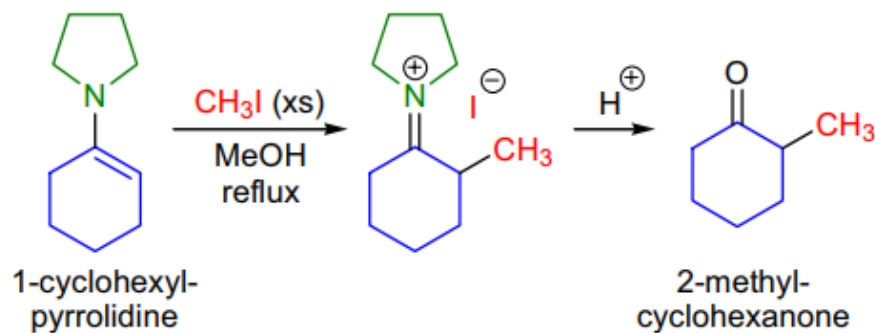
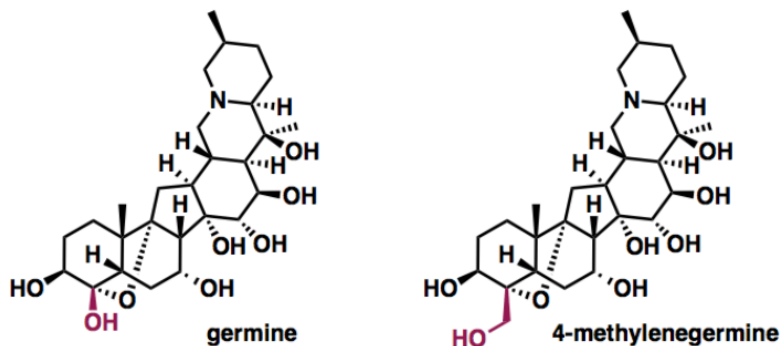


Stork-Zhao Olefination



Gilbert Stork 1921–2017
Columbia University

1945 [University of Wisconsin–Madison](#), PhD
under the supervision of [Samuel M. McElvain](#)
1946 [Harvard University](#): Instructor;
1948 Assistant Professor
1953 Columbia University: Associate Professor
1955 Professor;
1967–1993 Eugene Higgins Professor;
1993 Professor Emeritus



One would have to restart the whole synthesis. But I (G.S.) am now 95 years old...

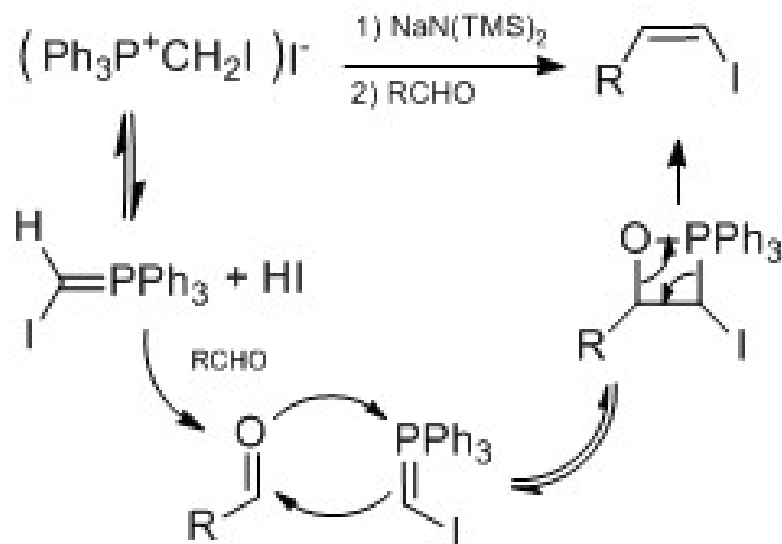
Stork enamine synthesis



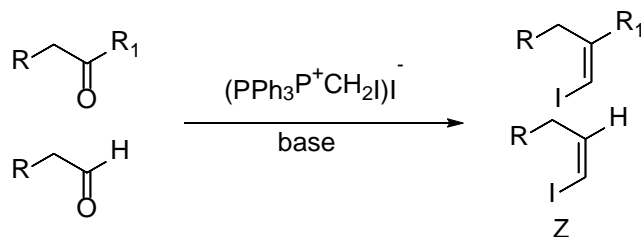
Kang Zhao

- 1982.9 - 1986.6 Shandong University ·
- 1988.9 - 1993.6 Columbia University, NY, USA ·
- 2001-至今 天津大学 首任药学院院长, 长江学者、

Stork-Zhao Olefination



Stork-Zhao Olefination



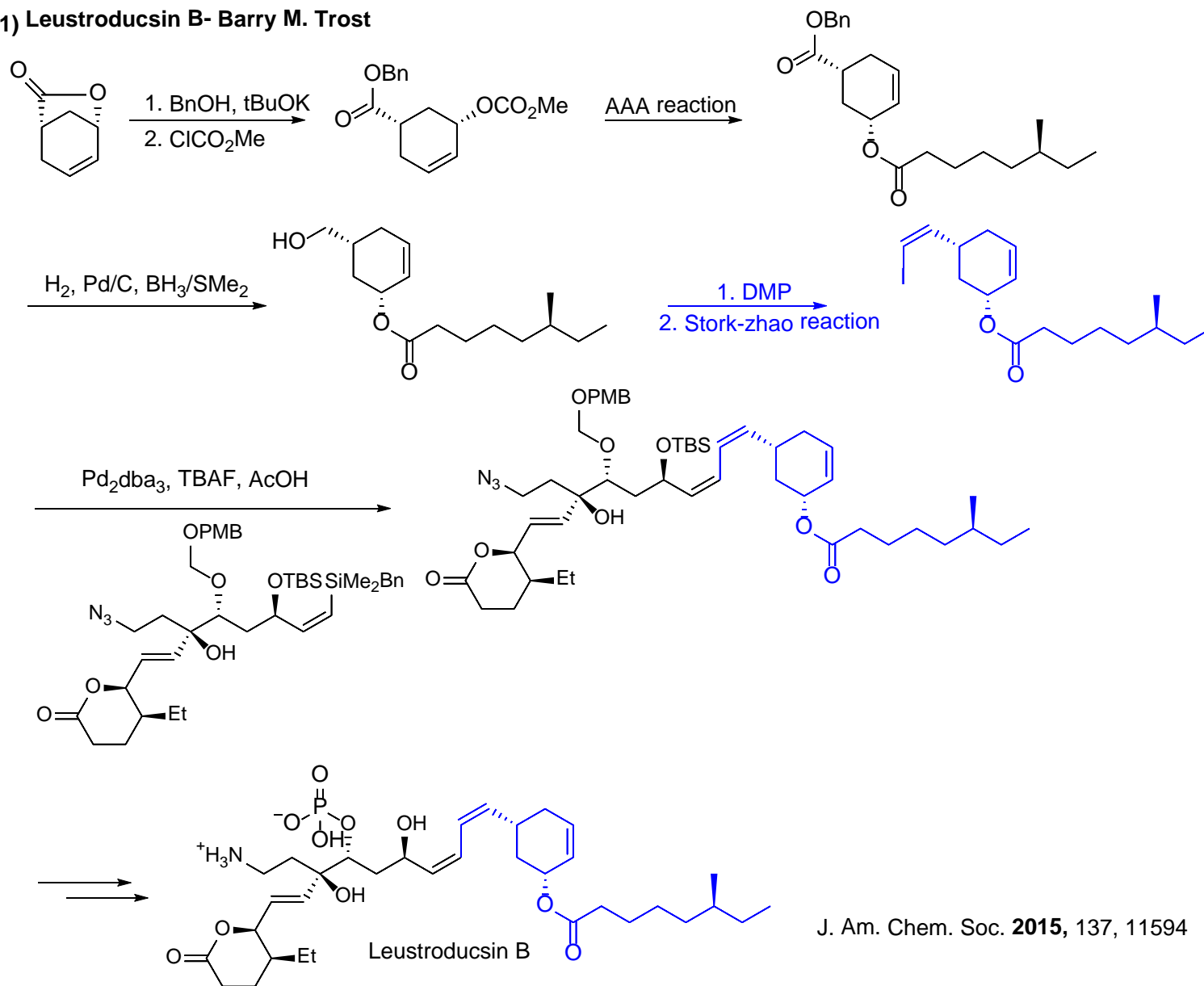
Conversion of Carbonyl Compounds to Vinyl Iodides

Carbonyl Compound	Solvent	ylide generation		reaction temperature ^a	Yield ^b	Z/E ^c
		temperature	time			
Methyl 6-oxohexanoate	THF	-23°C	8 min.	-23°C	74%	20:1
Citronellal	THF	-23°C	8 min.	-23°C	63%	12:1
Cyclohexanone	THF	-23°C	8 min.	-23°C	61%	
benzaldehyde	THF	-23°C	8 min.	-23°C	60%	4.6:1
	THF	20°C	1 min.	-78°C	63%	13:1
	THF/HMPA	20°C	1 min.	-78°C	96%	62:1
Nonyl aldehyde	THF	-23°C	8 min.	-23°C	76%	7.8:1
	THF	20°C	1 min.	-78°C	81%	8.3:1
	THF/HMPA	20°C	1 min.	-78°C	83%	9.4:1
Cyclohexanecarboxaldehyde	THF	-23°C	8 min.	-23°C	74%	6:1
	THF	20°C	1 min.	-78°C	72%	11:1
	THF/HMPA	20°C	1 min.	-78°C	71%	15.5:1

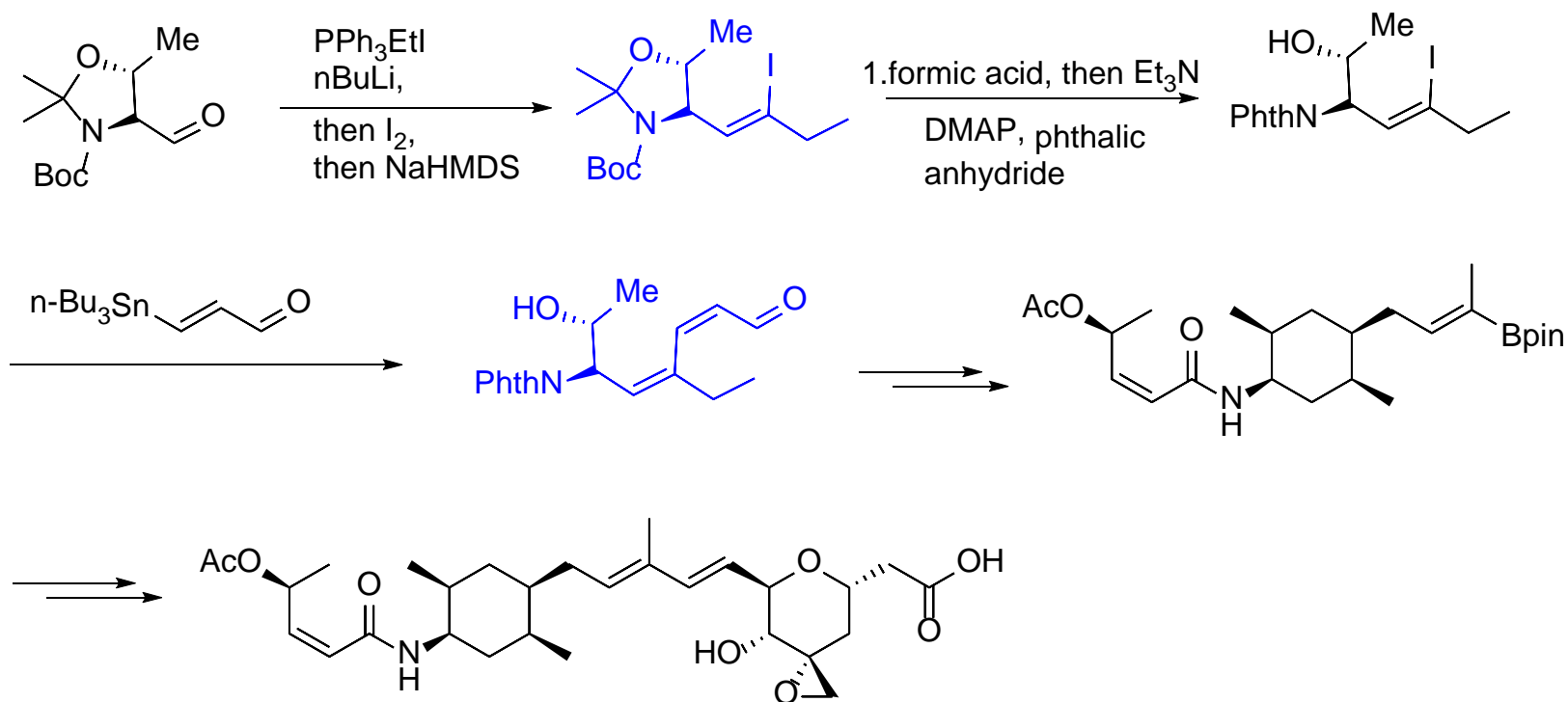
The stereoselectivity depend on temperature and HMPA

Application

1) Leustroducsin B- Barry M. Trost



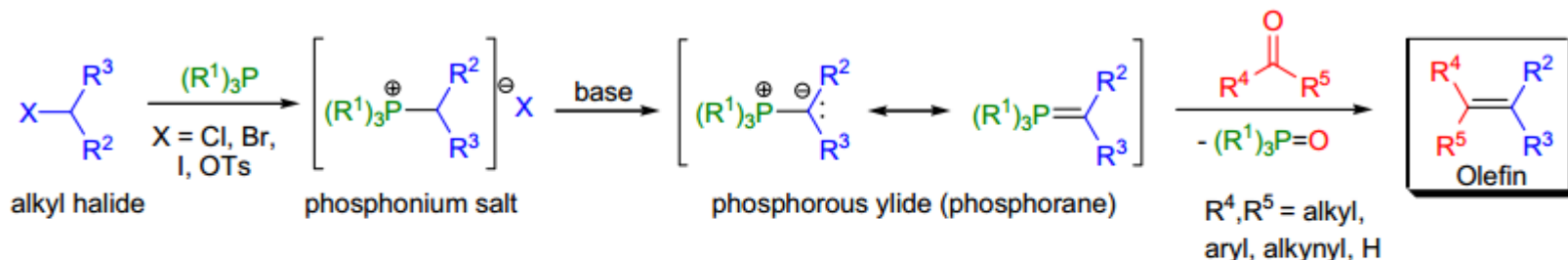
2) Thailanstatin A- K. C. Nicolaou



J. Am. Chem. Soc. **2016**, 138, 7532

The stereoselectivity is influenced by many factors

WITTIG REACTION



if $R^1 = \text{aryl}$ and $R^2, R^3 = \text{alkyl, H}$

⇒ "nonstabilized" ylide

if $R^1 = \text{aryl}$ and $R^2, R^3 = \text{aryl, alkenyl, benzyl, allyl, H}$

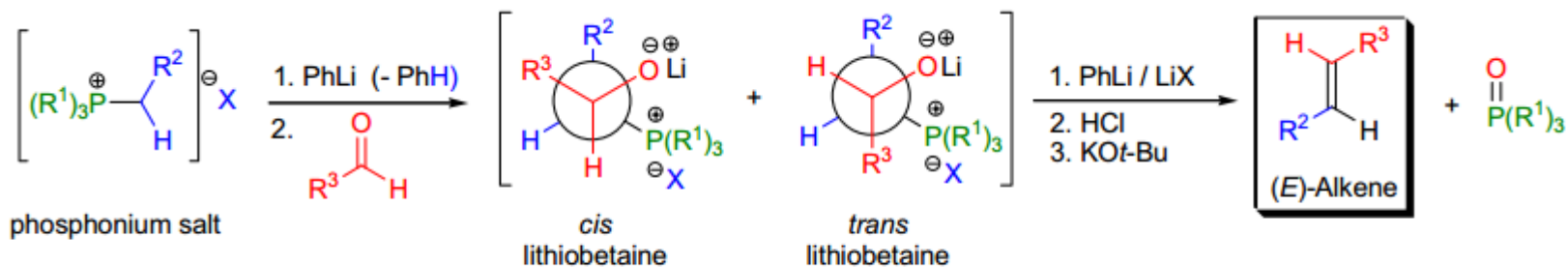
⇒ "semi-stabilized" ylide

if $R^1 = \text{aryl}$ and $R^2, R^3 = \text{-CO}_2\text{R, -SO}_2\text{R, -CN, -COR}$

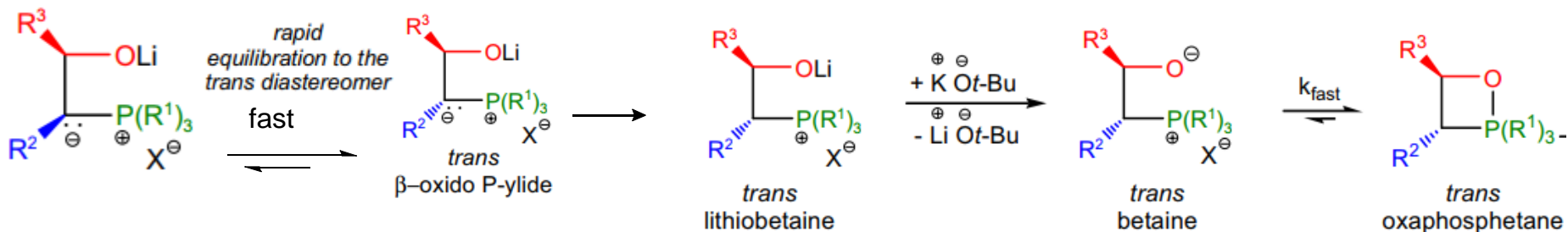
⇒ "stabilized" ylide

(E)-alkene

WITTIG REACTION - SCHLOSSER MODIFICATION

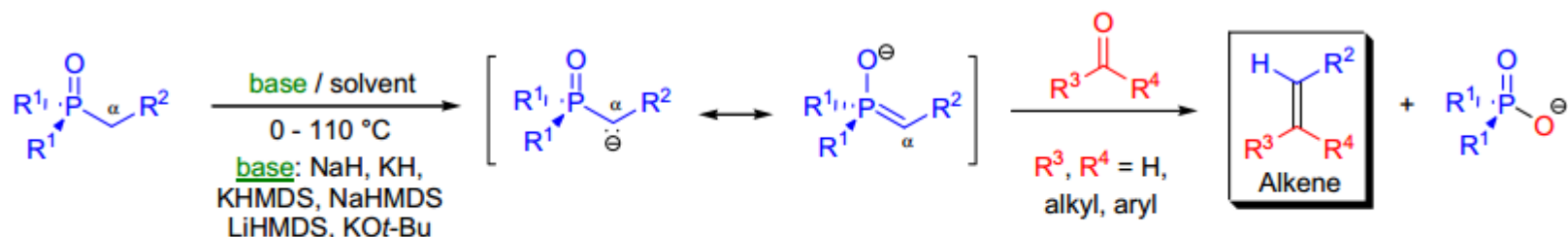


$R^1 = \text{aryl}; R^2 = \text{alkyl, H}; R^3 = \text{alkyl, aryl}; X = \text{Cl, Br, I}$



(E)-alkene

HORNER-WADSWORTH-EMMONS OLEFINATION



$R^1 = \text{aryl, alkyl}; R^2 = \text{alkyl, aryl, COR, CO}_2\text{R, CN, SO}_2\text{R}$

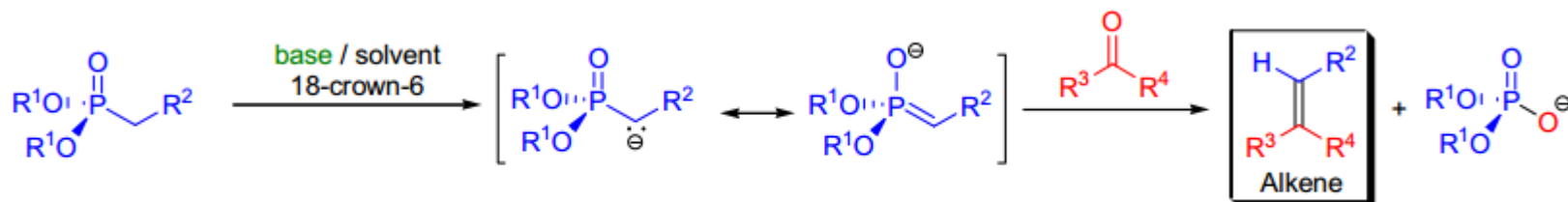
⇒ Horner-Wittig reaction

$R^1 = \text{O-aryl, O-alkyl, NR}_2; R^2 = \text{aryl, alkenyl, COR, CO}_2\text{R, CN, SO}_2\text{R}$

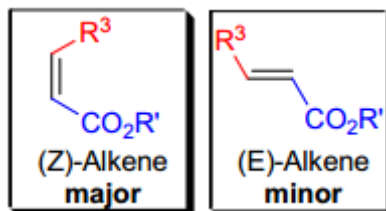
⇒ Wadsworth-Emmons reaction

(Z)-alkene

HORNER-WADSWORTH-EMMONS OLEFINATION – STILL-GENNARI MODIFICATION



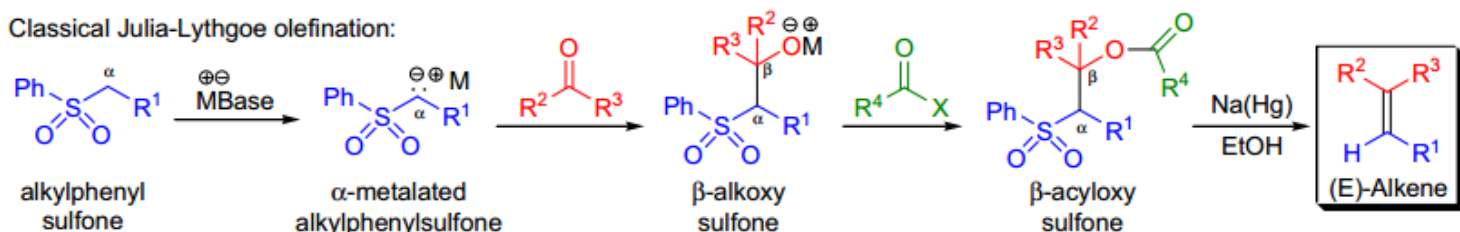
$R^1 = \text{CH}_2\text{CF}_3, \text{trifluoroalkyl}; R^2 = \text{COR, CO}_2\text{R, CN, SO}_2\text{R}; R^{3-4} = \text{H, alkyl, aryl}; \text{base} = \text{KH, KHMDS}$



(E)-alkene

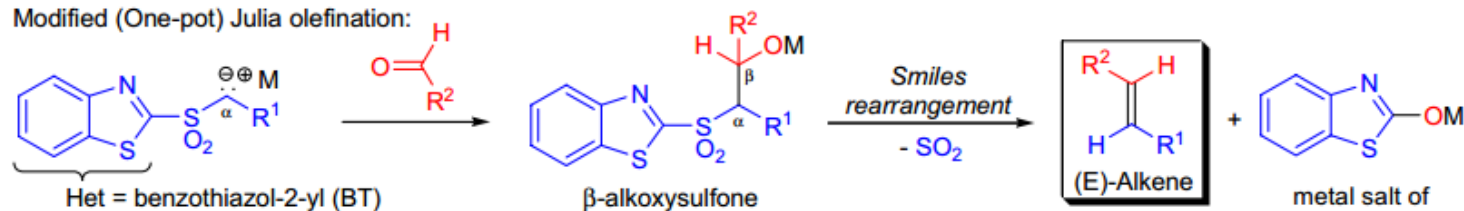
JULIA-LYTHGOE OLEFINATION

Classical Julia-Lythgoe olefination:



R¹ = H, alkyl, aryl; R², R³ = H, alkyl, aryl, alkenyl; R⁴ = alkyl, aryl; X = Cl, Br, OCOR

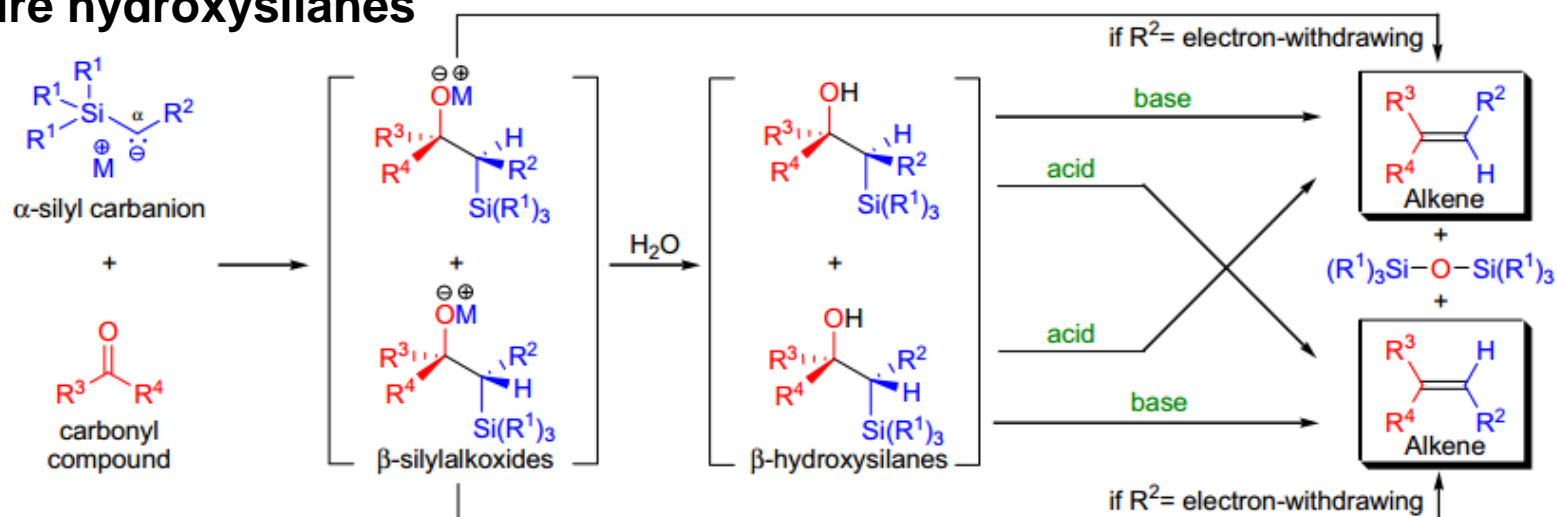
Modified (One-pot) Julia olefination:



R¹ = H, alkyl, aryl; R² = alkyl, aryl, alkenyl; Het = benzothiazol-2-yl (BT), pyridin-2-yl (PYR), 1-phenyl-1H-tetrazol-5-yl (PT)

The (E) or (Z)-alkene controlled by the pure hydroxysilanes

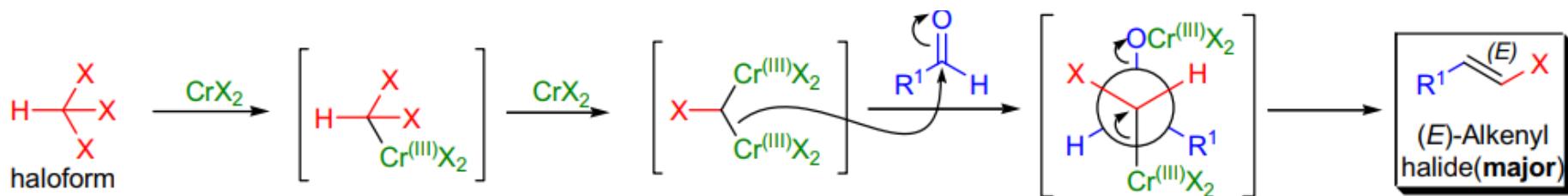
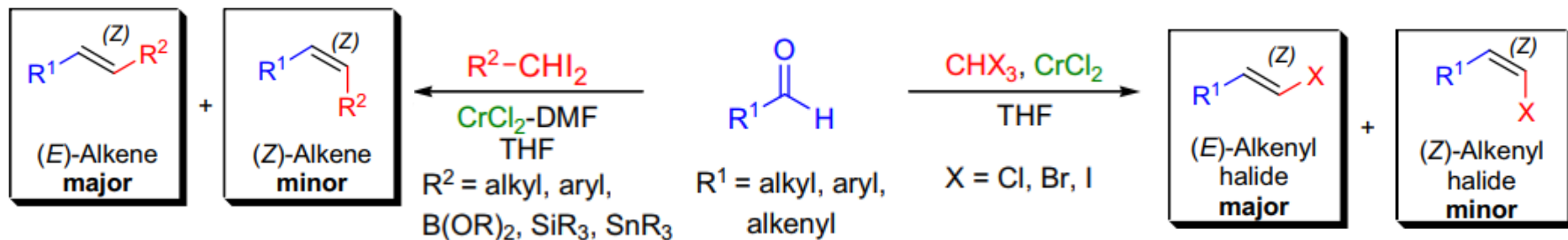
PETERSON OLEFINATION



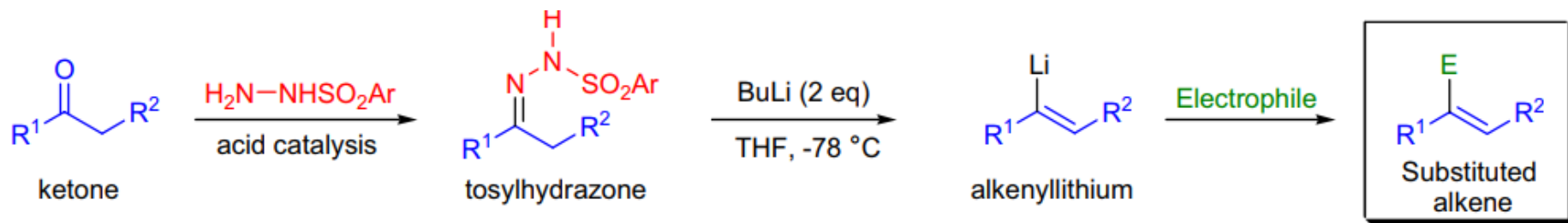
R¹ = alkyl, aryl; R² = alkyl, aryl, CO₂R, CN, CONR₂, CH=NR, SR, SOR, SO₂R, SeR, SiR₃, OR, BO₂R₂; R³, R⁴ = alkyl, aryl, H

(E)-alkene

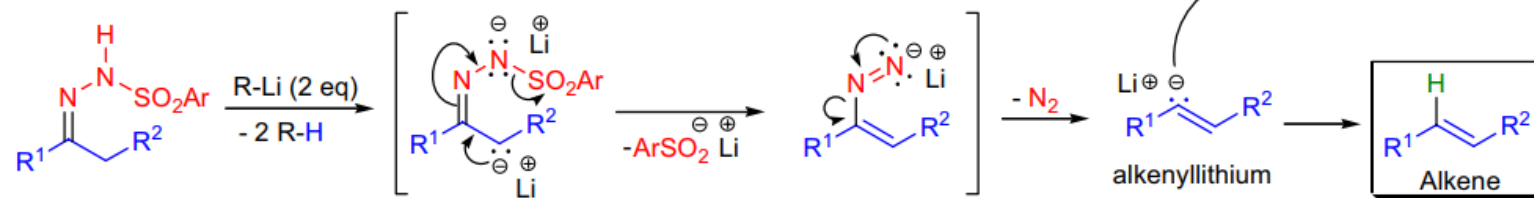
TAKAI-UTIMOTO OLEFINATION (TAKAI REACTION)



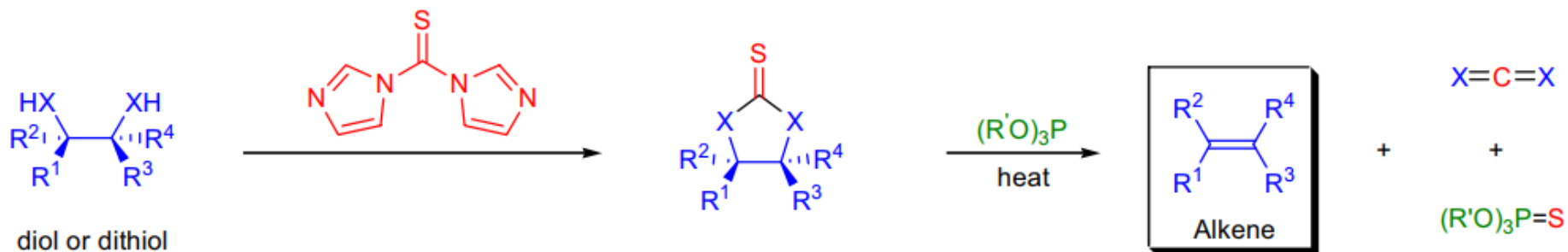
Shapiro reaction.



Carbanion Mechanism (Shapiro reaction):



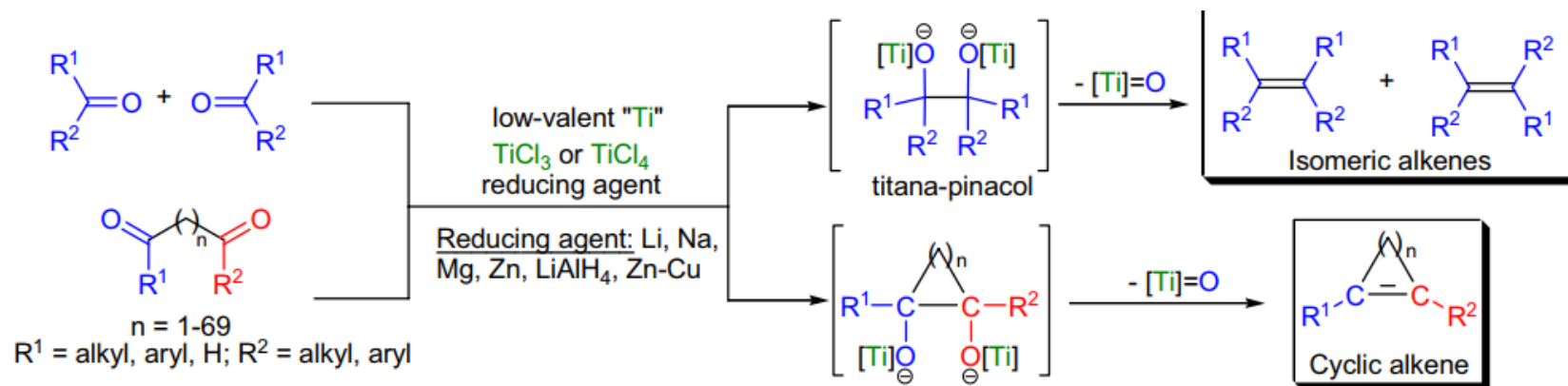
Corey-Winter olefination.



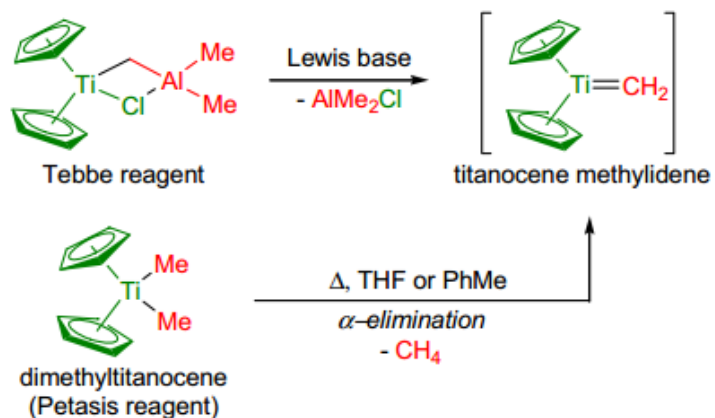
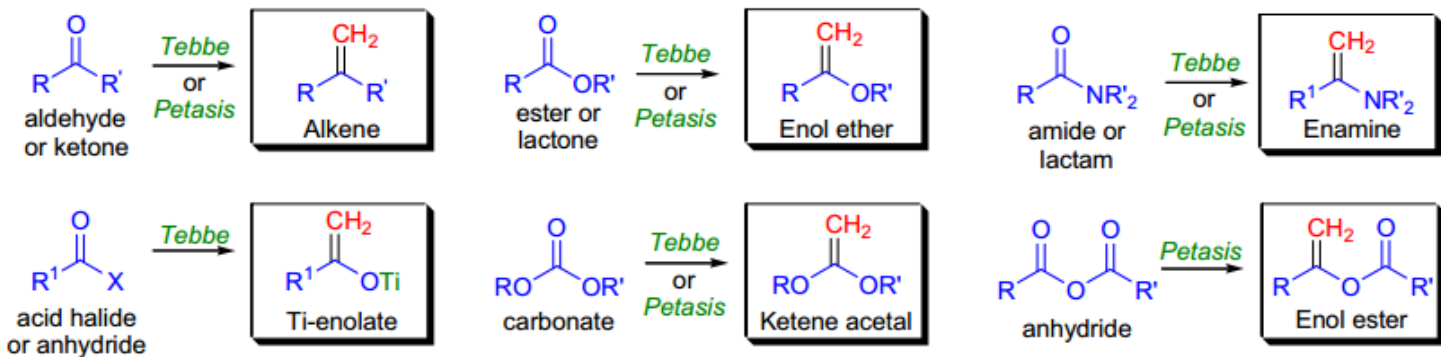
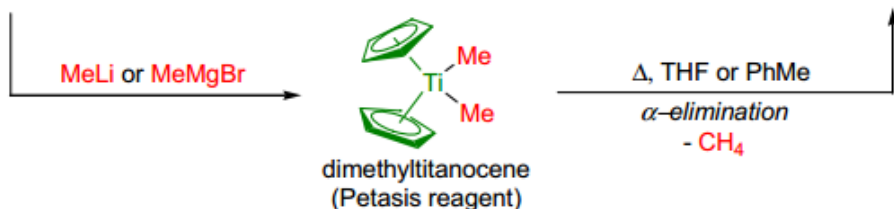
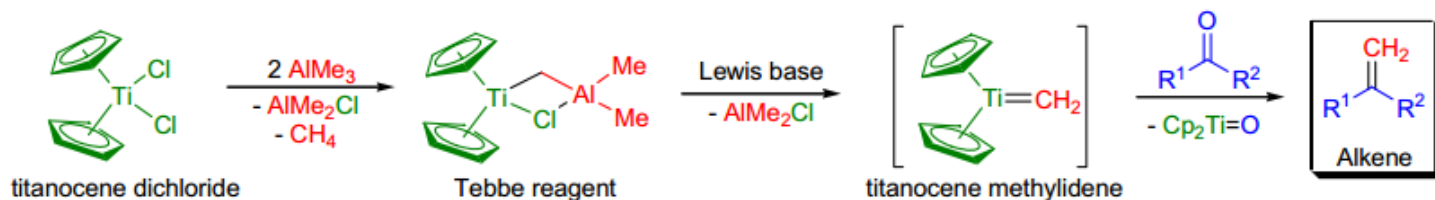
The stereochemistry of the product is only determined by the stereochemistry of the sm

Isomeric alkenes

McMURRY COUPLING



TEBBE OLEFINATION / PETASIS-TEBBE OLEFINATION



Isomeric alkenes

Johnson Olefination

