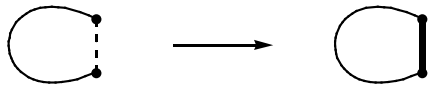


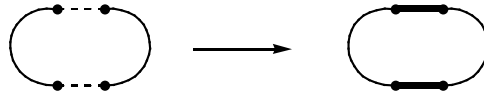
Cyclopentane Annulation¹⁾

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Cyclization

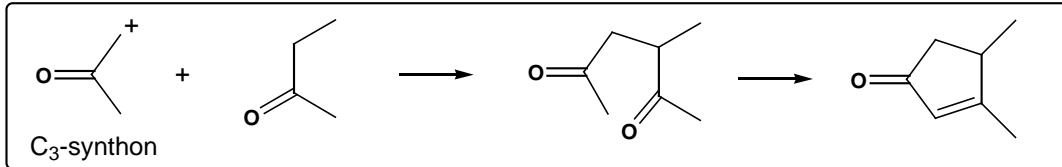


Annulation

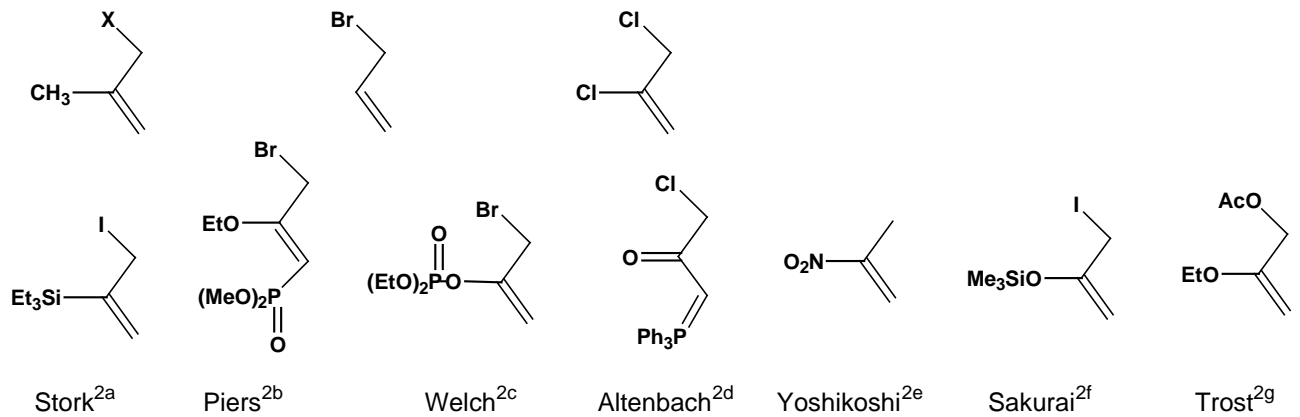


Cyclization

Cyclopentenone Annulation Strategy Based on Aldol or Wittig Cyclization



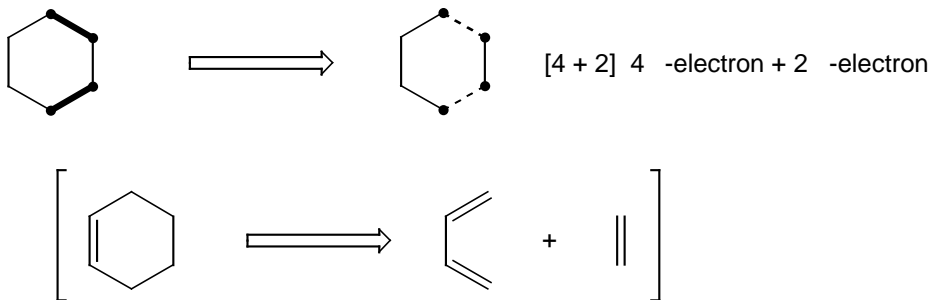
C₃-Synthons



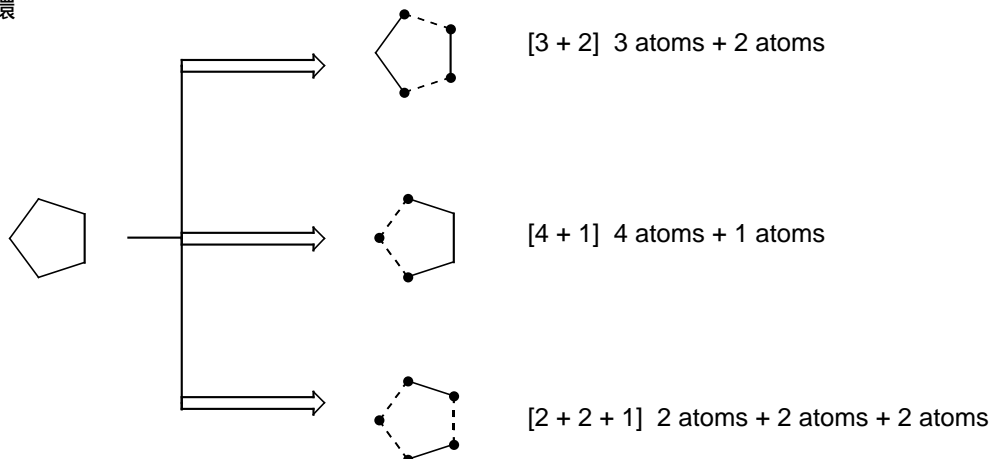
Annulation

六員環

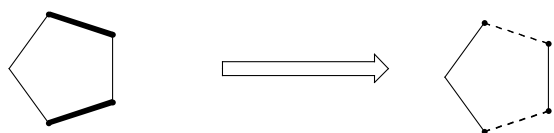
Diels-Alder Reaction



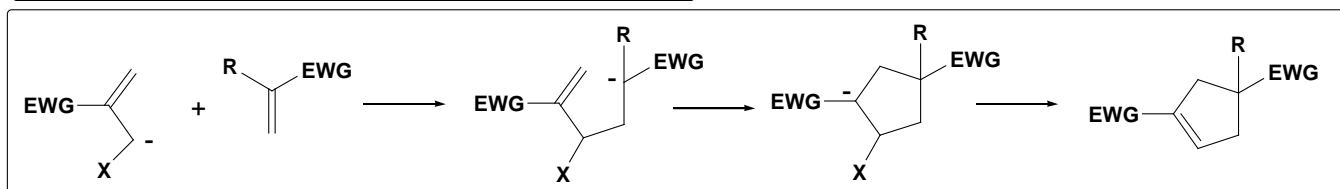
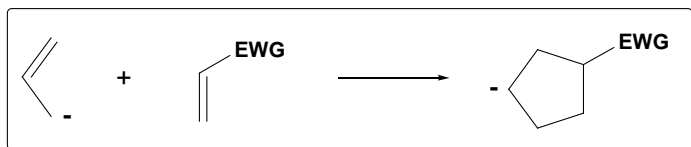
五員環



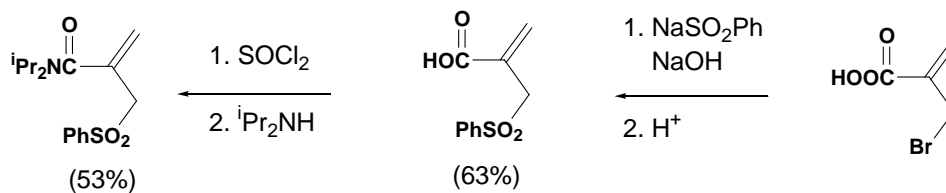
[3+2] Annulation



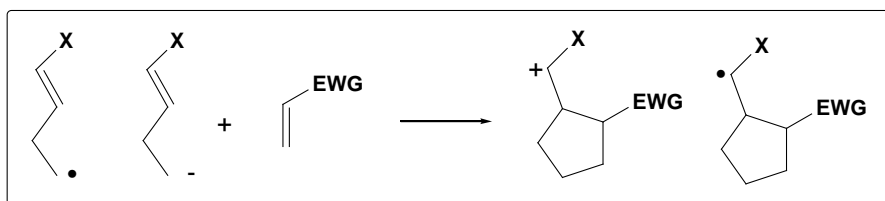
[I] Allylic Anion Synthons



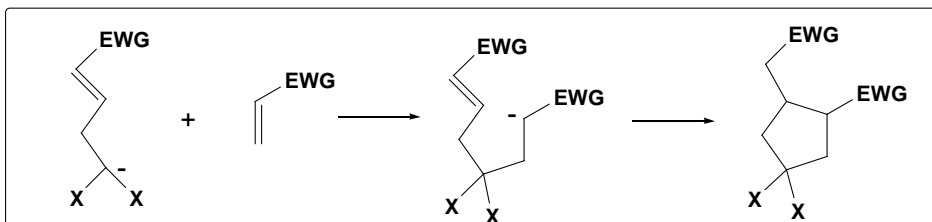
P.Beak³⁾



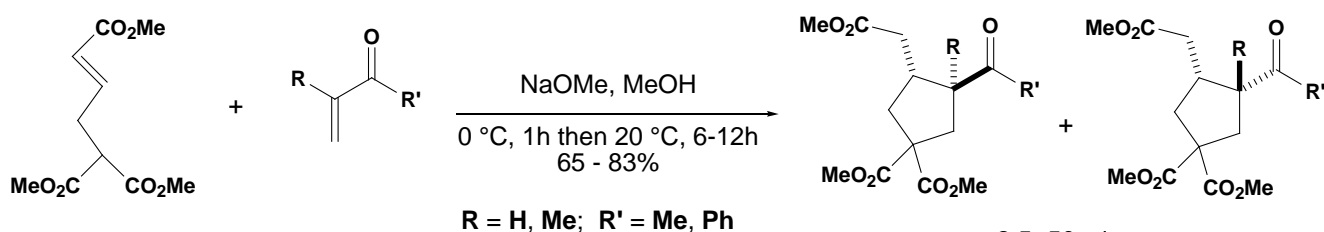
[II] Homoallylic Anion and Radical Synthons



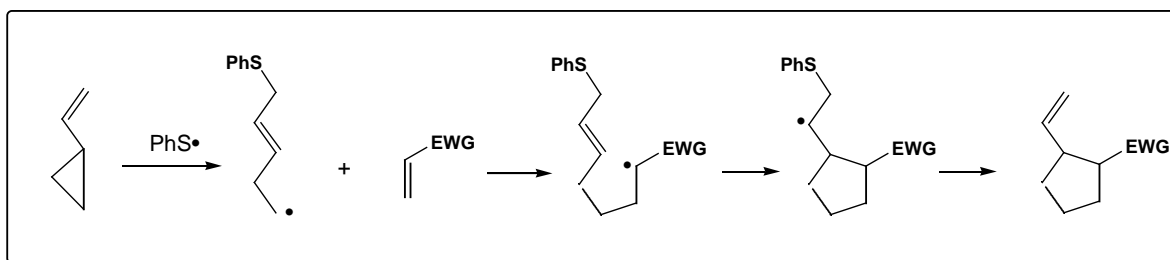
A. Homoallylic Anion



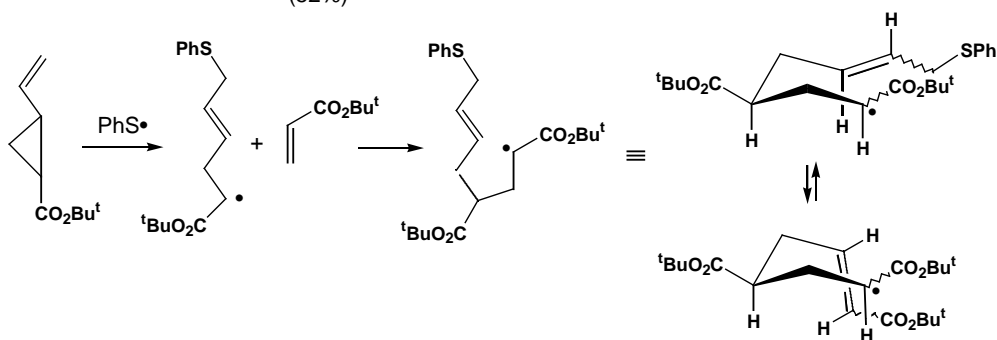
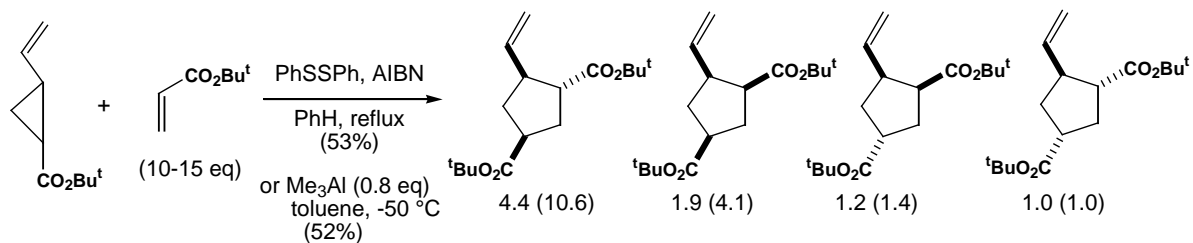
R.A.Bunce⁴⁾



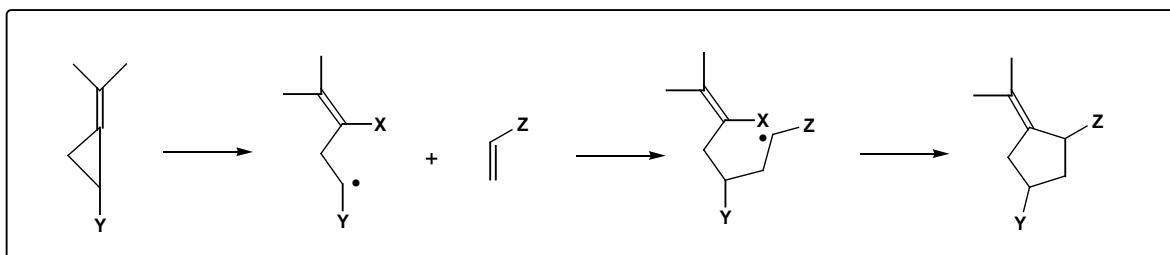
B. Vinylcyclopropane Precursor



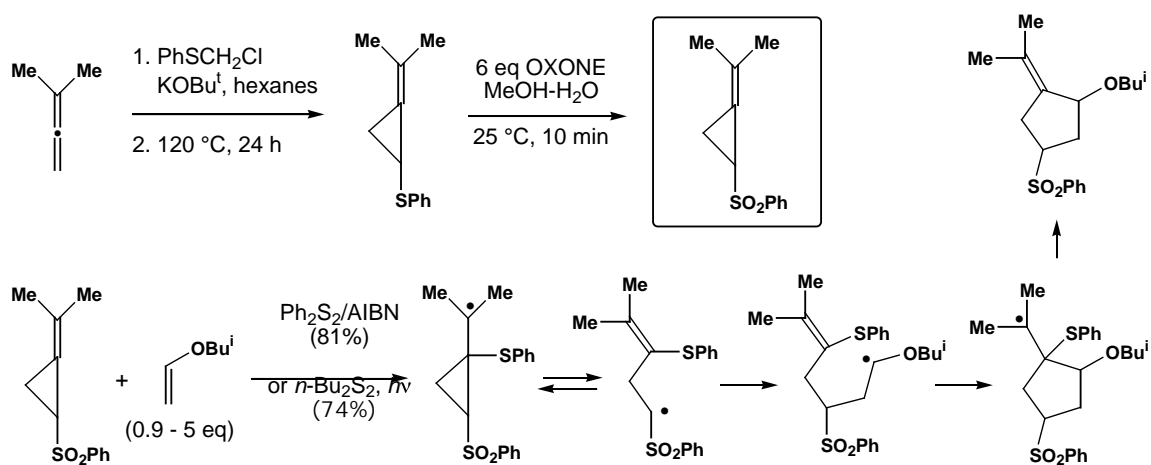
K.S. Feldman⁵⁾



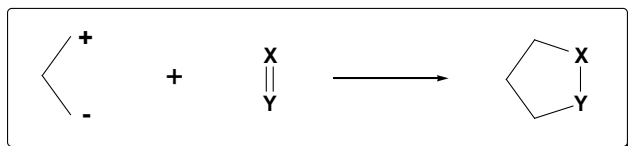
C. Methylene-cyclopropane Precursor



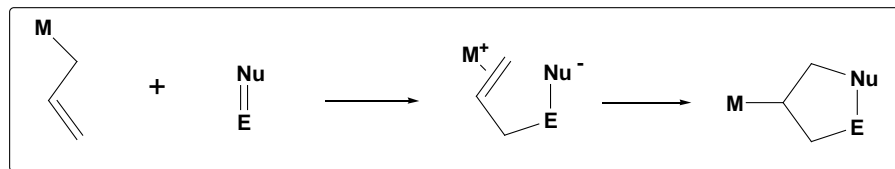
D.A. Singleton⁶⁾



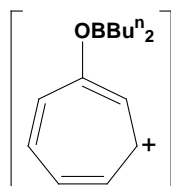
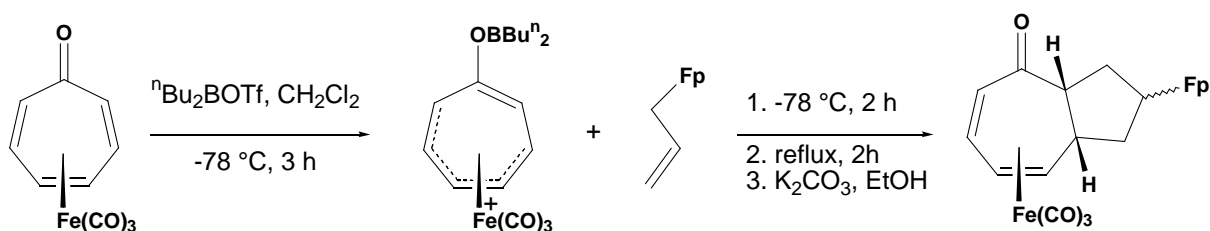
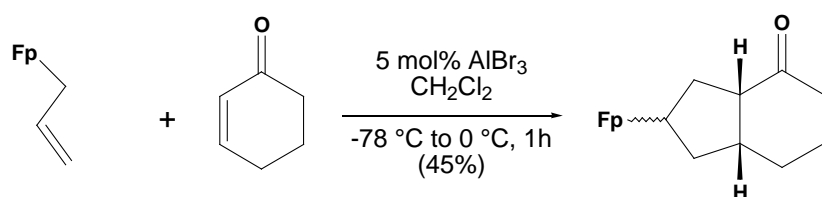
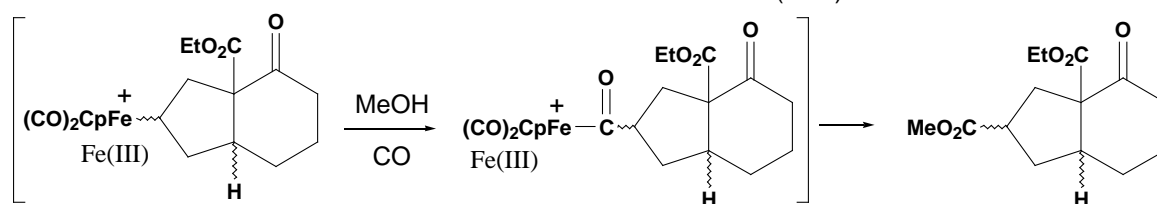
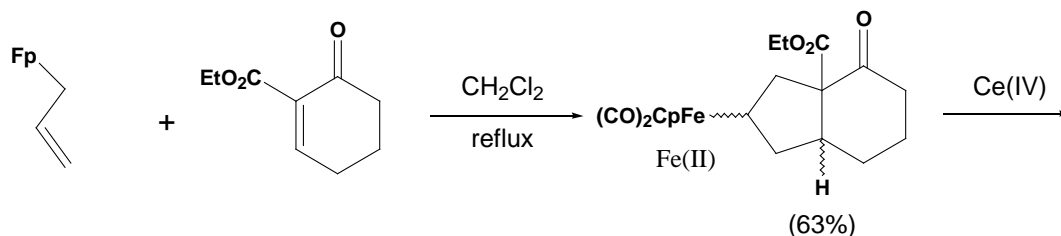
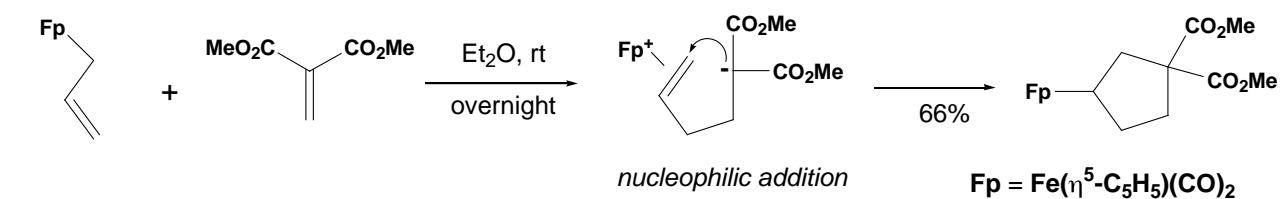
[III] Dimethylenmethane Synthons



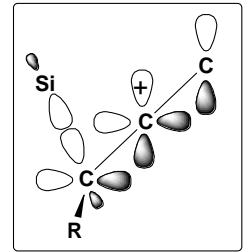
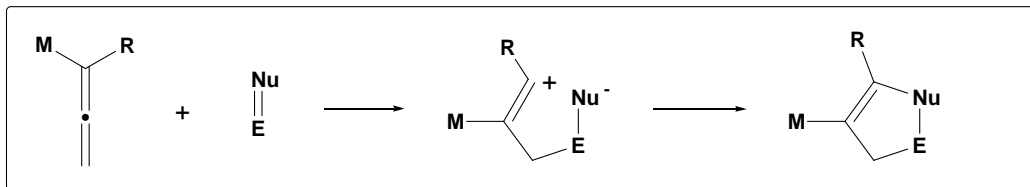
A. Allylic precursors



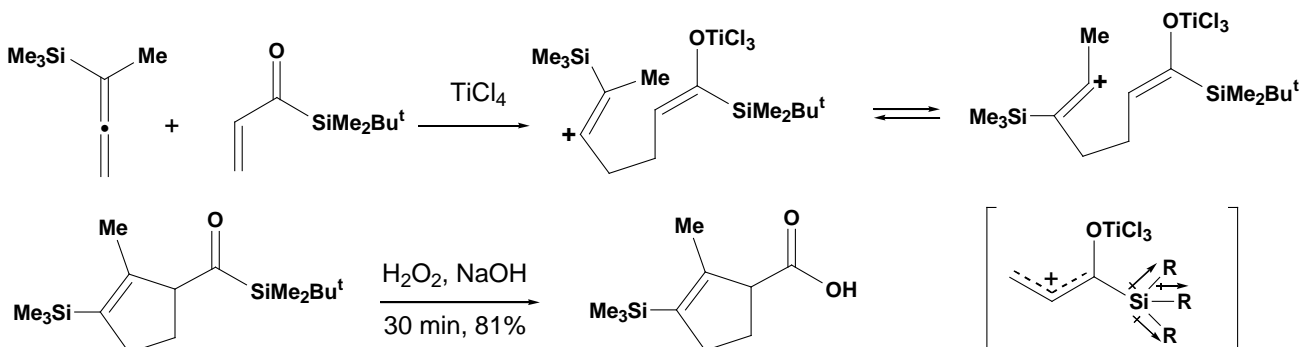
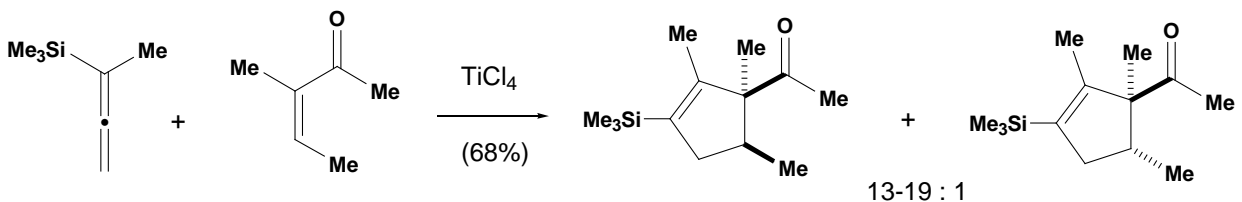
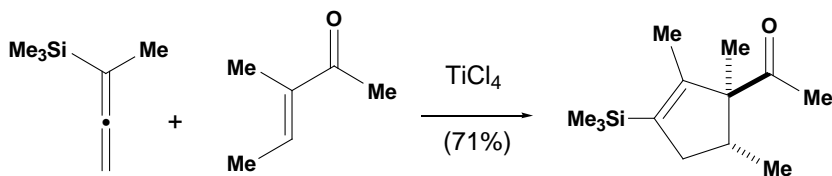
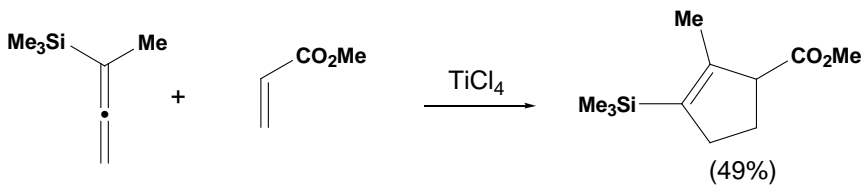
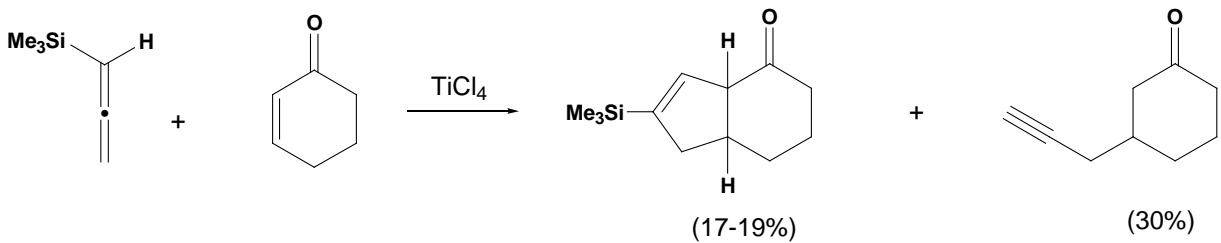
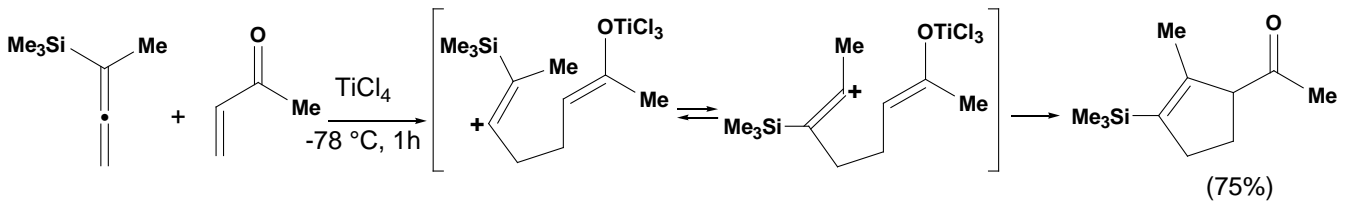
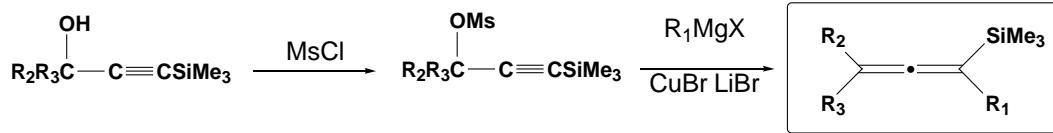
Rosenblum⁷⁾



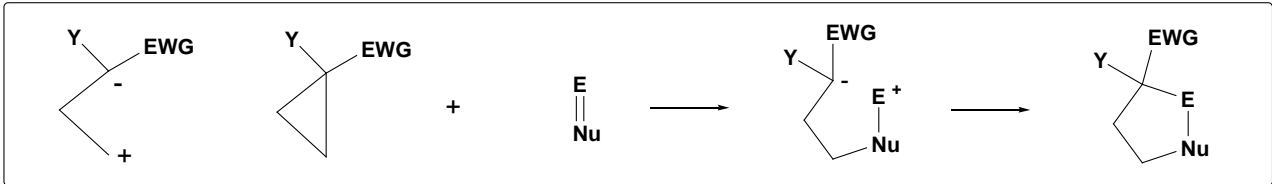
B. Allenylic precursor



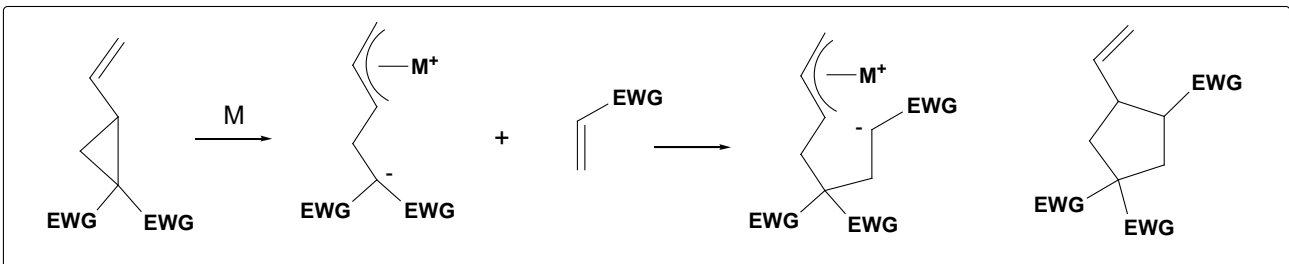
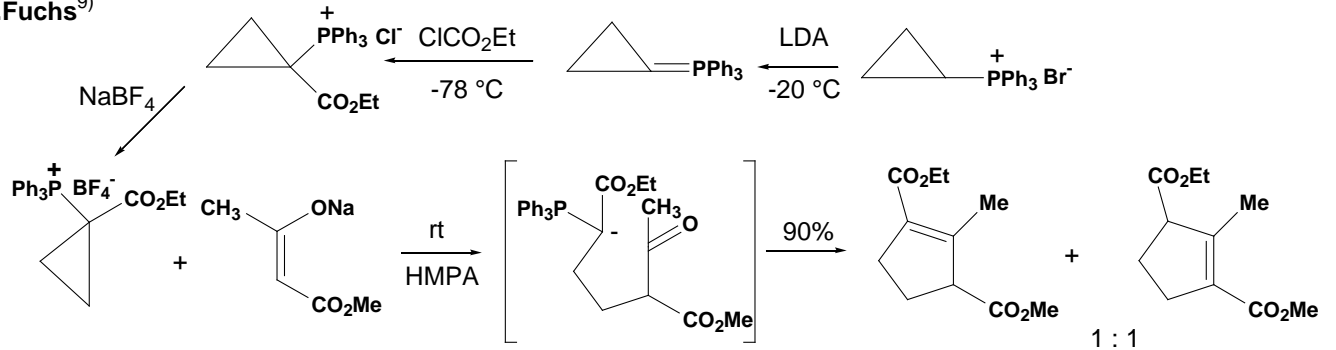
R.L. Danheiser⁸⁾



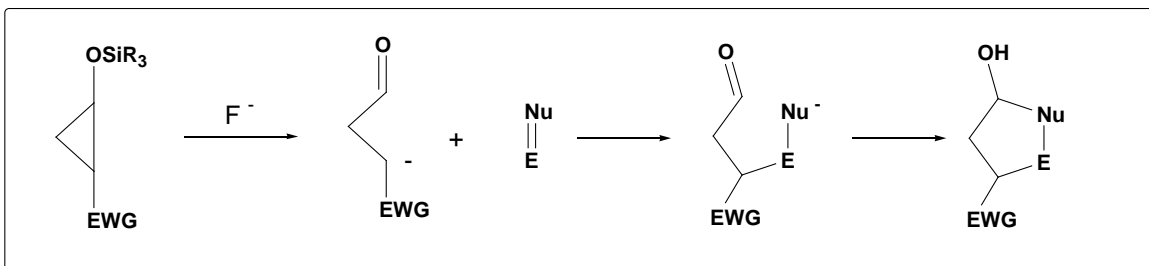
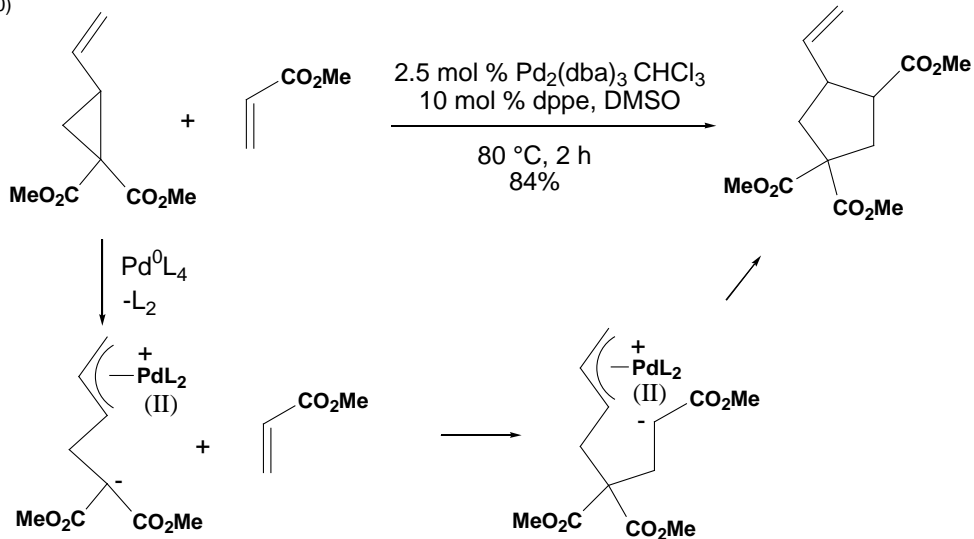
C. Cyclopropyl precursor



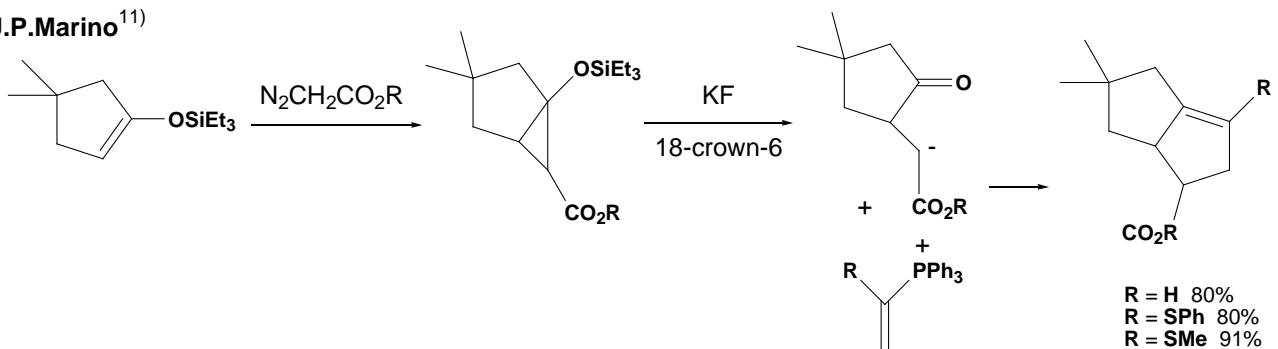
P.L.Fuchs⁹⁾



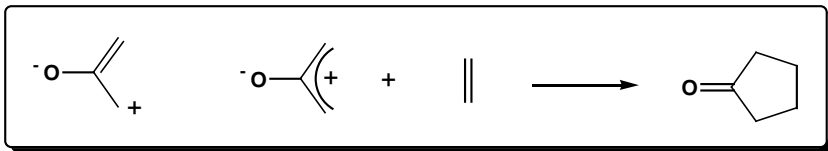
J.Tsuji¹⁰⁾



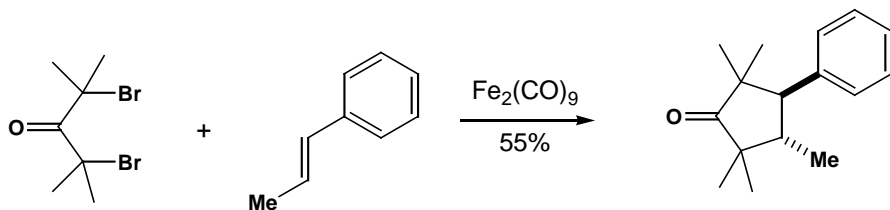
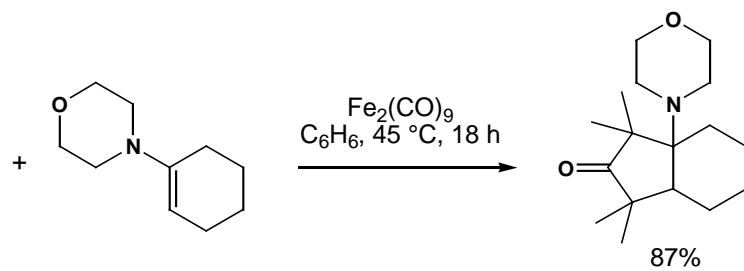
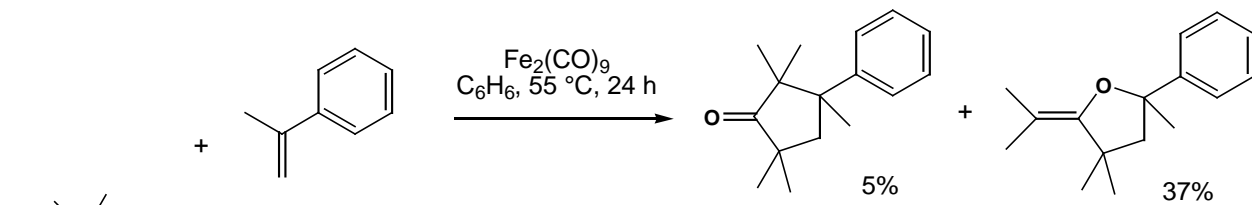
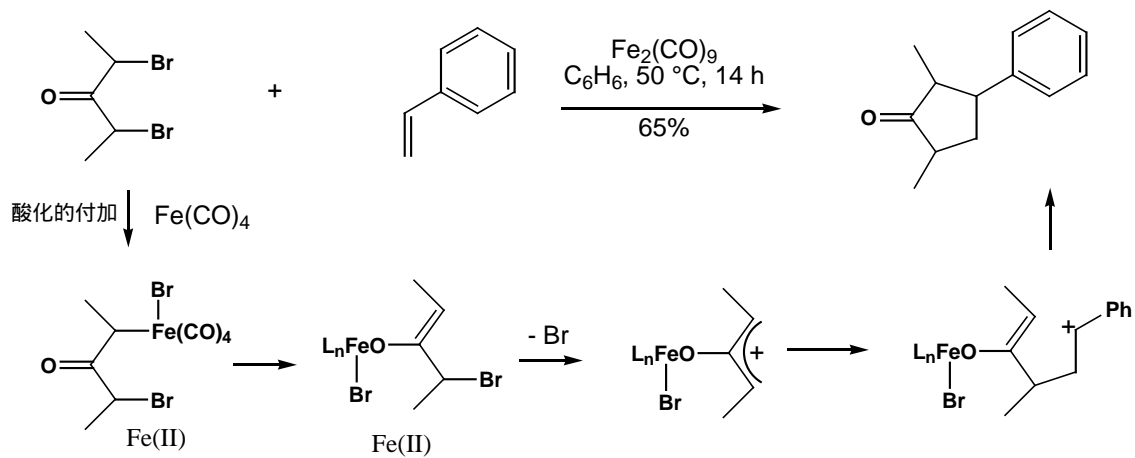
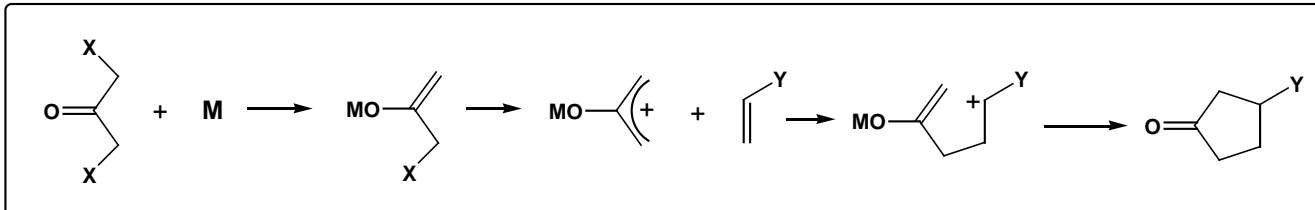
J.P.Marino¹¹⁾



[IV] 2-Oxyallyl Synthons



R. Noyori¹²⁾

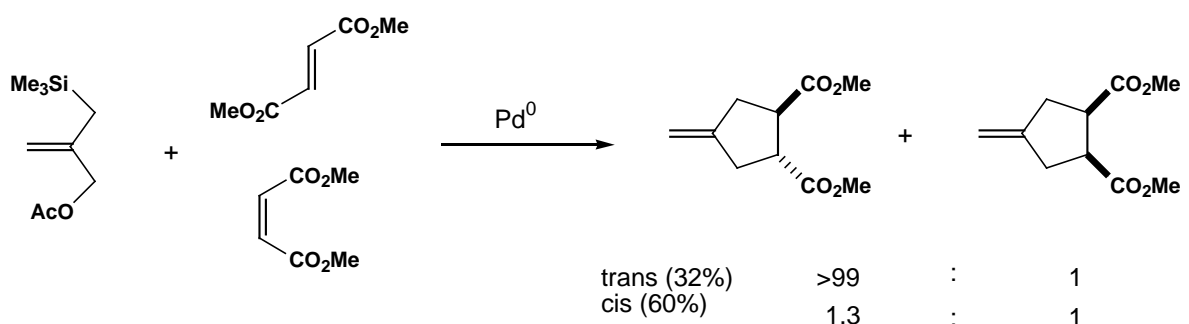
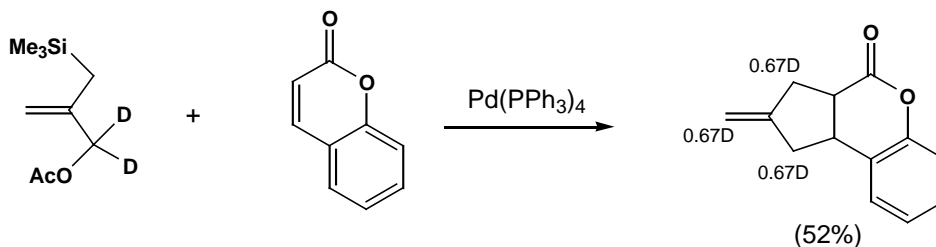
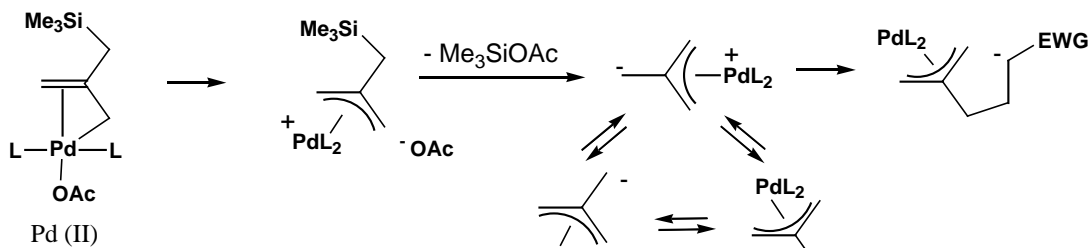
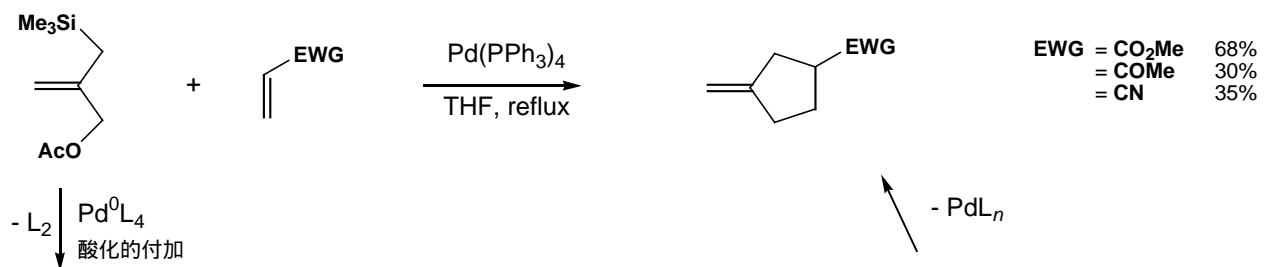
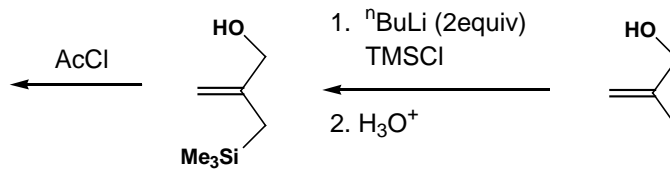
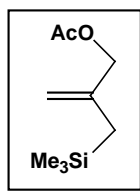
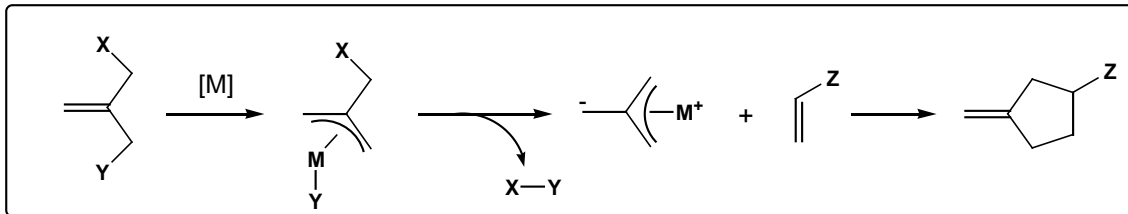


[V] Trimethylenemethane Synthons

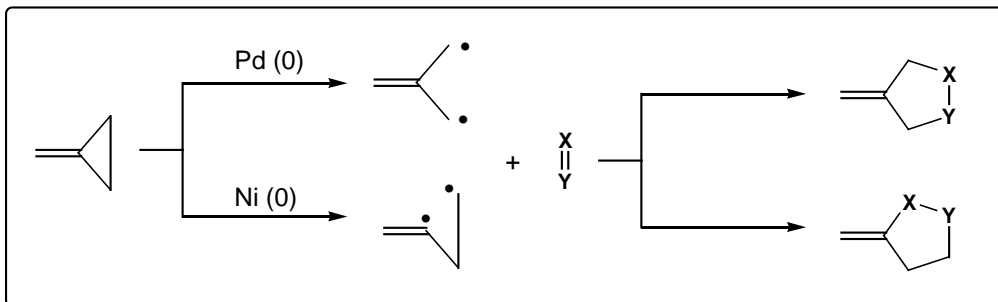


A. Bifunctional Conjunctive Reagents

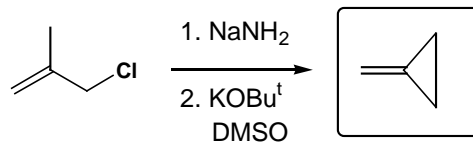
B.M. Trost¹³⁾



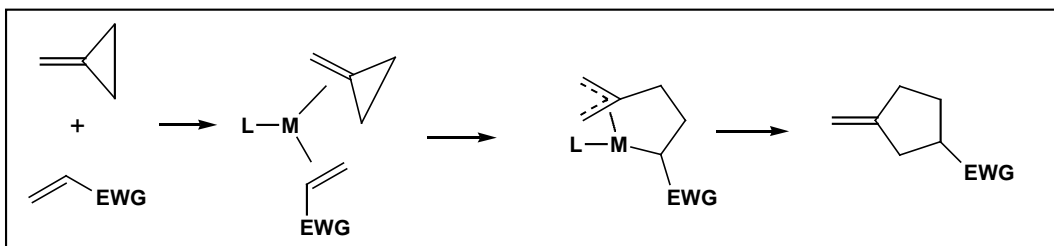
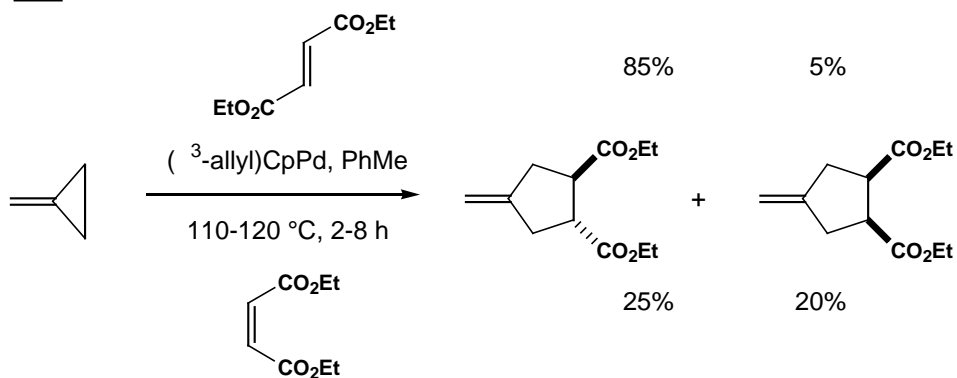
B. Methyleneecyclopropane



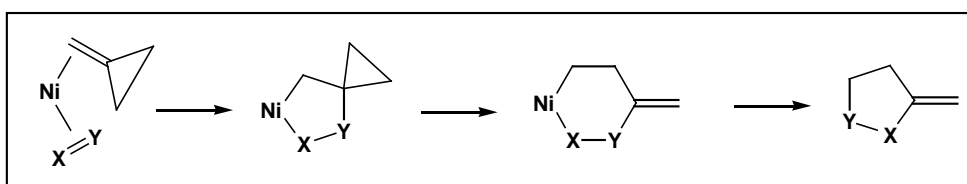
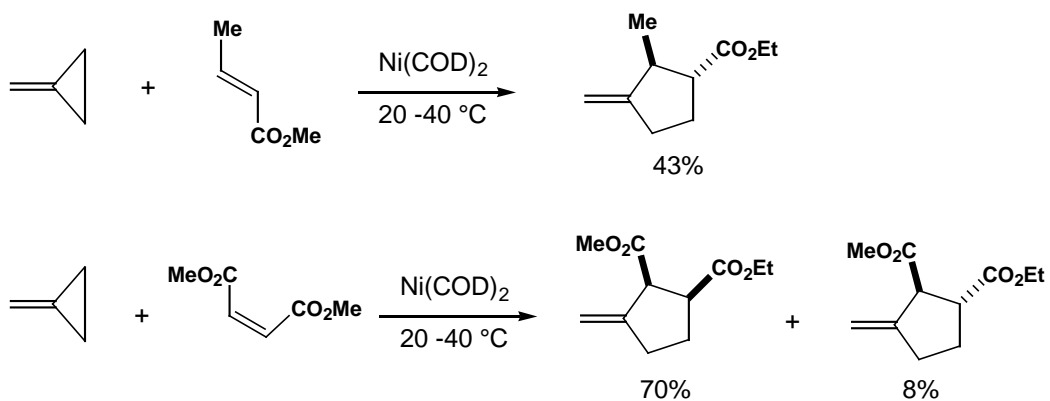
P. Binger¹⁴⁾



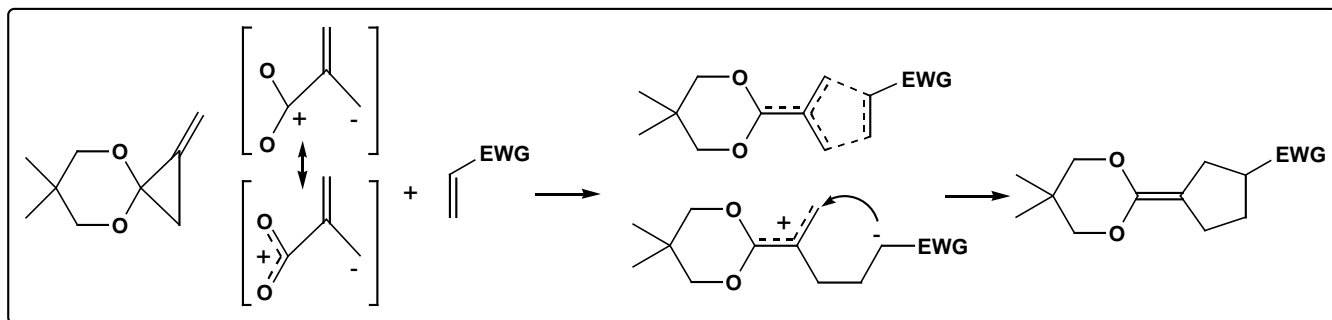
Pd



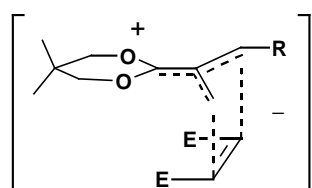
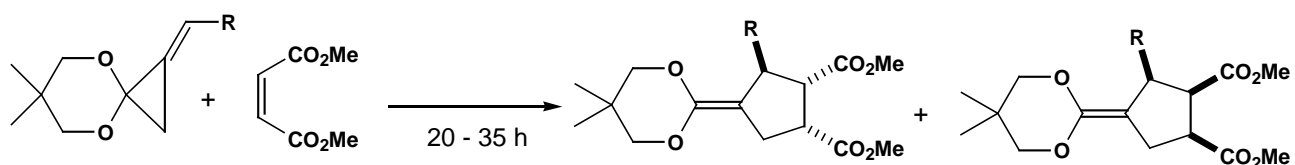
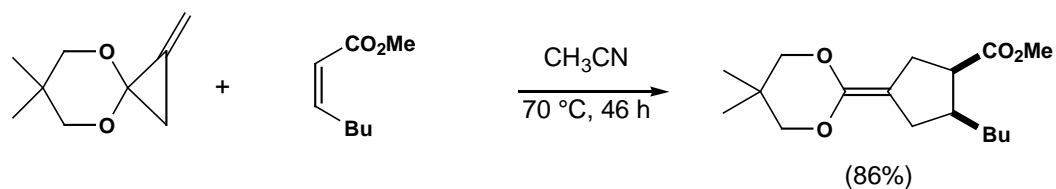
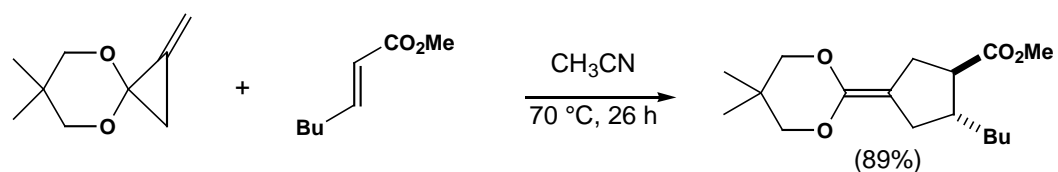
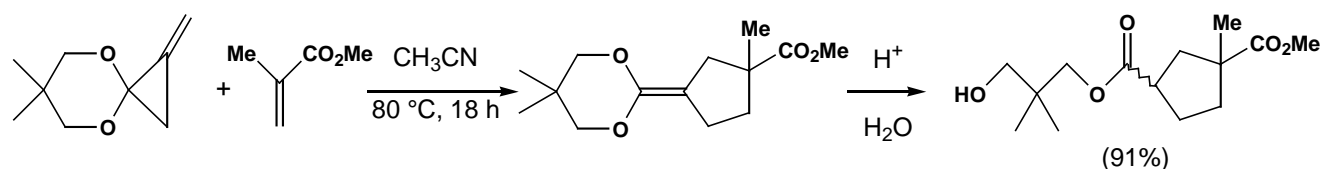
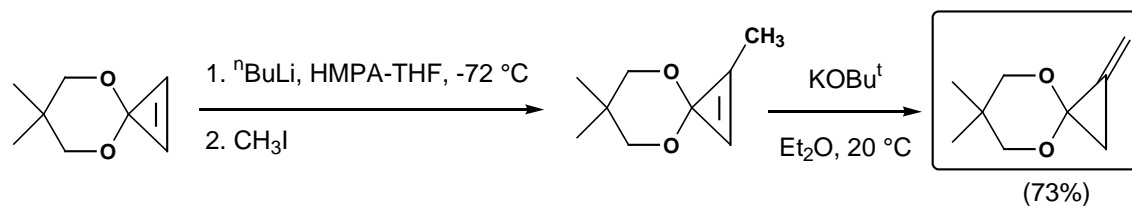
Ni



C. Methyleneecyclopropanone

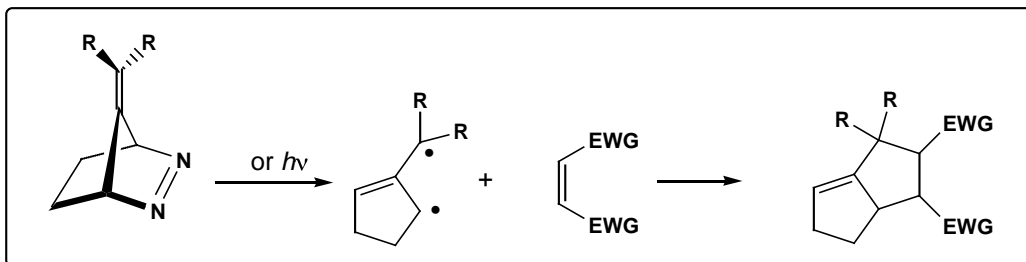


Eiichi Nakamura¹⁵⁾

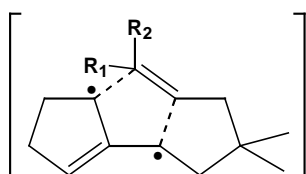
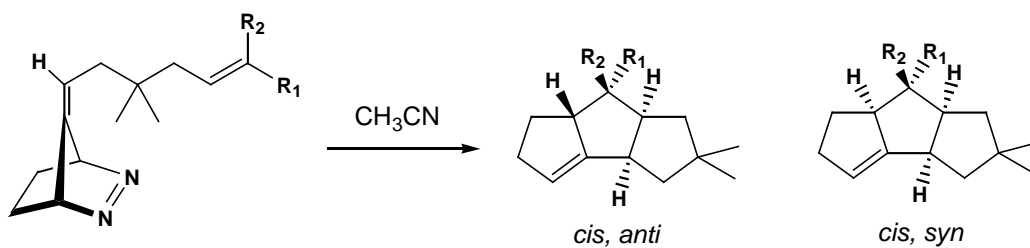
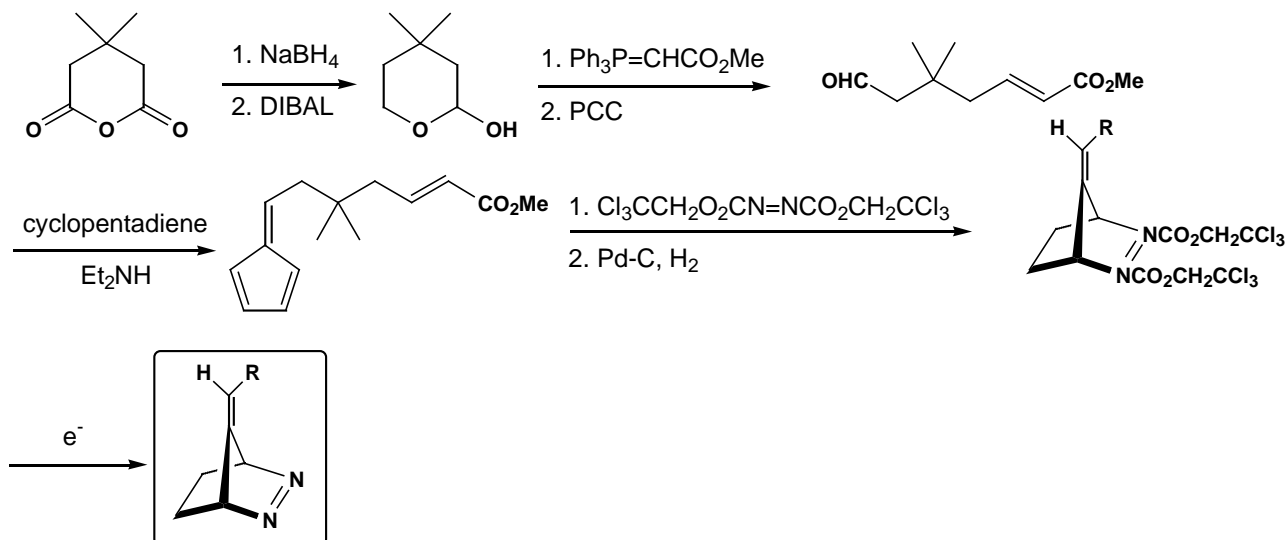


97	:	3	86%	toluene (2.6)
80	:	20	72%	DMF (36.7)
73	:	27	73%	DMSO-d6 (46.6)

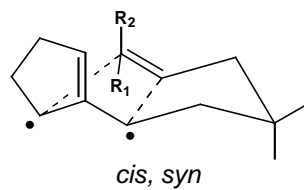
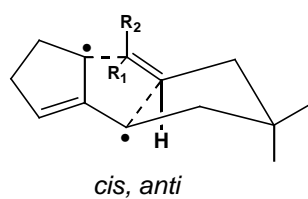
D. 1,3-Diyl Trapping



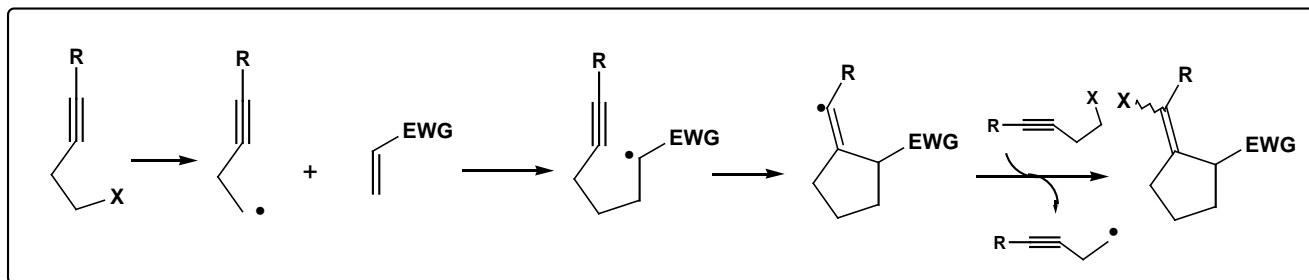
R.D. Little¹⁶⁾



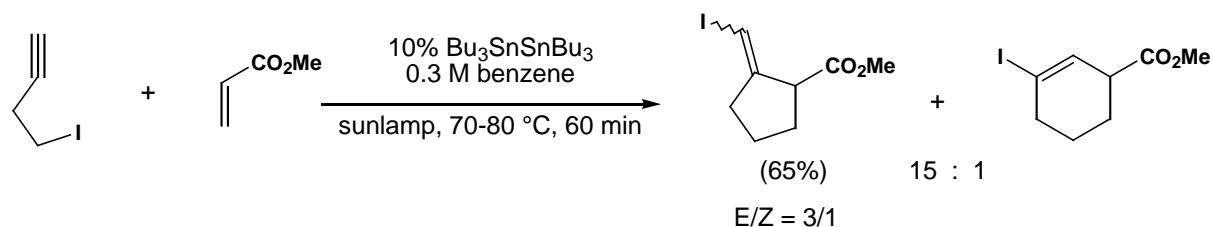
R_1	R_2	<i>cis, anti</i> : <i>cis, syn</i>	yield
CO_2Me	H	87 : 13	>85%
H	CO_2Me	75 : 25	87%



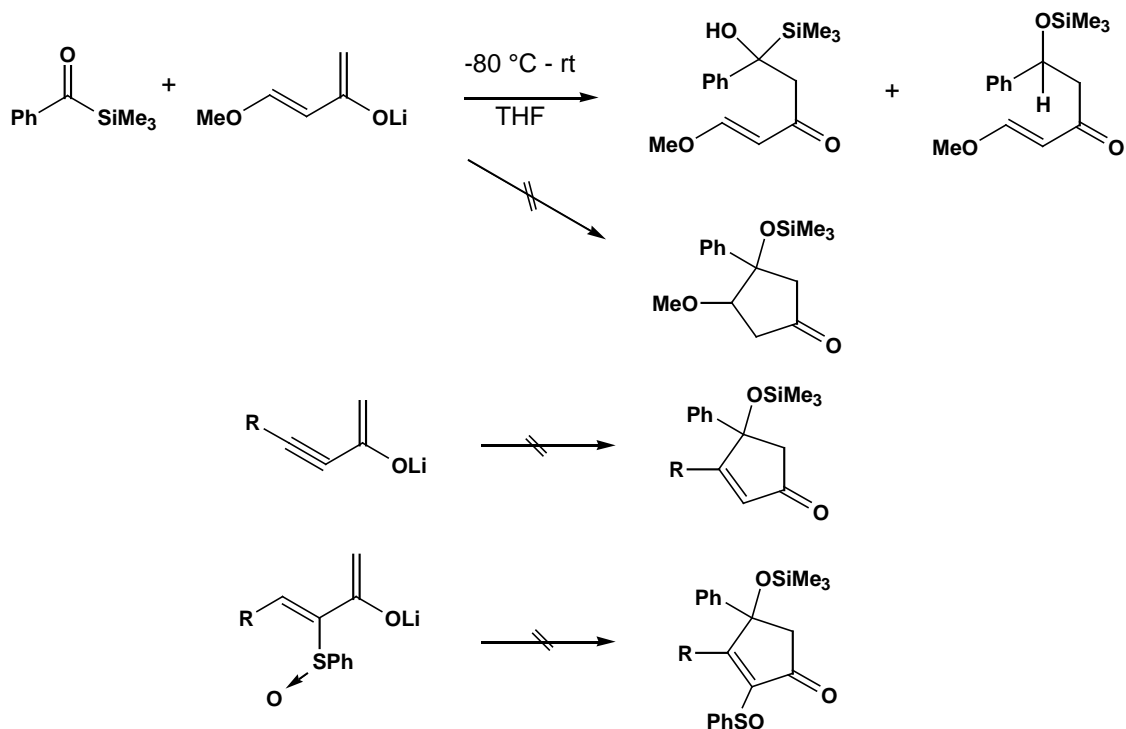
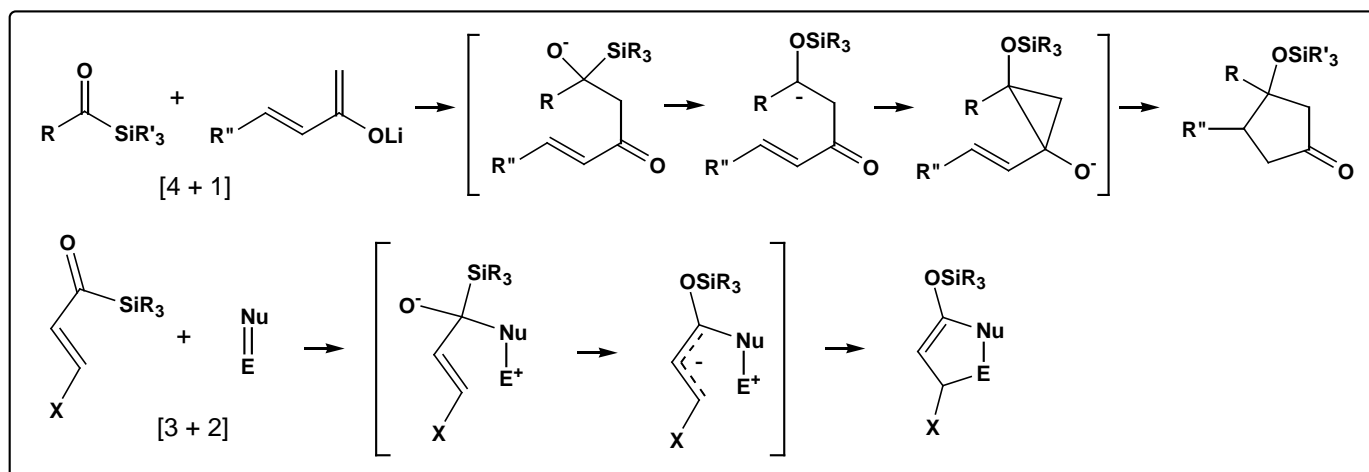
[VI] Atom Transfer Cycloadditions



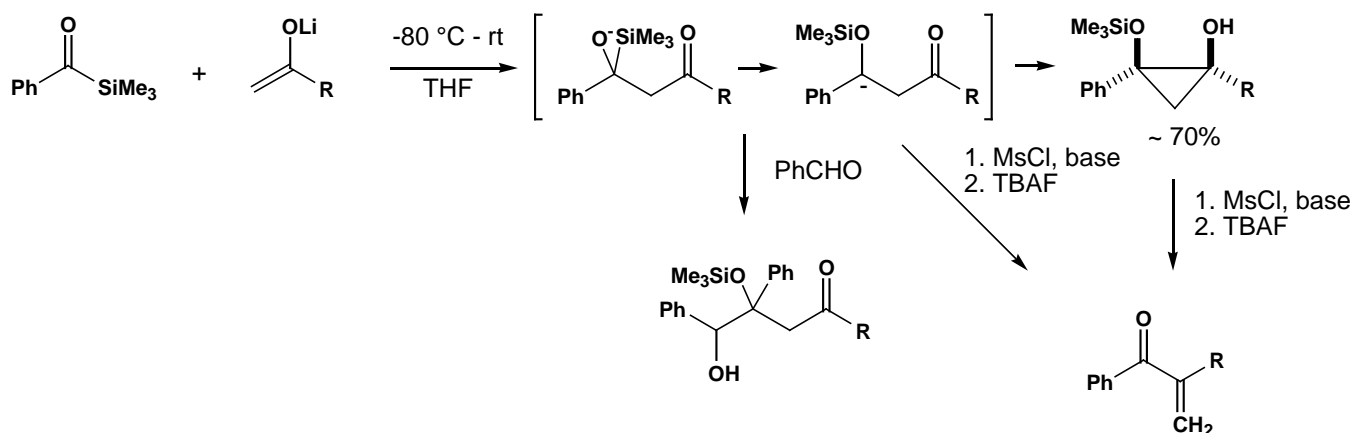
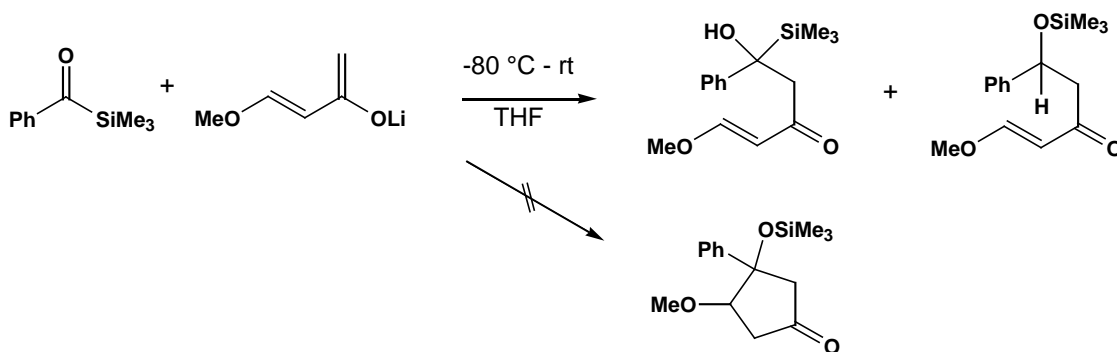
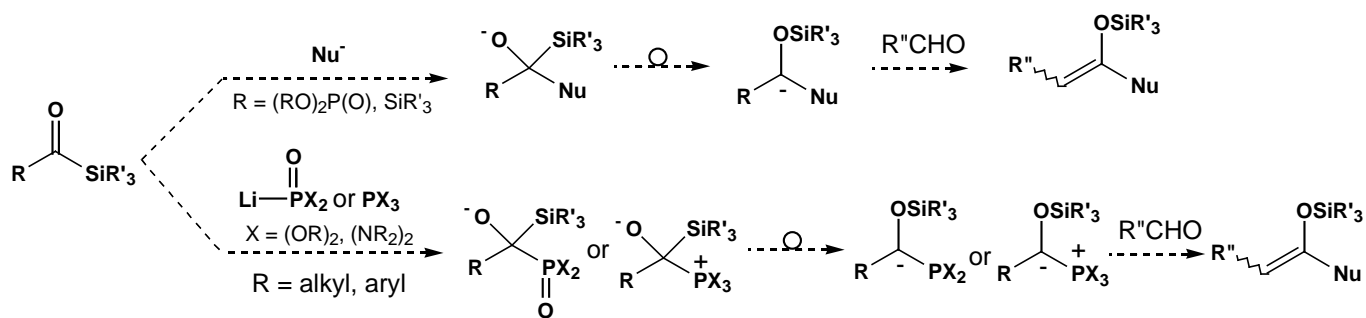
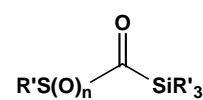
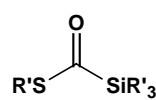
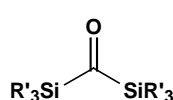
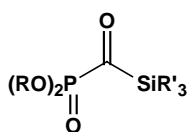
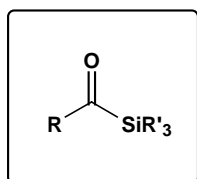
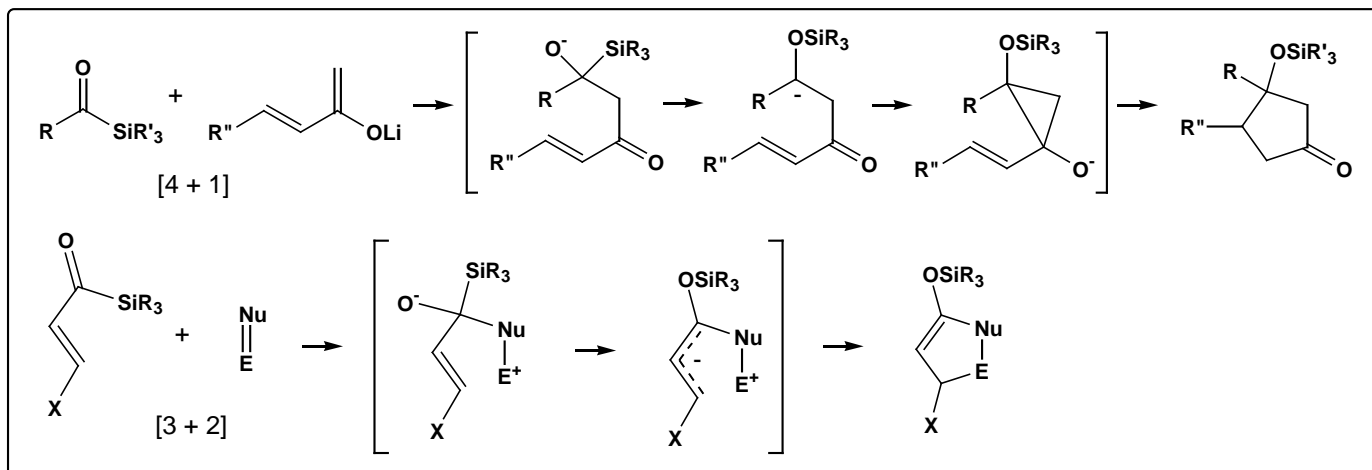
D.P. Curran¹⁷⁾

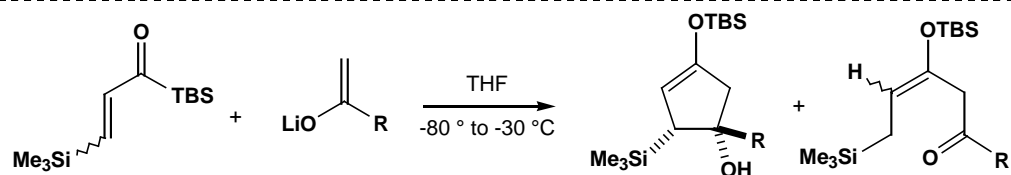
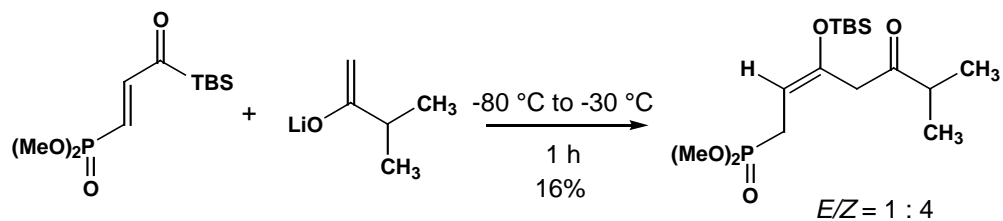
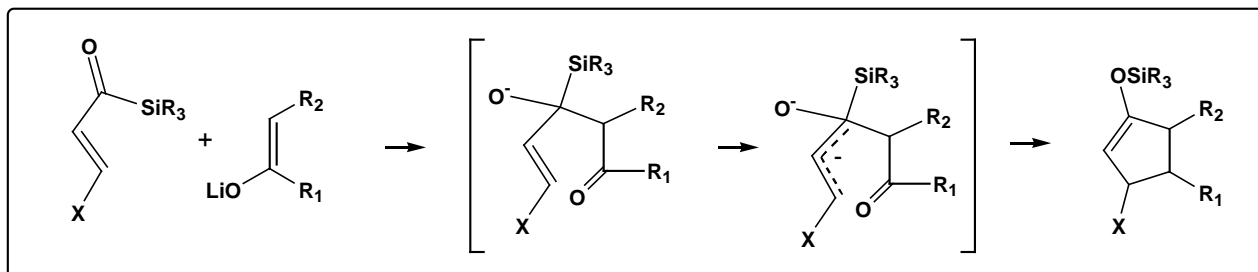


[VII] Brook Rearrangement Mediated Cycloadditions¹⁸⁾

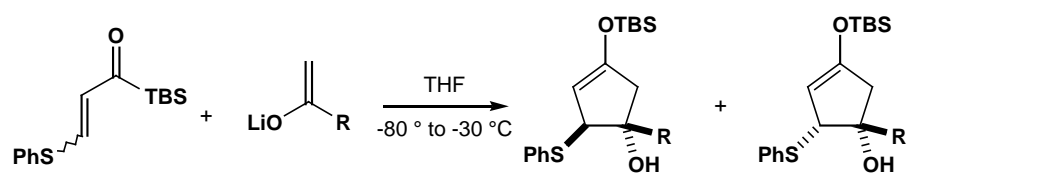


[VII] Brook Rearrangement Mediated Cycloadditions



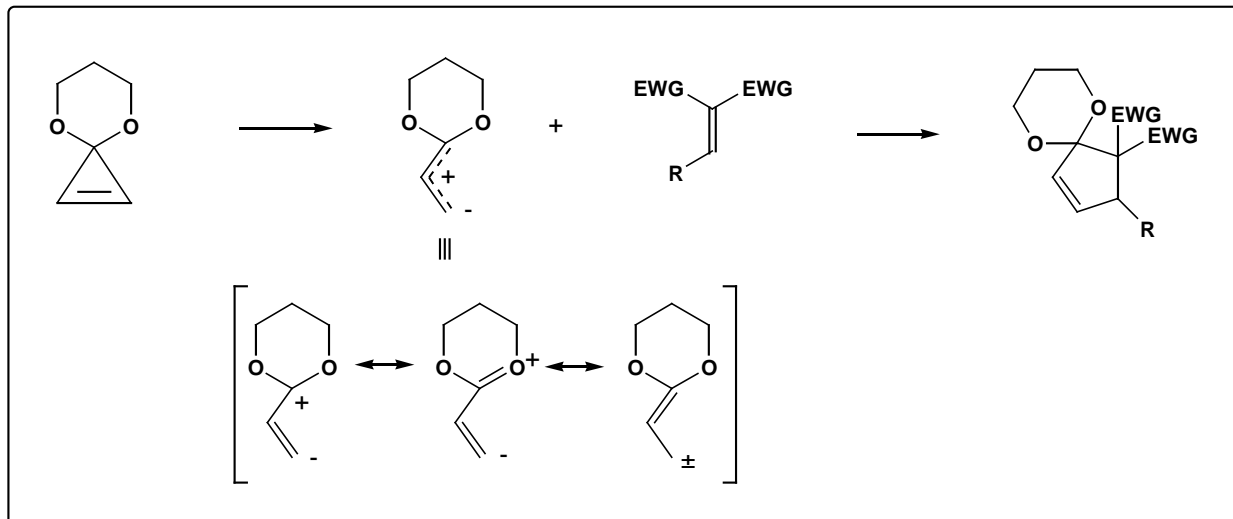


R		yield (%)	yield (%)	E : Z
<i>E</i>	Et	17	43	1 : 1
<i>Z</i>	Et	44	22	1 : 0
<i>E</i>	ⁿ Pr	11	57	3.6 : 1
<i>Z</i>	ⁿ Pr	41	17	6 : 1
<i>E</i>	ⁱ Pr	14	63	1.2 : 1
<i>Z</i>	ⁱ Pr	51	21	1 : 1.4

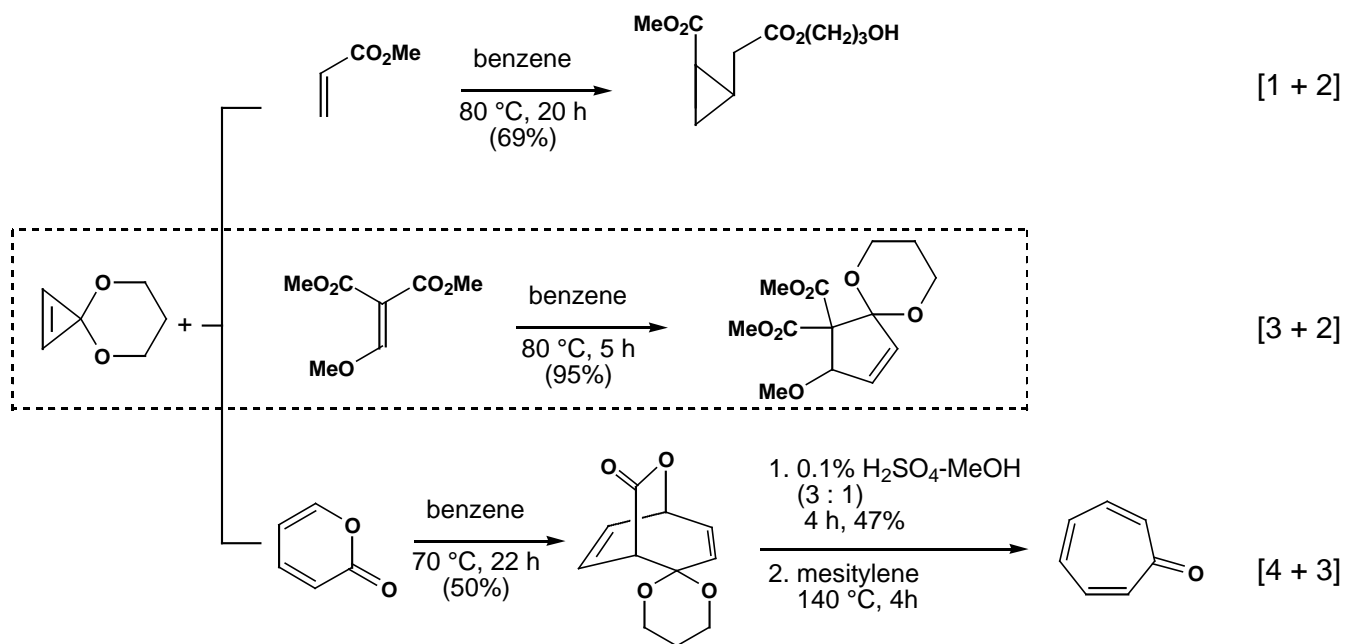
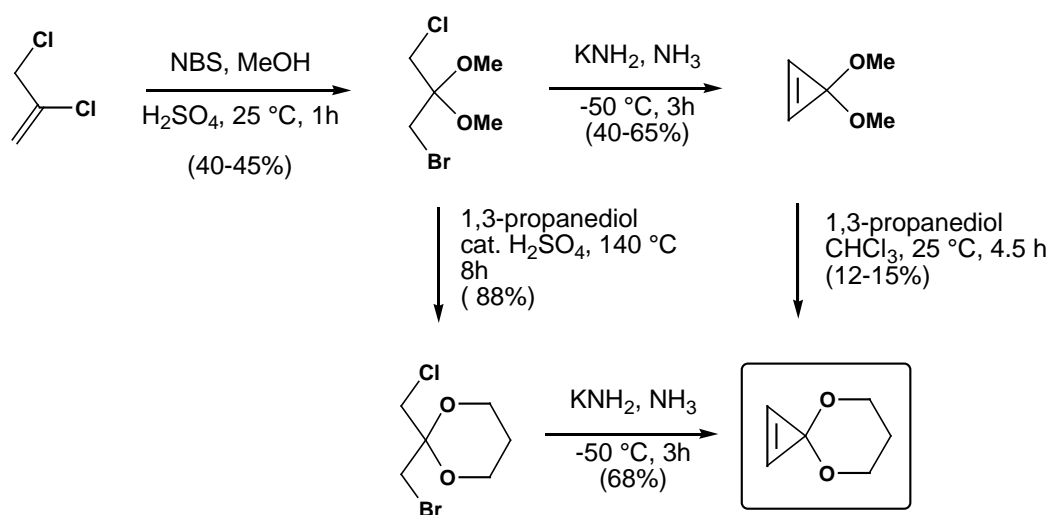


R		yield (%)	yield (%)
<i>E</i>	Et	68	5
<i>Z</i>	Et	62	3
<i>E</i>	ⁿ Pr	52	3
<i>Z</i>	ⁿ Pr	61	8
<i>E</i>	ⁱ Pr	54	12
<i>Z</i>	ⁱ Pr	48	12

[VIII] Vinylcarbene

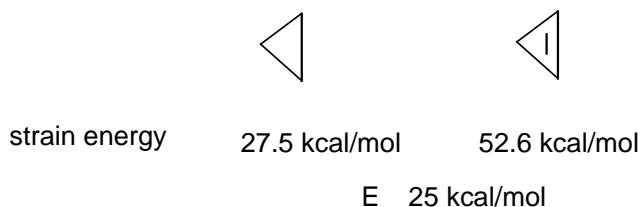
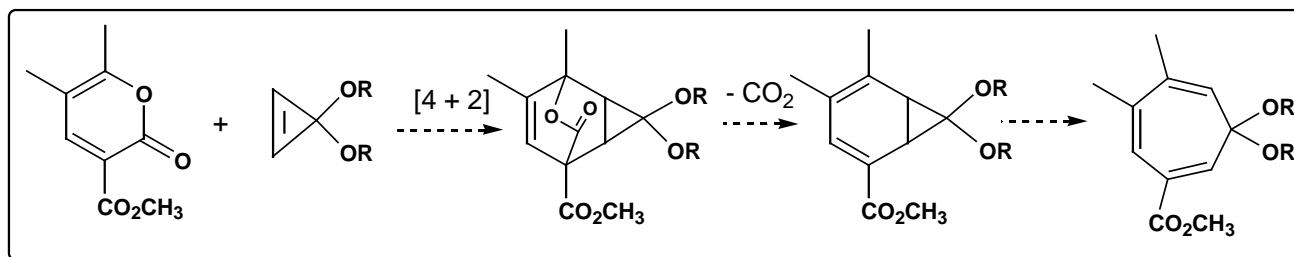


D.L. Boger¹⁹⁾

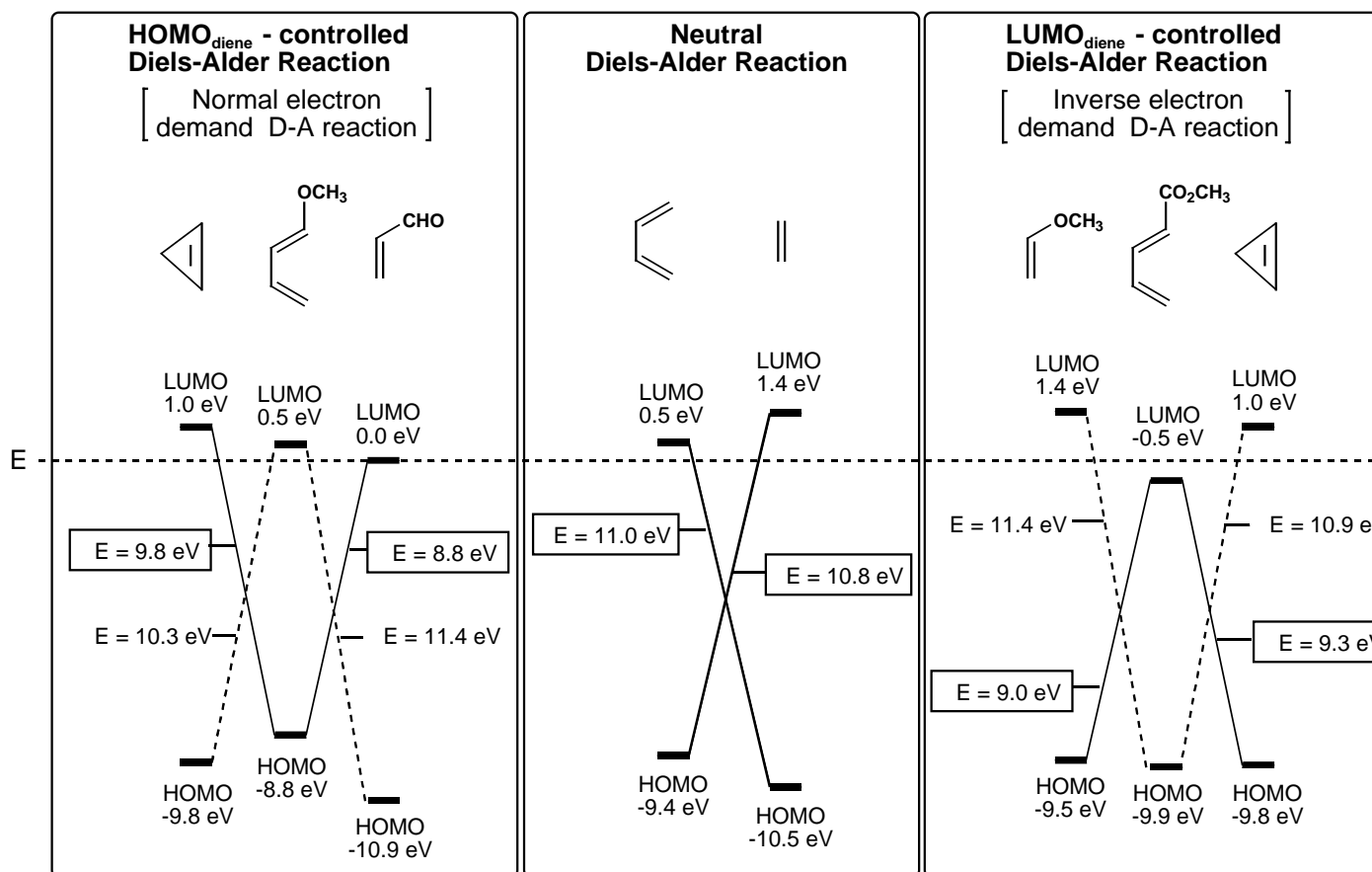


Boger らの当初の研究目的

cyclopropanone ketal のDiels-Alder 反応 (Inverse electron demand) を用いて cycloheptatriene 骨格を構築す



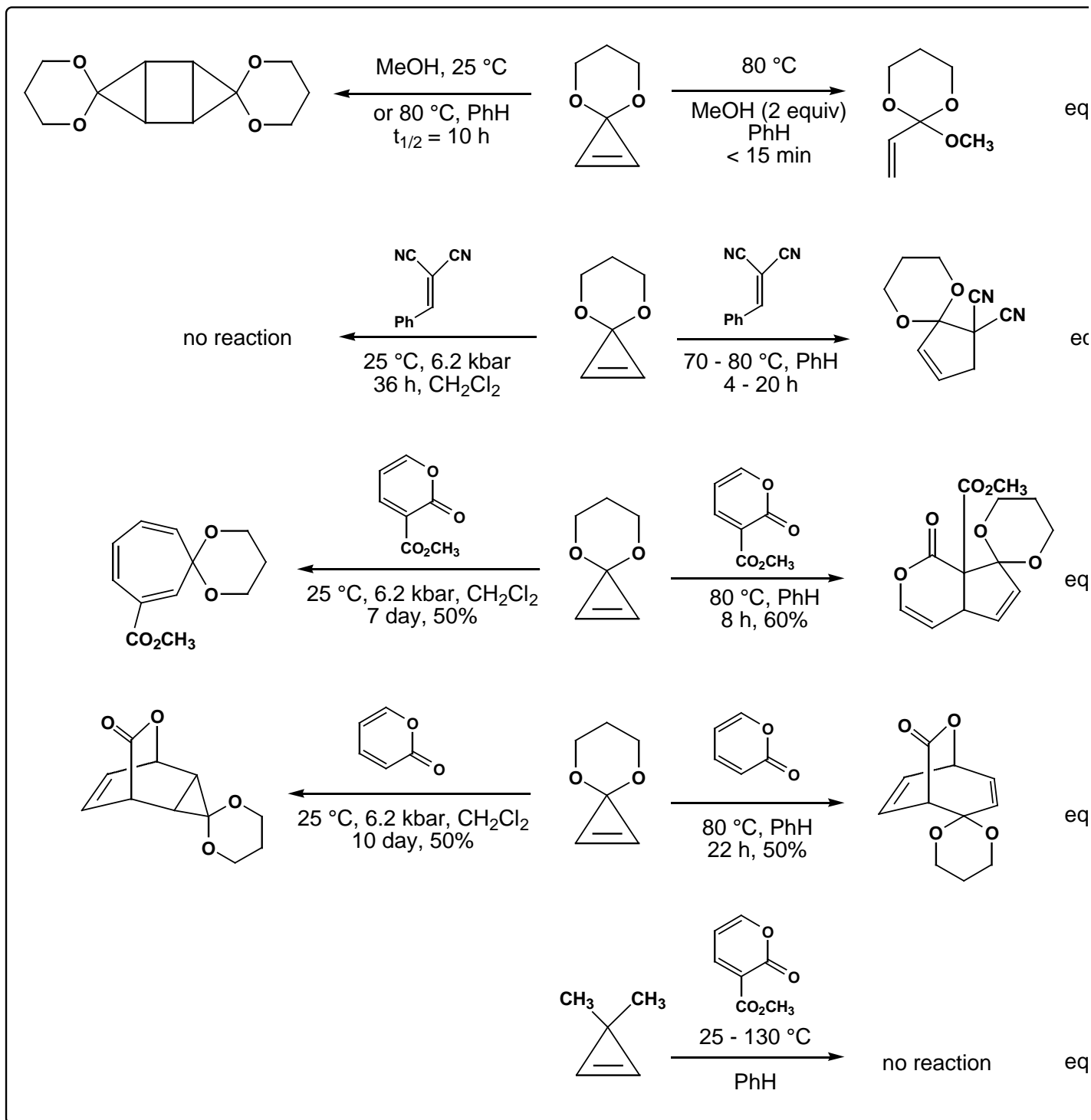
Dual participation of cyclopropene in normal and inverse electron demand Diels-Alder reactions, AM1 results



strained ring (e.g. cyclopropenone) に二重結合を導入すると, ethylene に較べて E_{LUMO} が下がり, E_{HOMO} が上がる.

Reaction Mechanism

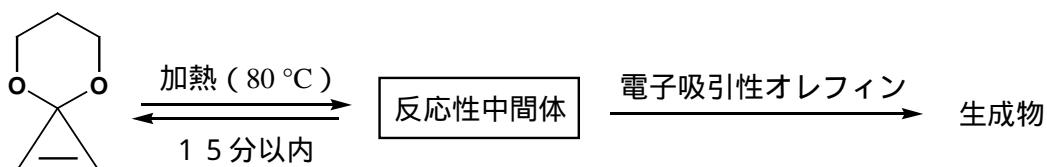
Establishment of a Reactive Intermediate in the [1 + 2], [3 + 2], and [3 + 4] cycloaddition reactions



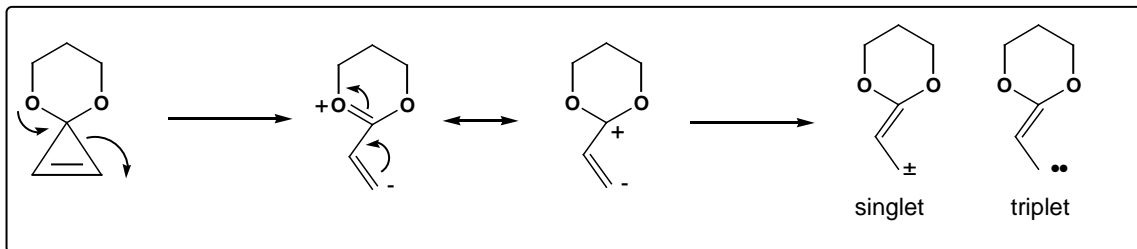
1. 反応性中間体の存在 .

2. 反応性中間体が生成するためには加熱 (~ 80 °C) が必要 .

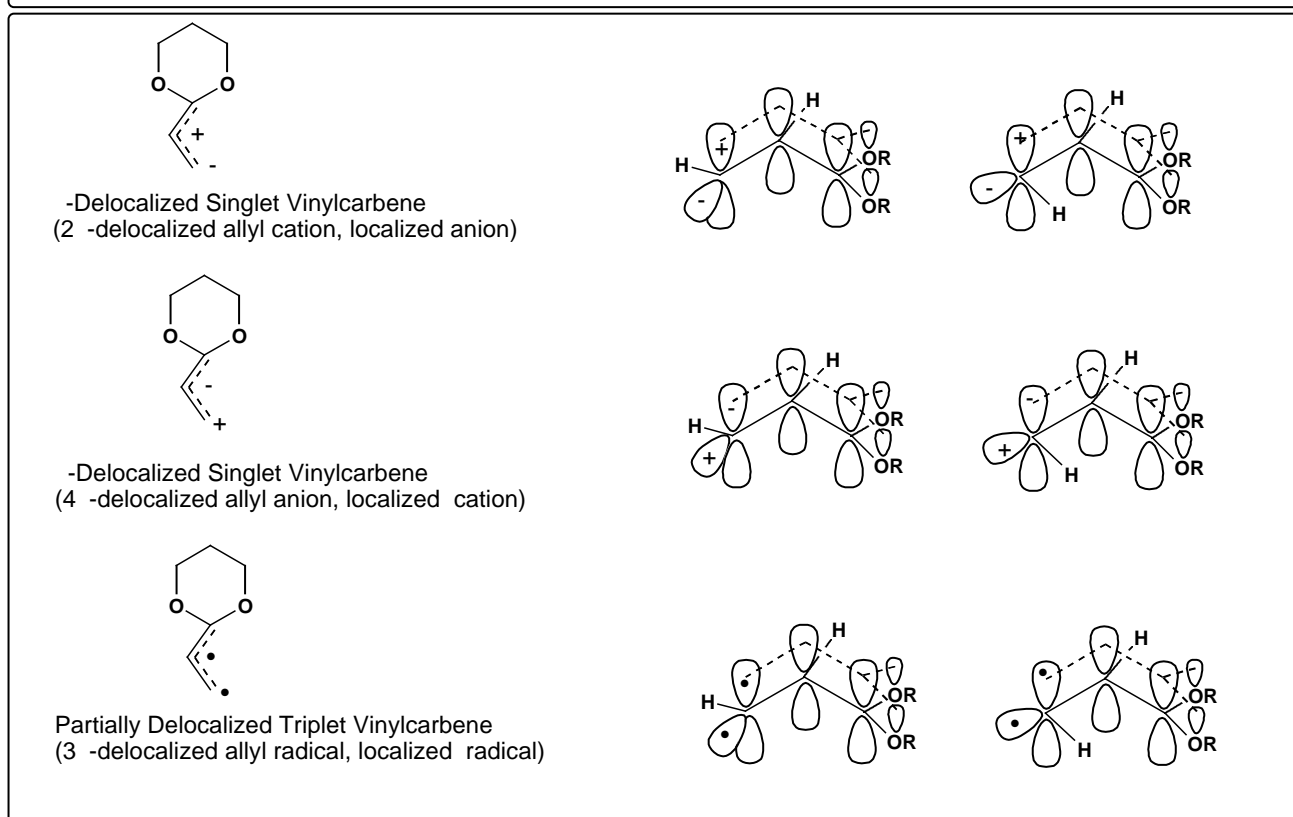
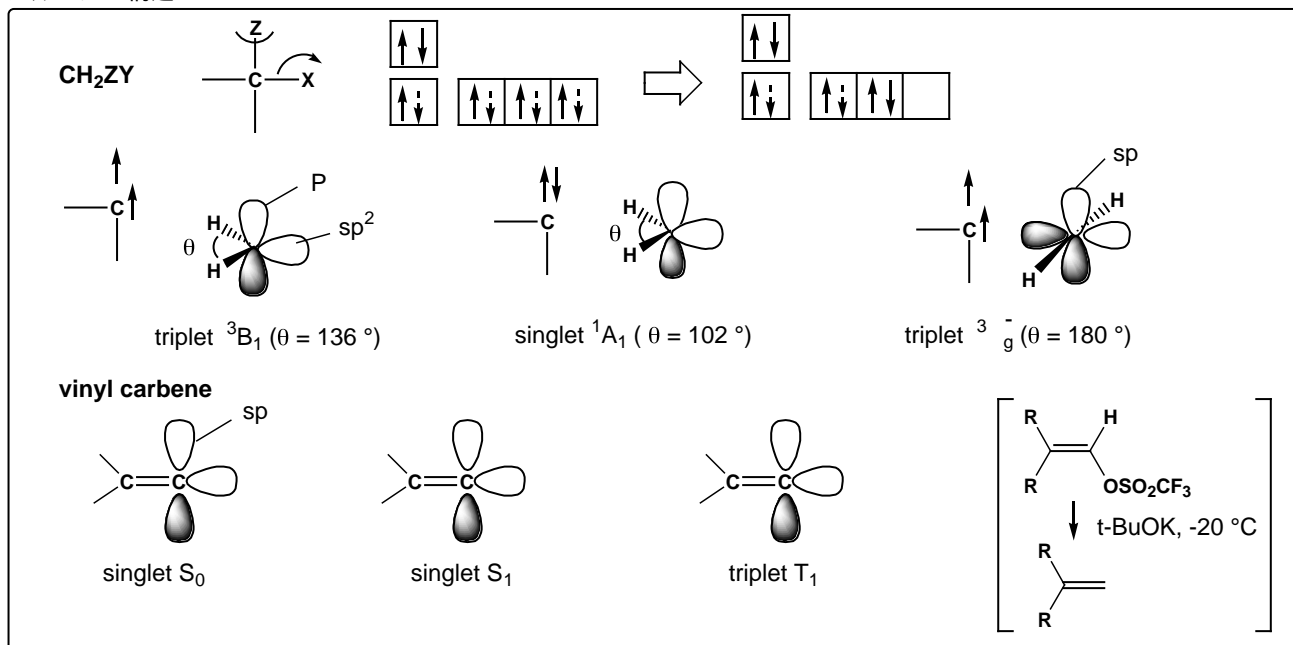
3. 反応性中間体の生成は可逆的で非常に速く (15 分以内) , 電子吸引性オレフィンとの反応が律速段階



反応性中間体の構造



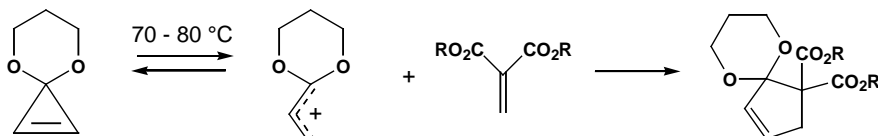
カルベンの構造



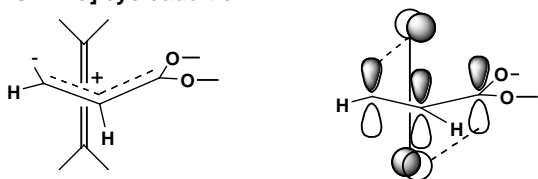
Reactive Intermediate が -Delocalized Singlet Vinylcarbene であるとする根拠

1. 電子吸引性オレフィンやジエンとのみ求核的カルベンとしての性質を示す (singlet carbene に特長的) .
2. singlet carbene に特有な酸性の O-H, C-H 結合への挿入反応がおきる .
3. 1,1-dimethoxyethylene, dihydropyran のような triplet carbene の捕捉剤とは反応しない .
4. free radical 捕捉剤や free radical 開始剤の影響を受けない .
5. 求電子性の基質との反応は cycloaddition だけで, 他の転位や付加脱離反応は受けない .
6. 溶媒の違いによる反応速度の変化は少ない .

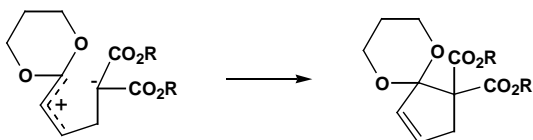
π -Delocalized singlet carbene を含む四種の可能性のあるメカニズム



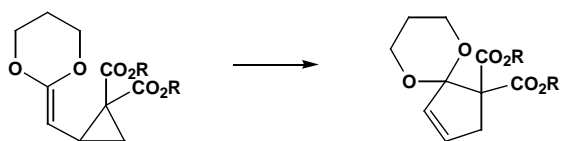
1. direct $[\pi 2s + \pi 2a]$ cycloaddition



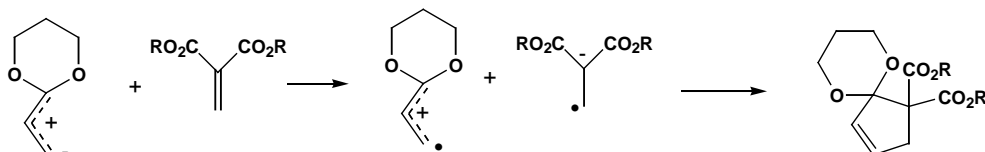
2. stepwise addition-cyclization



3. $[\omega 2s + \pi 2s]$ cycloaddition + vinylcyclopropane rearrangement



4. single-electron transfer + radical anion/radical cation combination



1. 溶媒の極性の違いにより大きな反応速度の変化は観察されない。

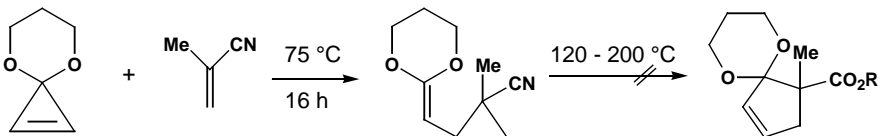
relative rate : DMF (2) > CH₃CN (1.4) > C₆H₆ (1) > C₅H₅N (0.9) > C₆H₅NO₂ (0.7)

zwitterion 中間体を経由する step-wise 機構 (2) は否定

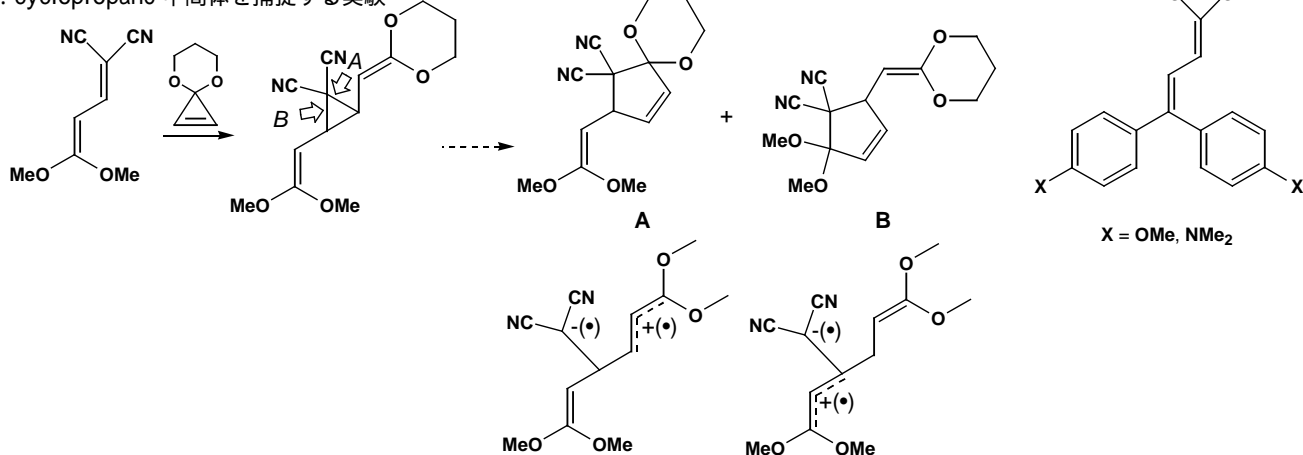
2. cyclopropane 中間体を経由する機構 (3) は次の実験事実から否定される。

cyclopropane 中間体を単離あるいは検出することはできなかった。

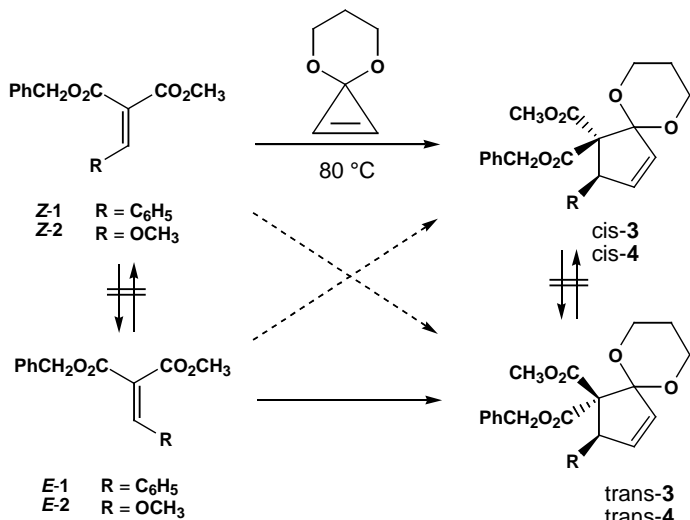
一つの電子吸引基しか持たないオレフィンとの反応により生成した三員環を、五員環が生成する温度 (70 - 80 °C) 以上に加熱 (120 - 200 °C) しても、五員環への転位は起きなかった。



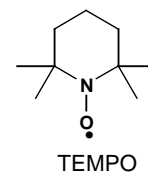
3. cyclopropane 中間体を捕捉する実験



X = OMe, NMe₂ とともに A タイプの成績体を与えたことから、cyclopropane 中間体の存在は除外される。



olefin	solvent	conditions	yield (%)	cis : tr
Z-1	PhH	20 h	66	64 : 36
Z-1	MeCN	20 h	60	90 : 10
E-1	PhH	20 h	71	27 : 73
E-1	MeCN	20 h	58	11 : 89
Z-2	PhH	24 h	76	79 : 21
Z-2	MeCN	24 h	63	81 : 19
E-2	PhH	20 h	67	29 : 71
E-2	PhH	16 h, 100 mol% TEMPO	64	25 : 75
E-2	PhH	16 h, 400 mol% TEMPO	52	29 : 71
E-2	PhH	16 h, 100 mol% C ₆ H ₄ (NO ₂) ₂	66	30 : 70
E-2	PhH	16 h, 400 mol% C ₆ H ₄ (NO ₂) ₂	65	25 : 75

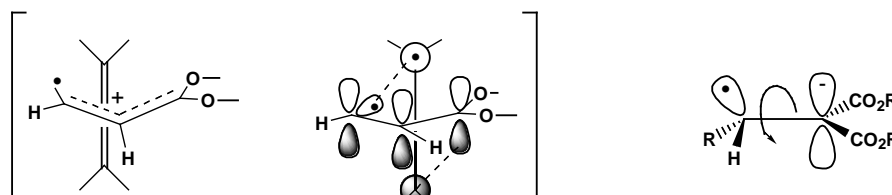
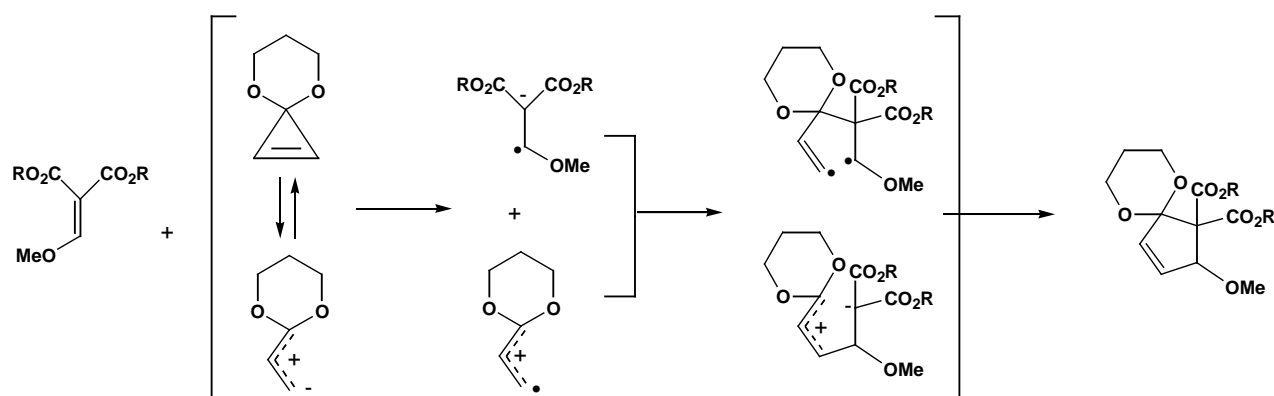
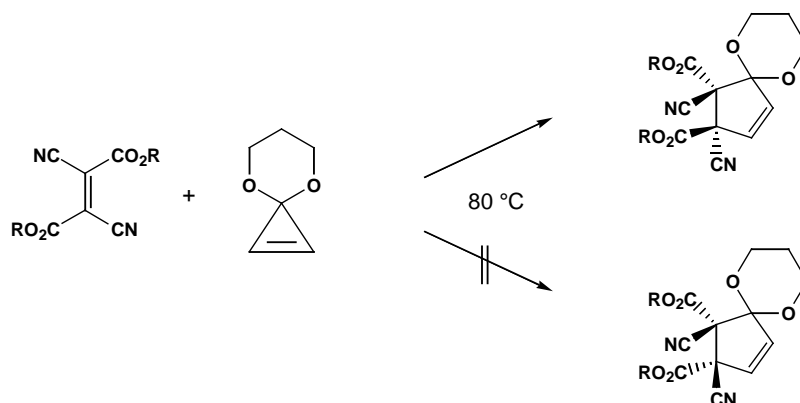


オレフィンの geometry は完全には保持されず，この傾向は極性の低い溶媒で大きい (PhH > MeCN) .
 TEMPO (ラジカル捕捉剤) により阻害されない .

このことから，

- 1) stepwise, biradical addition-cyclization , 2) zwitterion 中間体あるいは radical cation-radical anion combination
- 3) concerted [2s + 2a] は除外される .

しかし，Huisgen らが 1,3-dipolar cycloaddition が two-step addition-cyclization である事を証明するのに用いた次の例では完全に geometry が保持された .

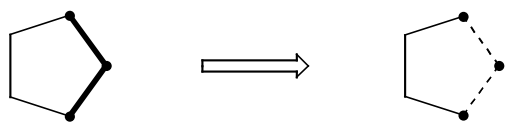


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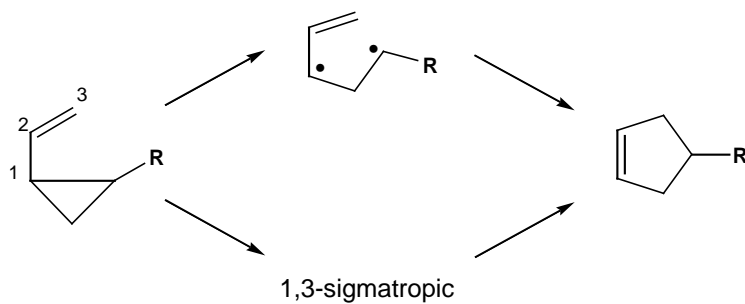
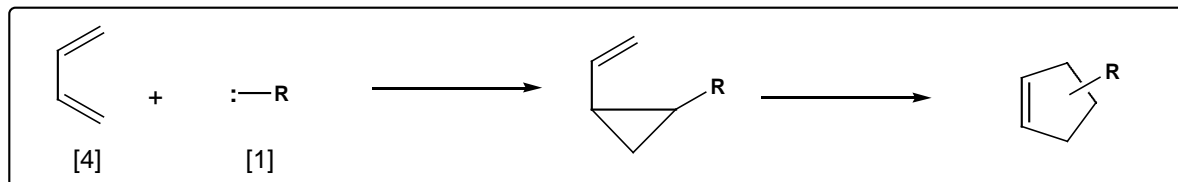
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(p) Trost, B.M., Chan, D.M.T. *J. Am. Chem. Soc.* **1982**, 104, 3733.
(q) Trost, B.M. *Angew. Chem. Int. Ed. Engl.* **1986**, 25, 1.
(r) Trost, B.M. *Pure Appl. Chem.* **1988**, 60, 1615.
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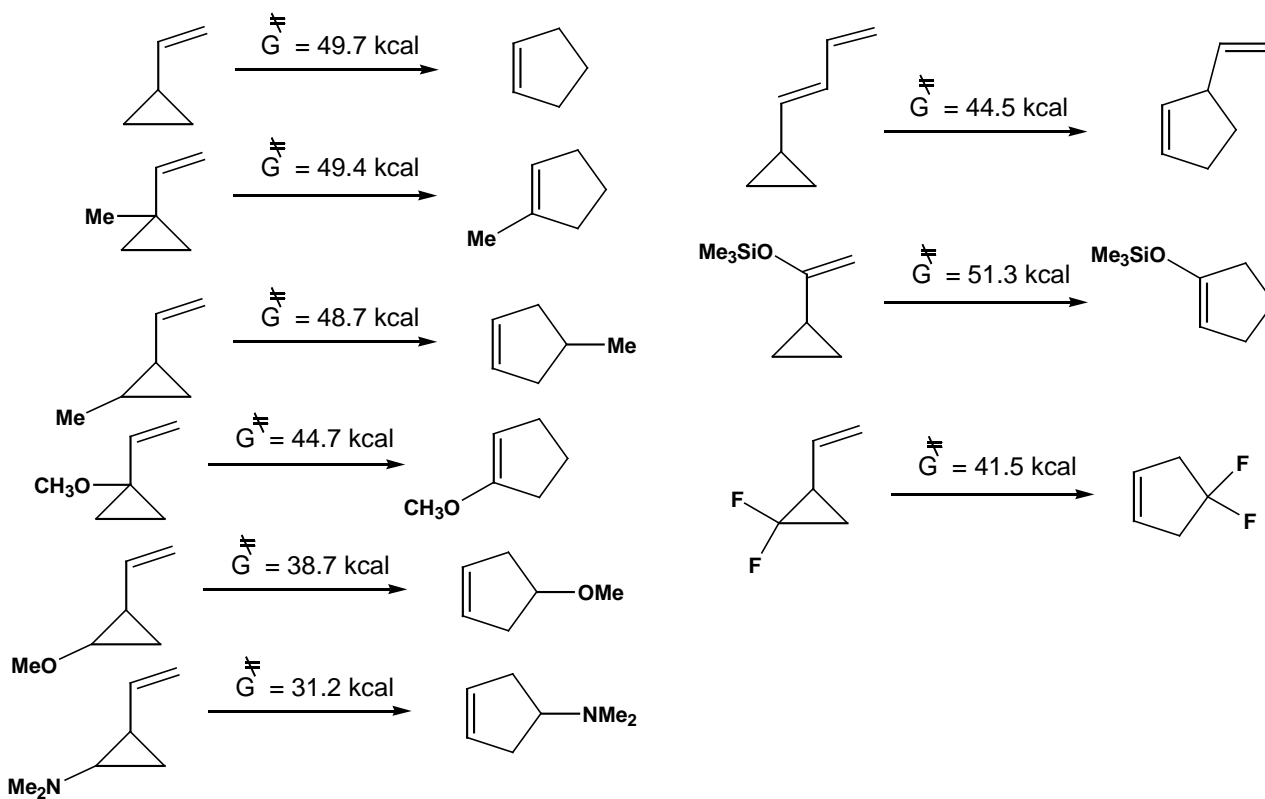
[4 + 1] Annulation



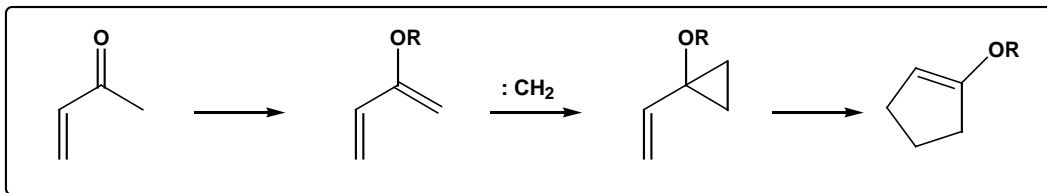
[I] Vinylcyclopropane Rearrangements¹⁾



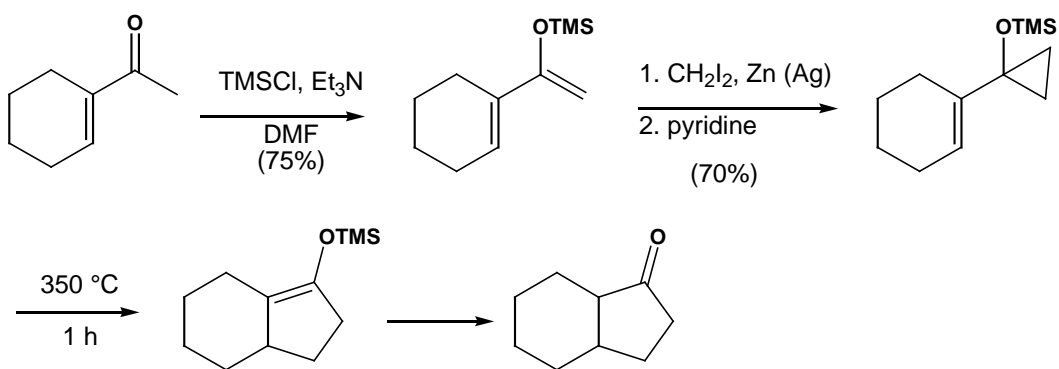
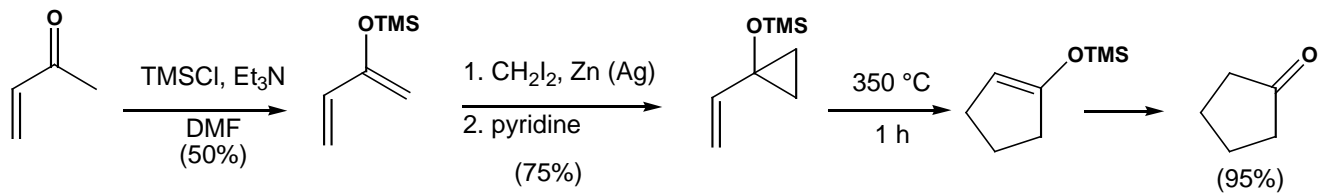
置換基効果^{1a)}



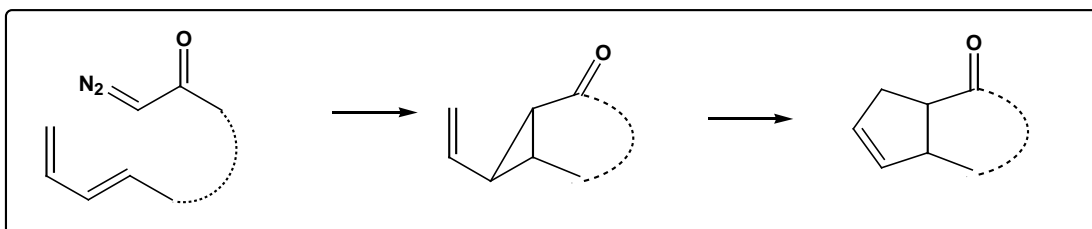
A. Intermolecular Vinylcyclopropane Rearrangements



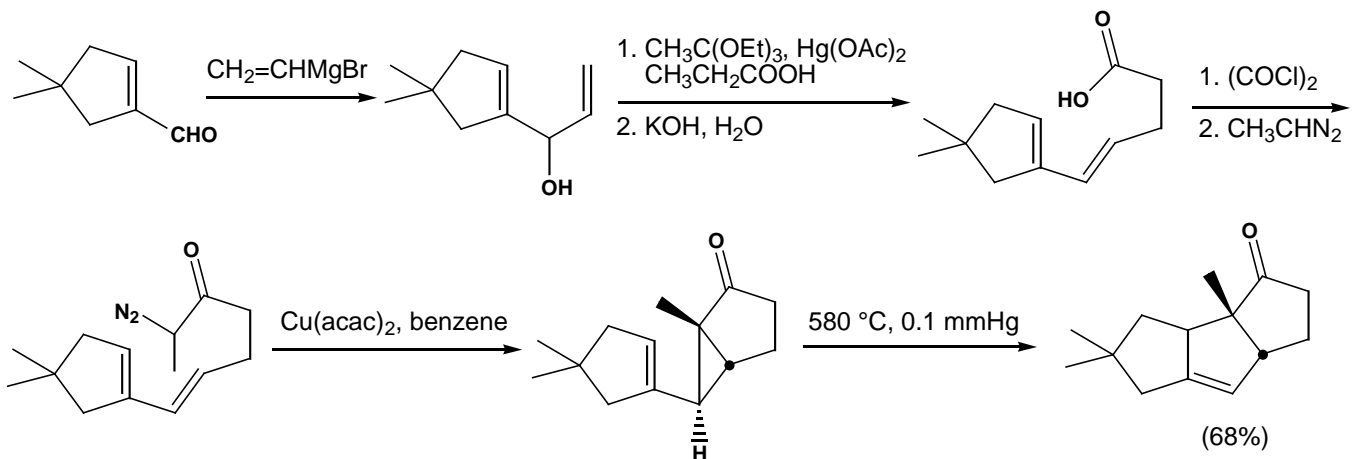
J.M.Conia²⁾



B. Intramolecular Vinylcyclopropane Rearrangements

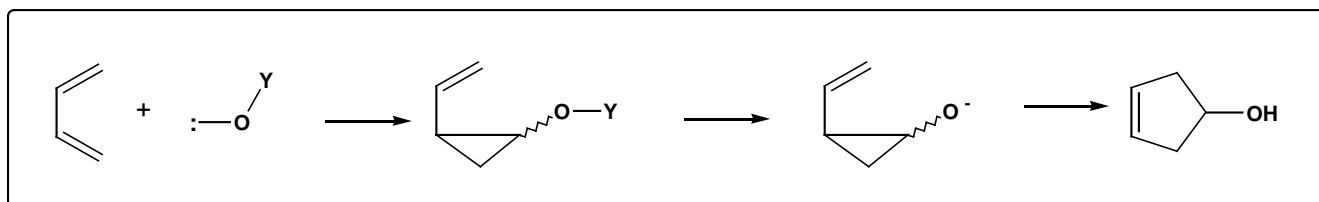


T.Hudlicky³⁾

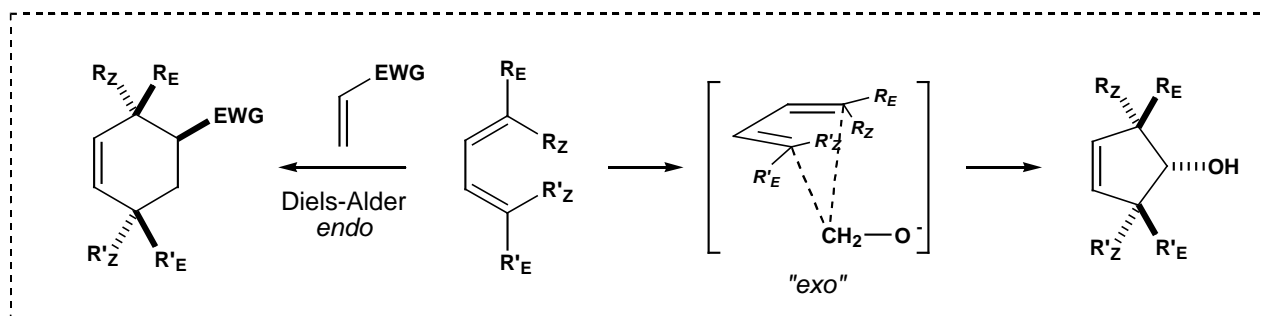
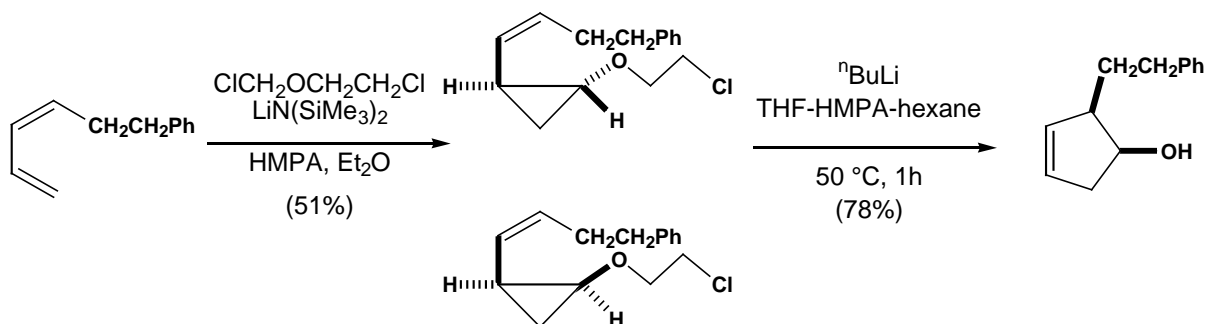
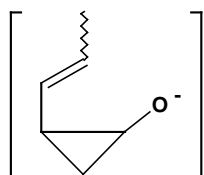
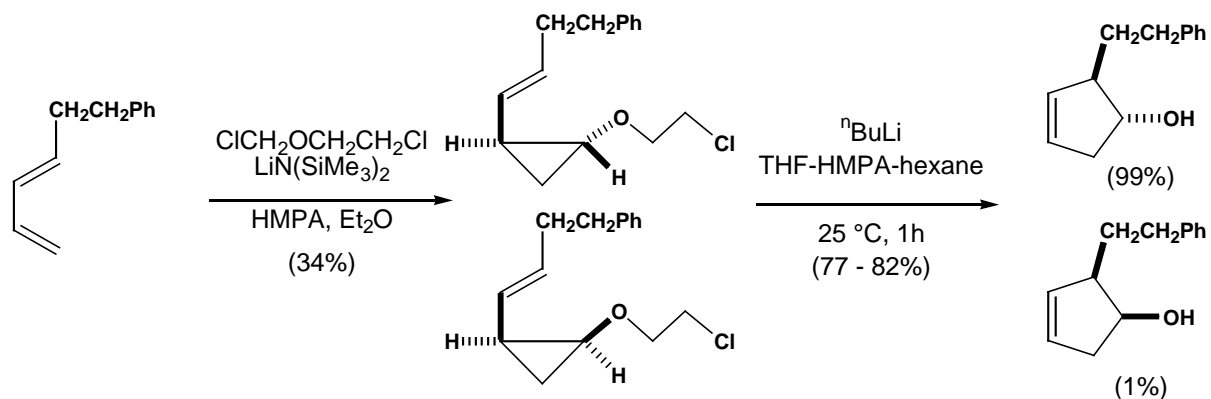


[II] Charge-accelerated Vinylcyclopropane Rearrangements

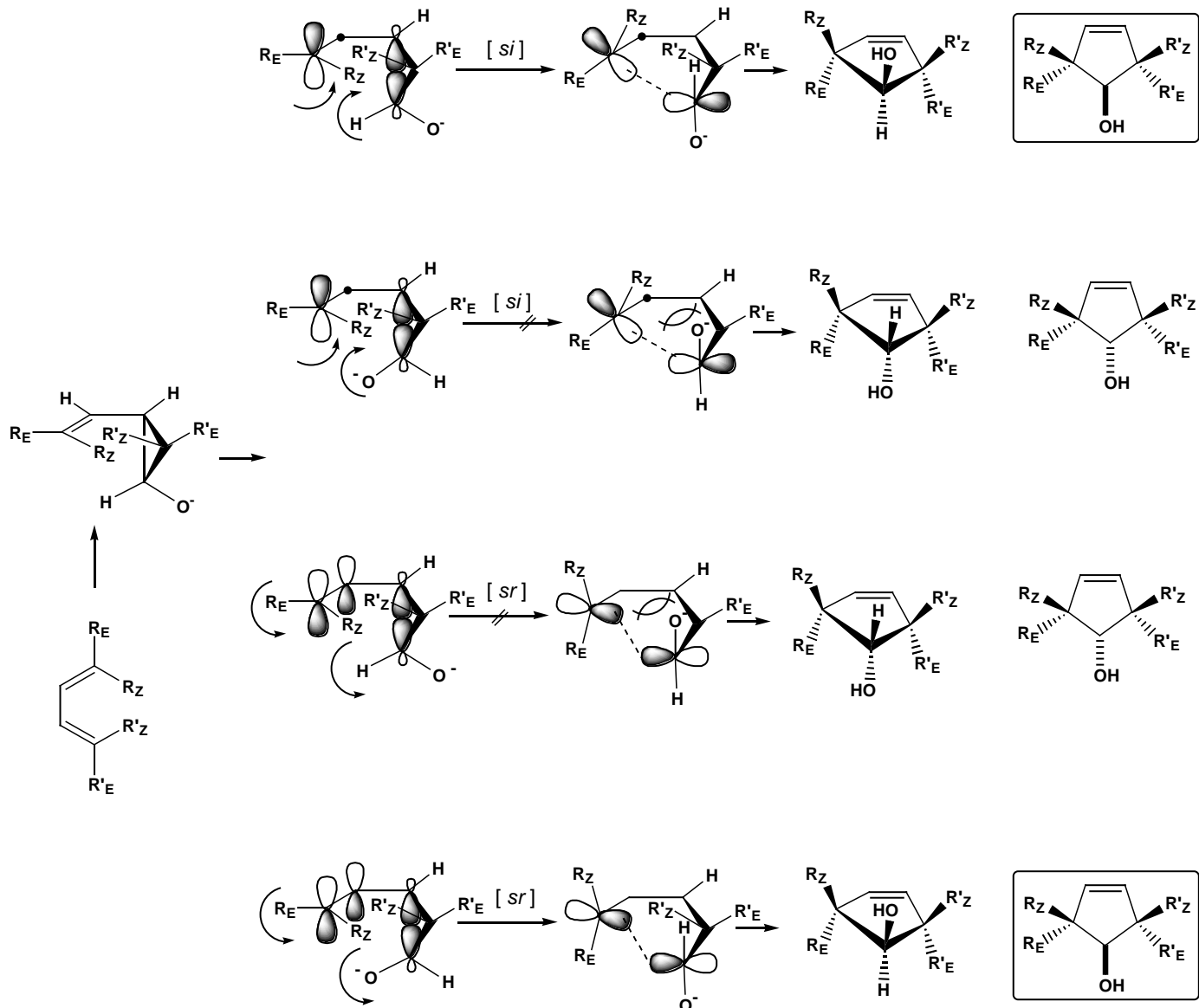
A. Oxyanion-accelerated Vinylcyclopropane rearrangements



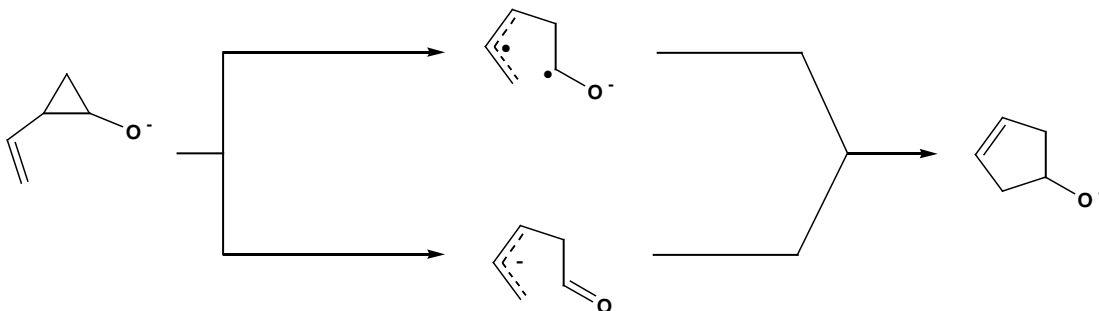
R.L.Danhesiser⁴⁾



A. Concerted 1,3-sigmatropic Shift Mechanism

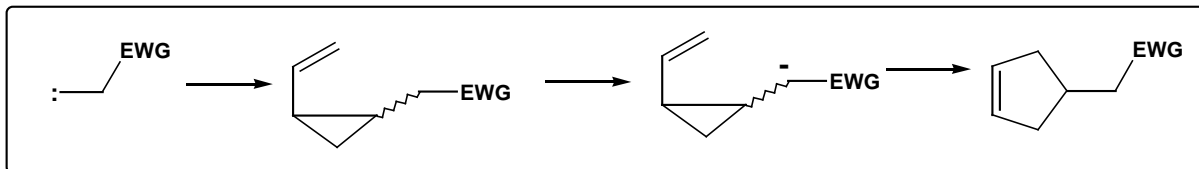


B. Step-wise Mechanism

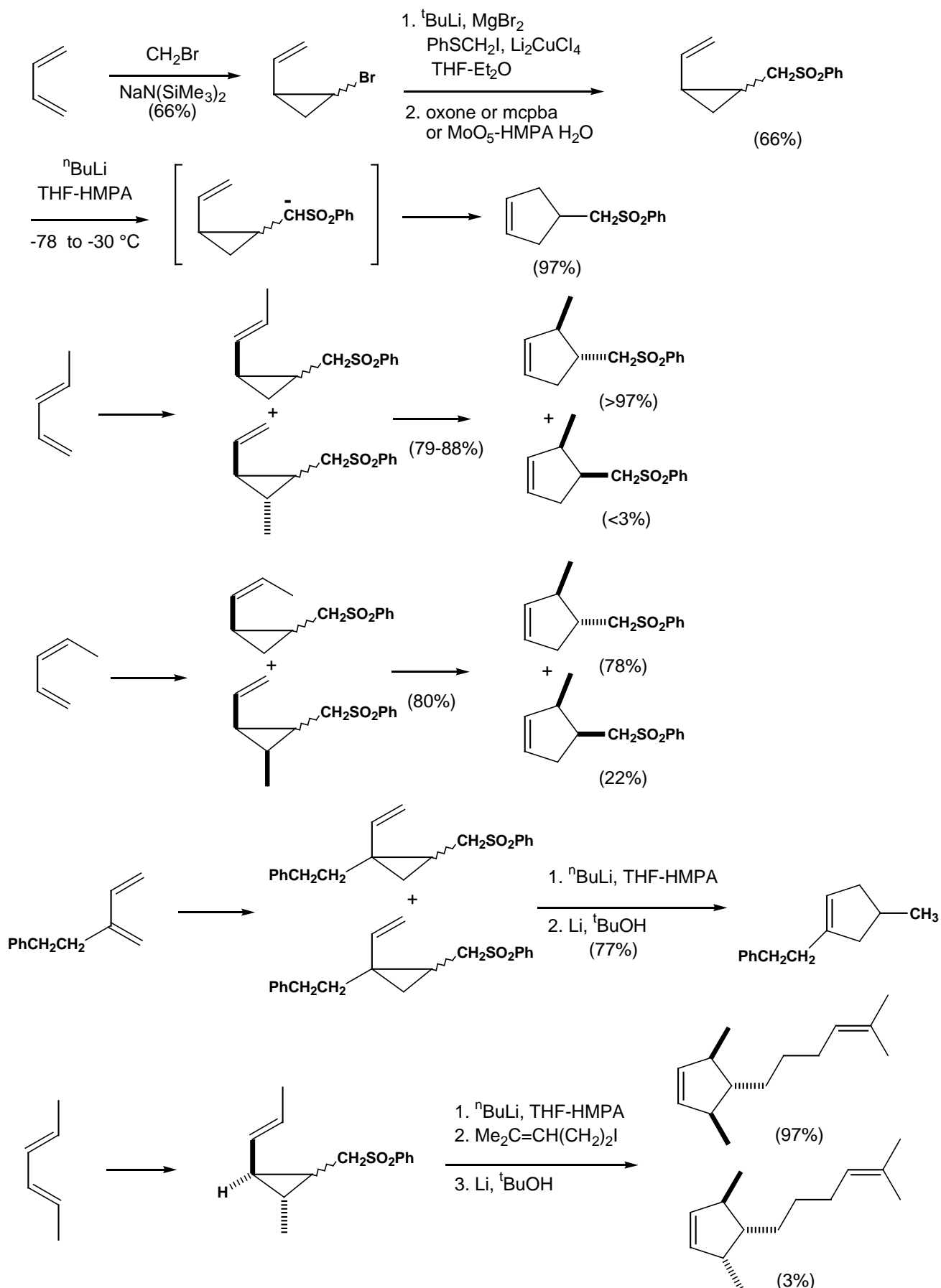


intermediates の環化が conformation の相互変換より速くなければならない。

B. Carbanion-accelerated Vinylcyclopropane Rearrangements



R.L. Danheiser⁵⁾



References

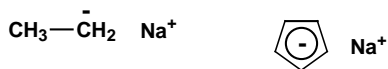
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Basic Organometallic Chemistry

Bond Types of the Metal-Carbon Bond

1. Ionic bonds

炭素とアルカリ金属およびアルカリ土類金属との結合に限定される



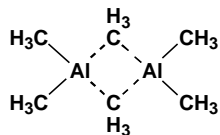
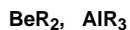
2. Sigma-Covalent Bonds

主として非遷移金属との結合

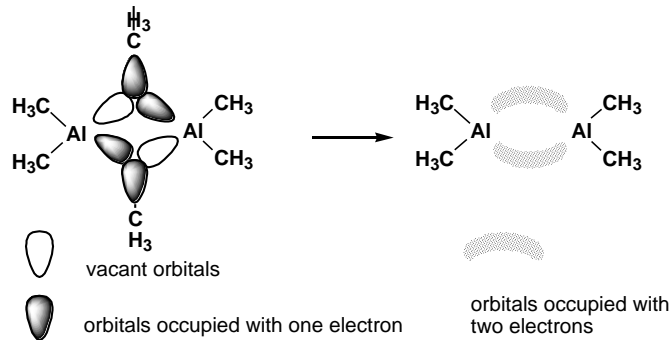


電気陰性度 (Sn : 1.72; Pb : 1.55; As : 2.20; Al : 1.47; C : 2.50)

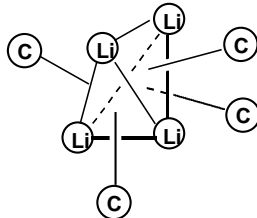
3. Electron Deficient Bonds



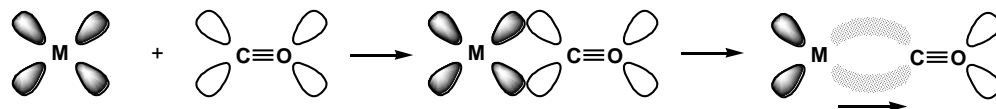
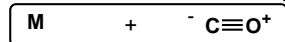
trimethylaluminum



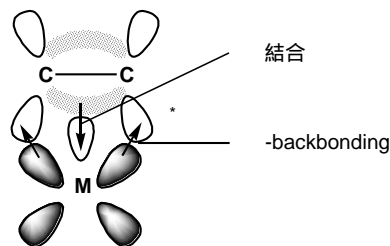
4. Delocalized Bonds in Polynuclear Systems



5. Dative Bonds with Participation of d-Orbitals



back-donation

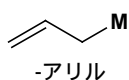


Sc 21 1.36 [Ar]3d ¹ 4s ²	Ti 22 1.54 [Ar]3d ² 4s ²	V 23 1.63 [Ar]3d ³ 4s ²	Cr 24 1.66 [Ar]3d ⁴ 4s ²	Mn 25 1.55 [Ar]3d ⁵ 4s ²	Fe 26 1.83 [Ar]3d ⁶ 4s ²	Co 27 1.88 [Ar]3d ⁷ 4s ²	Ni 28 1.91 [Ar]3d ⁸ 4s ²	Cu 29 1.90 [Ar]3d ¹⁰ 4s ¹
Y 39 1.22 [Kr]4d ¹ 5s ²	Zr 40 1.33 [Kr]4d ² 5s ²	Nb 41 1.6 [Kr]4d ³ 5s ²	Mo 42 2.16 [Kr]4d ⁵ 5s ¹	Tc 43 1.9 [Kr]4d ⁵ 5s ²	Ru 44 2.2 [Kr]4d ⁷ 5s ²	Rh 45 2.28 [Kr]4d ⁸ 5s ²	Pd 46 2.20 [Kr]4d ¹⁰	Ag 47 1.93 [Kr]4d ¹⁰ 5s ¹
La 57 1.10 [Xe]5d ¹ 6s ²	Hf 72 1.3 [Xe]5d ² 6s ²	Ta 73 1.5 [Xe]5d ³ 6s ²	W 74 2.36 [Xe]5d ⁴ 6s ²	Re 75 1.9 [Xe]5d ⁵ 6s ²	Os 76 2.2 [Xe]5d ⁶ 6s ²	Ir 77 2.20 [Xe]5d ⁷ 6s ²	Pt 78 2.28 [Xe]5d ⁹ 6s ¹	Au 79 2.54 [Xe]5d ¹⁰ 6s ¹

Sc 21	atomic number
1.36	electronegativity
[Ar]3d ¹ 4s ²	electronic configuration

Oxidation States (酸化状態)

(hapto, ハプト) 中心金属に結合した配位子の原子数



1 アリル



5-シクロペンタジエニル (Cp)



2



3 アリル ()



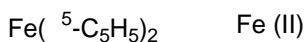
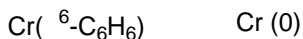
6-ベンゼン



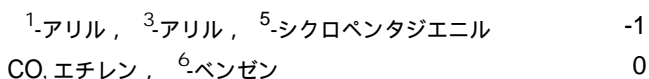
4

酸化数

配位子を閉殻電子構造の形にして取り去ったときに中心金属上に生じる電荷



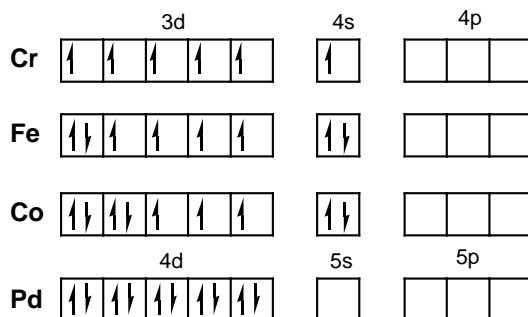
形式電荷



18-Electron Rule (18 電子則)

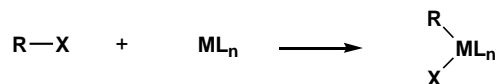
中心金属の d 電子の数と配位子から与えられる電子の数の合計は 18 (希ガスの電子配置) を越えることはできない。

	金属の電子配置	金属の価電子数	配位子からの電子	全価電子数
Cr(CO) ₆	3d ⁵ 4s ¹	6	2 × 6	6 + 12 = 18
Fe(CO) ₅	3d ⁶ 4s ²	8	2 × 5	8 + 10 = 18
Co ₂ (CO) ₈	3d ⁷ 4s ²	9	4 × 2	9 + 8 + 1 = 18
Fe(⁵ -C ₅ H ₅)(CO) ₂ CH ₃	3d ⁶ 4s ²	8	5 + (2 × 2) + 1	8 + 10 = 18

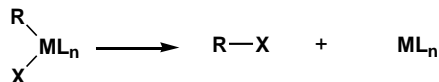


遷移金属化合物の代表的な反応

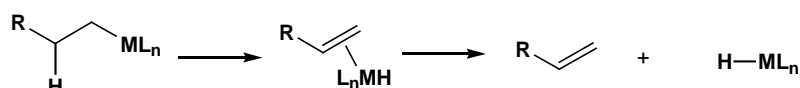
1. Oxidative Addition (酸化付加)



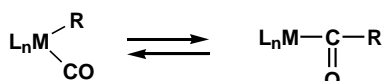
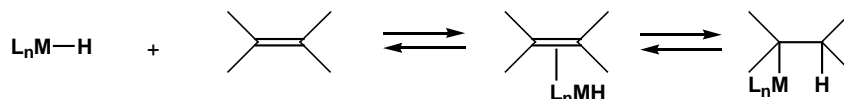
2. Reductive Elimination (還元脱離)



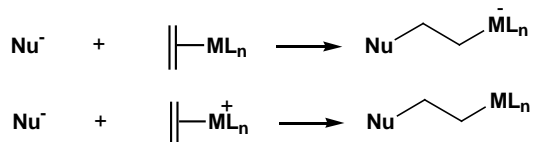
3. β -Elimination (脱離)



4. Insertion Reaction (挿入反応)



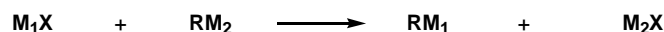
5. Nucleophilic Addition (求核付加)



6. Electrophilic Addition (求電子付加)



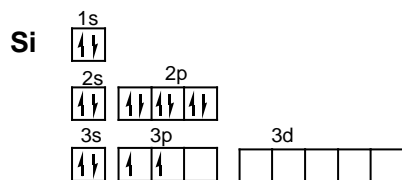
7. Transmetalation (トランスメタレーション)



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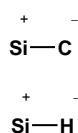
Properties of Organosilicon Compounds



Bond strength and Bond lengths

Bond	Bond Dissociation Energy (kcal/mol)	Bond Length (Å)
C-H	100	1.09
Si-H	81	1.48
C-C	80	1.54
Si-C	76	1.89
C-O	81	1.41
Si-O	127	1.63
C-F	108	1.39
Si-F	193	1.60

Inductive Effect

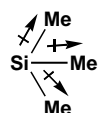


R_3Si は全体として電子供与基として働く

Pauling Electronegativities	
Si	1.90
C	2.55
O	3.44
F	3.93

Field Effect

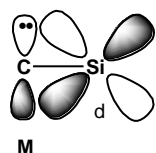
R_3Si の dipole moment の、隣接した π -システムに対する影響



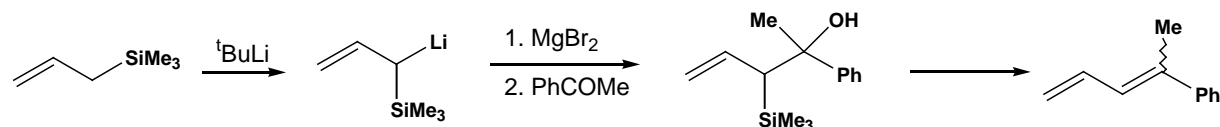
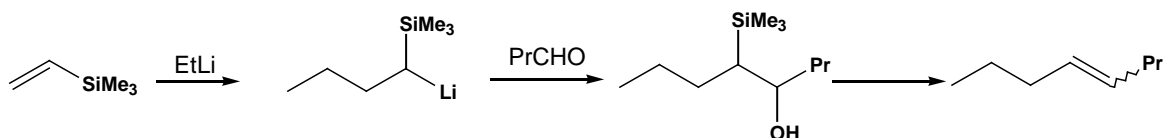
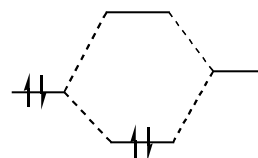
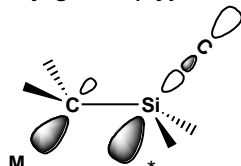
全体として電子吸引基として働く

Stabilization of α -carbon-metal bonds

$p\pi-d\pi$ bonding

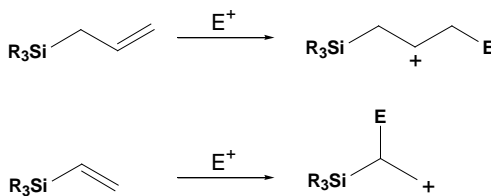
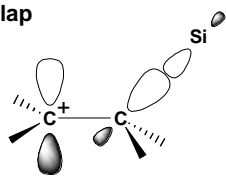


$\sigma-\pi$ conjugation (hyperconjugation)

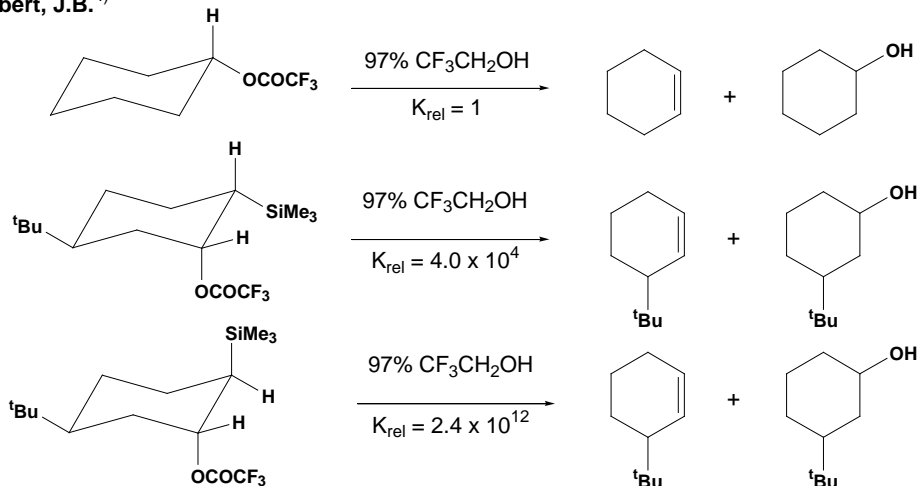


Stabilization of β -carbocations (β -effect)

σ - π overlap



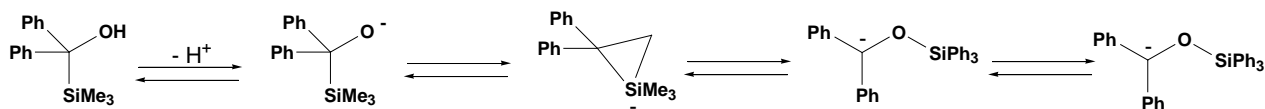
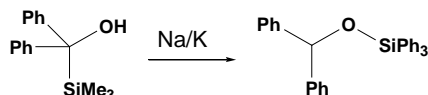
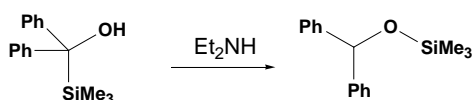
Lambert, J.B.⁴⁾



Calculated Stabilization Energy (kcal/mol)⁵⁾

CH_3^+	0	CH_2CH^+	0
	34.0		9.1
	17.8		22.9
	46.4		29.5
	72.0		42.8

1,2-Rearrangement (Brook rearrangement)

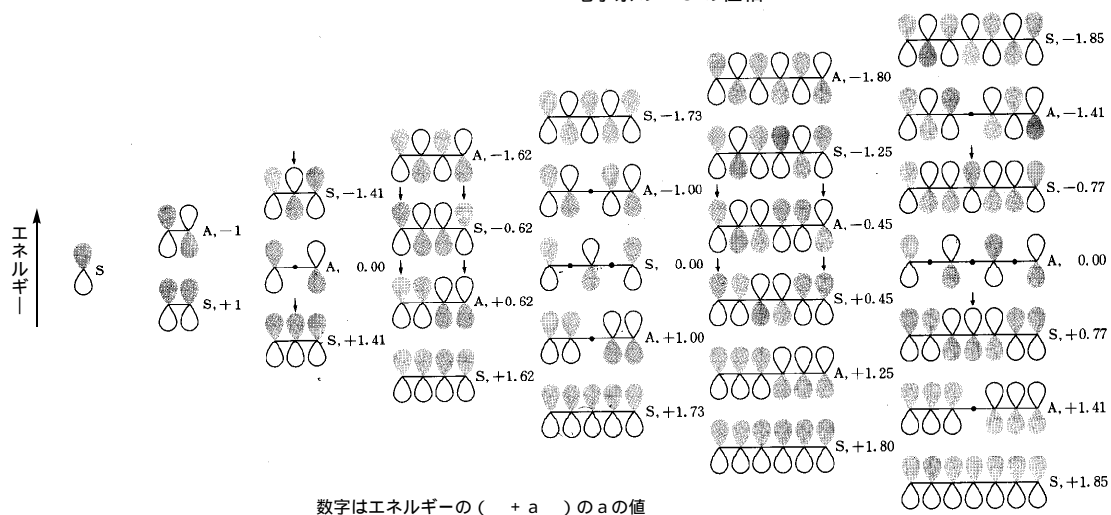


References

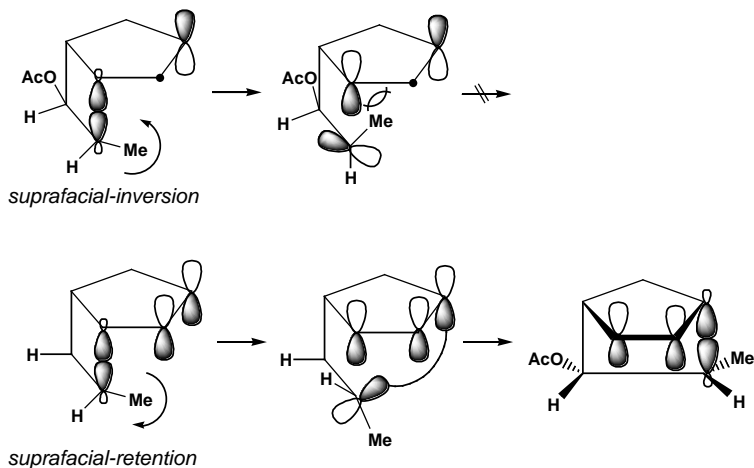
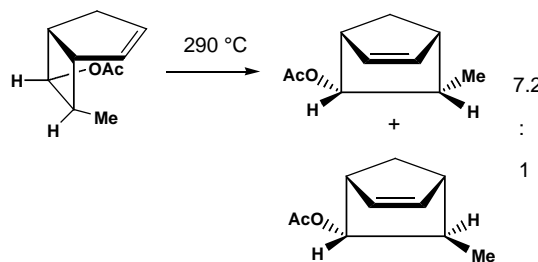
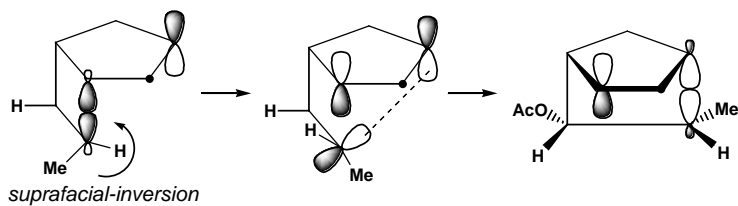
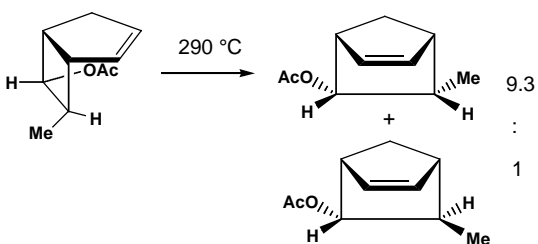
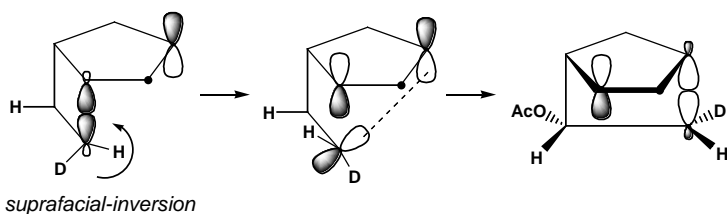
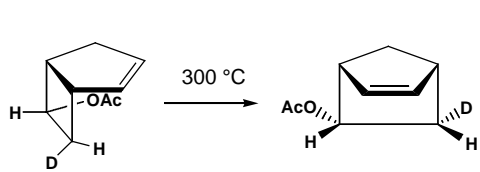
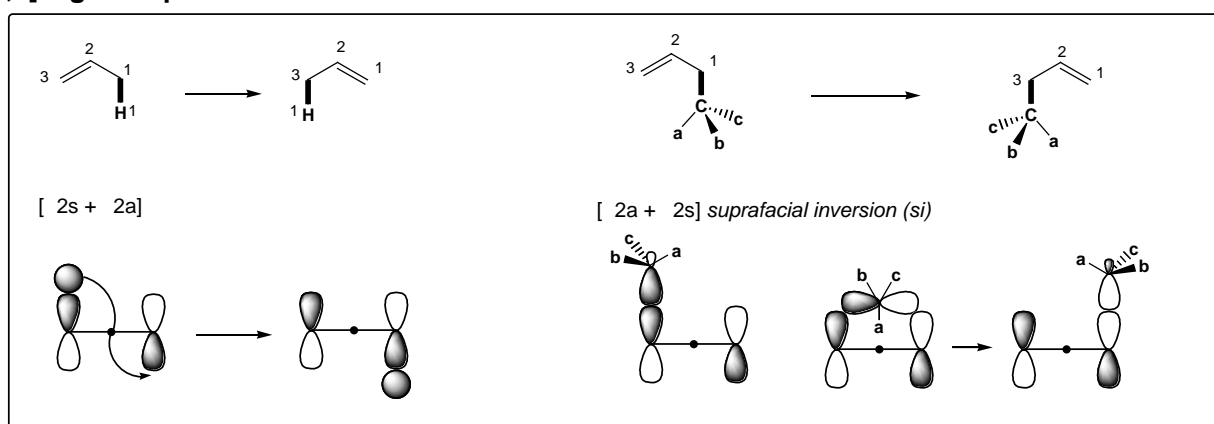
1. *The Chemistry of Organic Silicon Compounds*, Patai, S., Rappoport, Z. Eds, John Wiley & Sons, 1989, Part 1, Part 2.
2. Weber, W.P., *Silicon Reagents for Organic Synthesis*, Springer-Verlag, New York, 1983.
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b) Lambert, J.B. *Tetrahedron* **1990**, *46*, 2677.
5. Wieschke, S.W., Chandrasekhar, J., Jorgensen, W.L. *J. Am. Chem. Soc.* **1985**, *107*, 1436.

Sigmatropic Reaction

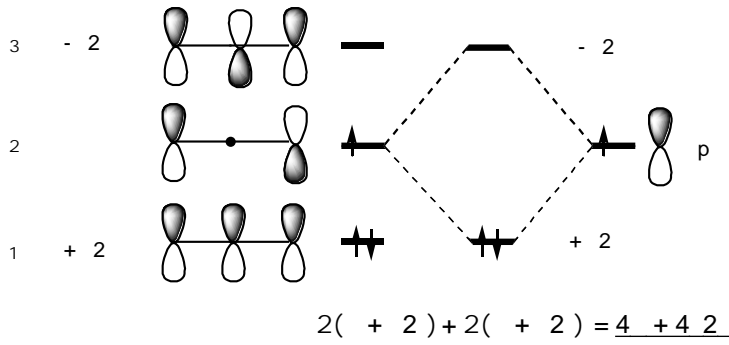
電子系の MO の位相



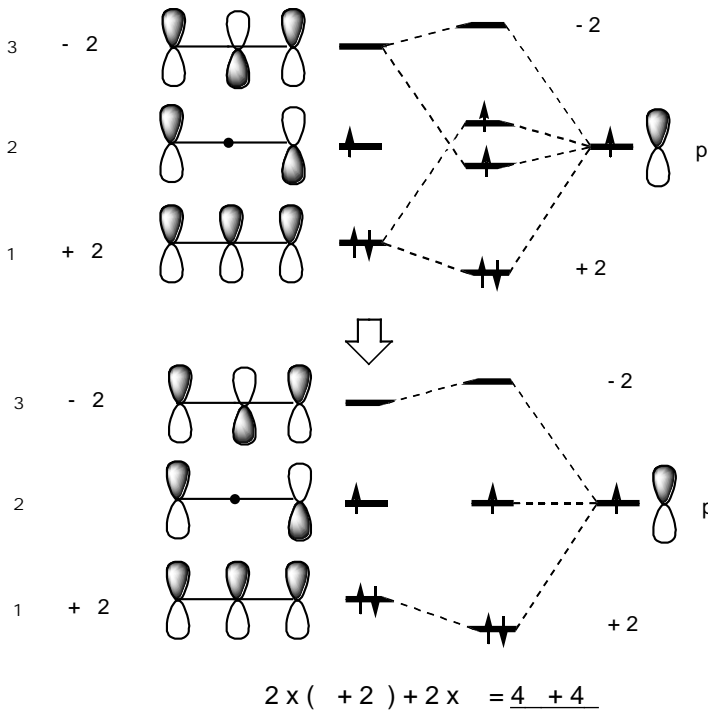
[1,3] sigmatropic reaction



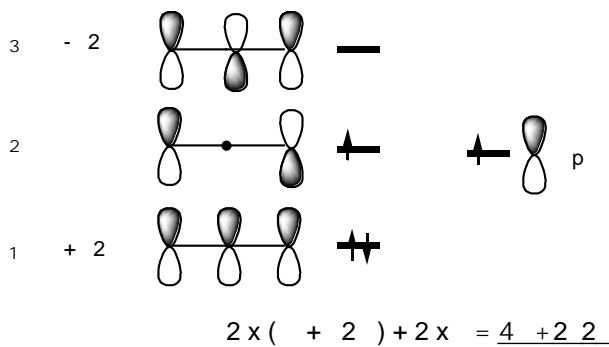
1. [$\pi 2s + \sigma 2a$]



2. [$\pi 2s + \sigma 2s$]



3. Radical mechanism



[$2s + 2a$] (許容) > [$2s + 2s$] (禁制) > radical

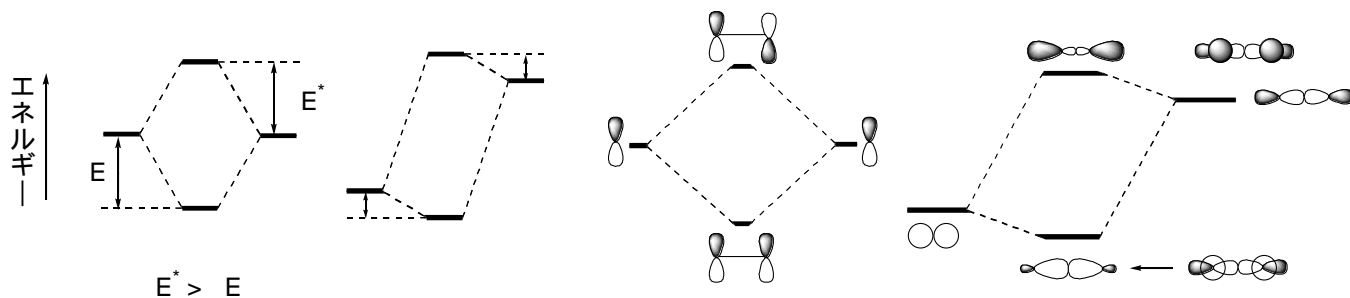
軌道相互作用

二つの軌道が相互作用すると、同位相で結合した軌道と逆位相で結合した軌道の二つができる。

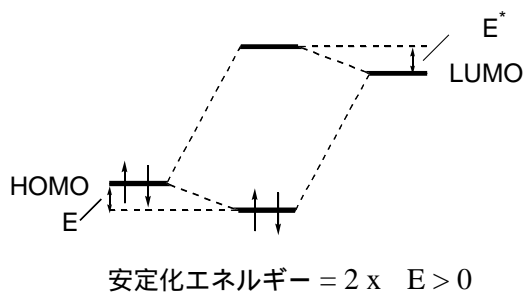
同位相の軌道（結合性軌道）のエネルギーは低く、逆位相の軌道（反結合性軌道）のエネルギーは高い。

二つの軌道が相互作用するとき、1) エネルギー差が小さければ小さいほど、2) 重なりが大きければ大きいほど、相互作用は強くなる（安定化、不安定化の度合いが大きくなる）。

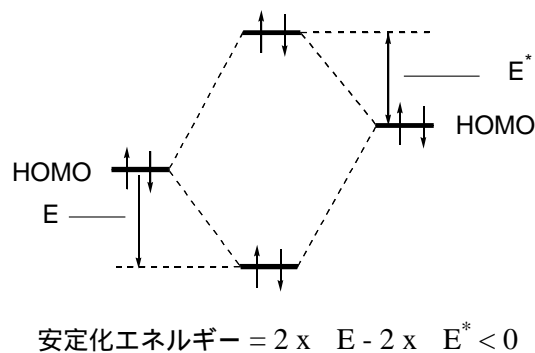
エネルギーの異なる軌道が相互作用した場合、同位相の軌道はもとの軌道のうち低いほうの軌道よりエネルギーが低く、逆位相の軌道はもとの高いほうの軌道よりエネルギーが高い。同位相の軌道は低いほうの軌道を主成分に持ち、逆位相の軌道は高いほうの軌道を主成分とする。



HOMO-LUMO Interaction



HOMO-HOMO Interaction

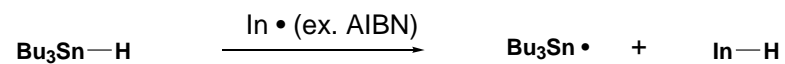


References

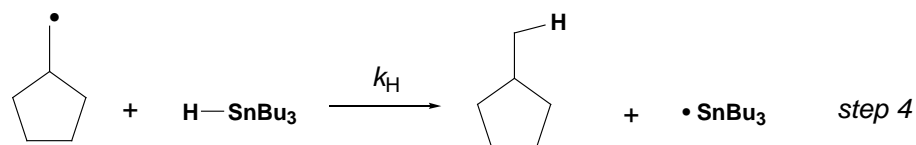
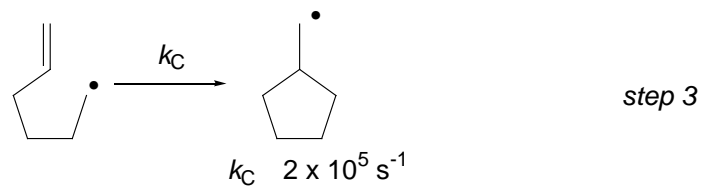
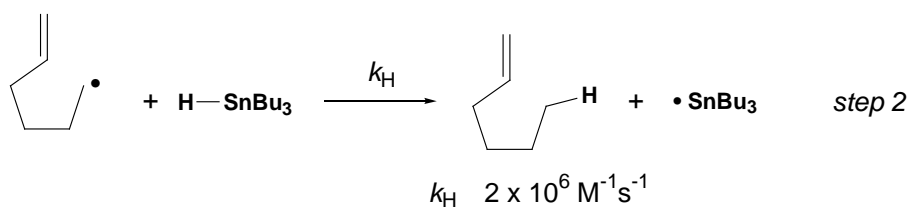
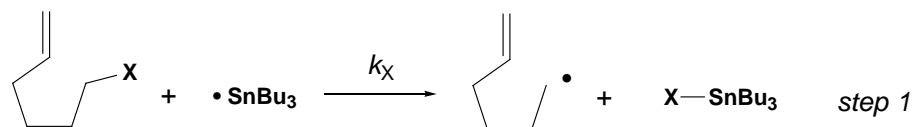
1. 井本 稔, ウッドワード・ホフマン則を使うために, 化学同人, 1978.
2. 井本 稔, 仲矢忠雄, 有機反応論(下), 東京化学同人, 1982.
3. 山辺信一, 稲垣都士, プログラム学習 入門フロンティア軌道論, 講談社サイエンティフィック, 1989.

Tin Hydride Method

Initiation



Propagation

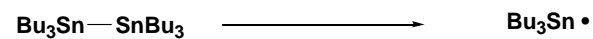


プロトン引き抜きの速度は基質の構造に依存しない。

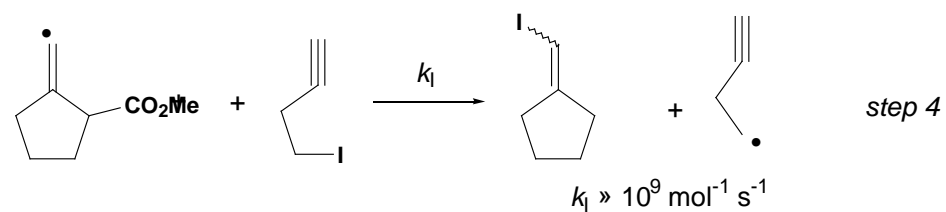
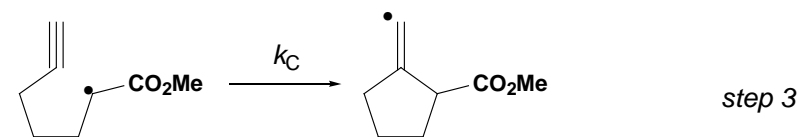
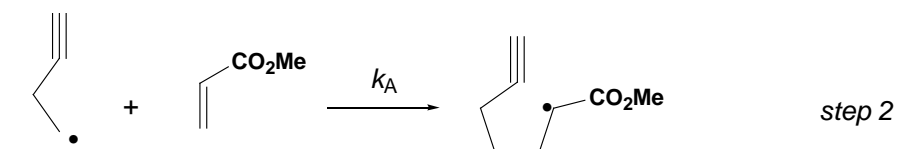
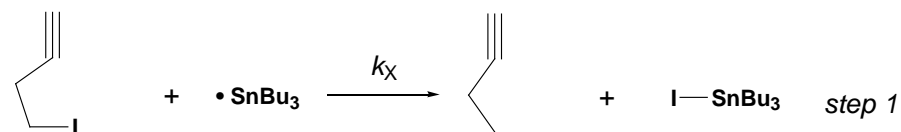
$$k_H (\text{step 2}) \quad k_H (\text{step 4})$$

Atom Transfer Method

Initiation



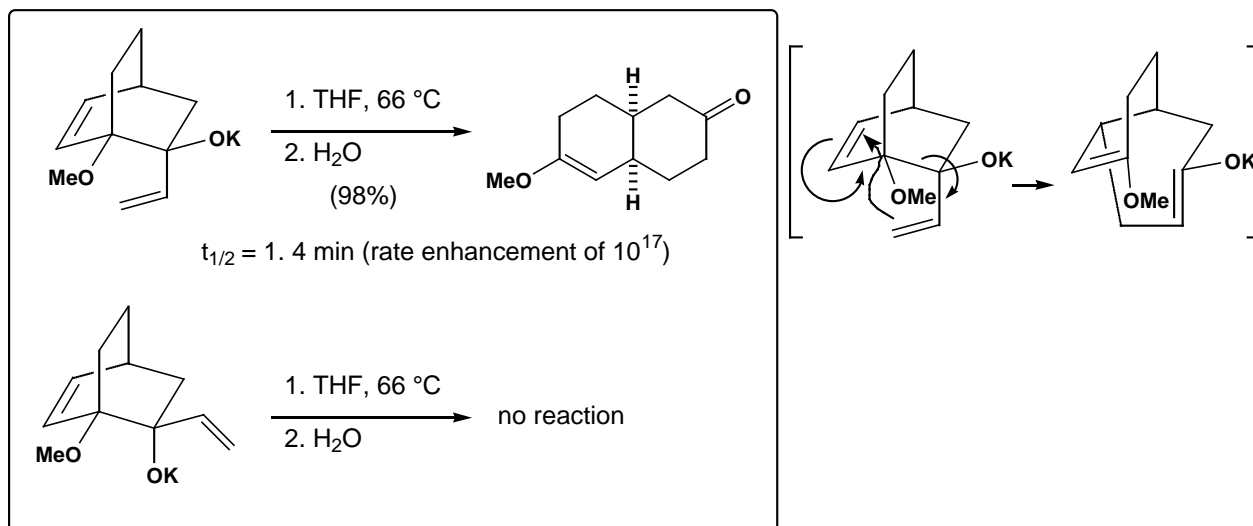
Propagation



$$k_I \gg k_C, k_A$$

Oxyanion-accelerated Rearrangements¹⁾

D.A.Evans (1975)²⁾



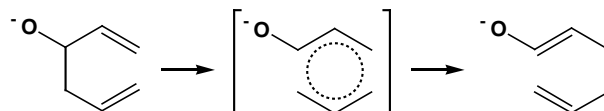
Oxyanion が反応を加速する理由

Evans³⁾

oxyanion が隣接した炭素-炭素結合を弱める .

結合解離エネルギーおよび ab initio 計算

Carpenter's Model⁴⁾



pericyclic reaction の反応速度に対する置換基の効果

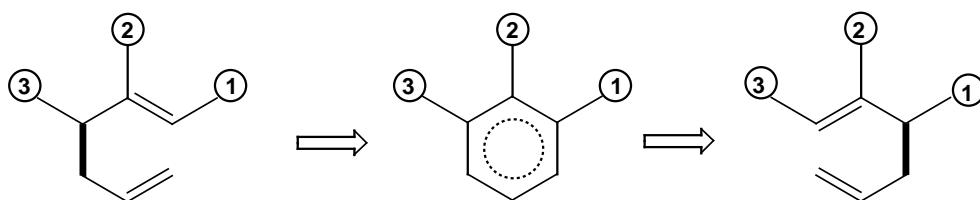
置換基の軌道と炭素骨格の軌道との conjugation の度合は原系から遷移状態に進むに連れて変化する . pericyclic reaction の遷移状態は完全に共役した軌道を含むので , 原系より遷移状態の方が非局在化の割合は大きい (特に置換基が原系において sp^3 炭素に結合している場合 , 大きいと予想される) . この非局在化の程度の違いを置換基の効果と考え , 置換基の種類および位置の違いによる原系と遷移状態のエネルギーの差を求める . 遷移状態としては環状の共役炭化水素をモデルとして使う (ex. Cope 転位には benzene) .

置換基モデルとして次のような四種類のモデルを考え , HMO 法により原系と遷移状態のエネルギーを求める (エネルギーは $n + x$) .

- : クーロン積分 (2p 軌道に電子が 1 個あって , 隣の 2p 軌道にある電子と無関係に存在する場合のその電子のエネルギー . すなわち電子の負電荷が核の正電荷と作用しあうことにより生ずるエネルギー . 約 -7 ~ -6 eV
- : 共鳴積分 (結合が形成されると , 電子が隣の原子との間で非局在化できるようになる . その時の安定化エネルギー . 約 -3 eV (負))

-electron acceptor (ACC) [R_3B , NO_2 etc]	: doubly occupied 2p orbital
-electron doner (Don) [MeO , Me_2N , K^+O^- etc]	: empty 2p orbital
non-polar conjugating substituent (Con)	: vinyl group
no substituent (0)	

Cope rearrangement



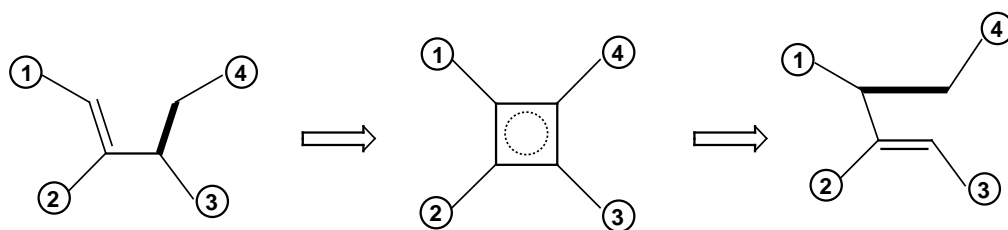
position	Substituent	Reactant (x)	Transition State (y)	
1,2	Pol	4.828	8.720	0.108
	Con	6.472	10.425	0.047
	0	4.000	8.000	0.000
3	Pol	4.000	8.720	-0.720
	Con	6.000	10.425	-0.425
	0	4.000	8.000	0.000

Reactant のエネルギー : $n + x$
 Transition state のエネルギー : $n + y$

偶数の環の場合、置換基が一つ加わる
 ことにより奇数の p 軌道をもつこと
 になり、非結合性軌道（エネルギーは
 ができる（" 電子系の MO の位相 "
 を参照）。置換基が Acc の場合はこの
 軌道には電子が入らず、Don の場合は
 入っても非結合性軌道なので全 電子
 エネルギーには寄与せず、Acc でも [中
 でもエネルギーは等しくなるので、こ
 場合単に polar 置換基 (Pol) として
 分類する。

position	Order of decreasing rates		
	1	2	3
1,2	0	Con	Pol
3	Pol	Con	0

1,3-Sigmatropic rearrangement



position	Substituent	Reactant	Transition state	
1,2	Pol	2.828	6.293	0.192
	Con	4.472	8.055	0.074
	0	2.000	5.657	0.000
3,4	Pol	2.000	6.293	-0.636
	Con	4.000	8.055	-0.398
	0	2.000	5.657	0.000

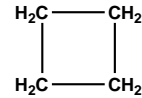
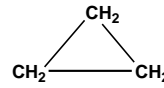
position	Order of decreasing rates		
	1	2	3
1,2	0	Con	Pol
3,4	Pol	Con	0

1. Comprehensive Organic Synthesis; Trost, B.M., Fleming, I., Eds.; Pergamon: Oxford, 1991; Vol. 5, pp 998-1035.
2. Evans, D.A.; Golob, A.M. *J. Am. Chem. Soc.* **1975**, *97*, 4765-4766.
3. a) Evans, D.A.; Baillargeon, D.J. *Tetrahedron Lett.* **1978**, 3315-3318, 3319-3322.
 b) Steigerwald, M.L.; Goddard, III, W.A.; Evans, D.A. *J. Am. Chem. Soc.* **1979**, *101*, 1994.
4. a) Carpenter, B.K. *Tetrahedron* **1978**, *34*, 1877-1884.
 b) Zoekler, M.T.; Carpenter, B.K. *J. Am. Chem. Soc.* **1981**, *103*, 7661-7663.

Chemistry of Cyclopropanes

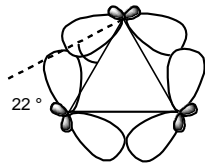
Strain Energy

	cyclopropane	cyclobutane
strain energy	27.5 kcal/mol	26.5 kcal/mol
Homolytic cleavage	61 kcal/mol	62.5 kcal/mol



Bonding in Cyclopropane¹⁾

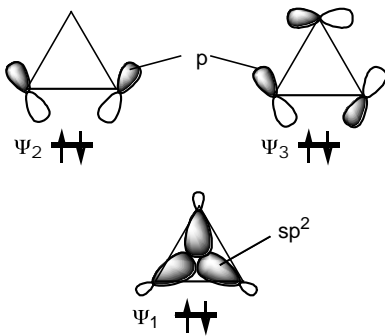
Coulson-Moffit model²⁾



軌道の重なりは ethane に比べて 20% 減少



Walsh Model³⁾



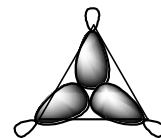
σ -Aromaticity

M.J.S.Dewar (1984)⁴⁾

cyclopropane	6	aromatic
cyclobutane	8	antiaromatic

D.Cremer (1986)⁵⁾

"surface orbital" Ψ_1 に起因する



three-center, two-electron bond

2 電子

-Aromaticity により cyclopropane の化学的物理的性質を説明することができる。

Strain energy

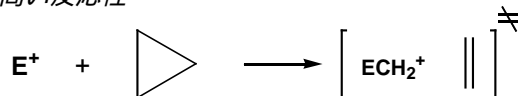
strain energy (27.5 kcal/mol) は、角度の歪みから予想される (104 kcal/mol) よりもはるかに安定である。

NMR

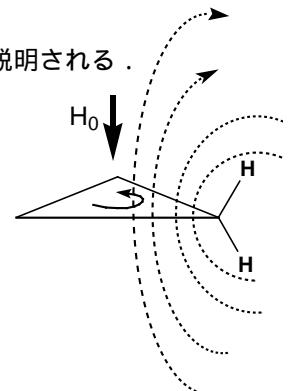
$J(^1\text{H}-^{13}\text{C})$, $J(^{13}\text{C}-^{13}\text{C})$ の値から cyclopropane はほぼ sp^2 混成

cyclopropane の ^1H NMR における高磁場シフト ($\sim 1\text{ppm}$) は環電流効果により説明される。

求電子剤との高い反応性



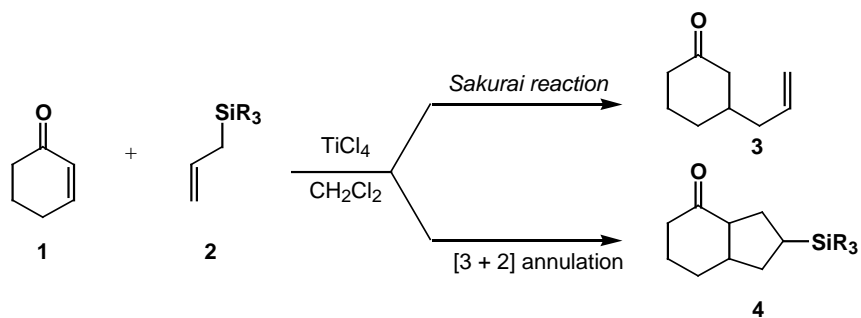
遷移状態において aromaticity を維持している。



1. Wong, H.M.C.; Hon, M.-Y.; Tse, C.-W.; Yip, Y.-C.; Tanko, J.; Hudlicky, T. *Chem. Rev.* **1989**, 89, 165-198.
2. Coulson, C.A.; Moffit, W.E. *J. Chem. Phys.* **1947**, 15, 151.
3. Walsh, A.D. *Nature (London)* **1947**, 165, 712.
4. Dewar, M.J.S. *J. Am. Chem. Soc.* **1984**, 106, 669-682.

論文を読み次の問に答えなさい。

- 1) **1** と **2** から, **3** および **4** が生成する機構を書きなさい(ただし, 立体化学は問わない)。
- 2) **R** が Me 基の場合 **3** が優先的に生成するが, **R** が i-Pr 基のようなかさ高い基の場合 **4** が主生成体となる。その理由を考えなさい。



- 3) propargylsilane の場合とは異なり, allylsilane の場合 C-3 に置換基がなくとも五員環を形成する理由を考えなさい。

