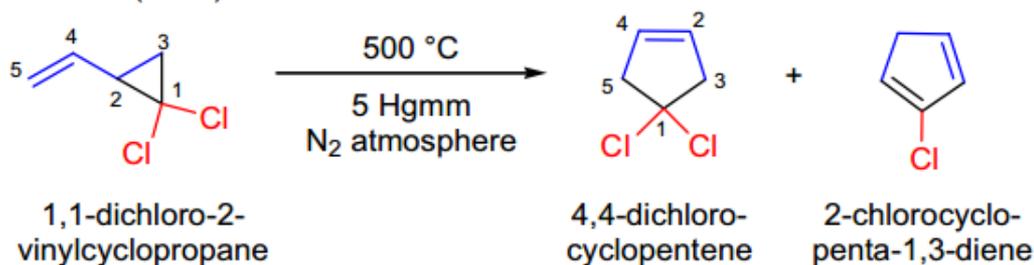
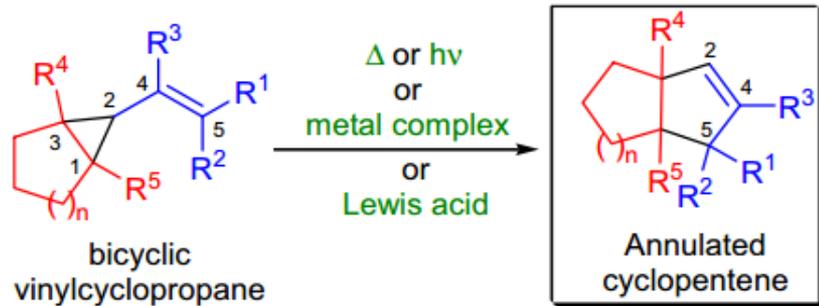
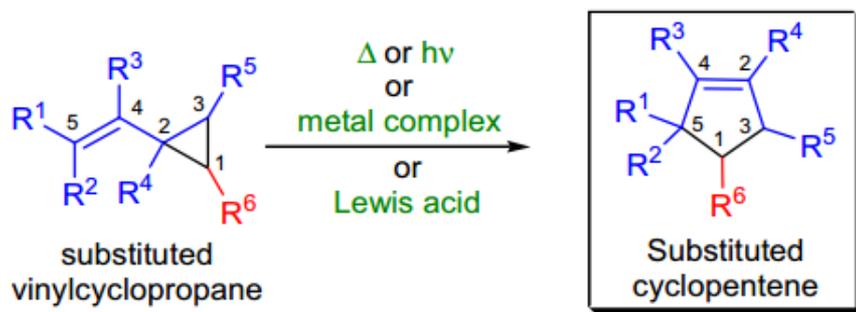
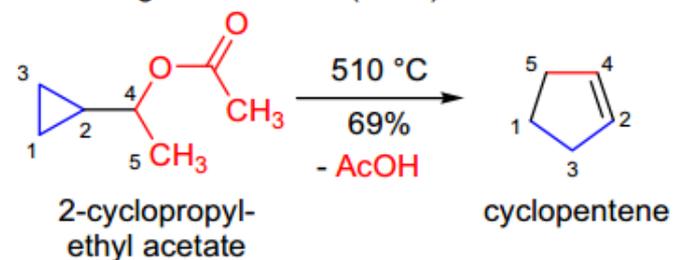


# Vinylcyclopropane-Cyclopentene Rearrangement

Neureiter (1959):



Overberger & Borchert (1960):

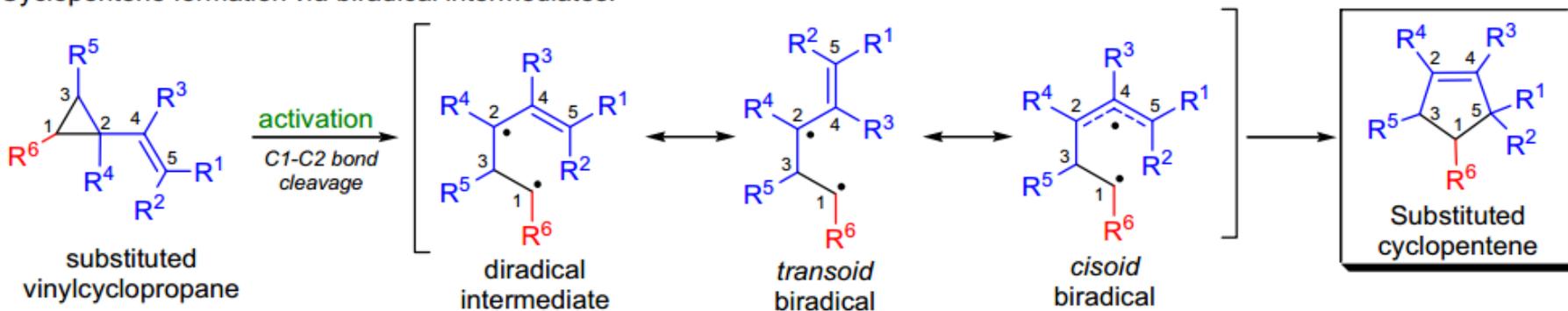


$R^{1-5}, R^6 = \text{H, alkyl, alkenyl, aryl, O-alkyl, NH}_2, \text{NH-alkyl, NR}_2; n = 1-3$

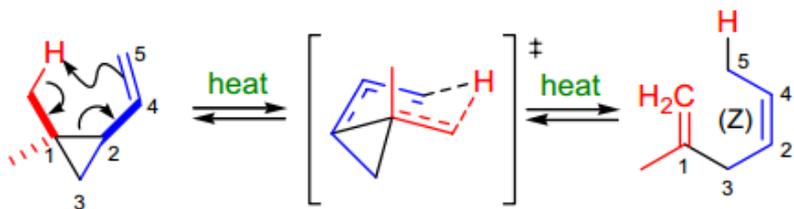
- 1) thermal-, photochemical-, transition metal-mediated, as well as Lewis acid mediated conditions can be applied to affect the transformation
- 2) the photochemical process works well only for a limited number and type of substrates.
- 3) the rearrangement of vinylcyclopropanes under thermal conditions is the most important transformation and it may take two major pathways: conversion to cyclopentenes or formation of open-chain alkenes or dienes;
- 4) the pathway taken depends on many factors such as the nature of substituents on the cyclopropane ring as well as the orientation of the  $\pi$ -system of the vinyl group relative to the cyclopropane ring (e.g., *cis*-alkylvinylcyclopropanes tend to undergo *[1,5]-sigmatropic H-shift (retro-ene reaction)* rather than forming cyclopentenes);
- 5) the rearrangement usually requires high temperatures (often this means running the reaction in a flash vacuum pyrolysis apparatus), but the degree of substitution and the presence of extended conjugation and heteroatoms lower the activation energy and also the required temperature
- 6) heteroatom substitution (e.g., *O*-alkyl,  $\text{NH}_2$ , *S*-alkyl, etc.) on the cyclopropane moiety has a dramatic activation energy-lowering effect, whereas substitution on the vinylic moiety does not have a significant influence.
- 7) the rearrangement can be highly regio- and stereoselective provided that the cyclopropane is opened regioselectively.
- 8) The stereochemical outcome of the rearrangement is determined by the energetics of the substituted cyclopentene product.

# Mechanism

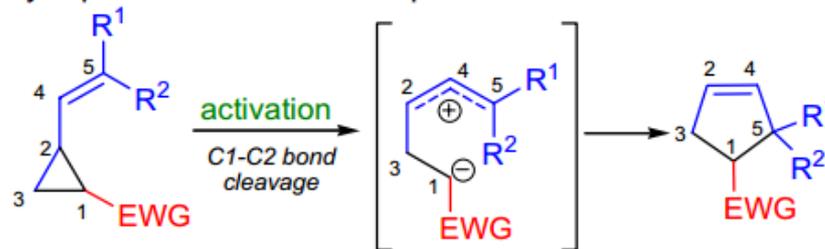
Cyclopentene formation *via* biradical intermediates:



Competing retro-ene reaction (reversible process):

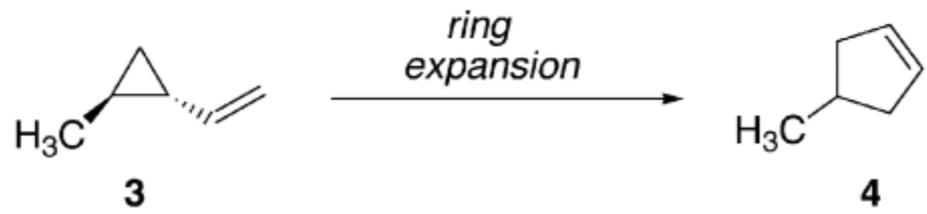
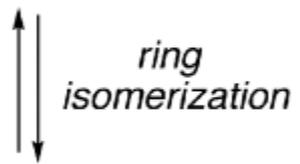
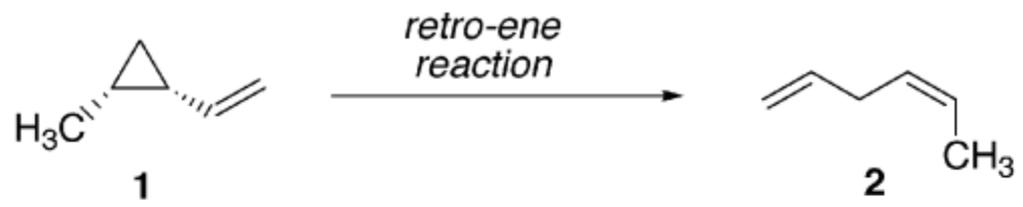


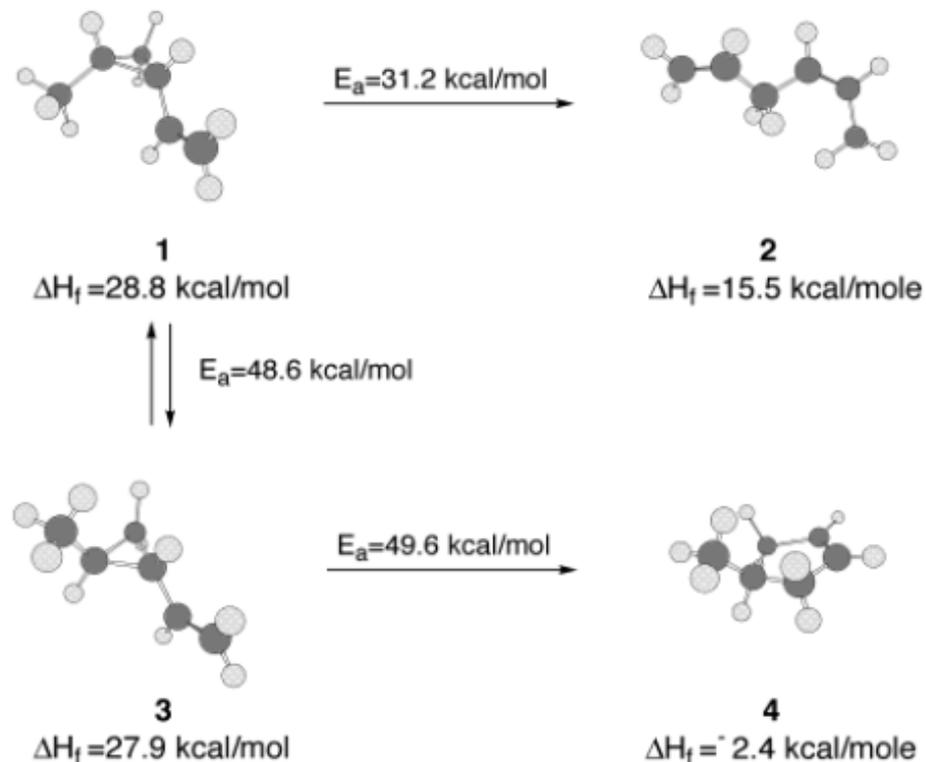
Cyclopentene formation *via* dipolar intermediates:



a diradical-mediated two-step and/or orbital-symmetry-controlled pericyclic process?





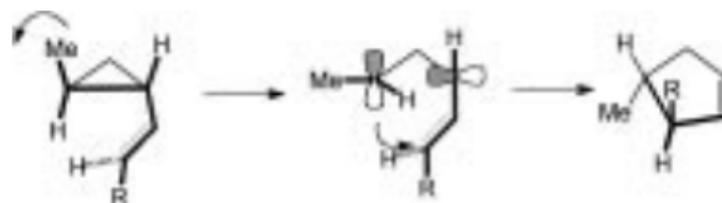
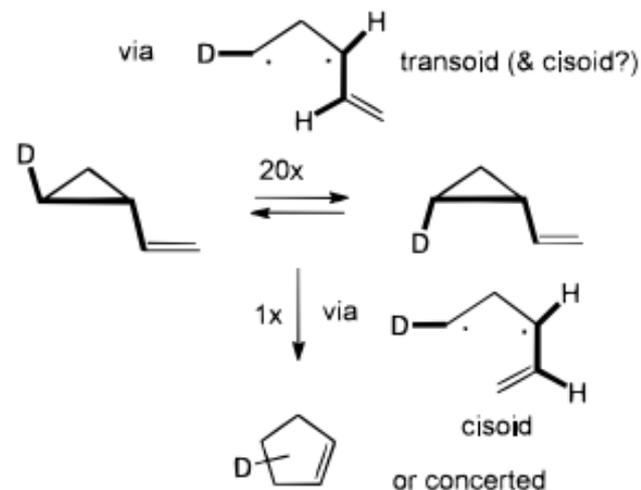
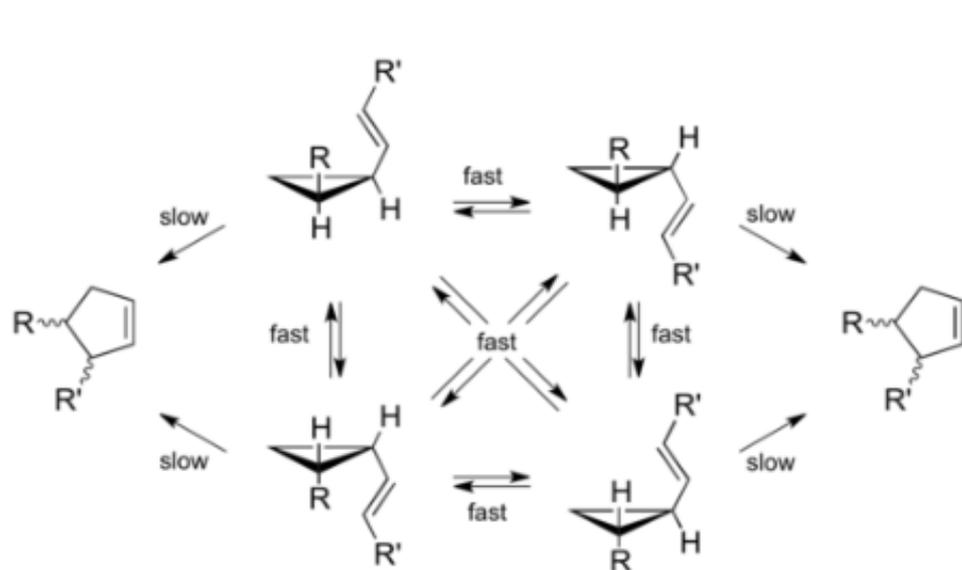
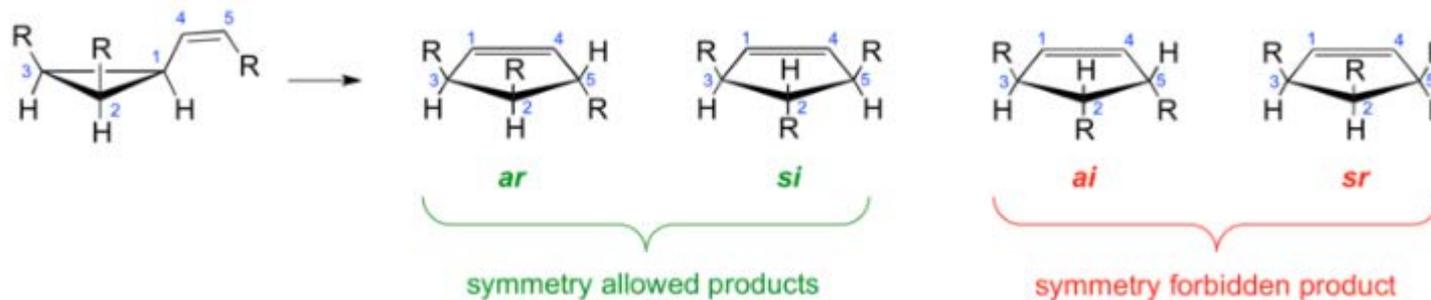


**Table 1. Effect of Substituents on the Activation Energy and Reaction Temperature of the Vinylcyclopropane Ring Expansion**

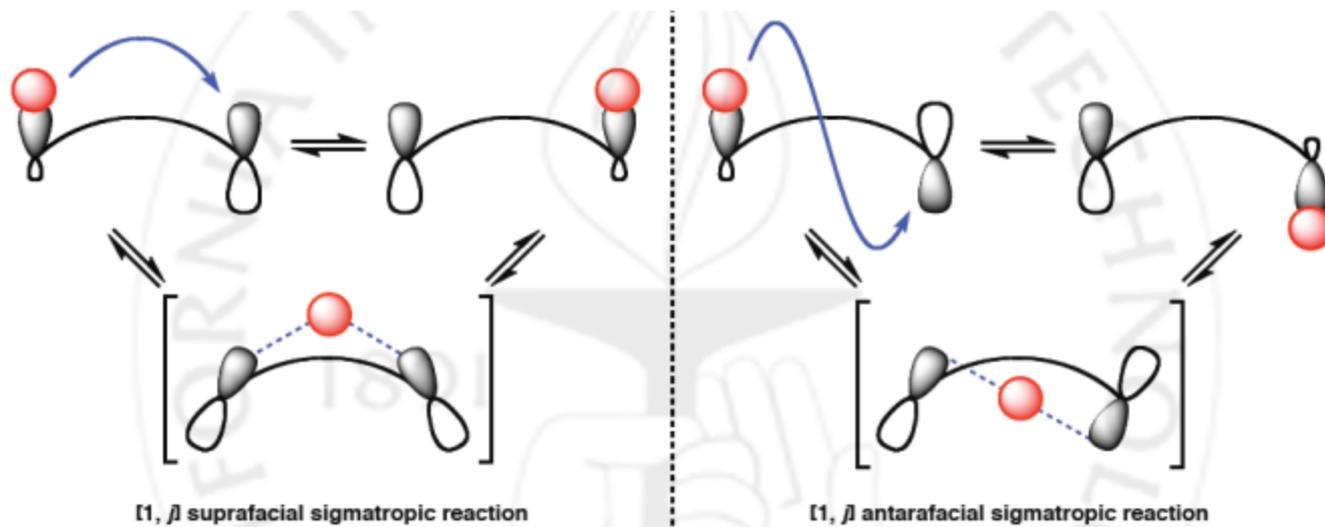
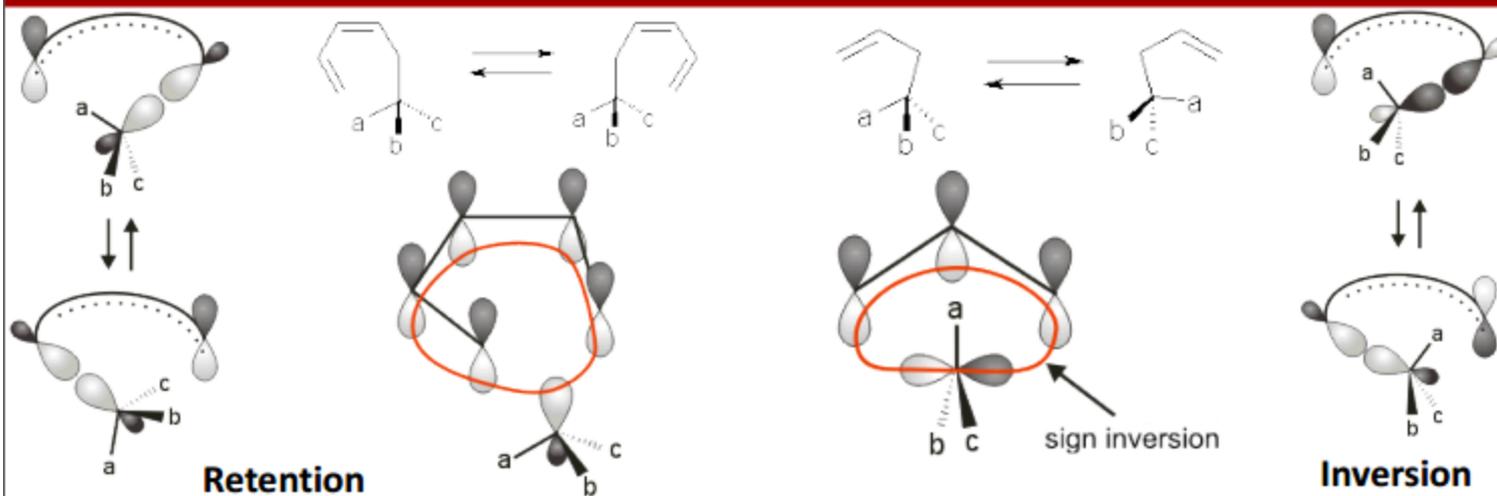
X[C1]C=C1 >> X[C1]C=CC1 (heat)

X	$E_a$	typical temperature range
H	49.7	500–600
Me	48.6	500–600
Ph	44.7	250–300
OMe	41.0	220–250
$F_{\text{disubstituted}}$	40.3	200–225
NMe <sub>2</sub>	31.1	175–200

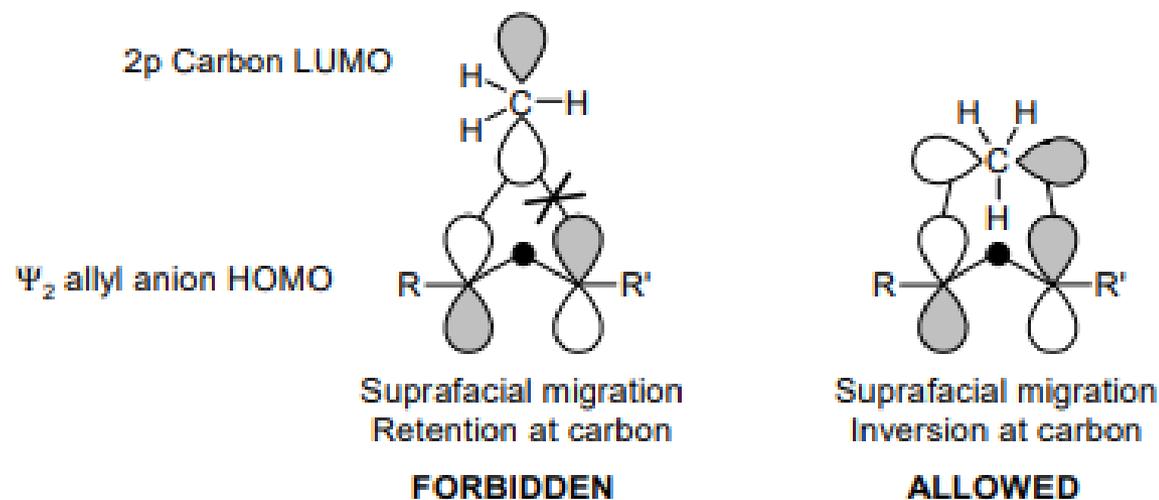
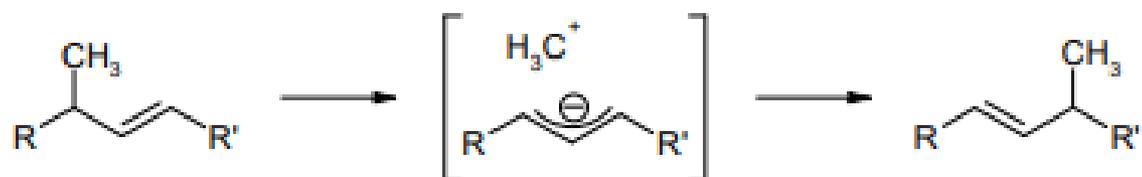
Observing the formation of *ai*- and *sr*-cyclopentene products would support the notion that a stepwise, non-concerted mechanism is operative whereas their absence would point towards a fully concerted mechanism.



# Chemical Reactions-Rearrangement



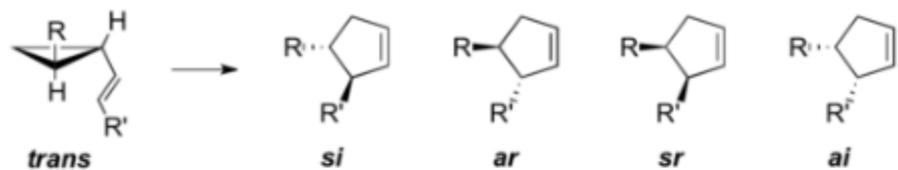
## [1,3] Sigmatropic Rearrangements: C migration



**A summary of the Woodward-Hoffmann rules.**

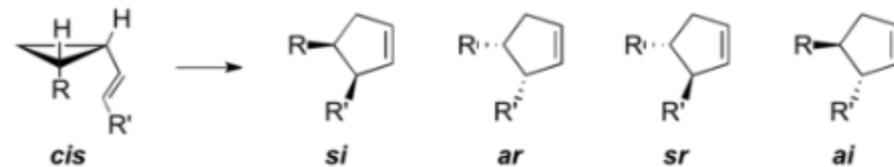
Reaction conditions	Thermal	Photochem.	Thermal	Photochem.
no. electrons	$4n+2$	$4n$	$4n$	$4n+2$
Electrocyclisation	Disrotation Suprafacial	Disrotation Suprafacial	Conrotation Antarafacial	Conrotation Antarafacial
Cycloaddition	Suprafacial	Suprafacial	Antarafacial	Antarafacial
Sigmatropic reactions	Suprafacial	Suprafacial	Antarafacial	Antarafacial

The data clearly indicated that the mechanistic preferences of the rearrangements are system dependent.



Entry	Year	R	R'	<i>si</i> (%)	<i>ar</i> (%)	<i>sr</i> (%)	<i>ai</i> (%)
1	1976	Me	Me	65	8	22	5
2	1977	CN	Me	54	13	11	22
3	1991	Me	D	55	15	18	13
4	1993	Me	Ph	60	10	19	11
5	1994	Ph	Me	44	20	25	11
6	1994	D	D	40	13	23	24
7	1995	Ph	Ph	67	12	17	4
8	1996	Ph- <i>d</i> <sub>5</sub>	D	58	8	24	10

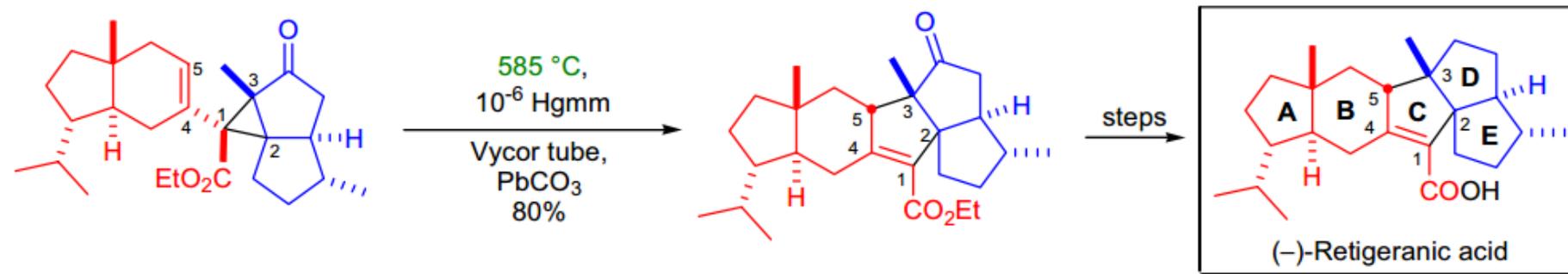
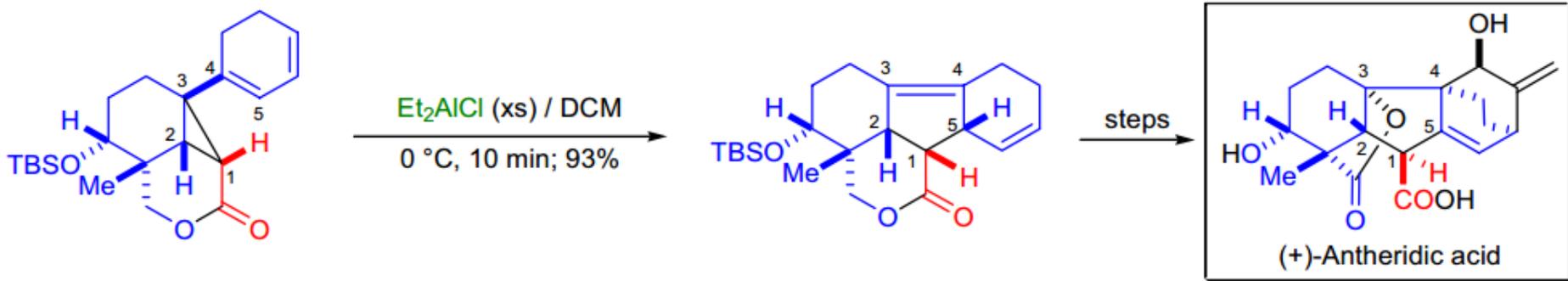
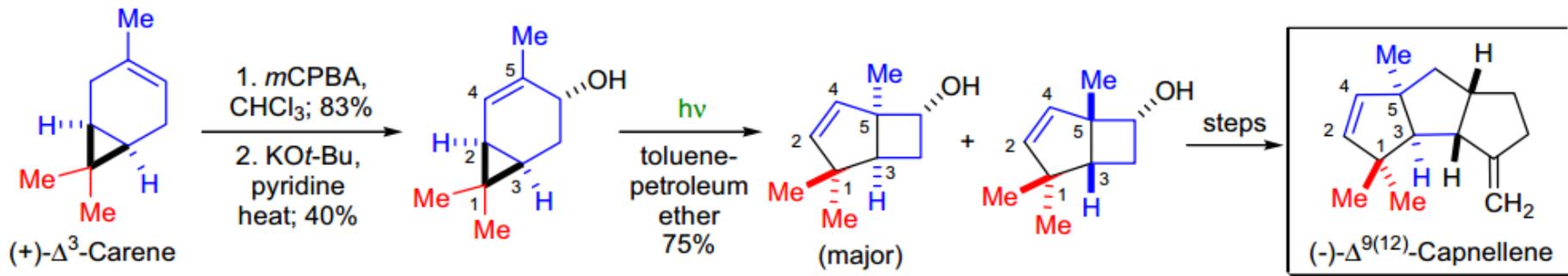
*trans*-vinylcyclopropanes tend to form more of the symmetry-allowed *ar*- and *si*-cyclopentenenes supportive of a concerted mechanism



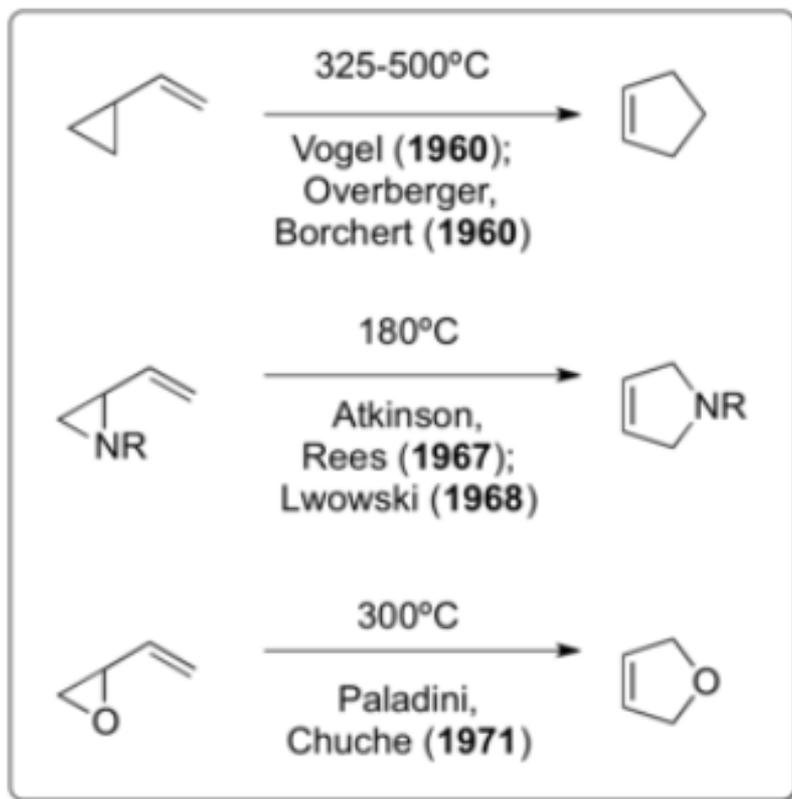
Entry	Year	R	R'	( <i>si</i> + <i>ar</i> ) (%)	( <i>sr</i> + <i>ai</i> ) (%)
9	1977	CN	Me	36	64
10	1994	Ph	Me	10	90
11	1995	Ph	Ph	9	91
12	1996	Ph- <i>d</i> <sub>5</sub>	D	48	52

the *cis*-vinylcyclopropanes preferentially yield the symmetry-forbidden *ai*- and *sr*-products suggesting a more stepwise, diradical mechanism.

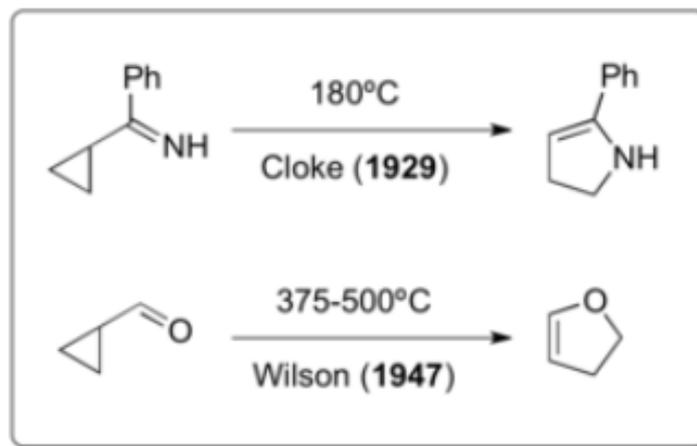
# Synthetic Applications



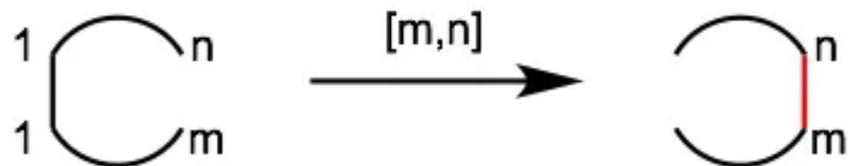
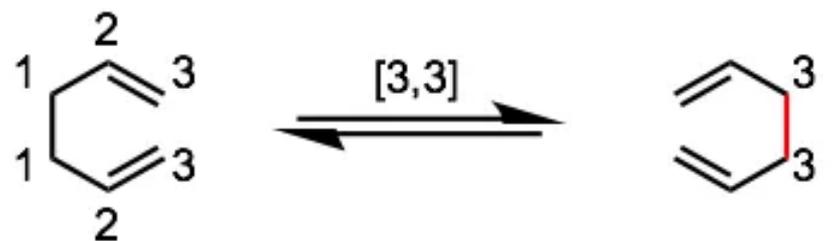
## Related reaction



## Cloke–Wilson Rearrangement

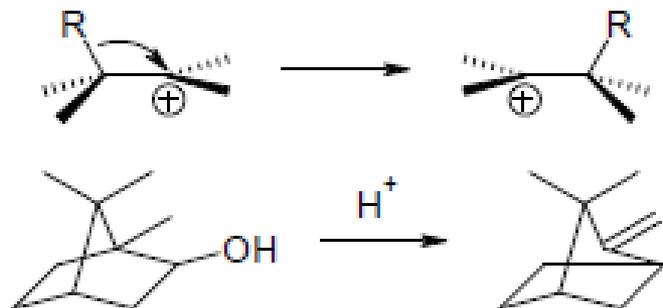


# [m,n] Sigmatropic reaction

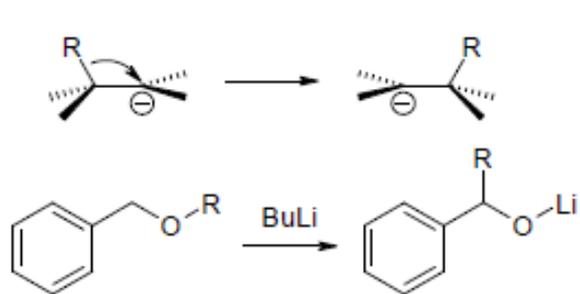


[1,2]-C shift :

Wagner-Meerwein Rearrangement

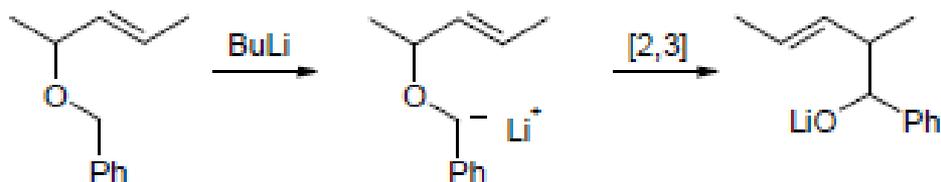


Wittig Rearrangement



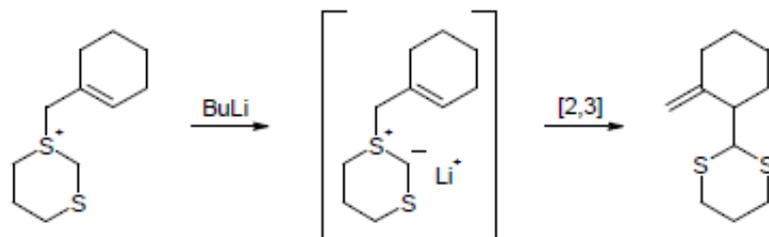
[2,3]-C shift

Wittig Rearrangement<sup>1</sup> (X=O, Y=C)



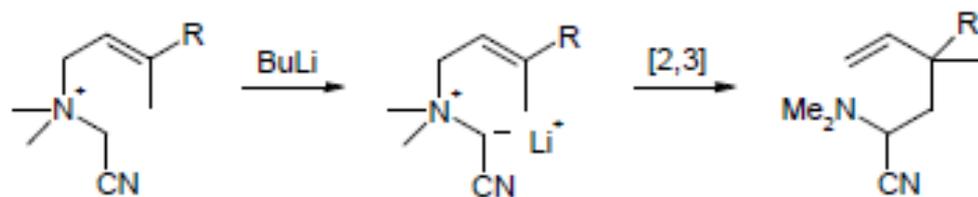
[2,3]-C shift

Sulfonium Ylide Rearrangement<sup>2</sup> (X=S, Y=C)

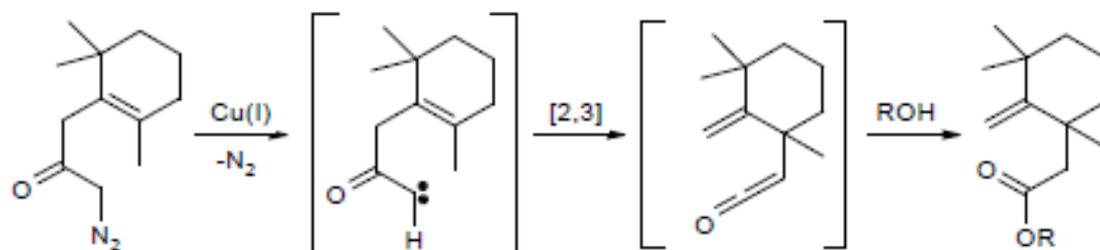


## [2,3]-C shift

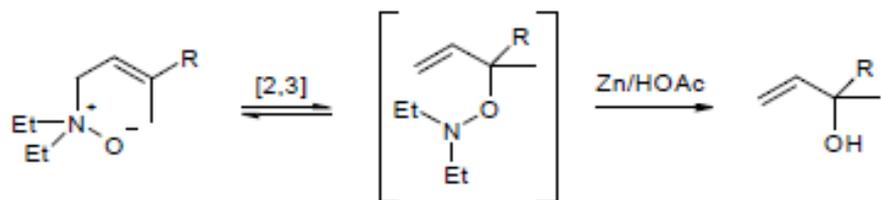
### Ammonium Ylide Rearrangement<sup>3</sup> (Stevens R.) (X=N, Y=C)



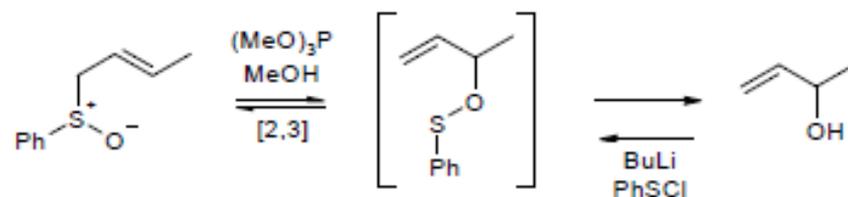
### All-carbon Rearrangement<sup>4</sup> (X=C, Y=C)



### Meisenheimer Rearrangement<sup>5</sup> (X=N, Y=O)

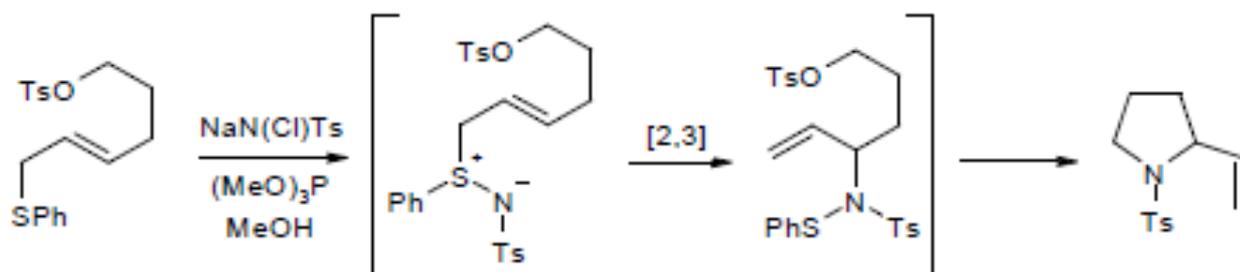
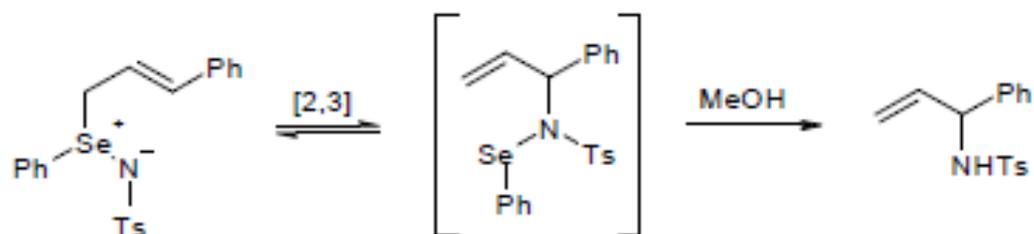


### Sulfoxide Rearrangement<sup>6</sup> (X=S, Y=O)



### Mislow–Evans rearrangement

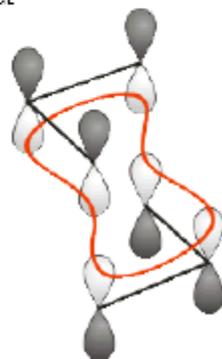
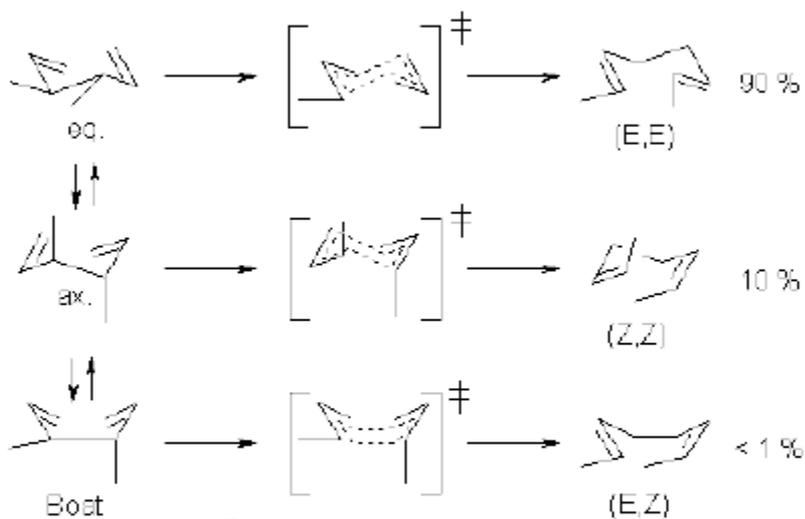
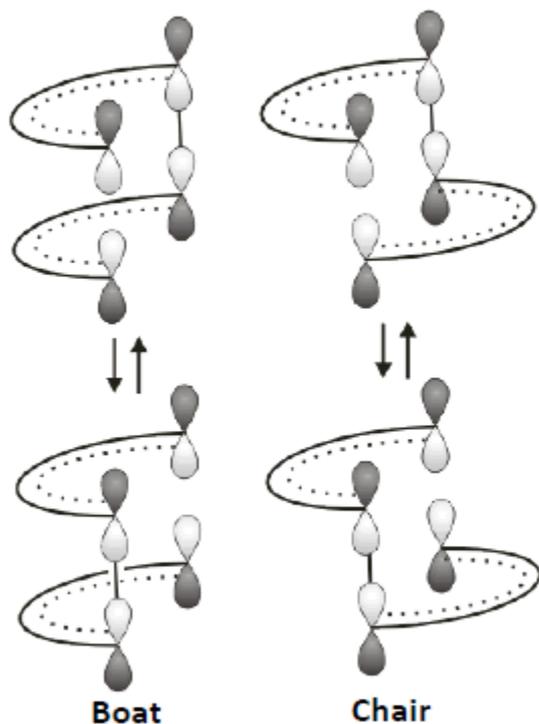
## Related Rearrangements<sup>7,8</sup>



[3,3]-C shift :

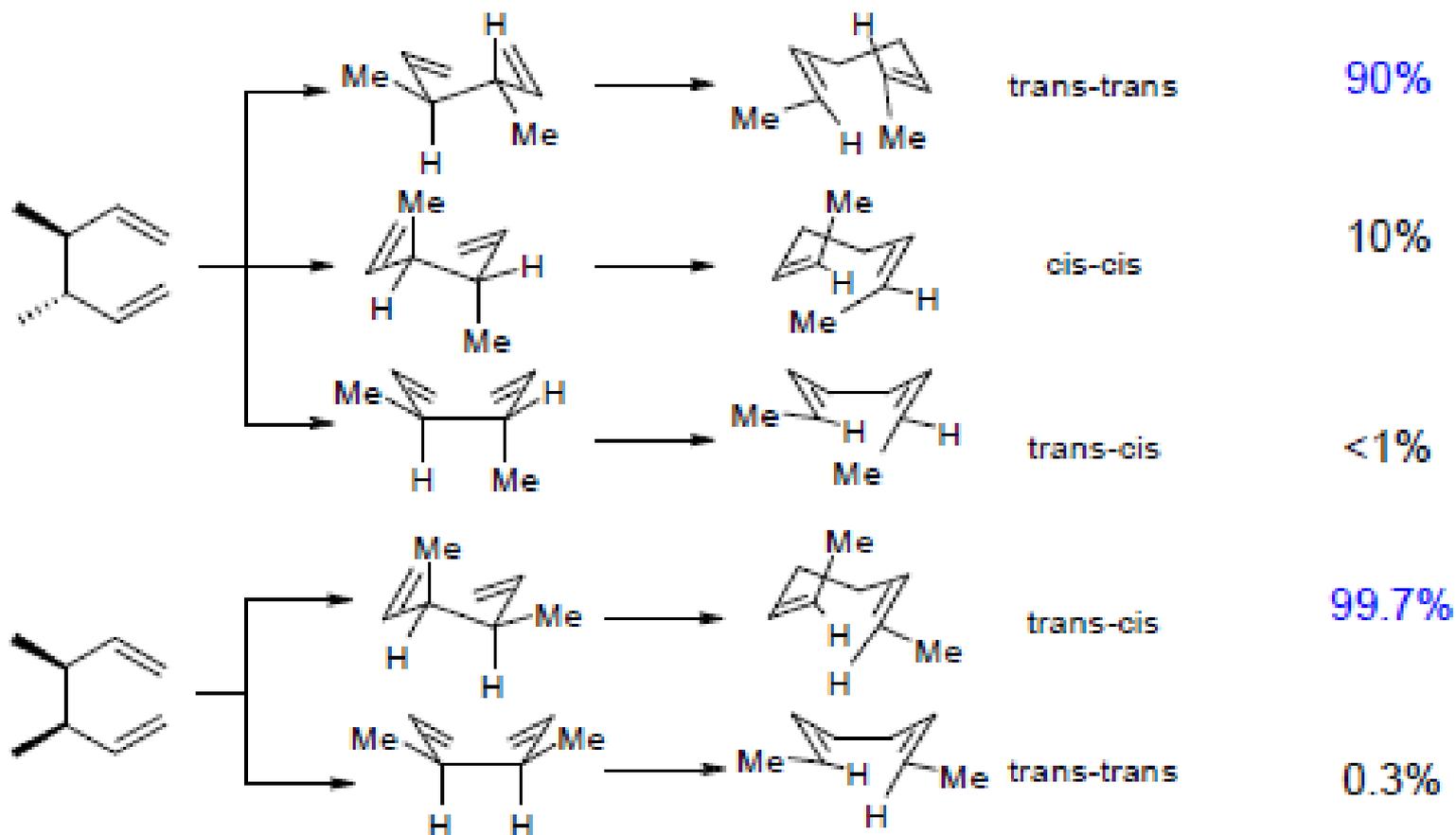
## Chemical Reactions-Rearrangement

Stereochemistry of [n,m] Sigmatropic Rearrangements



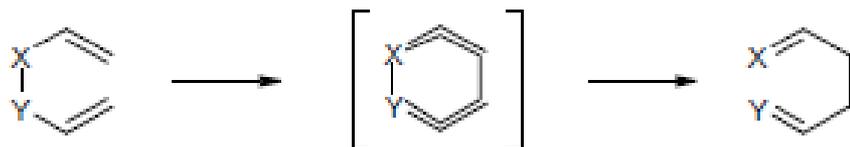
[3,3] Sigmatropic  
•6 Electrons  
•Hückel aromatic  
•Supra-supra

# Cope Rearrangement: Boat vs. Chair Transition State



[3,3]-C shift :

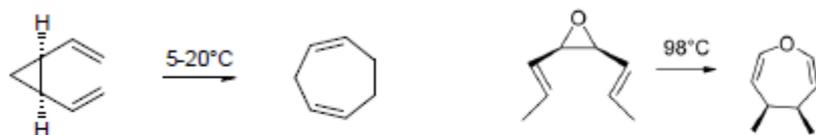
## Cope x Claisen Rearrangement



X, Y = C, O, N, etc

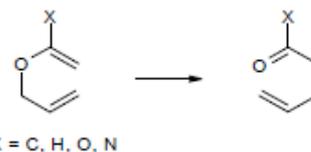


### Cope Rearrangement: Use of ring strain<sup>18</sup>



- Relief of ring strain upon rearrangement

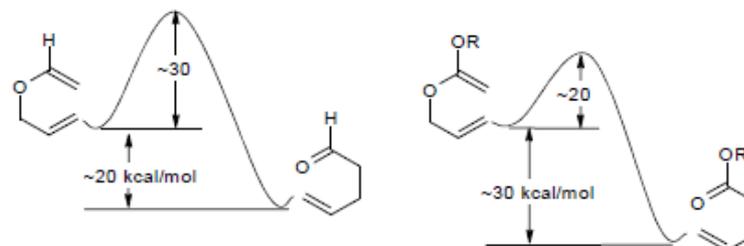
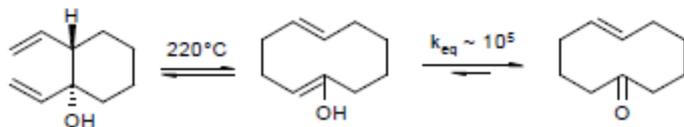
### Claisen Rearrangement



X = C, H, O, N

- Thermodynamic driving force: (C-O)  $\pi$ -bond and (C-C)  $\sigma$ -bond formation
- X=Heteroatom leads to higher exothermicity and reaction rate

### Oxy-Cope Rearrangement<sup>19</sup>

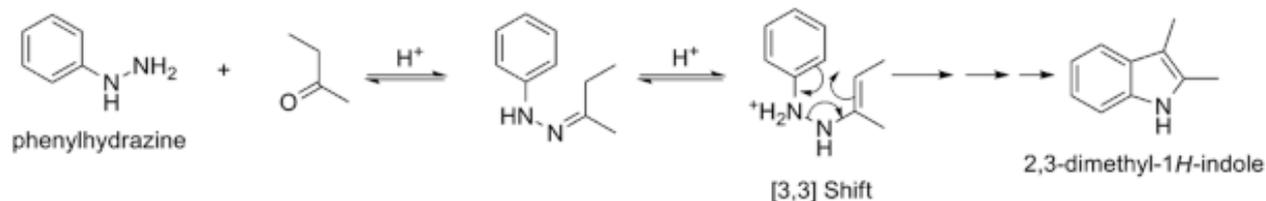




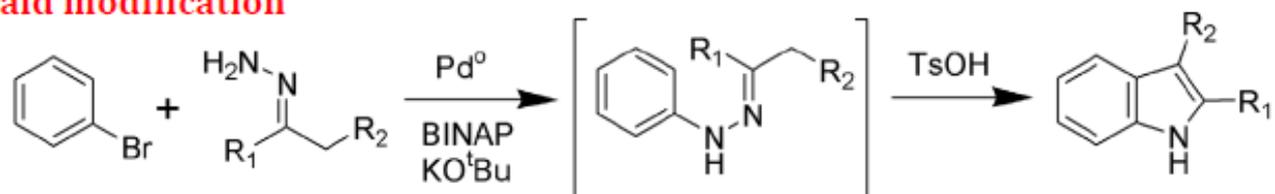
# Chemical Reactions-Rearrangement

## 6-Electron systems, [3,3] sigmatropic- Fischer Indole

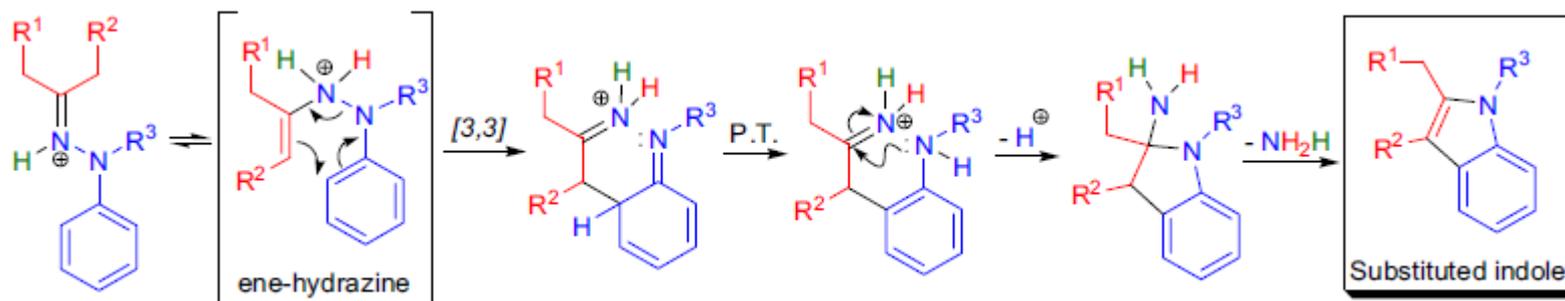
Fischer Indole Synthesis



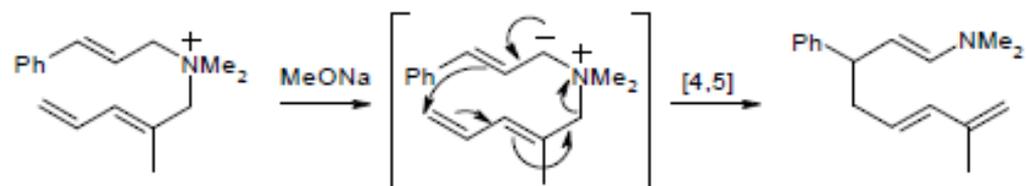
## Buchwald modification



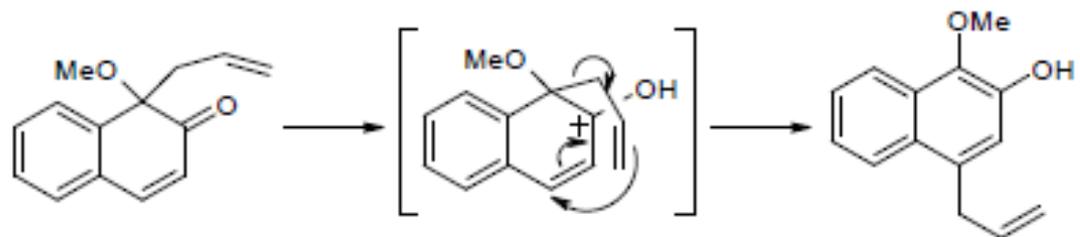
*Journal of the American Chemical Society*, 120 (26): 6621–6622.



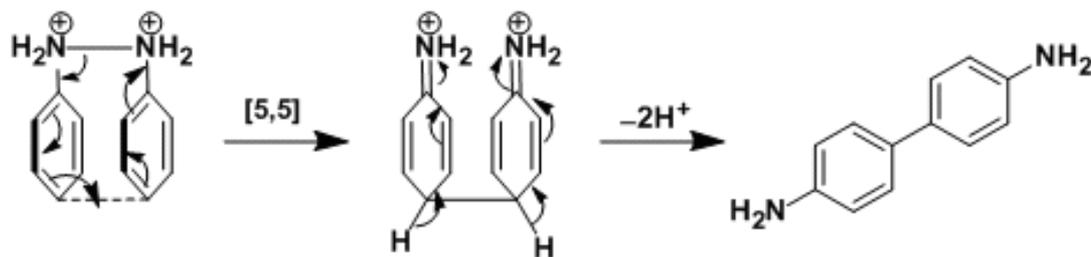
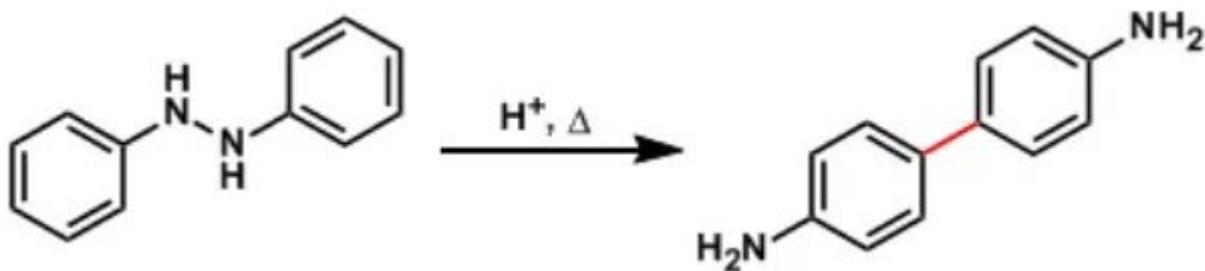
## [4,5]-C shift



## [3,4] shift



## [5,5] Sigmatropic Rearrangements



该化合物进行的是[3,3]- $\sigma$ 键重排反应重排发生在邻位(diazaCope重排)