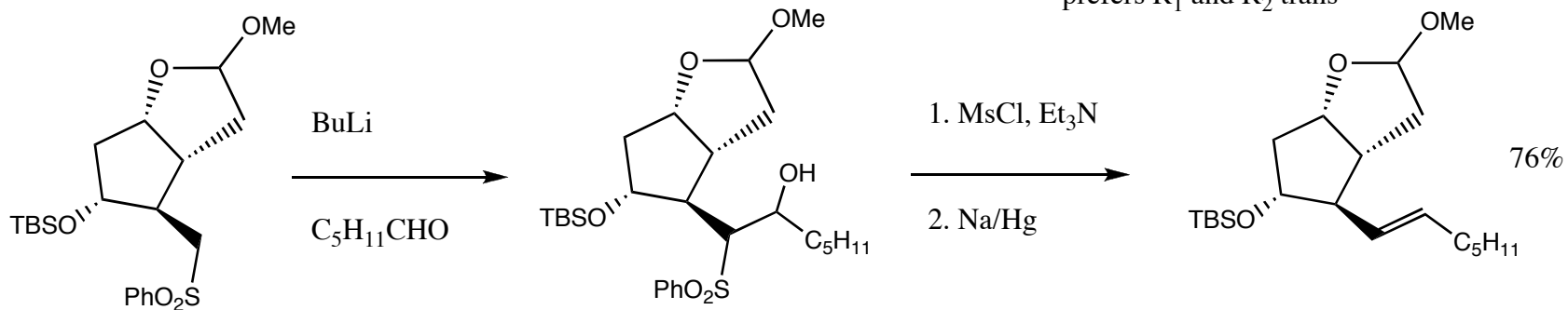
Synthesis, **2000**, 1223

Julia Olefination: *E*-selective synthesis

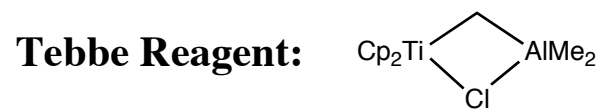
mixture of diastereomers:



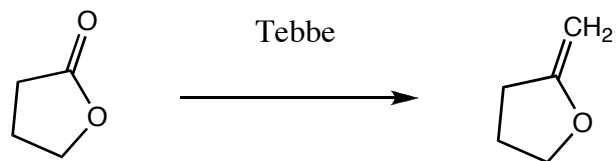
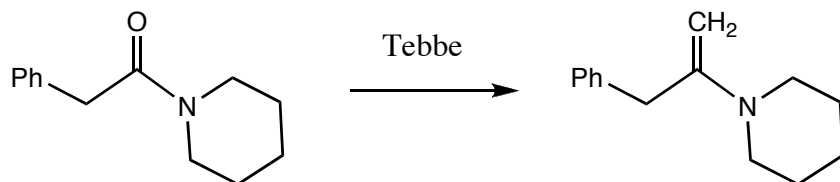
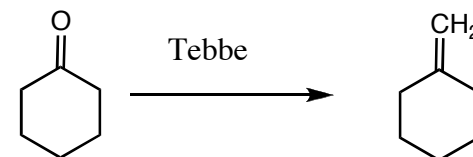
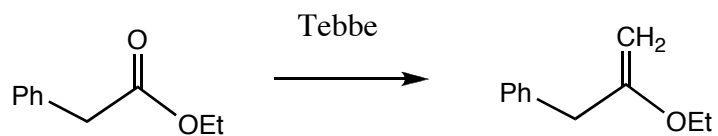
TL 1973, 4833.



TL, 1990, 7105
see also:
JOC, 1995, 3194
Org. Lett. 2005, 2373.

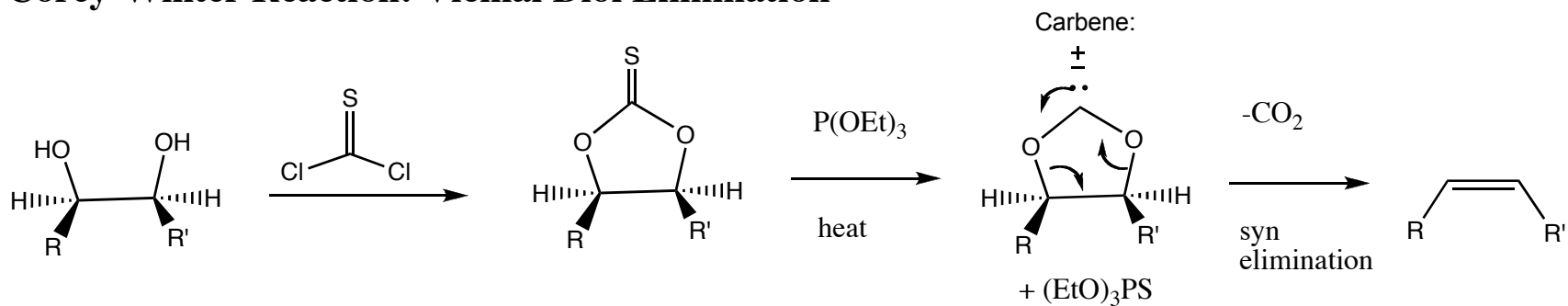


Reacts with aldehydes, ketones, esters, lactones, amides to give methylene compounds:



see also: Petasis reagent: Cp_2TiMe_2 *JACS*, **1990**, 6392.

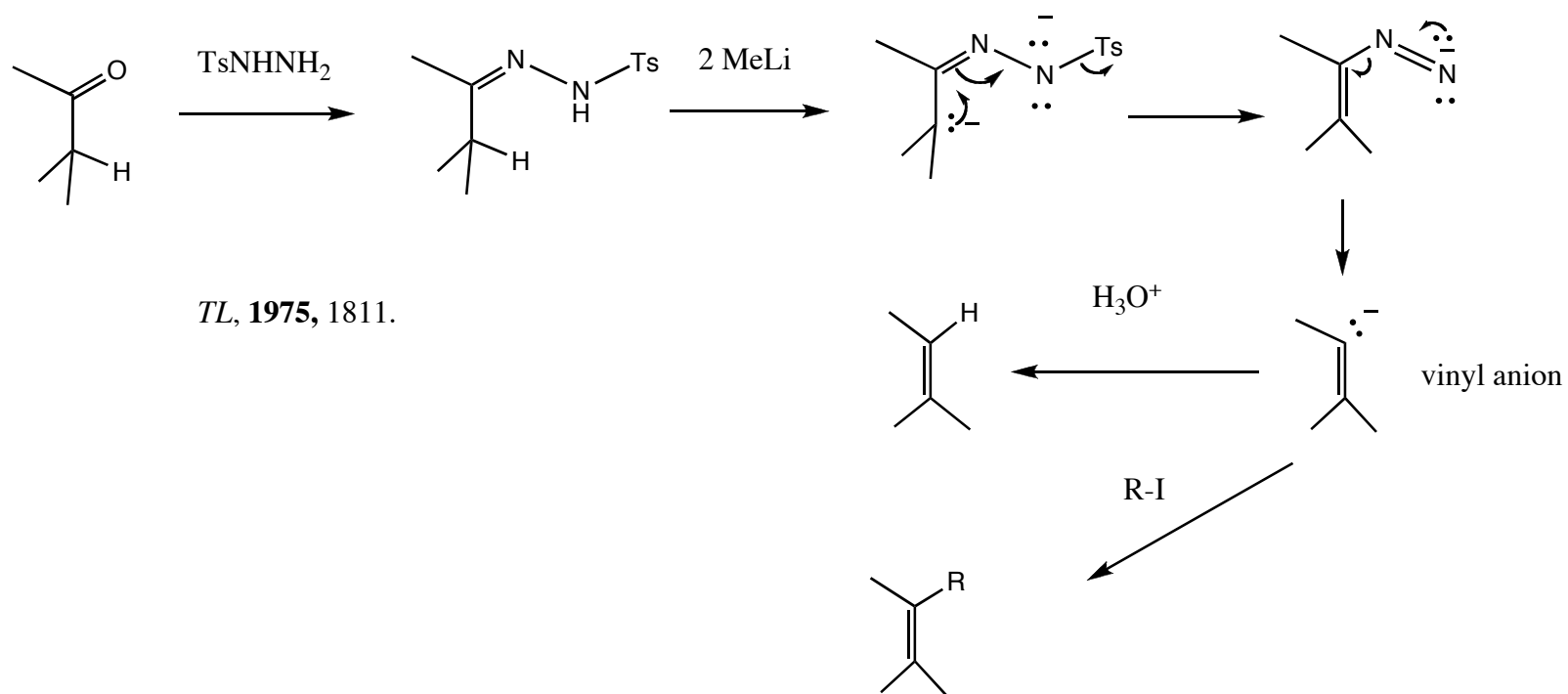
Corey-Winter Reaction: Vicinal Diol Elimination



JACS, 1963, 2677

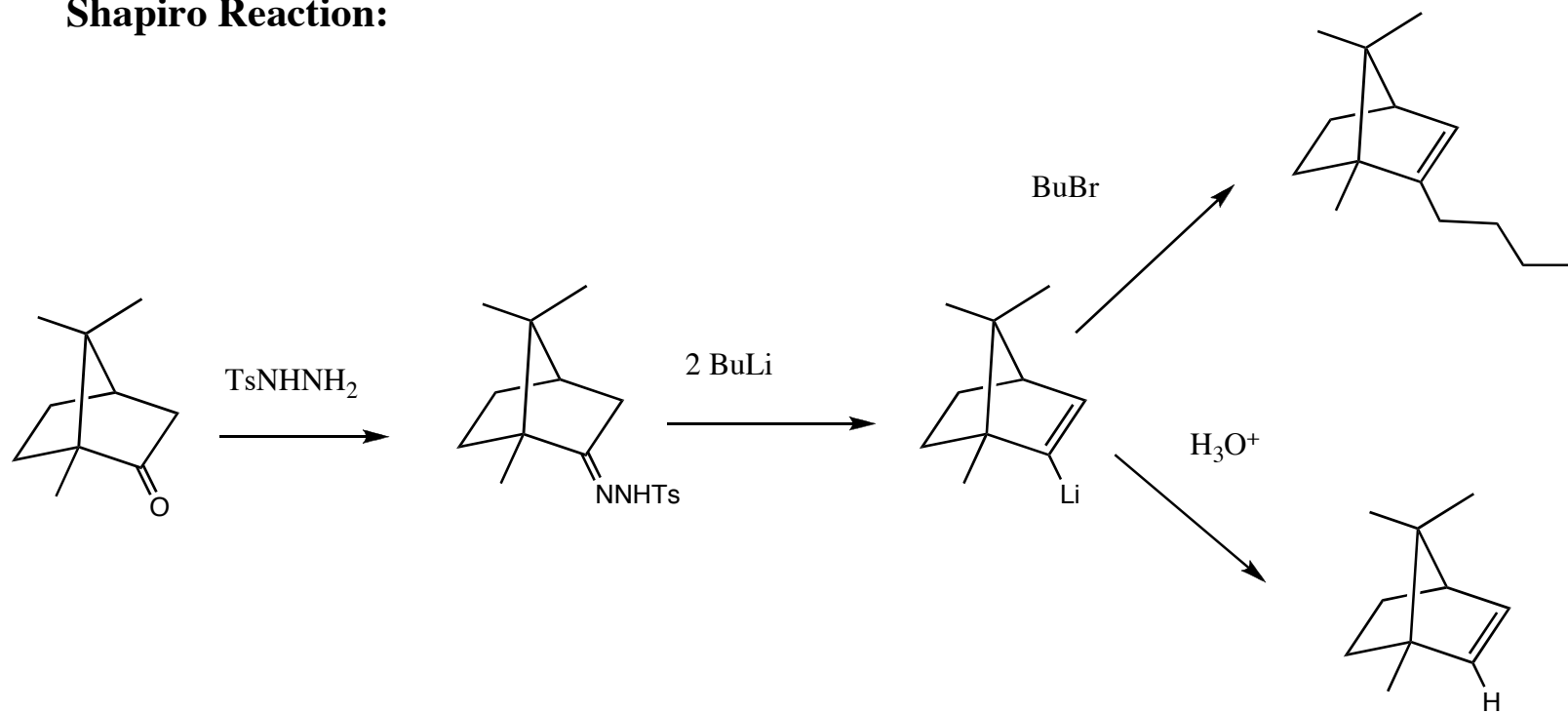
JACS, 1965, 934

Shapiro Reaction:



TL, 1975, 1811.

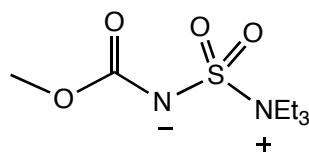
Shapiro Reaction:



Acc. Chem. Res. **1983**, 55.

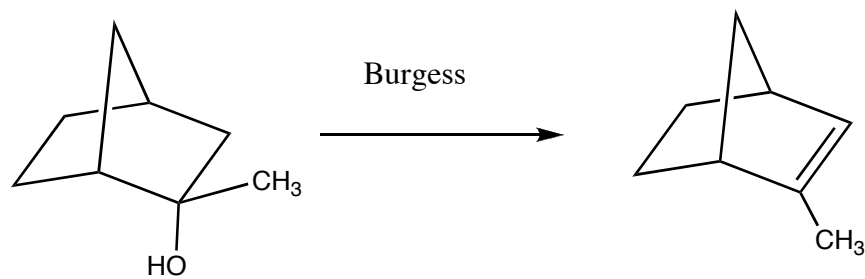
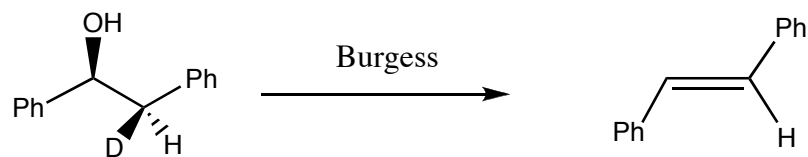
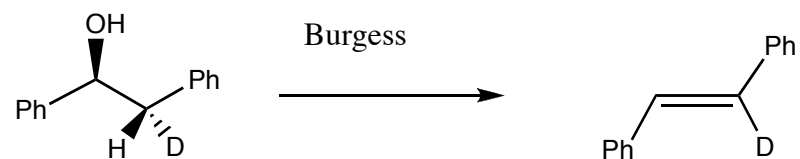
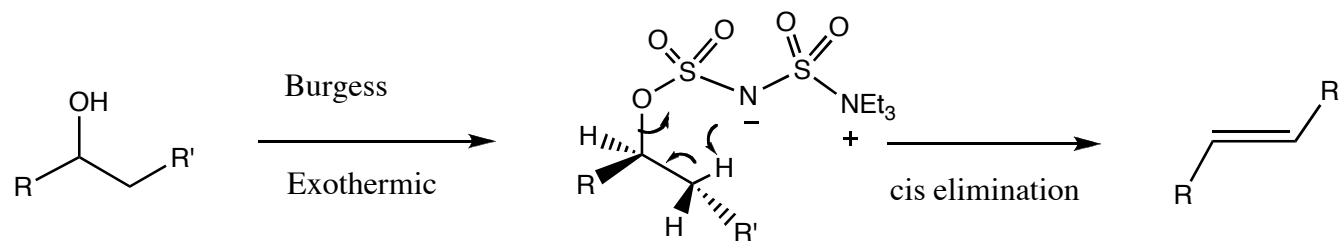
Dehydration of alcohols to form alkenes

Burgess Reagent:



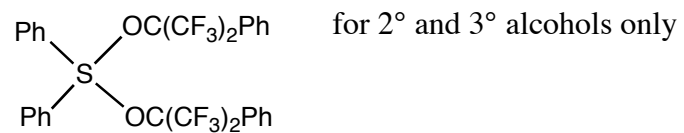
for 2° and 3° alcohols only

JACS, **1970**, 5224
JOC, **1973**, 26

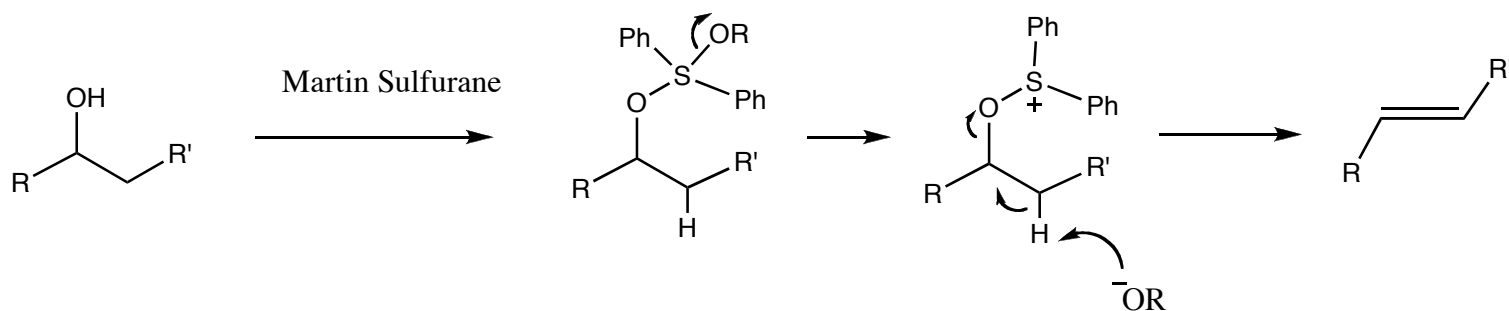


JACS, **1990**, 8433

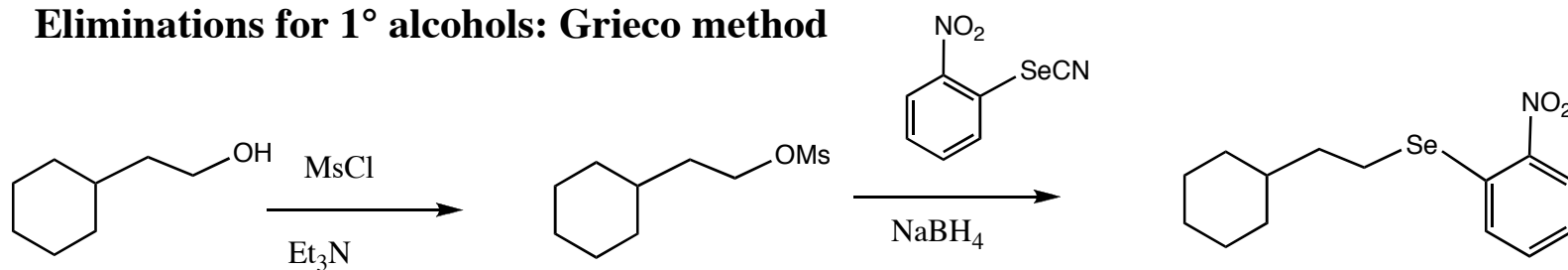
Martin Sulfurane:



JACS, 1971, 4327
JOC, 1973, 26



Eliminations for 1° alcohols: Grieco method



JOC, 1975, 1450.

Other selenide eliminations:

see *JACS*, 1973, 5813

JOC, 1975, 542.

