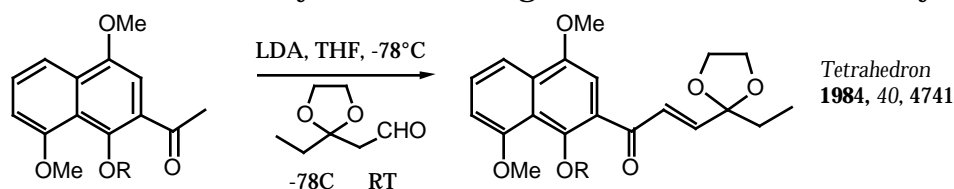


C=C Bond Formation

C&S Chapt. 2 # 5,6,8,9,12

1. Aldol Condensation
2. Wittig Reaction (Smith, Ch. 8.8.A)
3. Peterson Olefination
4. Julia-Lythgoe Olefination
5. Carbonyl Coupling Reactions (McMurry Reaction) (Smith Ch. 13.7.F)
6. Tebbe Reagent
7. Shapiro and Related Reaction
8. – Elimination and Dehydration
9. From Diols and Epoxides
10. From Acetylenes
11. From Other Alkenes-Transition Metal Catalyzed Cross-Coupling and Olefin Metathesis

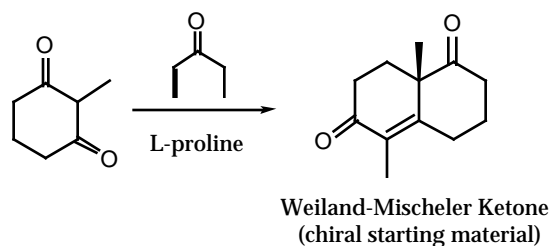
Aldol Condensation - Aldol condensation initially give β -hydroxy ketones which under certain conditions readily eliminated to give α,β -unsaturated carbonyls.



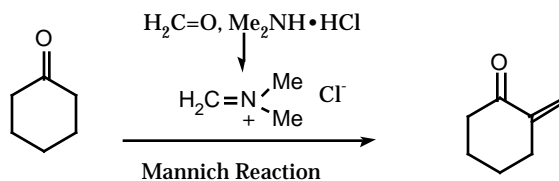
Robinson Annulation : Sequential Michael addition/aldol condensation between a ketone enolate and an alkyl vinyl ketone (i.e. MVK) to give a cyclohex-2-en-1-one

JOC **1984**, 49, 3685

Synthesis **1976**, 777.



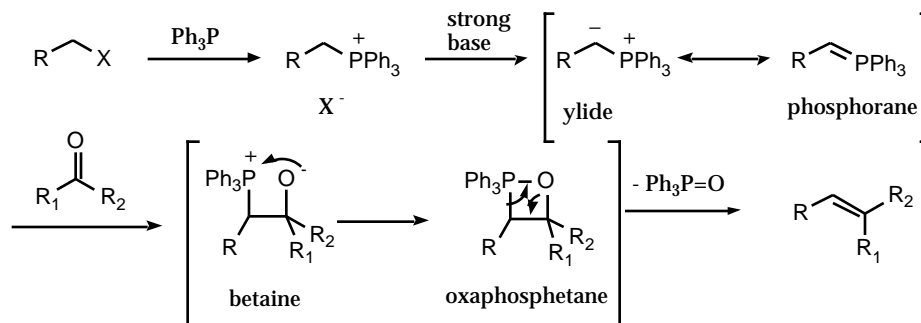
Mannich Reaction - α,β -unsaturated carbonyls (α -methylene carbonyls)



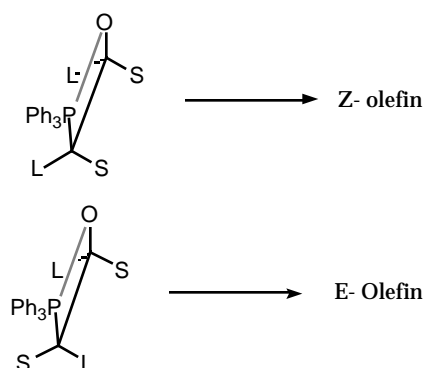
Wittig Reaction review: *Chem. Rev.* **1989**, 89, 863.

mechanism and stereochemistry: *Topic in Stereochemistry* **1994**, 21, 1

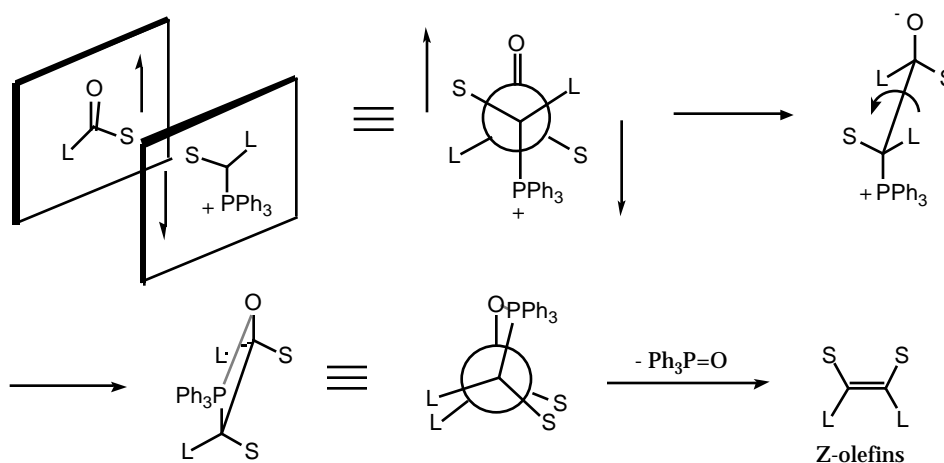
- reaction of phosphonium ylide with aldehydes, ketones and lactols to give olefins



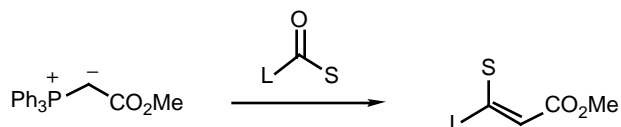
- Olefin Geometry



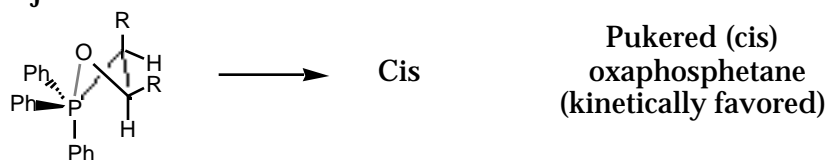
- With "non-stabilized" ylides the Wittig Reaction gives predominantly Z-olefins.
Seebach et al *JACS*



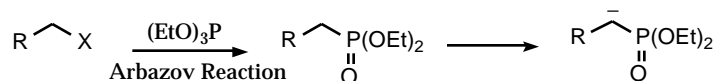
- "Stabilized ylides" give predominantly E-olefins



- Betaine formation is reversible and the reaction becomes under thermodynamic control to give the most stable product.
- There is NO evidence for a betaine intermediate.
- Vedejs Model:

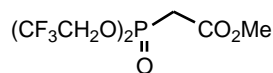


Phosphonate Modification (Horner-Wadsworth-Emmons)

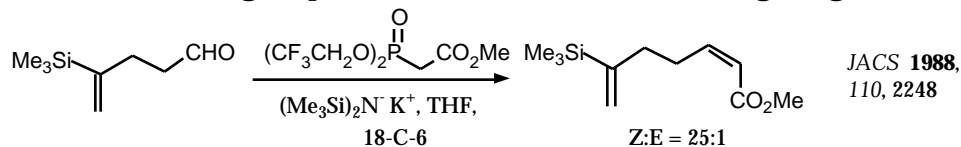


- R is usually restricted to EWG such as CO₂H, CO₂Me, CN, SO₂Ph etc. and the olefin geometry is usually E.

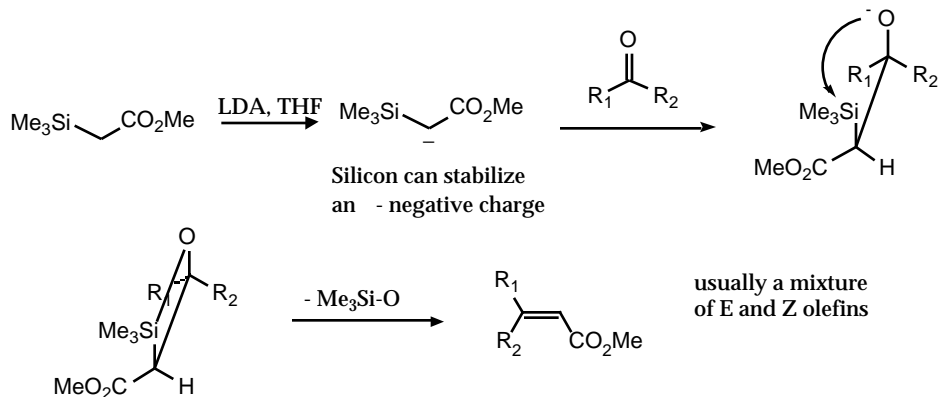
- Still Modification TL **1983**, 24, 4405.



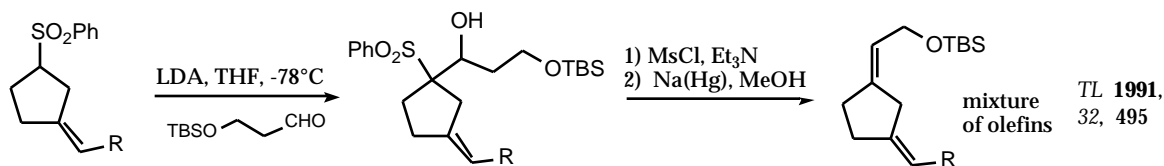
- CF₃CH₂O- groups make the betaine less stable, giving more Z-olefin.



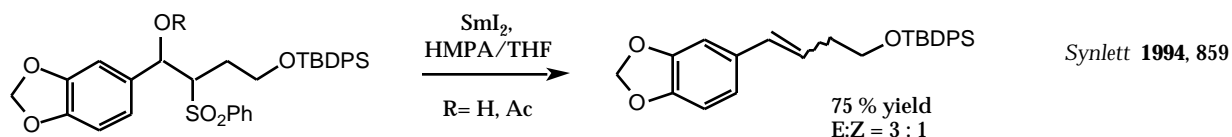
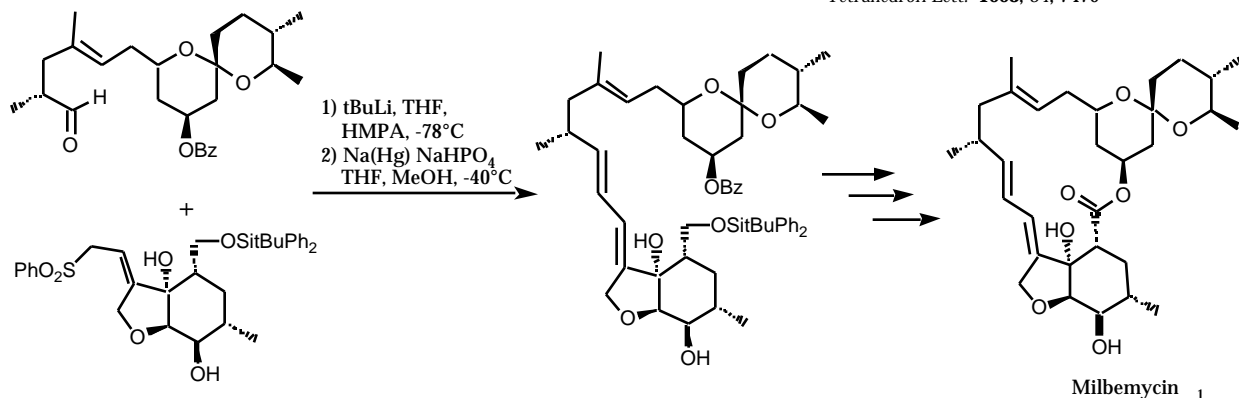
Peterson Olefination review: *Synthesis* **1984**, 384 *Organic Reactions* **1990**, 38 1.



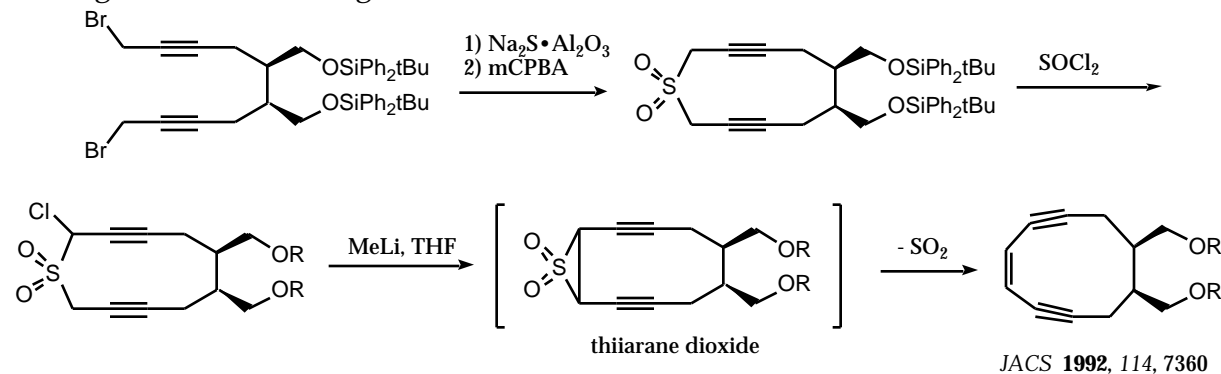
Julia-Lythgoe Olefination TL 1973, 4833 Tetrahedron 1987, 43, 1027



Tetrahedron Lett. 1993, 34, 7479



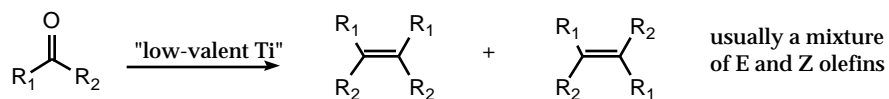
Ramberg-Bäcklund Rearrangement



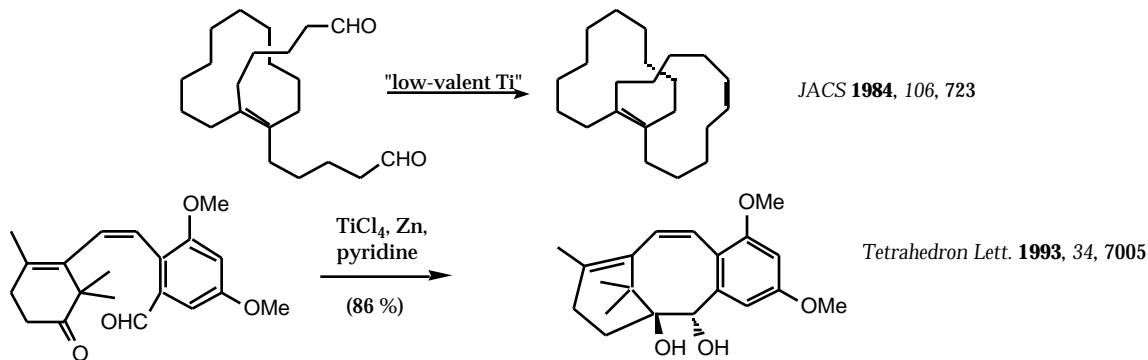
Carbonyl Coupling Reactions (McMurry Reaction)

Reviews: Chem. Rev. 1989, 89, 1513.

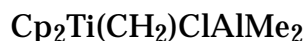
- reductive coupling of carbonyls with low valent transition metals, $\text{Ti}(0)$ or $\text{Ti}(II)$, to give olefins



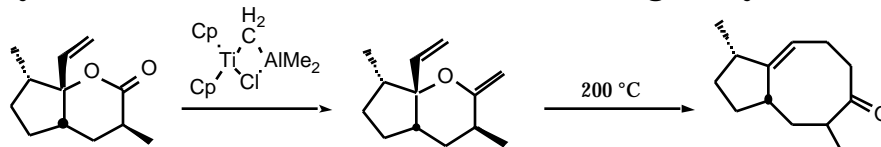
excellent method for the preparation of strained (highly substituted) olefins
- Intramolecular coupling gives cyclic olefins



Tebbe Reagent



- methylenation of ketones and lactones. The later gives cyclic enol ethers.

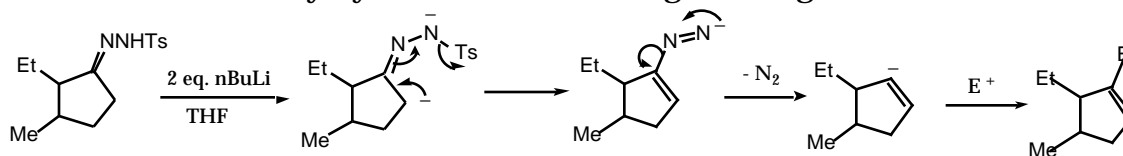


- Cp_2TiMe_2 will also do the methylenation chemistry
JACS **1990**, 112, 6393.

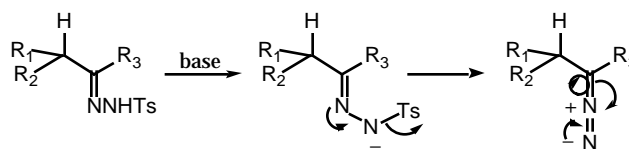
Shapiro and Related Reactions

Organic Reactions **1990**, 39, 1 : **1976**, 23, 405

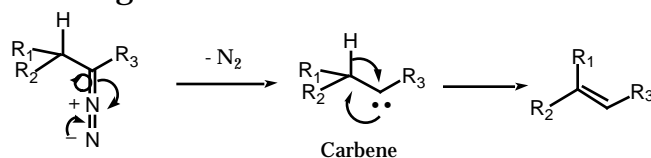
- Reaction of a tosylhydrazone with a strong base to give an olefin.



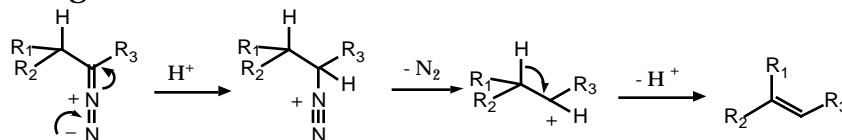
Bamford-Stevens Reaction- initial conversion of a tosylhydrazone to a diazo intermediate



a: aprotic- decomposition of the diazo intermediate under aprotic conditions gives an olefin through a carbene intermediate.



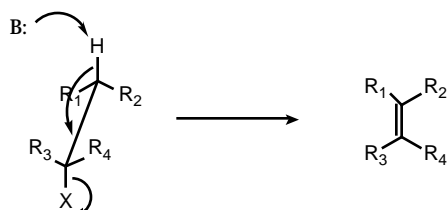
b. protic- decomposition of the diazo intermediate under protic conditions an olefin through a carbonium ion intermediate.



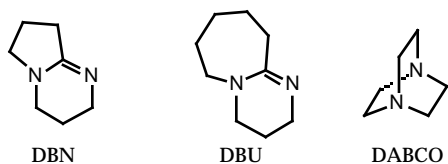
- Eliminations

Anti Eliminations

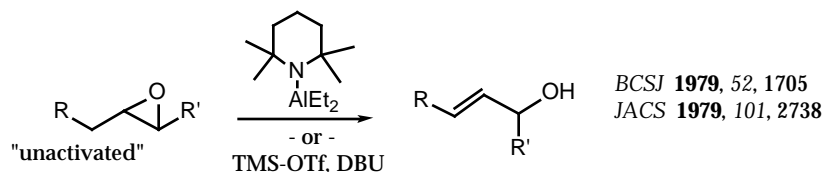
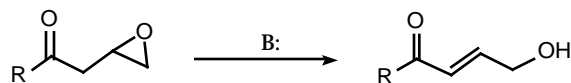
- elimination of HX from vicinal saturated carbon centers to give a olefin, usually base promoted.
- base promoted E₂- type elimination proceeds through an anti-periplanar transition state.



- typical bases: NaOMe, tBuOK, DBU, DBN, DABCO, etc.

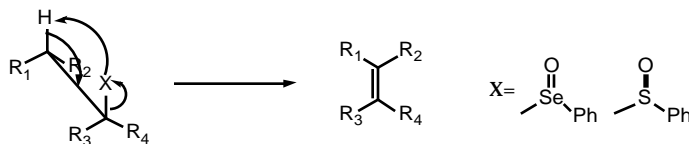
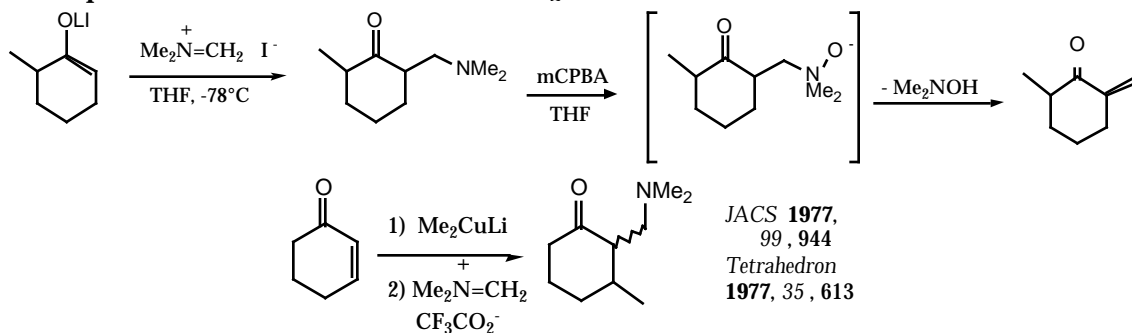


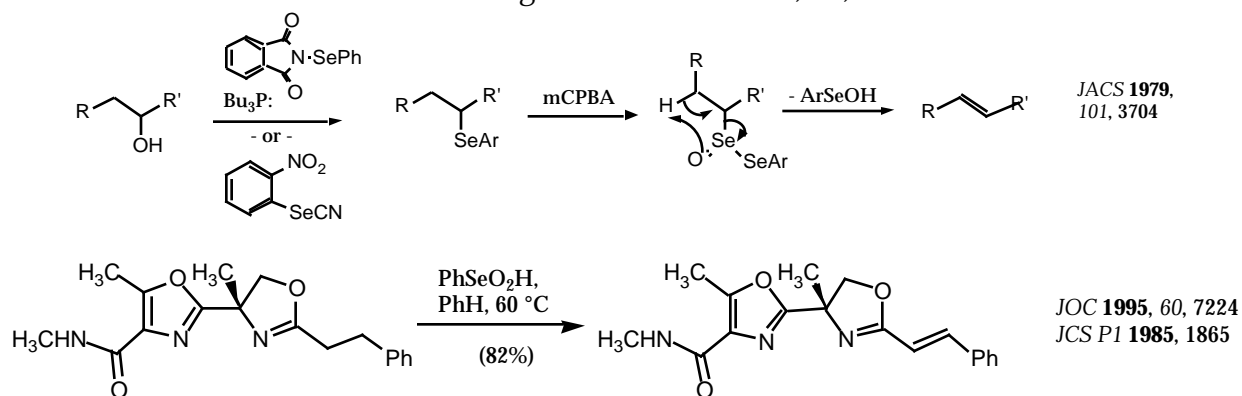
- X: -Br, -I, -Cl, -OR, epoxides



Syn Elimination

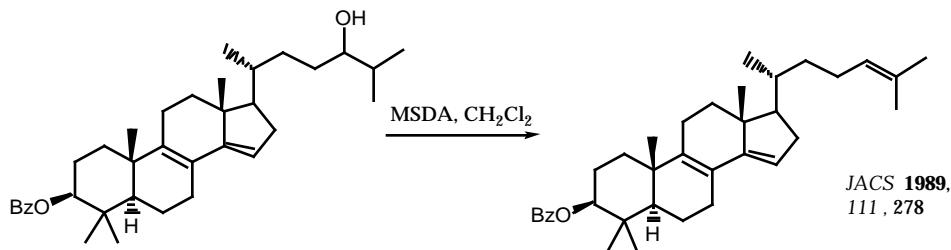
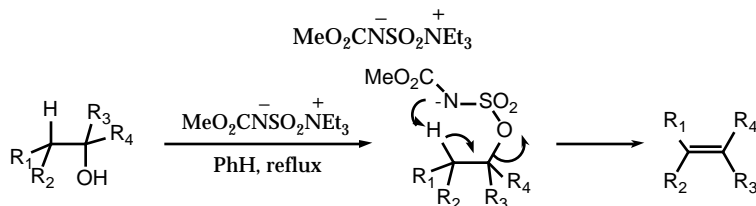
- often an intramolecular process

Cope Elimination- elimination of R₂NOH from an amine oxide

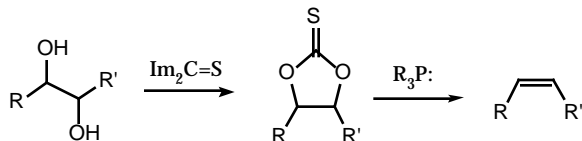
Selenoxide Elimination *Organic Reactions* **1993**, 44, 1.

Dehydration of Alcohols

- alcohols can be dehydrated with protic acid to give olefins via an E₁ mechanism.
 - other reactions dehydrate alcohols under milder conditions by first converting them into a better leaving group, i.e. POCl₃/ pyridine, P₂O₅
- Martin sulfurane; Ph₂S[OCPh(CF₃)₂]₂ *JACS*, **1972**, 94, 4997 dehydration occurs under very mild, neutral conditions, usually gives the most stable olefin

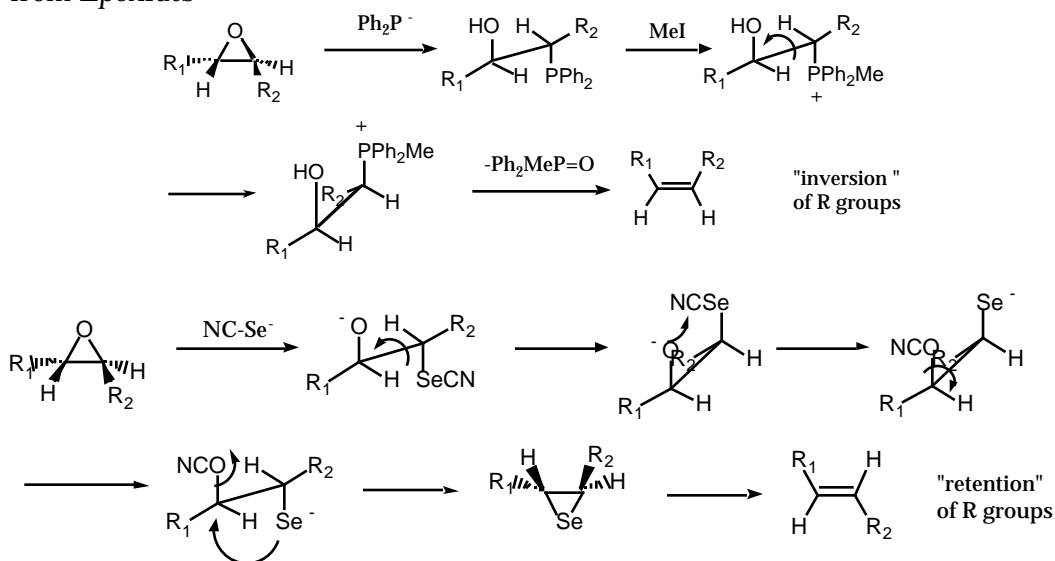
Burgess Reagent (inner salt) *JOC*, **1973**, 38, 26 occurs via a syn elimination

Olefins from Vicinal Diols

Corey-Winter Reaction *JACS* **1963**, 85, 2677; *TL* **1982**, 1979; *TL* **1978**, 737

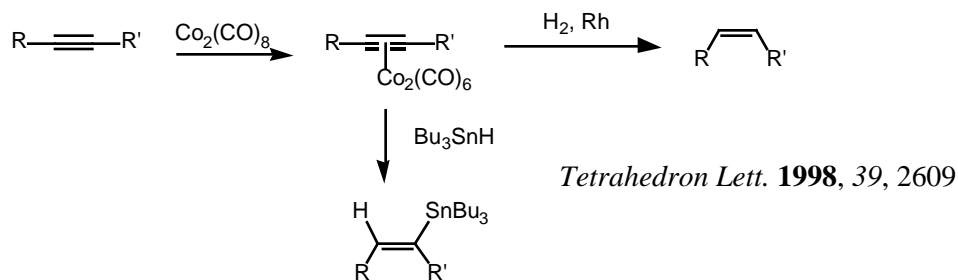
- vic-diols can be converted to olefins with K_2WCl_6 *JCSCC* **1972**, 370; *JACS* **1972**, 94, 6538
- This reaction worked best with more highly substituted diols and give predominantly syn elimination.
- Low valent titanium; McMurry carbonyl coupling is believed to go through the vic-diol. vic-diols are smoothly converted to the corresponding olefins under these conditions. *JOC* **1976**, 41, 896

Olefins from Epoxides



From Acetylenes

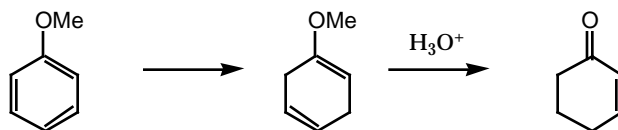
- Hydrogenation with Lindlar's catalyst gives cis-olefins



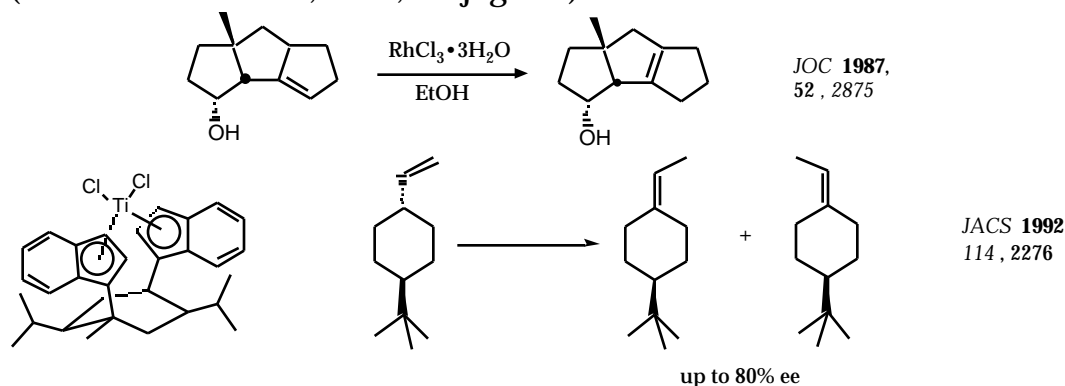
From Other Olefins

Sigmatropic Rearrangements

- transposition of double bonds

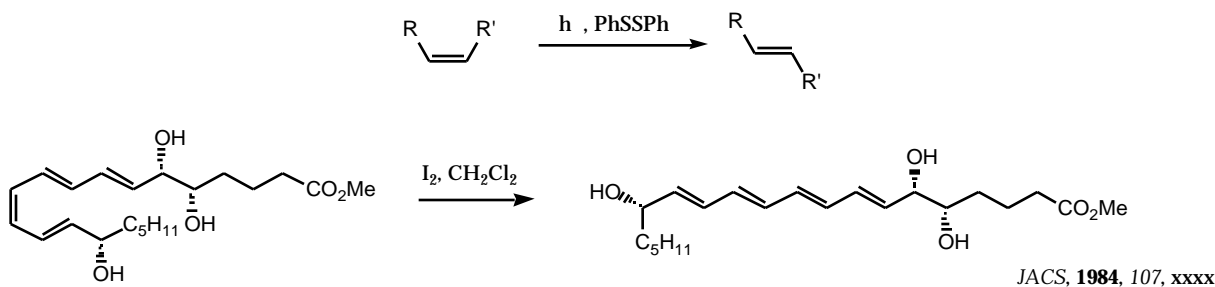
Birch Reduction *Tetrahedron* **1989**, 45, 1579

Olefin Isomerization- a variety of transition metal ($\text{RhCl}_3 \cdot \text{H}_2\text{O}$) catalyst will isomerize double bonds to more thermodynamically favorable configurations (i.e. more substituted, trans, conjugated)



Olefin Inversion *Tetrahedron* **1980**, 557

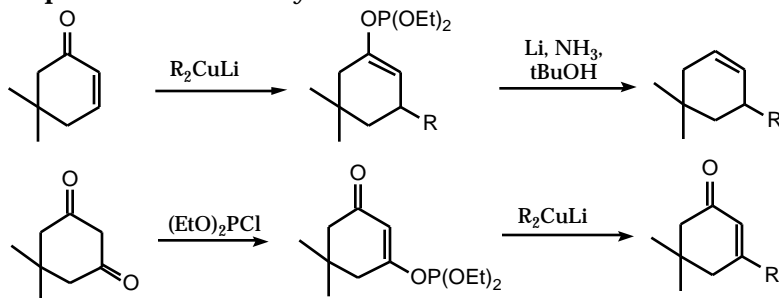
- Conversion of cis to trans olefins
- Conversion of trans to cis-olefins



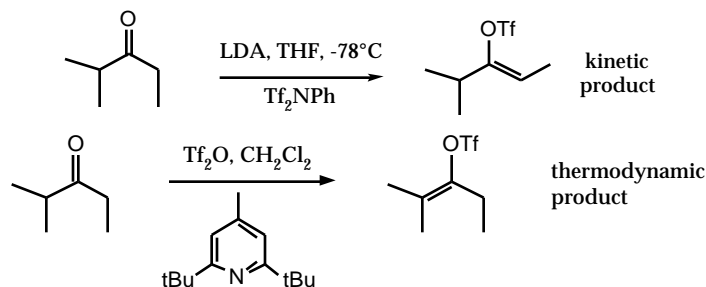
Transition Metal Catalyzed Cross-Coupling Reactions

Coupling of Vinyl Phosphonates and Triflates to Organometallic Reagents

- vinyl phosphates review: *Synthesis* **1992**, 333.

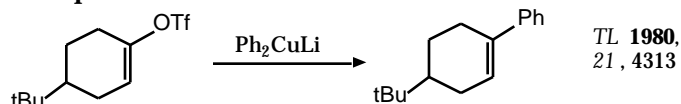


- preparation of enol triflates *Synthesis* **1997**, 735



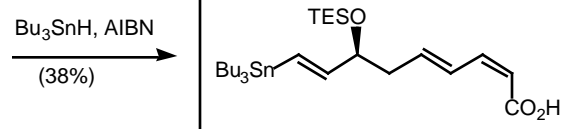
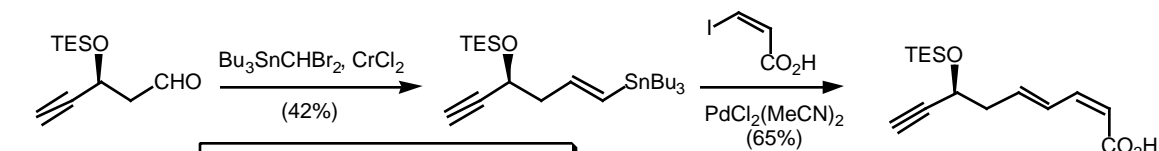
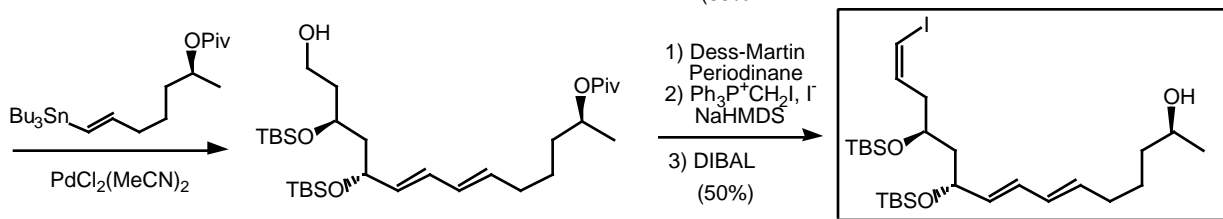
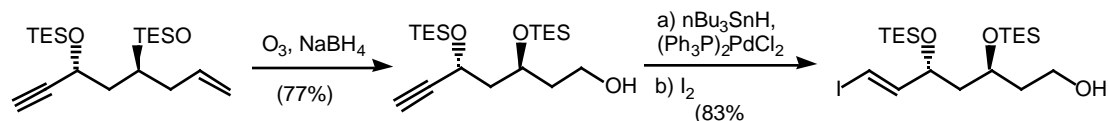
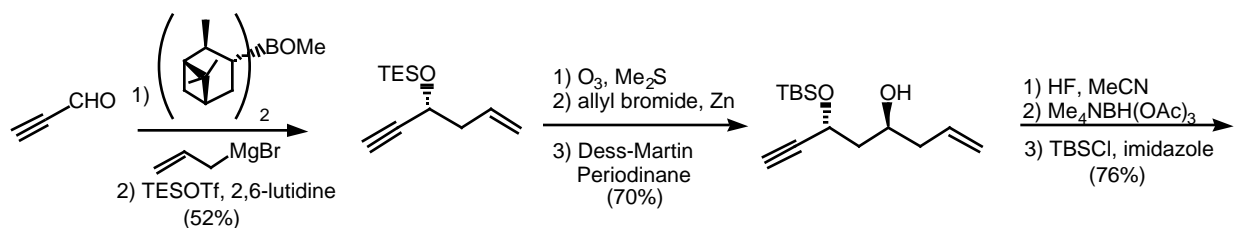
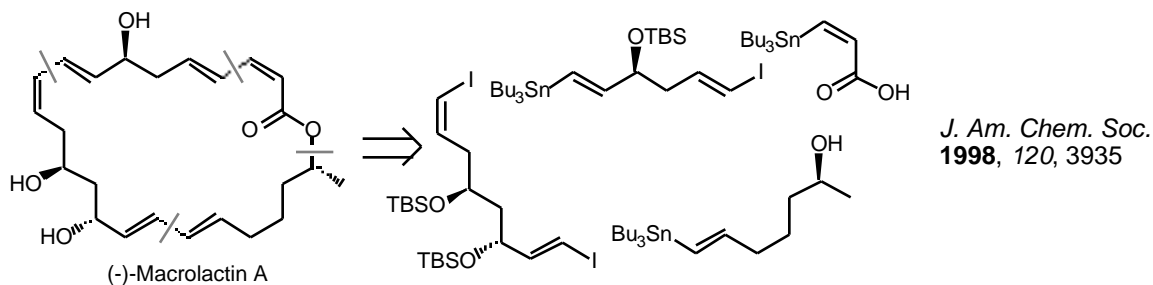
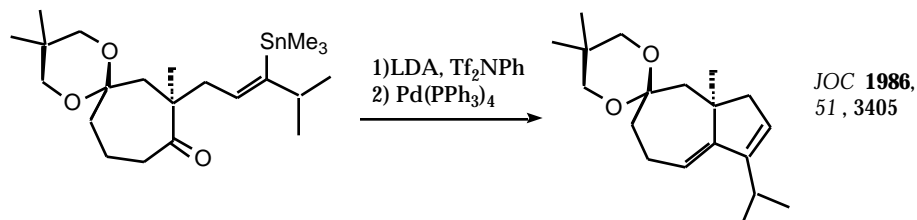
- reaction with cuprates.

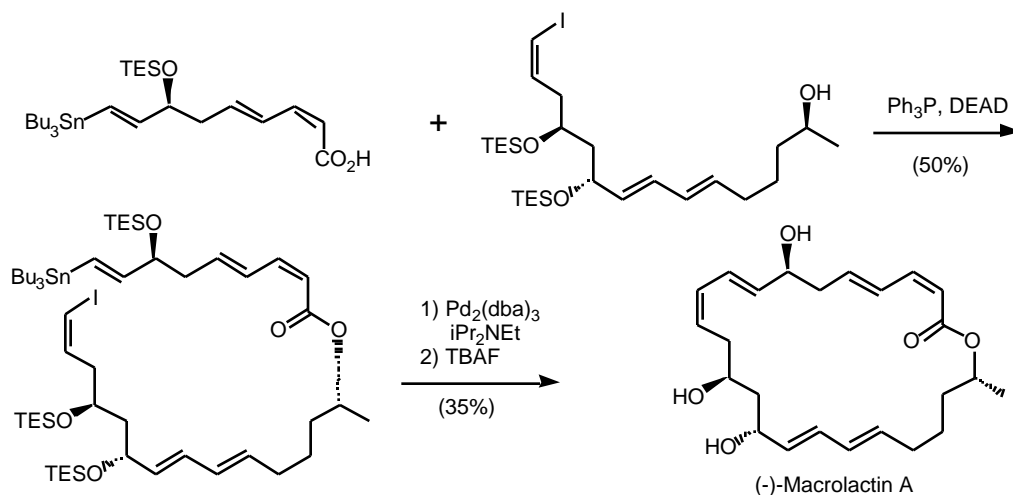
Acc. Chem. Res. **1988**, 25, 47



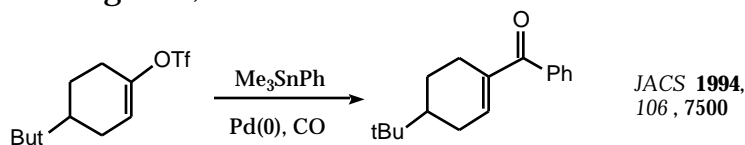
- palladium (0) catalyzed cross-coupling of vinyl or aryl halides or triflates with organostannanes (Stille Reaction)

Angew. Chem. Int. Ed. Engl. **1986**, 25, 508.; Organic Reactions **1997**, 50, 1-652

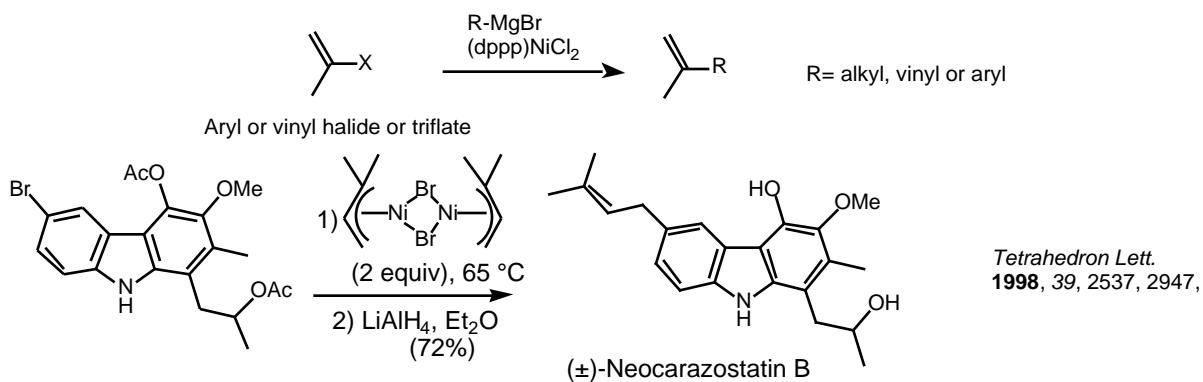




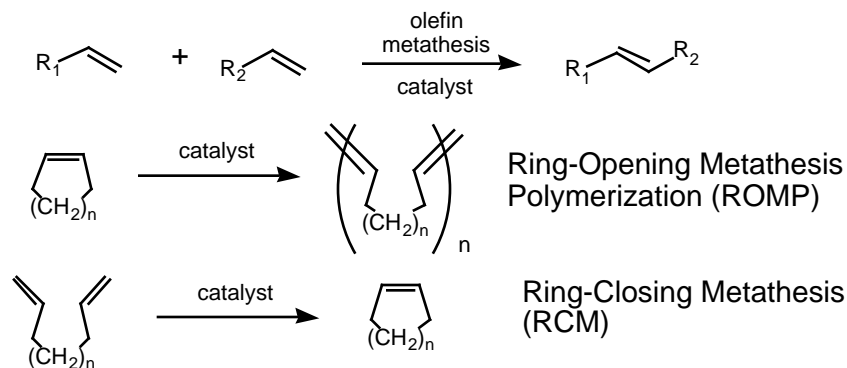
palladium (0) catalyzed carbonylations- coupling of a vinyl triflate with a organostanane to give α,β -unsaturated ketones.



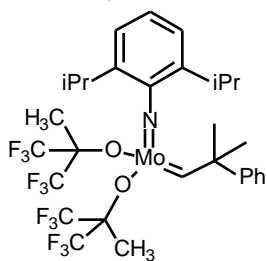
Nickel (II) Catalyzed Cross-Coupling with Grignard Reagents (Kumada Reaction): *Pure Appl. Chem.* **1980**, *52*, 669 *Bull. Chem. Soc. Jpn.* **1976**, *49*, 1958



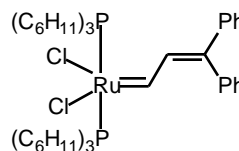
Olefin Metathesis *Tetrahedron* **1998**, *54*, 4413, *Acc. Chem. Res.* **1995**, *25*, 446.



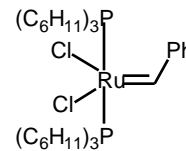
Metathesis Catalysts:



Schrock's Catalyst



Grubbs' Catalyst



Mechanism:

