SECTION 8

Aromaticity

Antiromaticity

Electrocyclic Reaction –

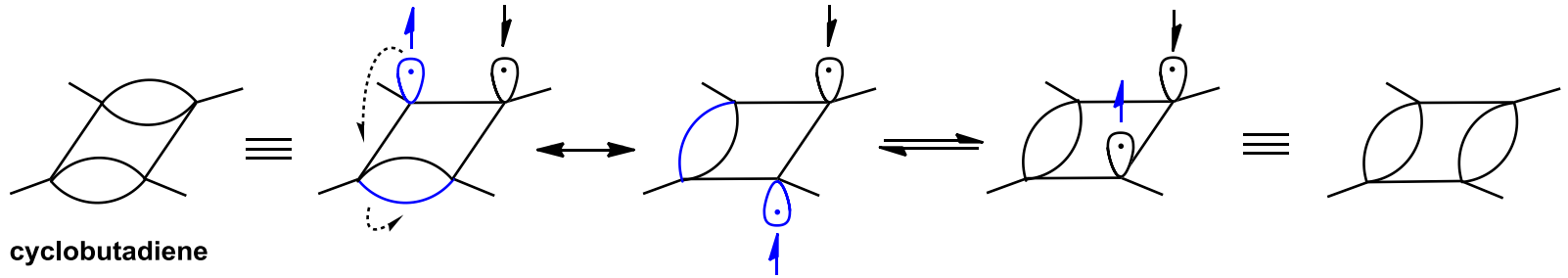
Diels-Alder Reaction

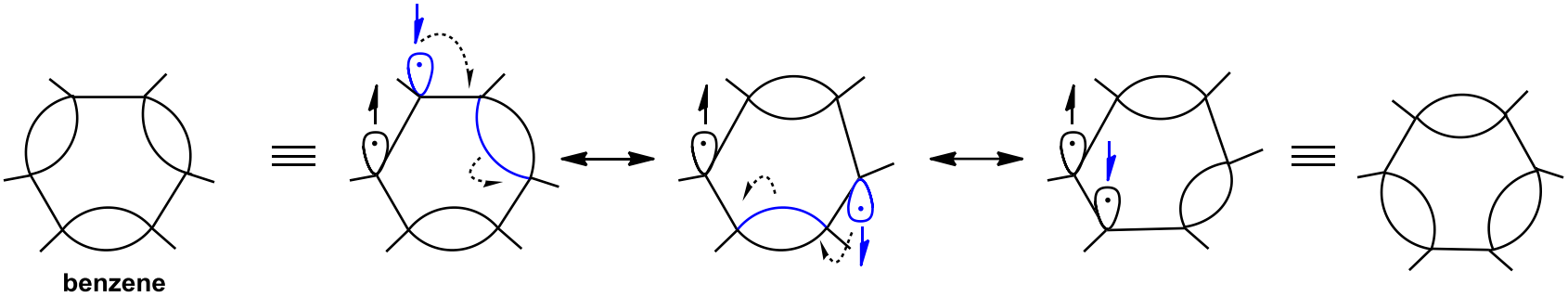
(2018)

G. Deslongchamps, P. Deslongchamps. **Org. Biomol. Chem.** 2011, 9, 5321-5333.

G. Deslongchamps, P. Deslongchamps. **Tetrahedron** 2013, 69, 6022-6033.

Cyclobutadiene and Benzene



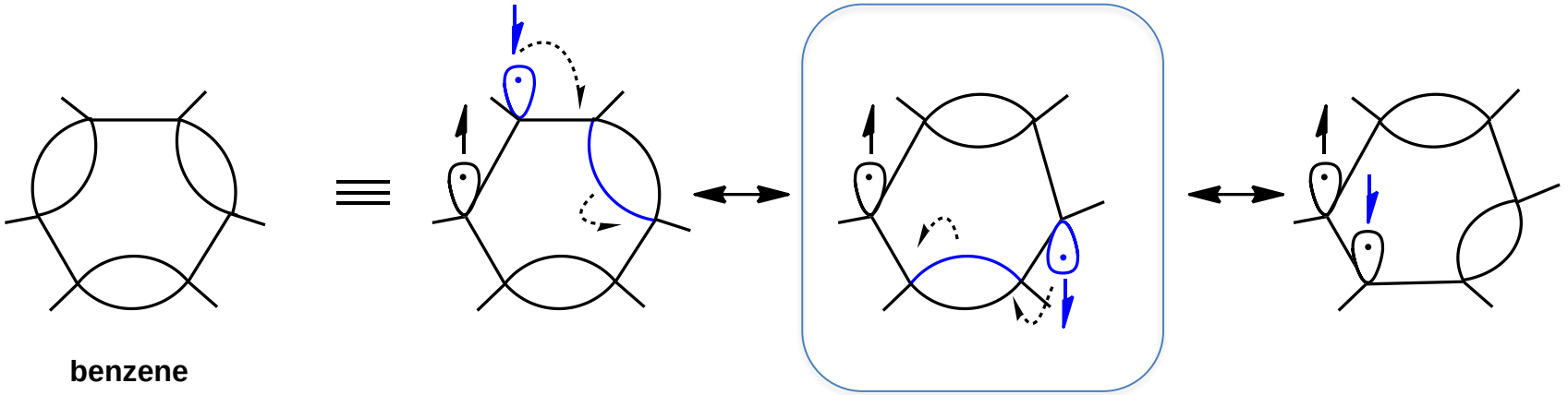


"Based on energetic considerations, the bent bond model serves as a better framework with which to describe the electronic structure in systems exhibiting resonance than the σ,π model"

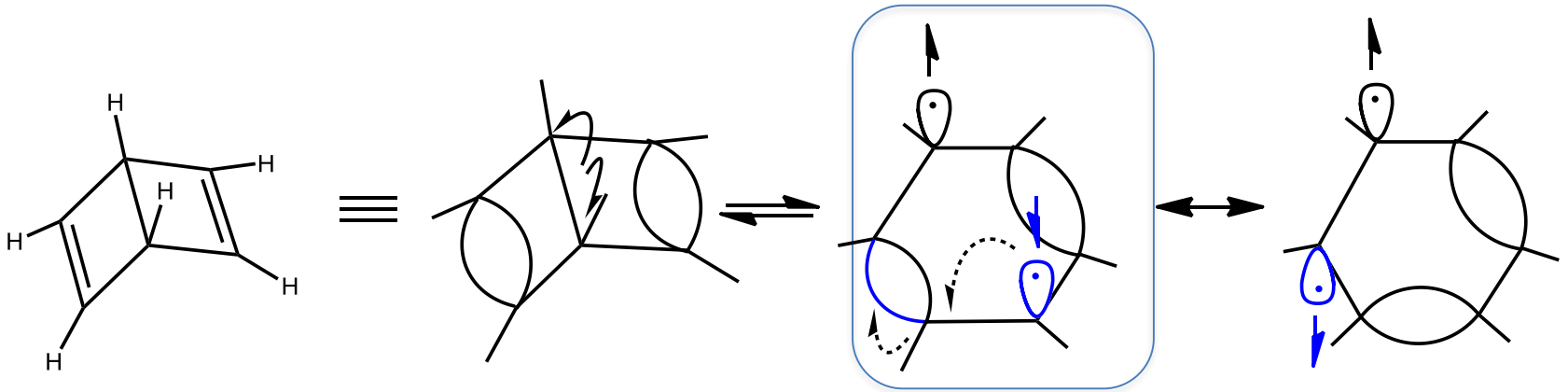
In the Nature of Multiple Bonds: Benzene, Bent Bonds and Resonance.
P. A. Schultz, R. P. Messner. *J. Am. Chem. Soc. Chem*. **1993**, *115*, 10943-10951.

G. Deslongchamps, P. Deslongchamps. *Org. Biomol. Chem*. **2011**, *9*, 5321-5332.

Dewar Benzene and Benzene



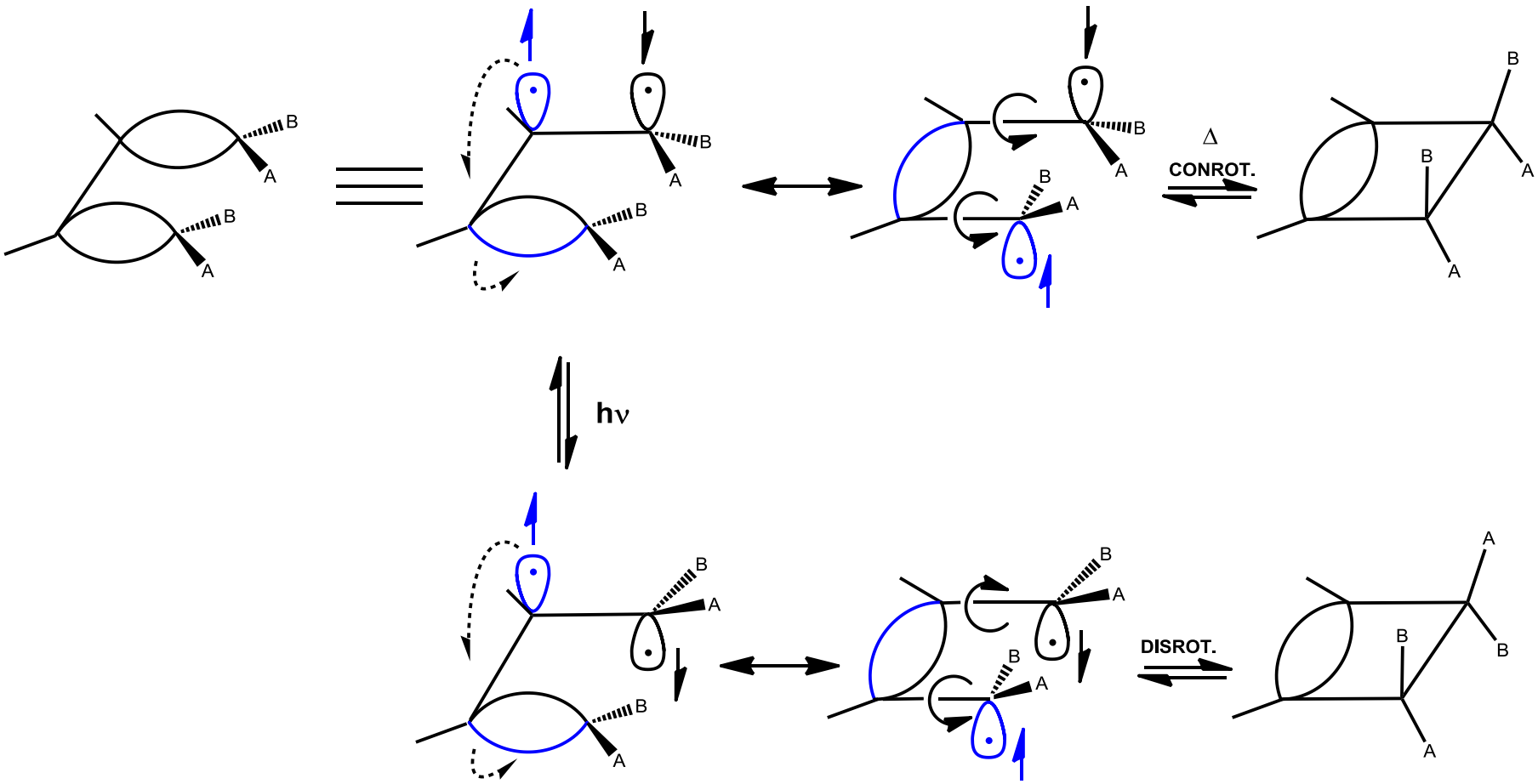
benzene



Dewar benzene

E. E. van Tamelen, S. P. Pappas, K. L. Kirk, *J. Am. Chem. Soc.,* **1971**, *93*, 6092.
G. Deslongchamps, P. Deslongchamps. *Org. Biomol. Chem*. **2011**, *9*, 5321-5332.

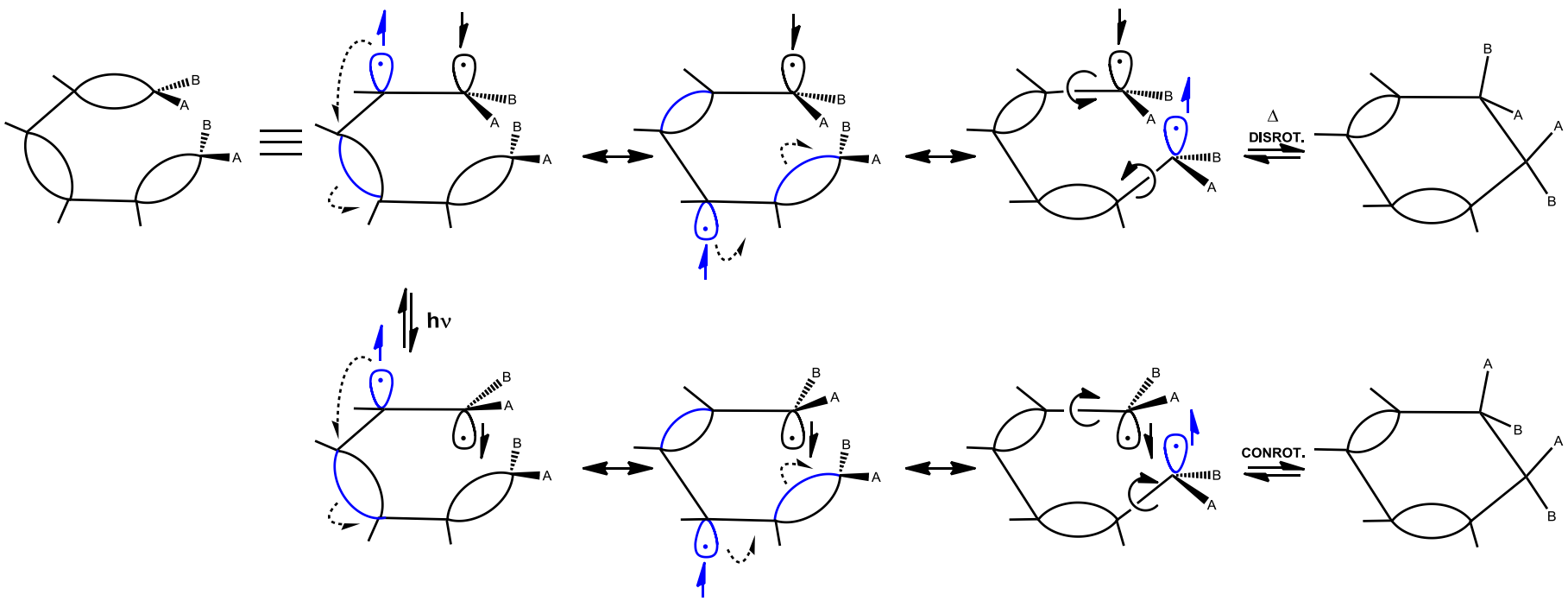
1,3-Butadiene Electrocyclization



R.B. Woodward, R. Hoffman, *J. Am. Chem. Soc.,* **1965**, *87*, 2511.

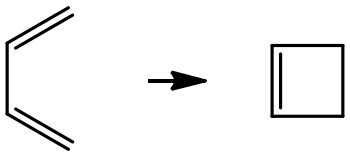
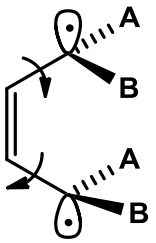
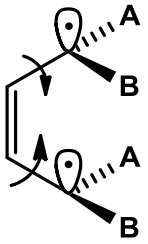
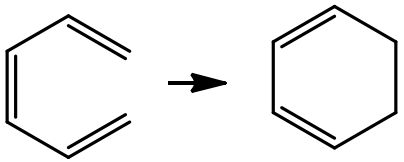
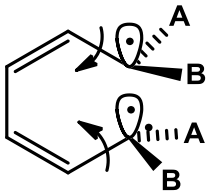
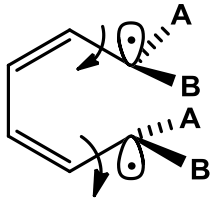
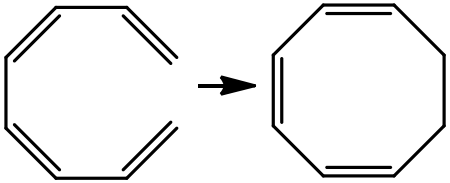
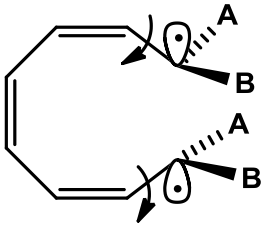
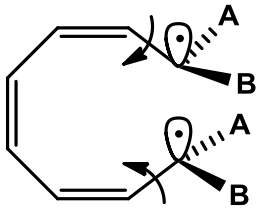
G. Deslongchamps, P. Deslongchamps. *Org. Biomol. Chem*. **2011**, *9*, 5321-5332.

1,3,5-Hexatriene Electrocyclization

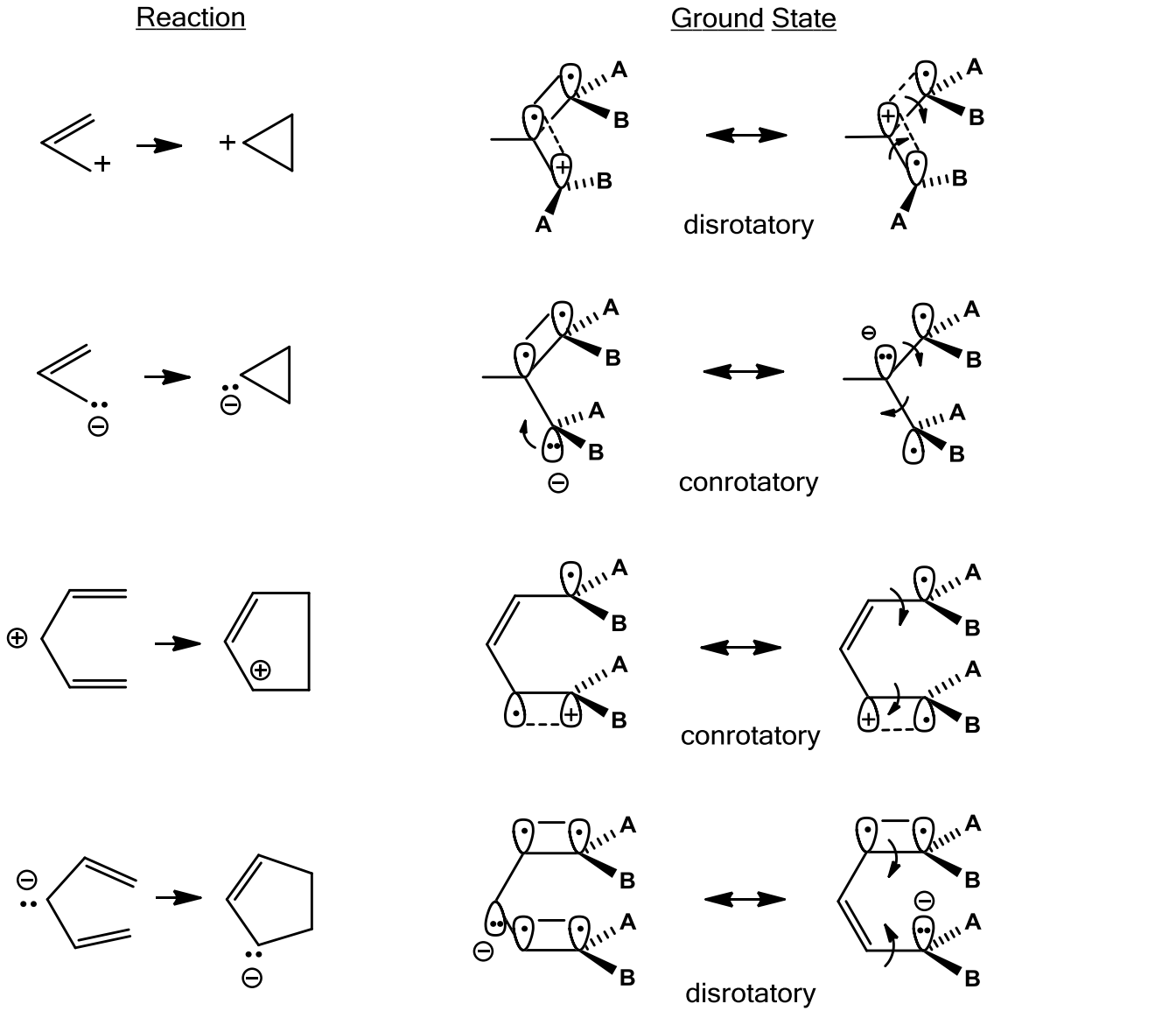


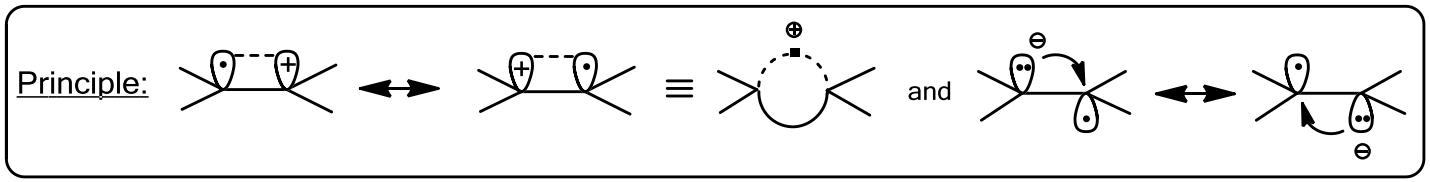
G. Deslongchamps, P. Deslongchamps. *Org. Biomol. Chem*. **2011**, *9*, 5321-5332.

Conrotatory and Disrotatory Electrocyclic Reactions (1)

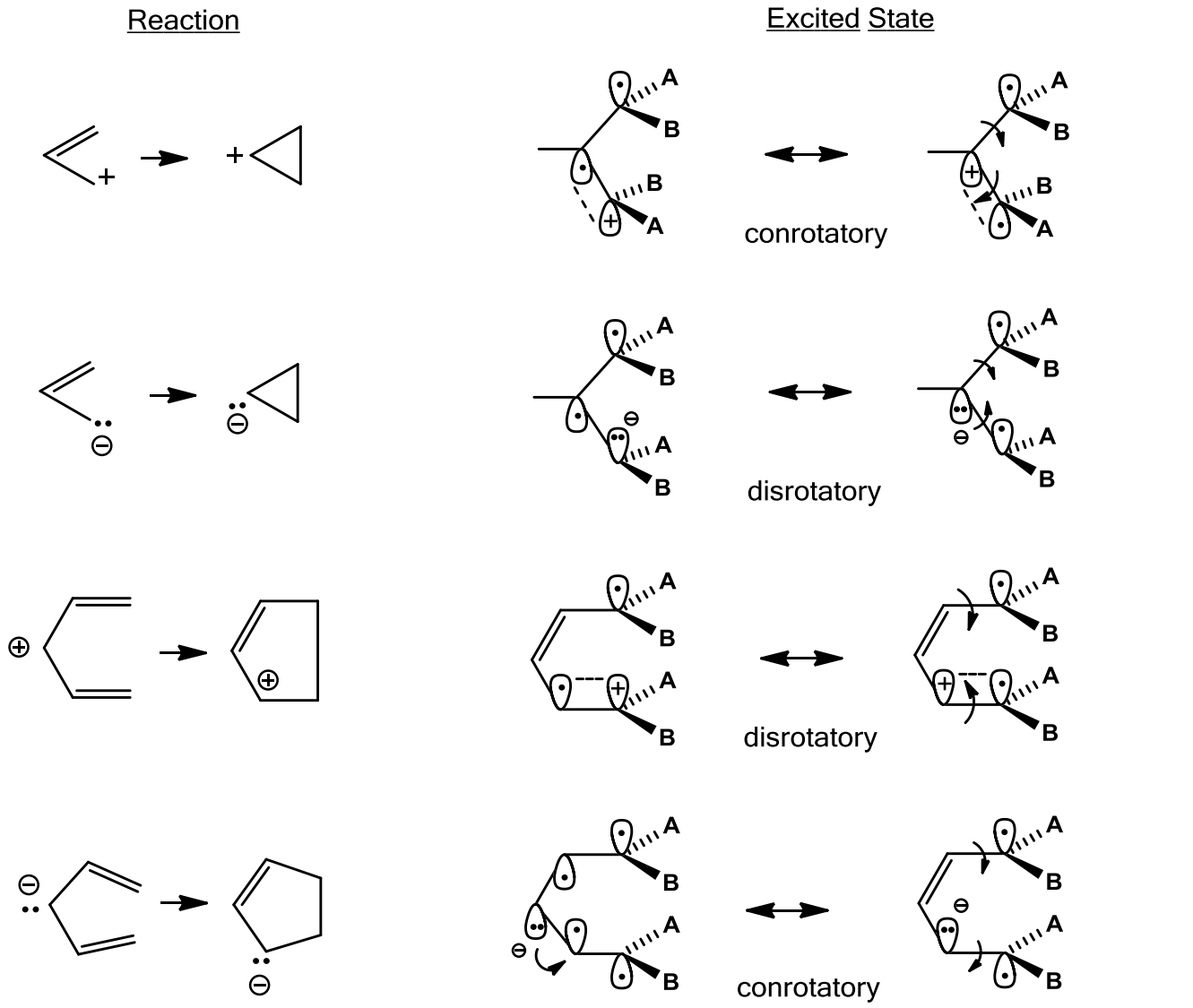
Reaction	Ground State	Excited State
	 conrotatory	 disrotatory
	 disrotatory	 conrotatory
	 conrotatory	 disrotatory

Conrotatory and Disrotatory Electrocyclic Reactions (2)

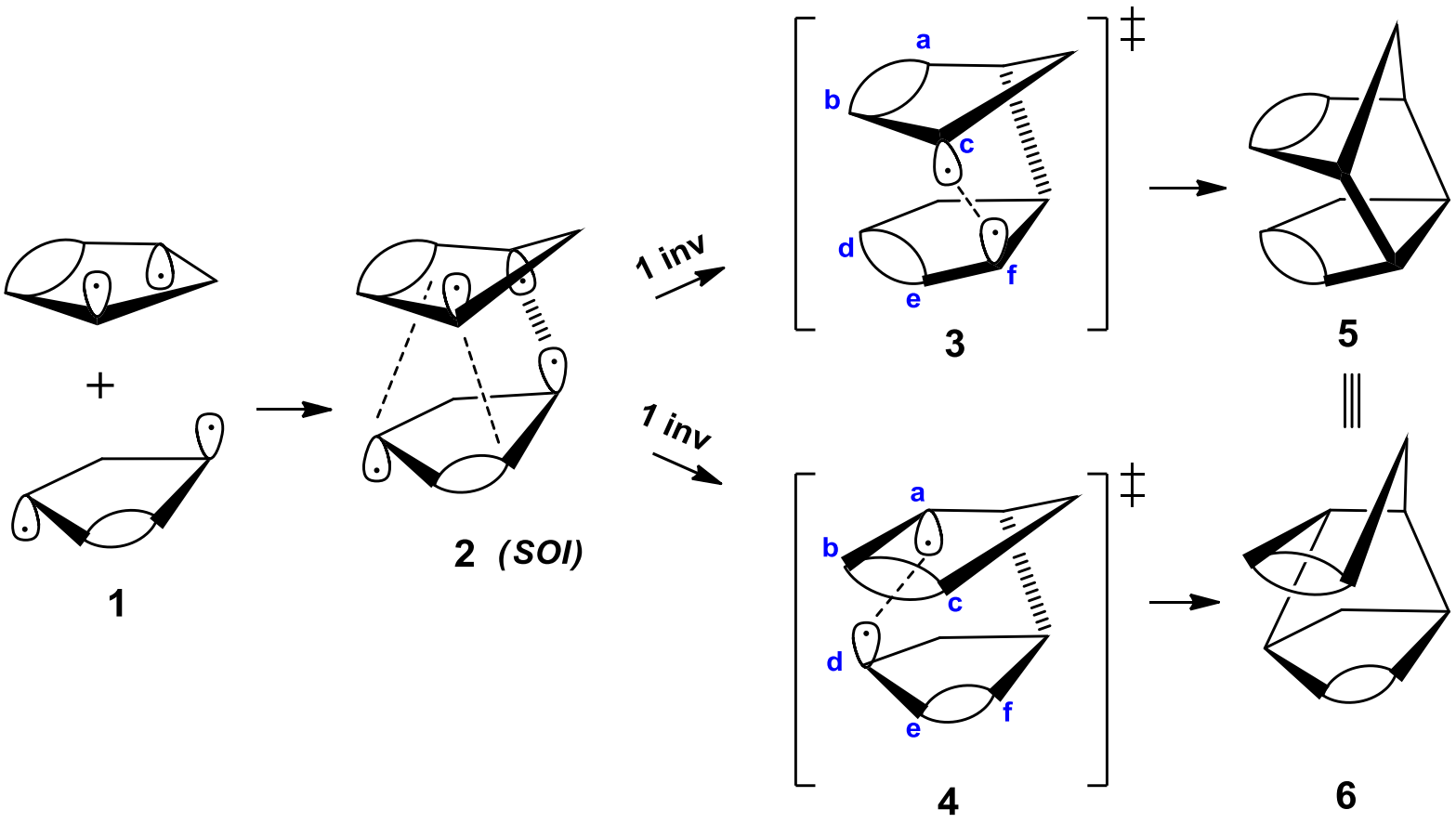




Conrotatory and Disrotatory Electrocyclic Reactions (3)

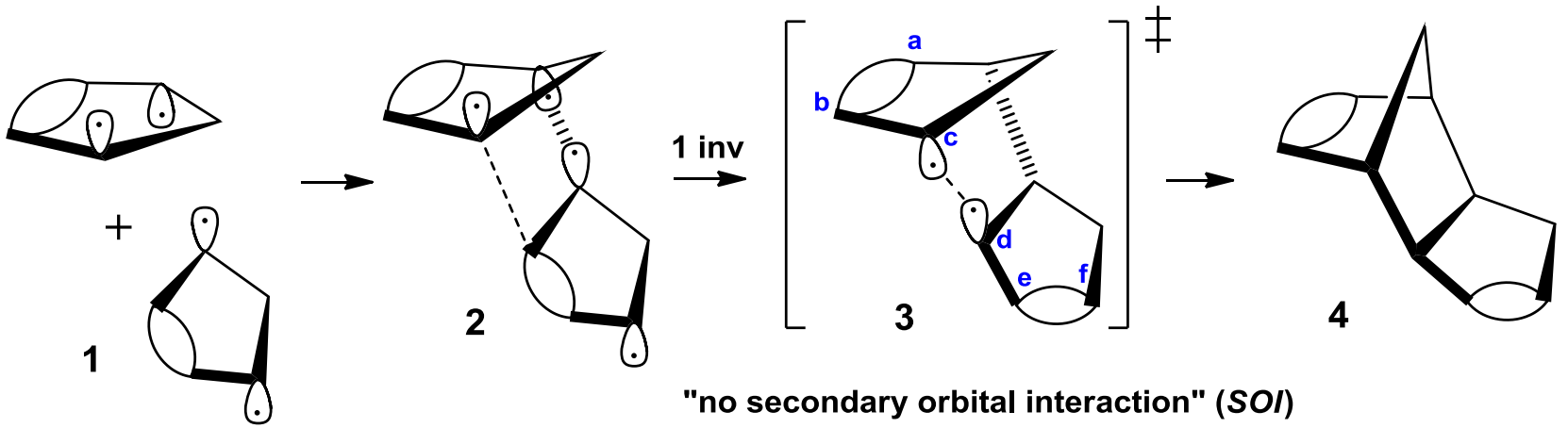


Endo Dimerization of Cyclopentadiene



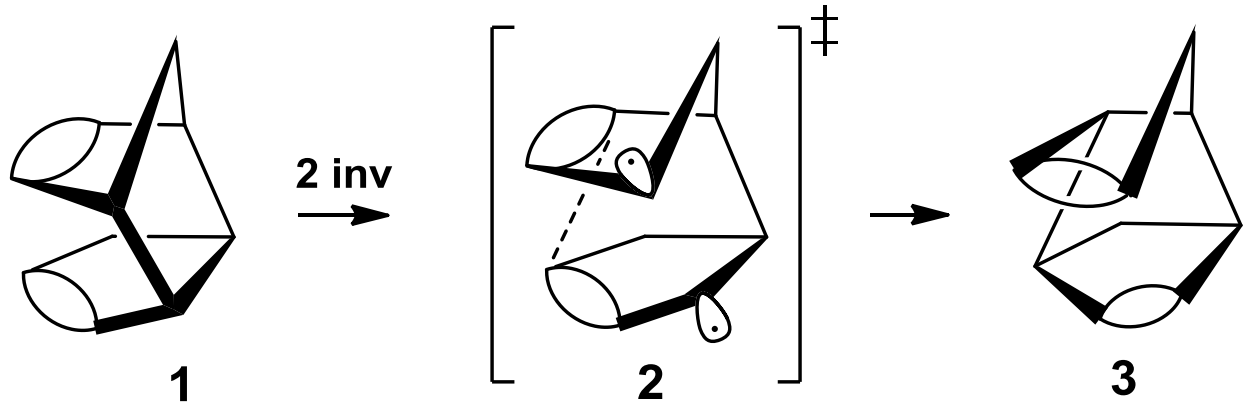
P. Caramella, P. Quadrelli, L. Toma. *J. Am. Chem. Soc.* **2002**, *124*, 1130-1132.
C. S. Wannere, A. Paul, R. Herges, K. N. Houk, H. F. Schaefer, P. von Ragué Schleyer, P. *J. Comput. Chem.* **2006**, *28*, 344-361.
G. Deslongchamps, P. Deslongchamps. *Tetrahedron* **2013**, *69*, 6022-6033.

Exo Dimerization of Cyclopentadiene



G. Deslongchamps, P. Deslongchamps. *Tetrahedron* **2013**, *69*, 6022-6033.

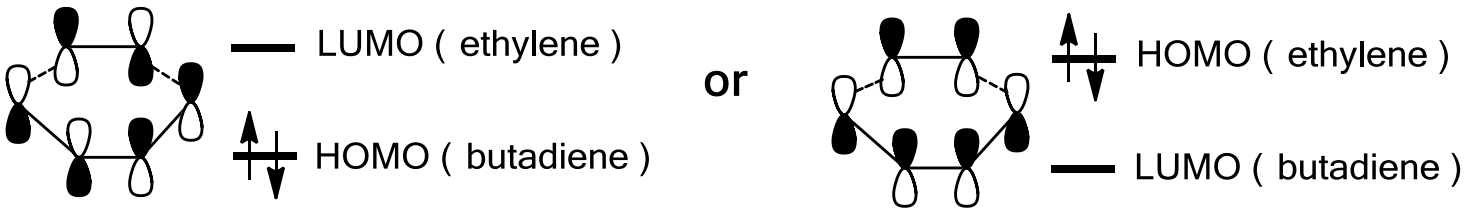
Bent Bond Model for Cope Rearrangement



R. B. Woodward, T. J. Katz. *Tetrahedron* **1959**, *5*, 70-89 .
G. Deslongchamps, P. Deslongchamps. *Tetrahedron* **2013**, *69*, 6022-6033.

Bent Bonds and the Antiperiplanar Hypothesis – A Simple Model to Predict Diels-Alder Reactivity

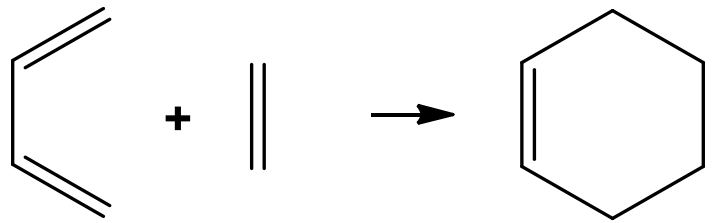
Diels-Alder : $\sigma-\pi$ and FMO Theory



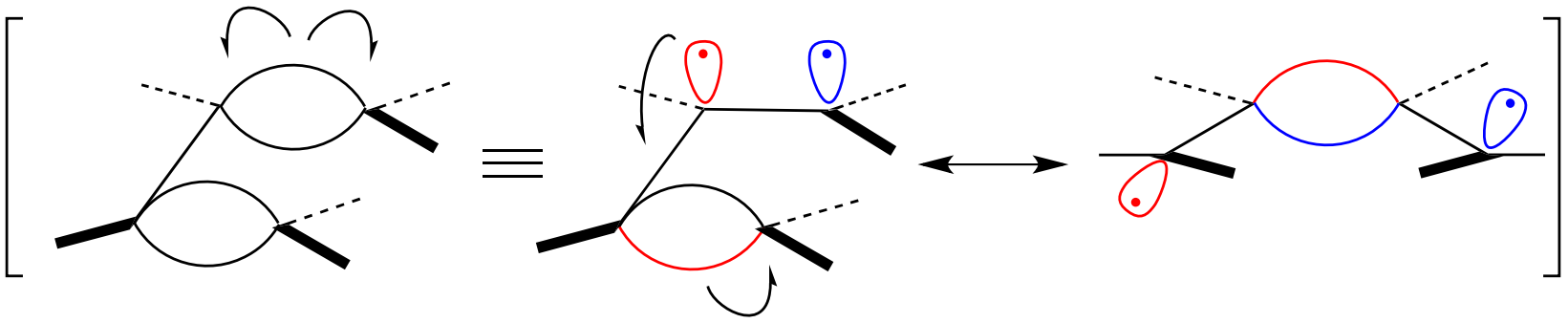
N.B. Either way, interaction of a HOMO and LUMO of ethylene and butadiene can occur because of the phasing matches

HOMO = Highest Occupied Molecular Orbital
LUMO = Lowest Unoccupied Molecular Orbital

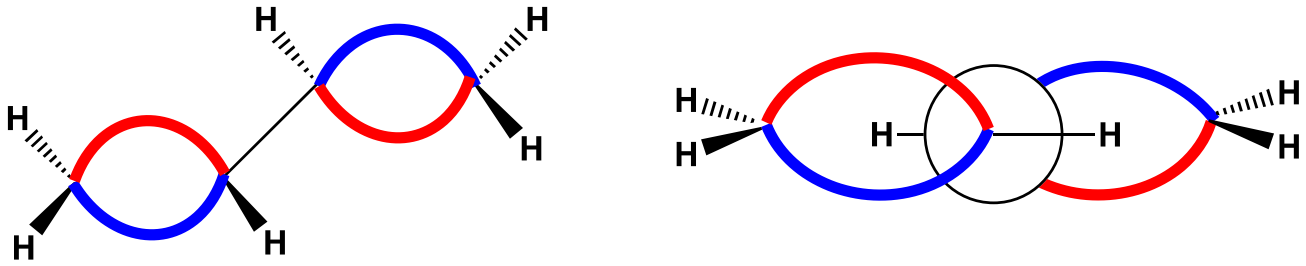
Resonance Structures for *s-cis* 1,3-Dienes



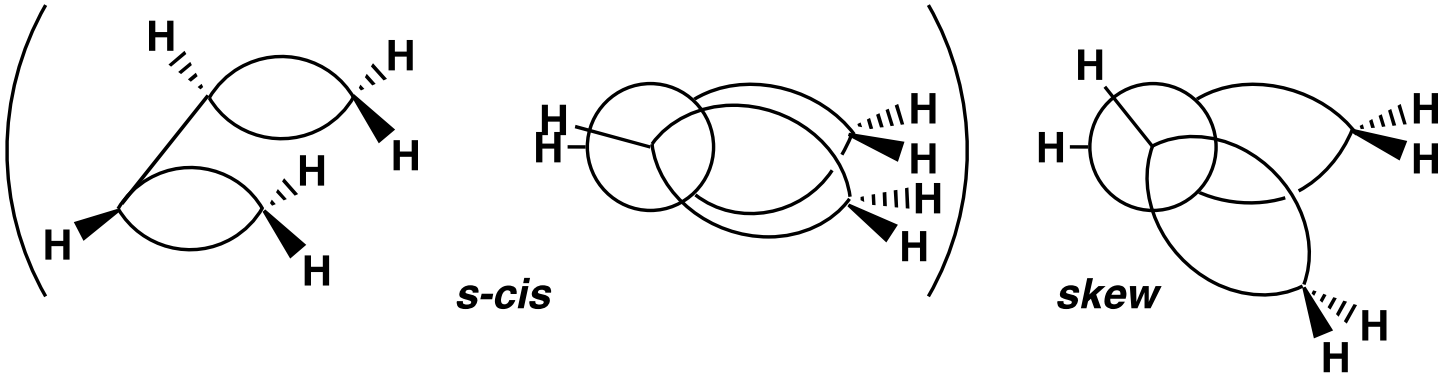
diene dienophile D.A. adduct



S-trans 1,3-Butadiene in Perspective View (left) and Newman Projection (right)



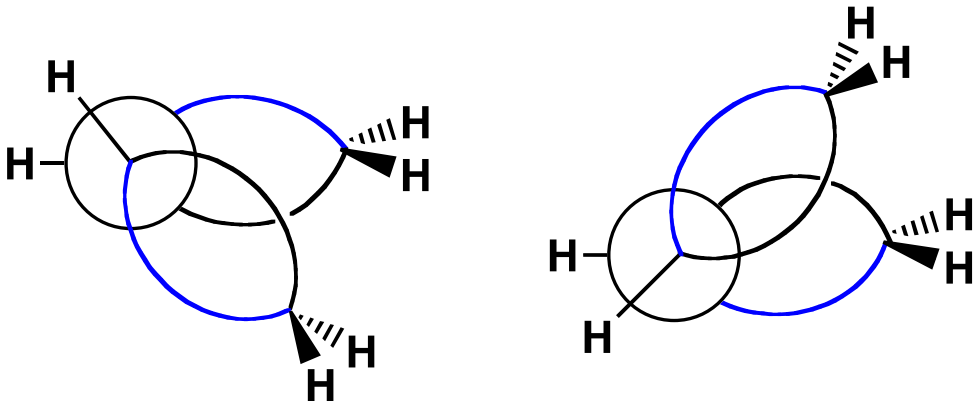
Bent Bond Models of *s-cis* (left) and *skew* (right) 1,3-Butadiene



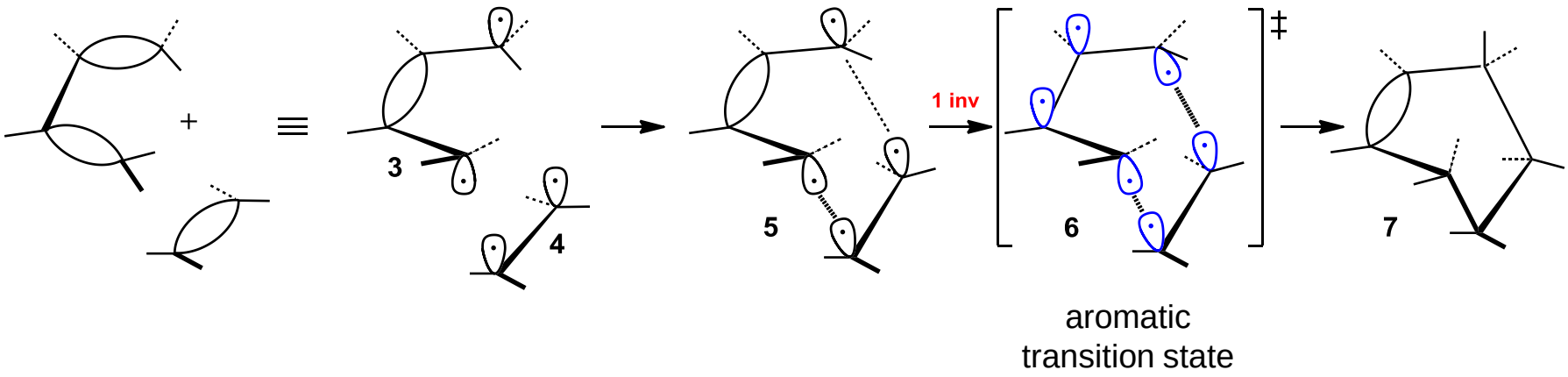
M. E. Squillacote, R. S. Sheridan, O. L. Chapman, F. A. L. Anet, *J. Am. Chem. Soc.,* **1979**, *101*, 3657-3659.

M. C. McCarthy *et al. J. Am. Chem. Soc.,* **2018**, *57*, 1821-1825.

Bent Bond Models of *Skew* 1,3-Butadiene Viewed as Newman Projections



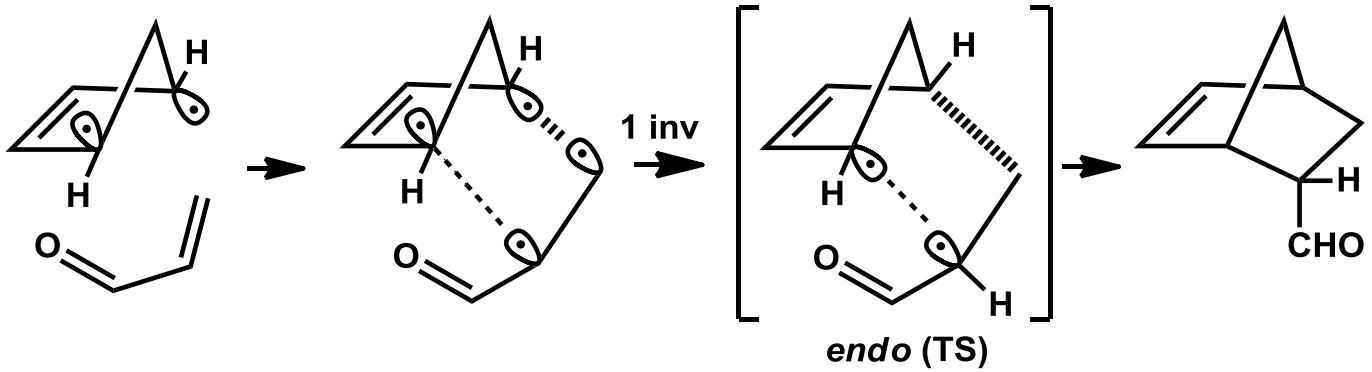
Bent-Bond Model for Cycloaddition of *s-cis* 1,3-Butadiene with Ethylene



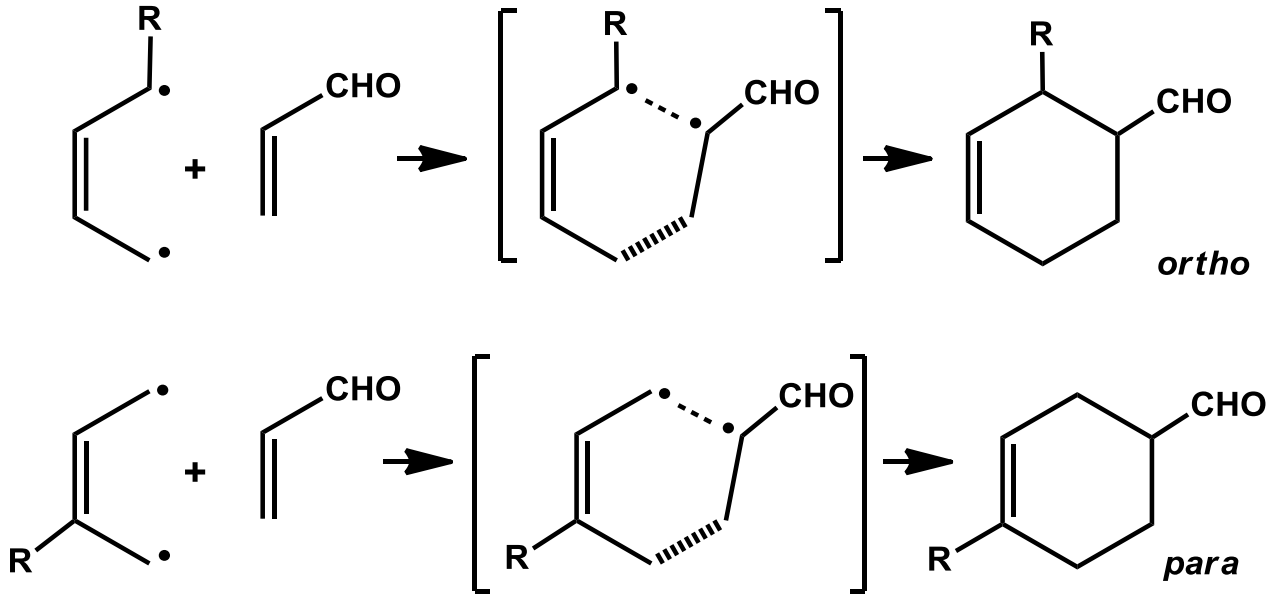
M. G. Evans, E. Warhurst, *Trans. Faraday Soc*., **1938**, *34*, 614-624.
M. G. Evans, *Trans. Faraday Soc*., **1939**, *35*, 824-834.
M. J. S. Dewar, *Angew. Chem. Int. Ed. Engl.,* **1971**, *10*, 761-776.
G. Deslongchamps, P. Deslongchamps. *Tetrahedron* **2013**, *69*, 6022-6033.

S-cis Diene and Acrolein Diels-Alder

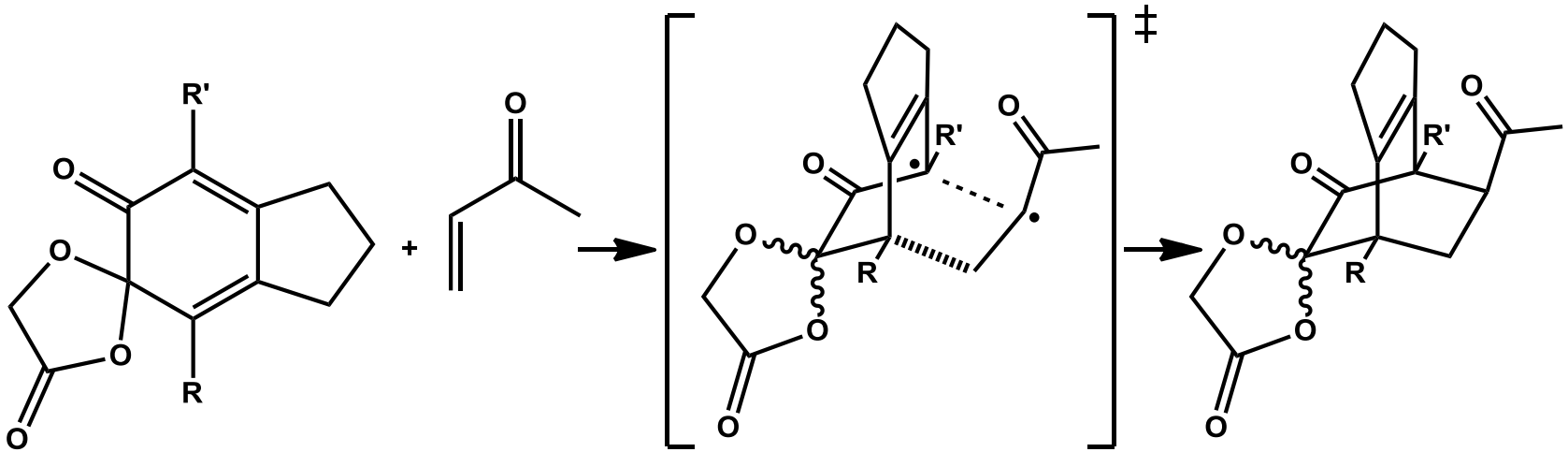
with cyclopentadiene



with 1-alkyl and 2-alkyl butadiene (*ortho* and *para* rules)



Masked *ortho*-Benzoquinones as Diels-Alder Dienes and Asynchronicity



1: R = H, R' = CH_3 (15x faster)

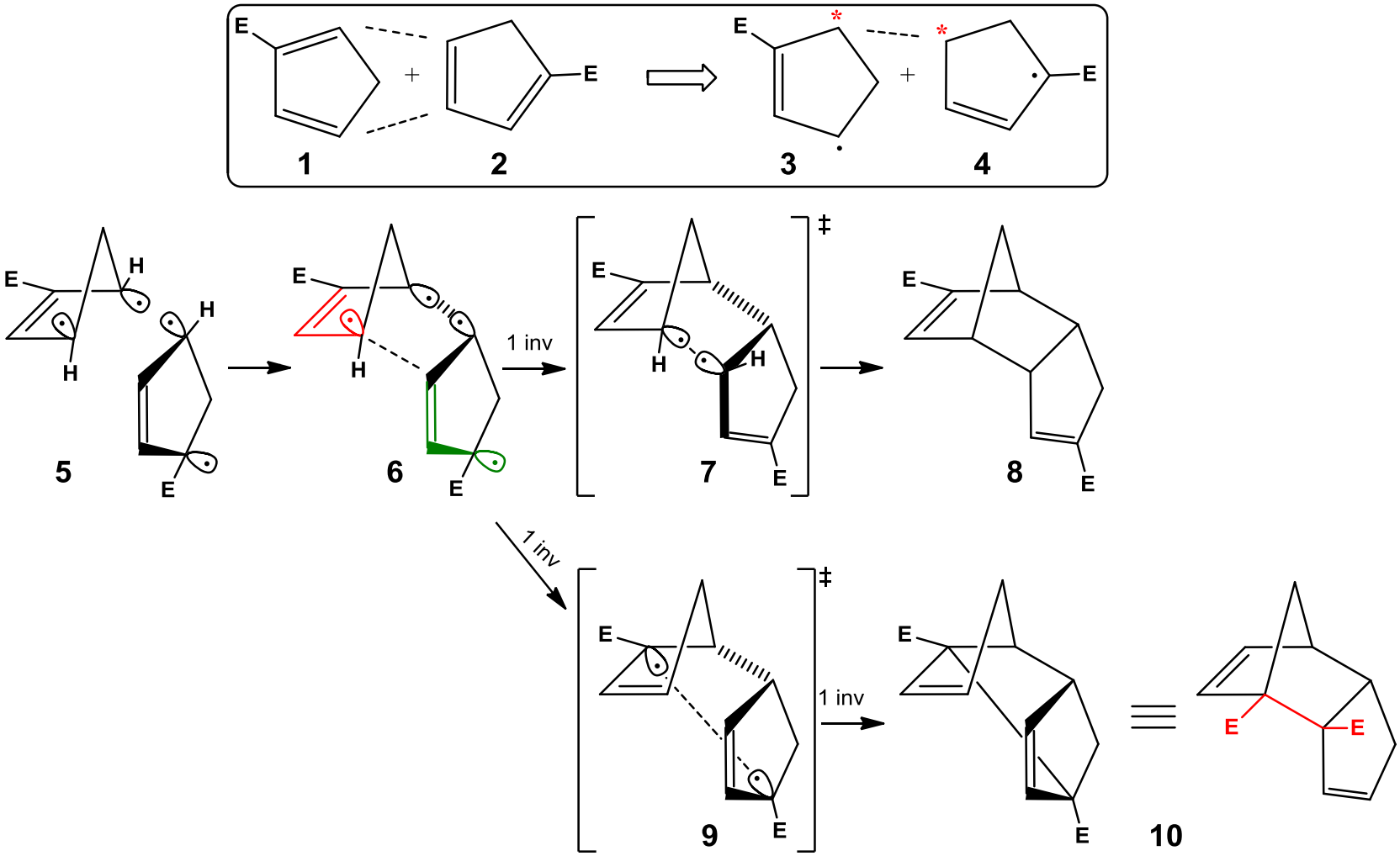
2: R = CH_3, R' = H

3

4

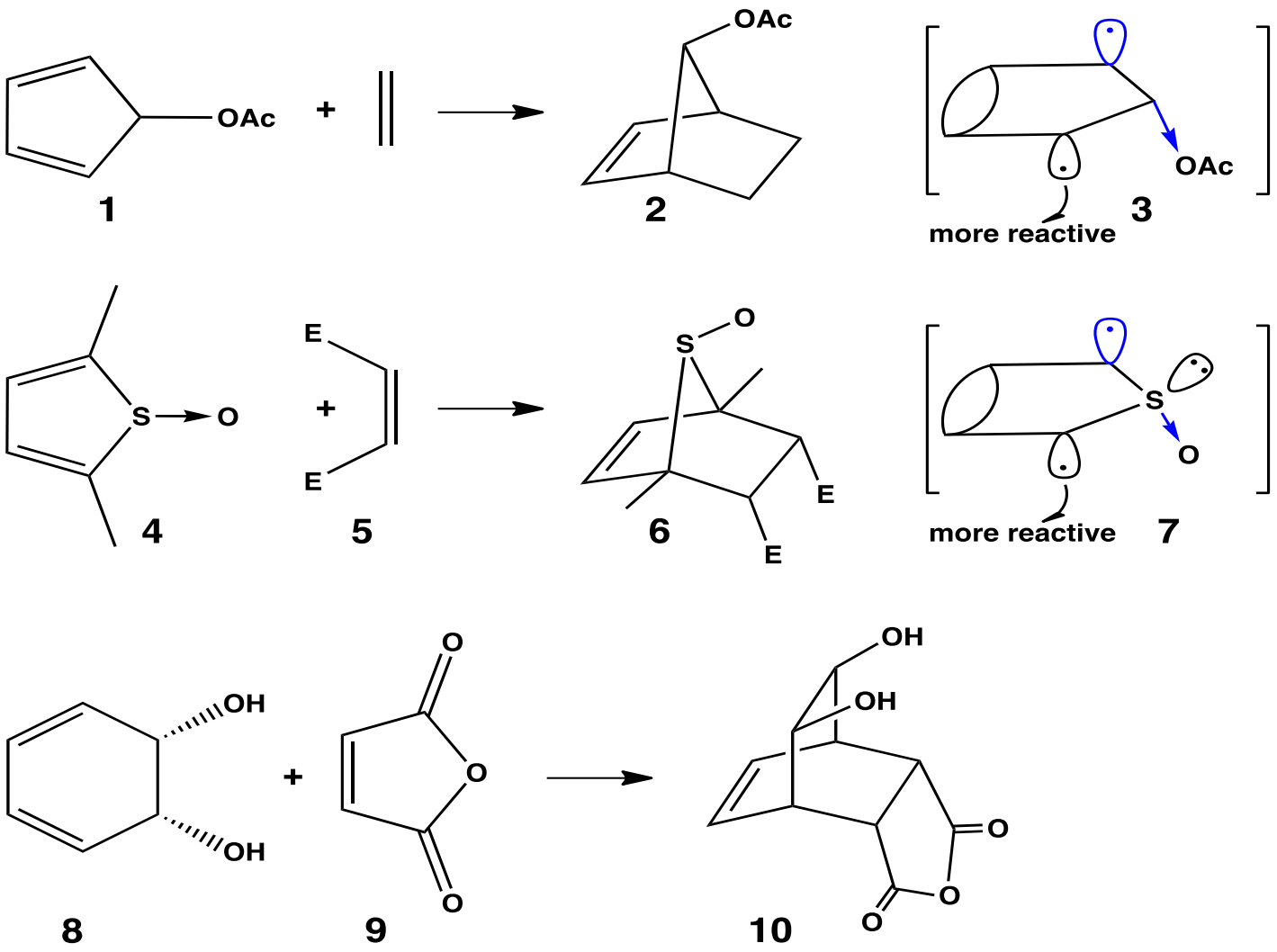
Y. L. Dory, A. L. Roy, P. Soucy, P. Deslongchamps, *Org. Lett.,* **2009**, *11,* 1197-1200.

Formation of Thiele's Acid (E = CO_2H)



J. Thiele. *Chem. Ber.* **1901**, *1*, 68-71.
G. Deslongchamps, P. Deslongchamps. *Tetrahedron* **2013**, *69*, 6022-6033.

Resonance Structures Decide Facial Selectivity of Dienes

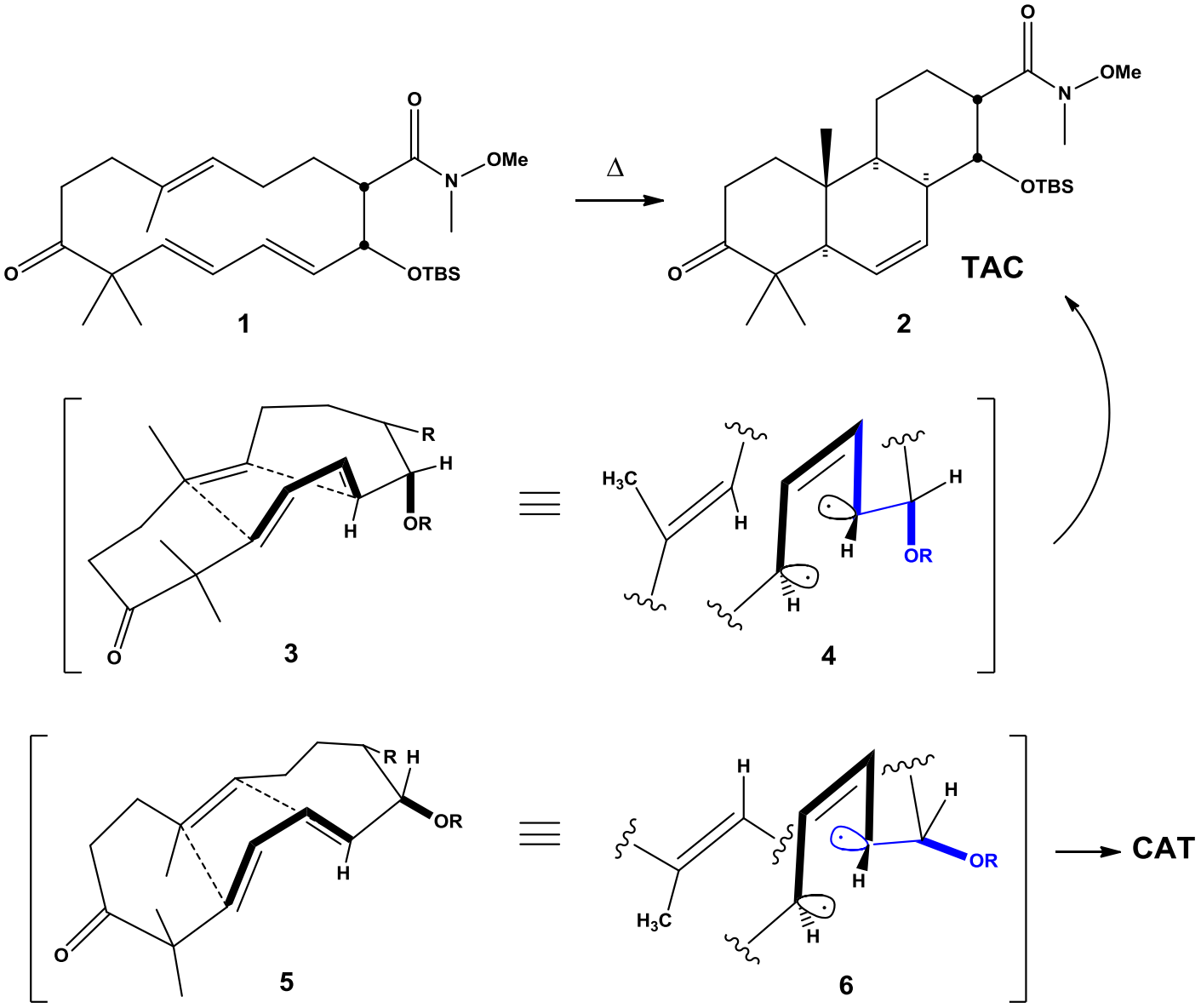


S. Weinstein, M. Shatausky, C. Norton, R. B. Woodward, *J. Am. Chem. Soc.,* **1955**, *77*, 4183-4184.

A. Naperstkow, J. B. Macaulay, M. J. Newslands, A. G. Fallis, *Tetrahedron Lett.,* **1989**, 5077-5080.

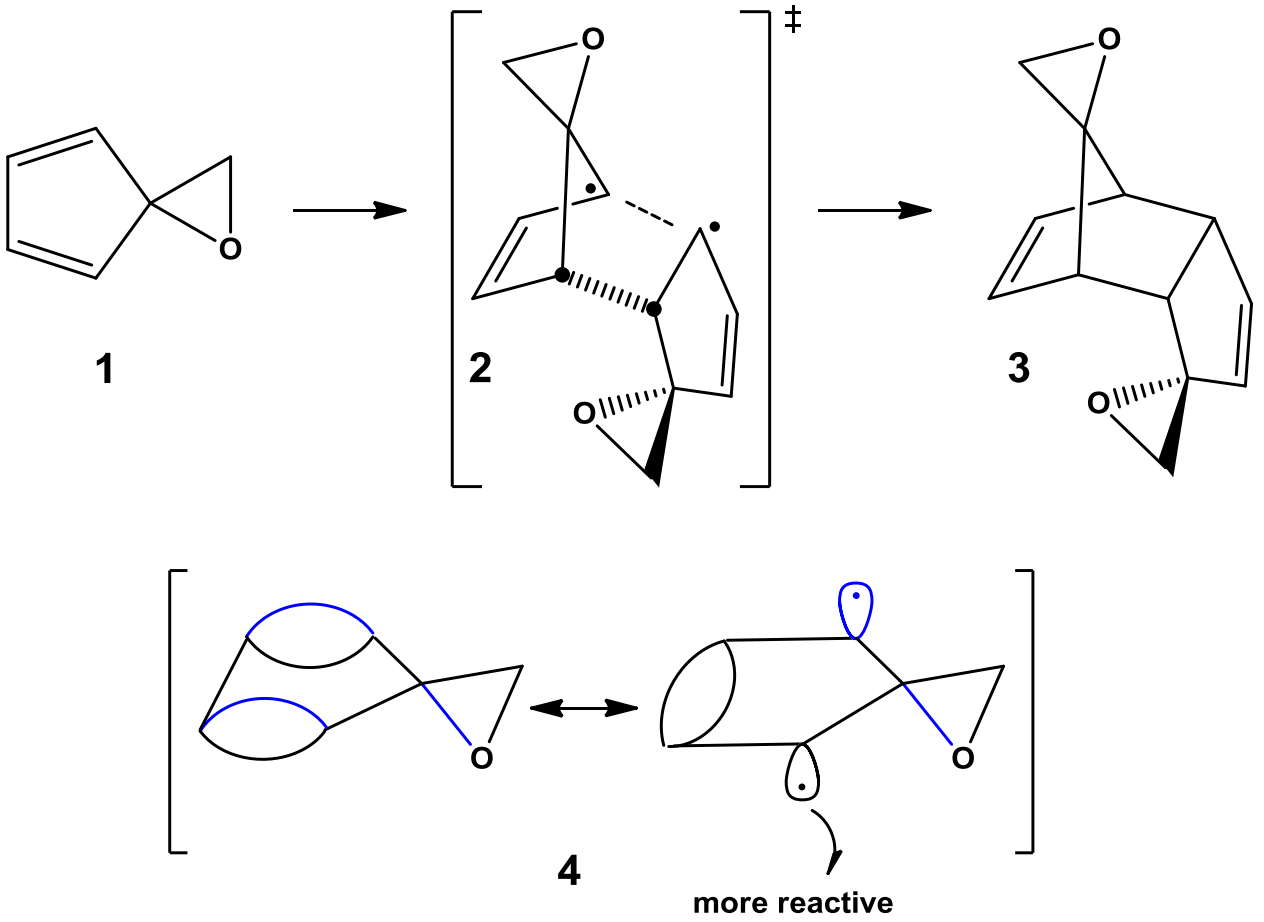
J. R. Gillard, D. J. Burnell, *J. Chem. Soc., Chem. Commun.,* **1989**, 1439-1440.

Stereoselectivity in Transannular Diels-Alder Reactions



S. Phoenix, M. S. Reddy, P. Deslongchamps, *J. Am. Chem. Soc.,* **2008**, *130*, 13989-13995.
E. Bourque, P. Deslongchamps, Y. L. Dory, *J. Org. Chem.,* **2003**, *68*, 2390-2397.

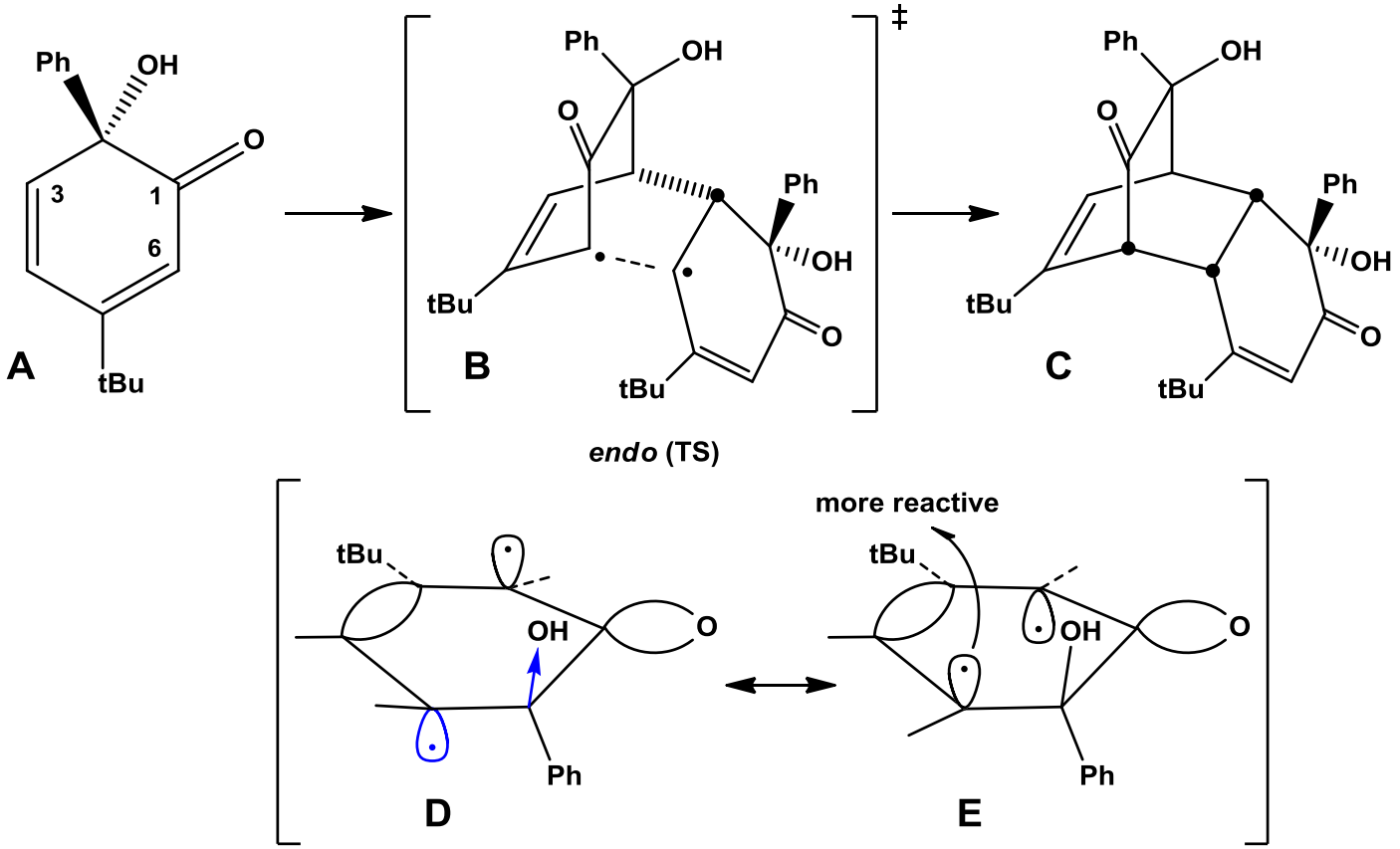
Dimerization of Epoxycyclopentadiene



R. D. J. Froese, M. G. Organ, J. D. Goddard, T. D. P. Stack, B. M. Trost, *J. Am. Chem. Soc.*, **1995**, *117*, 10931-10938.

Ortho-Quinol Dimerization

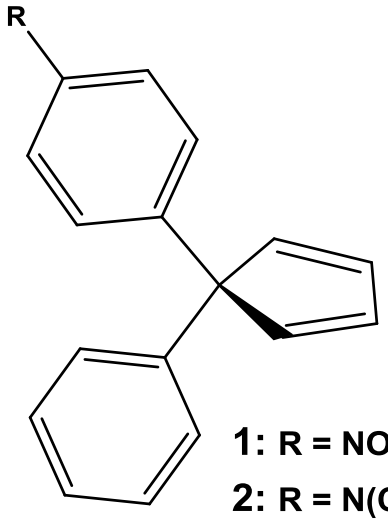
a rather revealing case



racemic A gives only *S*-*S* and *R*-*R* dimers (no S-R cross-over)

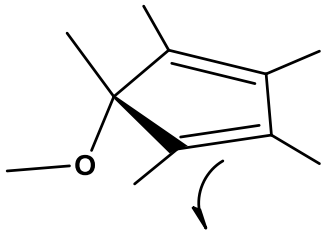
S. Quideau, L. Pouységu, D. Deffieux, *Synlett,* **2008**, *4*, 467-495.
G. Deslongchamps, P. Deslongchamps. *Tetrahedron,* **2013**, *69*, 6022-6033.

Other Facially Perturbed Dienes

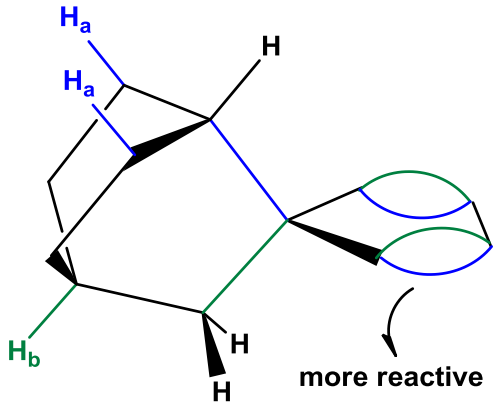


1: R = NO_2 (β)

2: R = $N(CH_3)_2$ (α)



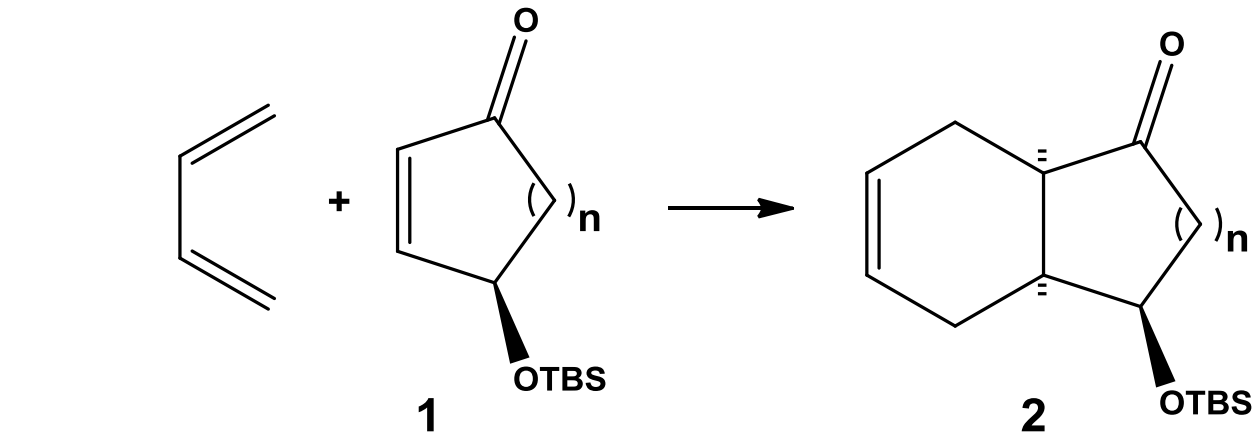
3

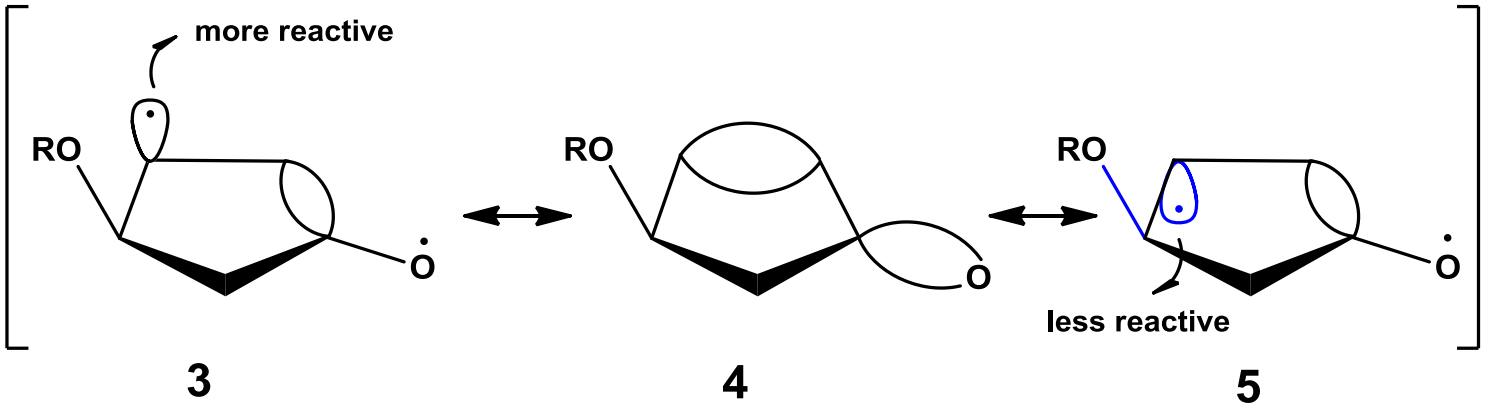


4

R. Halterman, B. A. McCarthy, M. A. McEvoy. *J. Org. Chem.* **1992**, *97*, 5585-5589.
D. J. Burnell, H. B. Goodgrand, S. M. Kaiser, Z. Valenta. *Can. J. Chem.* **1987**, *65*, 154-165.
G. Deslongchamps, P. Deslongchamps. *Tetrahedron* **2013**, *69*, 6022-6033.

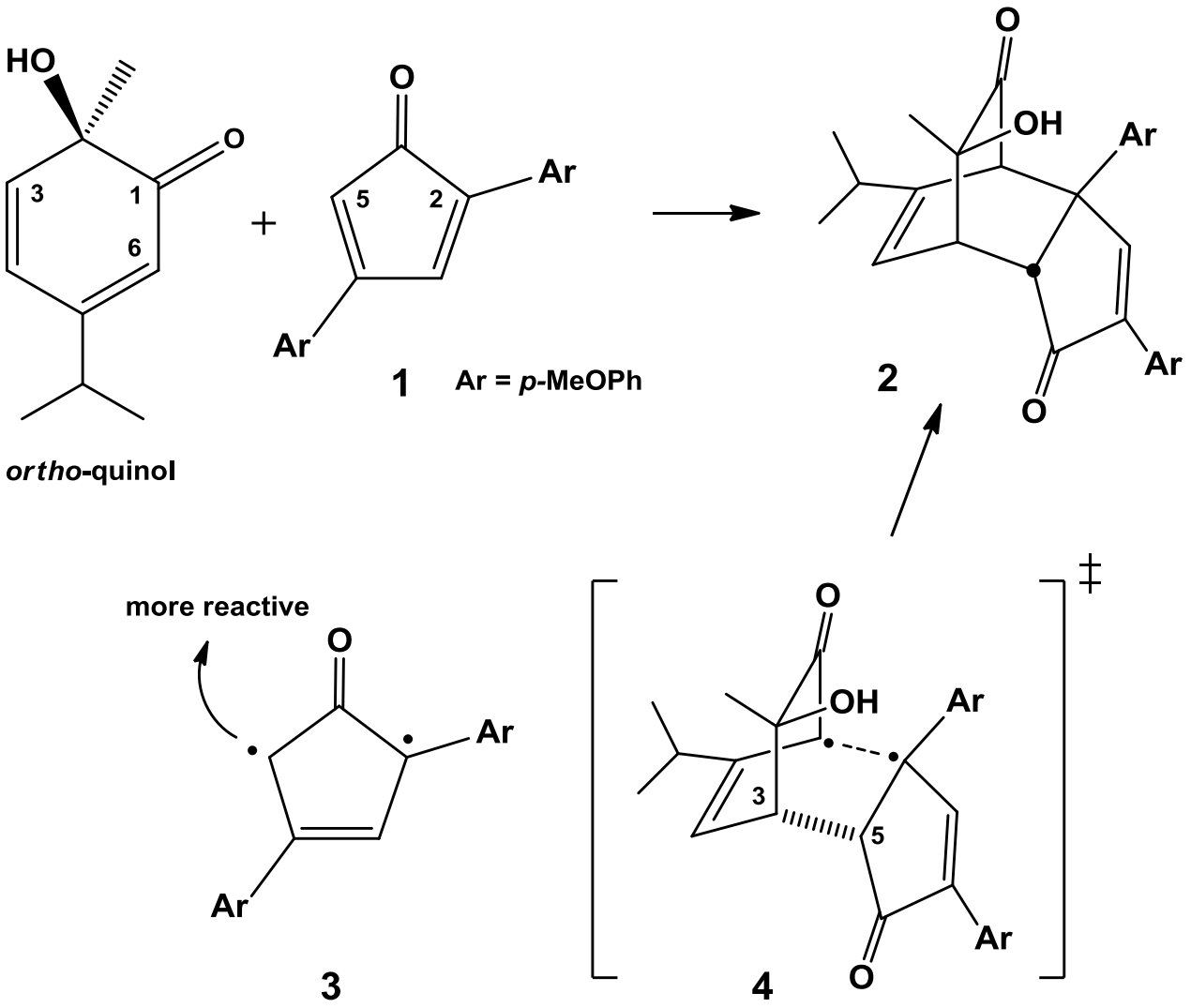
Effect of Dienophile Substituents on Diels-Alder Facial Selectivity





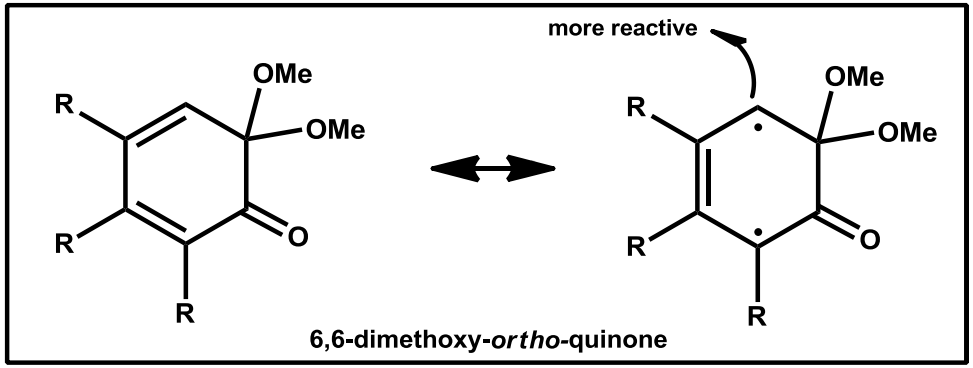
L. O. Jeroncic, M.-P. Cabal, S. Danishefsky. *J. Org. Chem.* **1991**, *56*, 387-395.
G. Deslongchamps, P. Deslongchamps. *Tetrahedron* **2013**, *69*, 6022-6033.

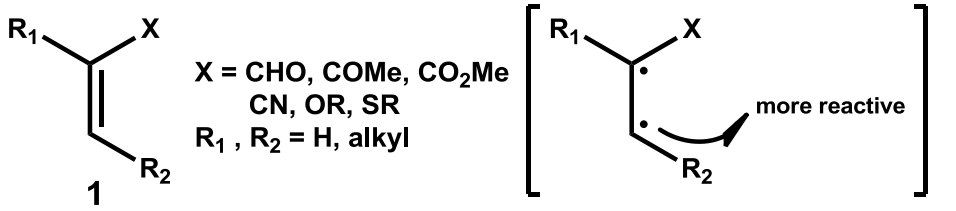
Cycloaddition of *ortho*-Quinol with Dirayl Cyclopentadienone

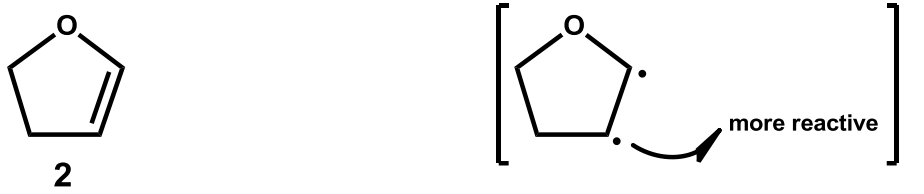


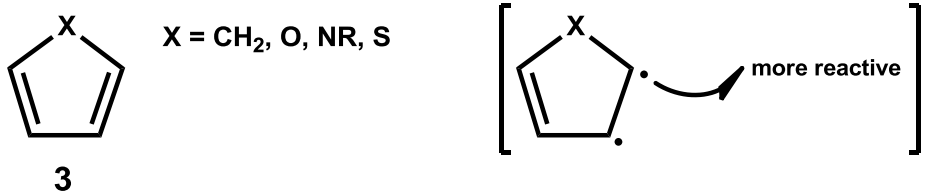
J. H. Porco *et al., J. Org. Chem.* **2011**, *76*, 8944-8954.
G. Deslongchamps, P. Deslongchamps. *Tetrahedron* **2013**, *69*, 6022-6033.

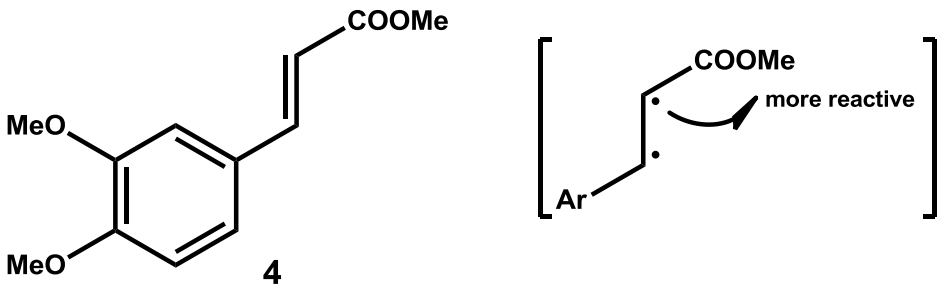
Dienophile Regioselectivities with Unsymmetrical Dienes such as 6,6-Dimethoxy-*ortho*-quinones





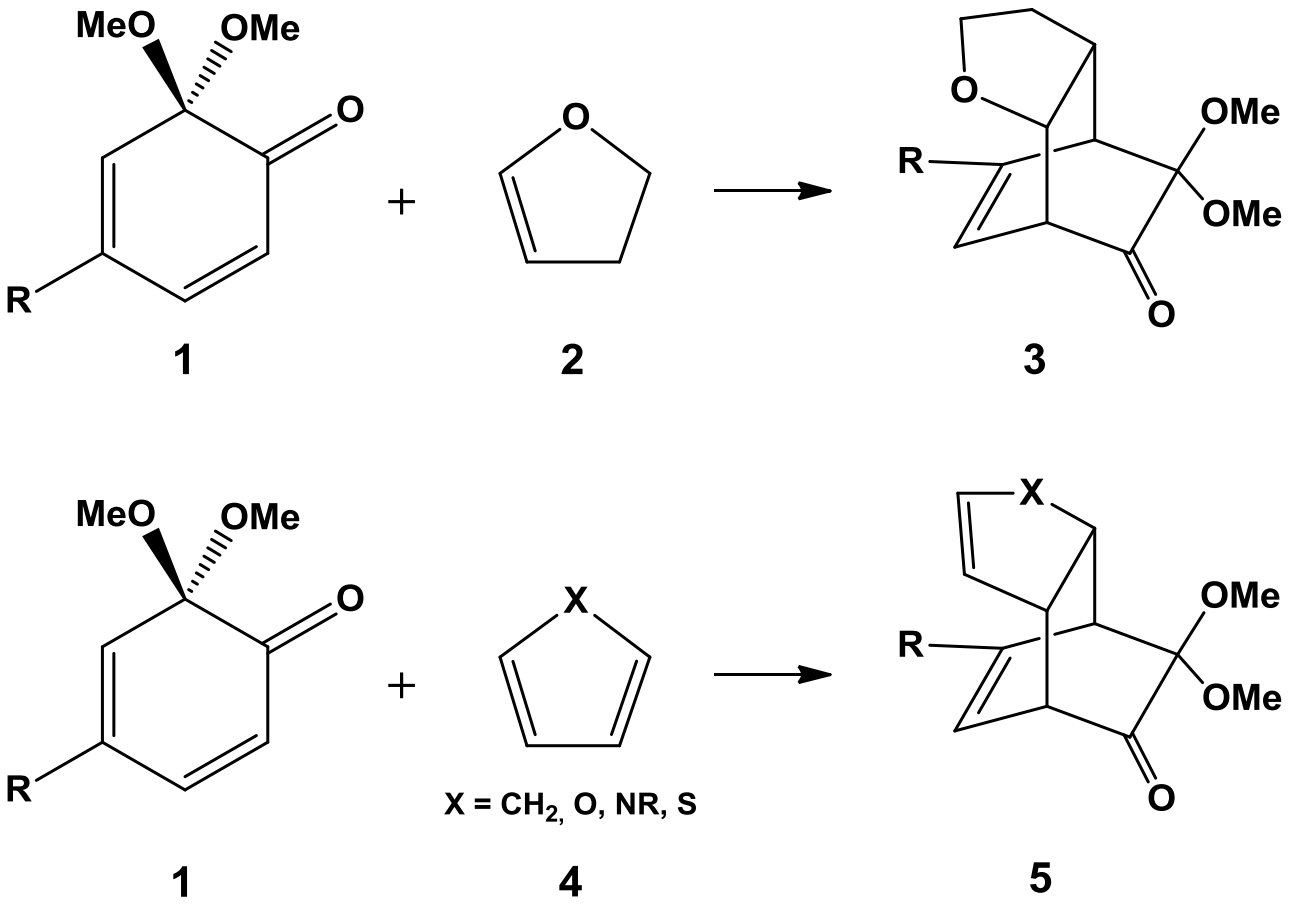






C.-C. Liao, R. K. Peddinti,
Acc. Chem. Res. **2002**, *35*, 856-866.
G. Deslongchamps, P. Deslongchamps.
Tetrahedron **2013**, *69*, 6022-6033.

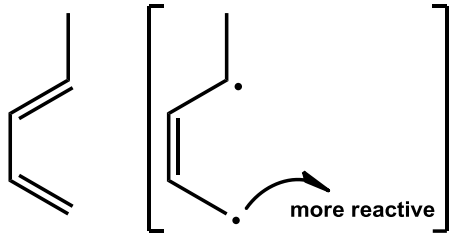
Regioselectivity Control with Dihydrofuran and Furan-type Dienophiles



C.-C. Liao, R. K. Peddinti, *Acc. Chem. Res.* **2002**, *35*, 856-866.
G. Deslongchamps, P. Deslongchamps. *Tetrahedron* **2013**, *69*, 6022-6033.

Regioselectivity Control with Unsymmetrical Dienes and Dienophiles

DIENES



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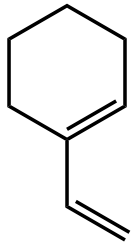

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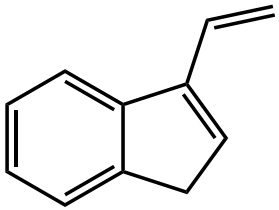

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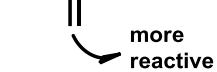
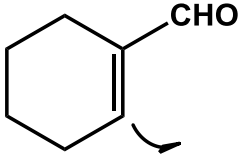
DIENOPHILES



R = Me, Br

4

5



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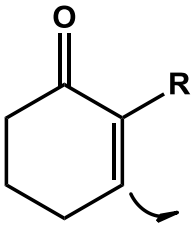

R = H, COOMe

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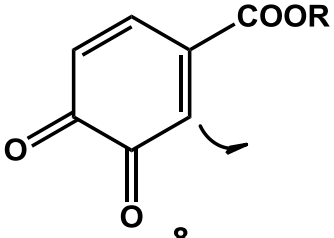

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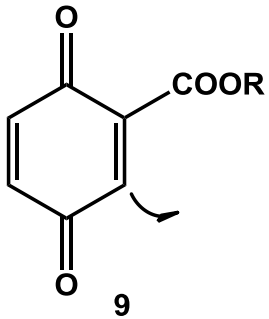
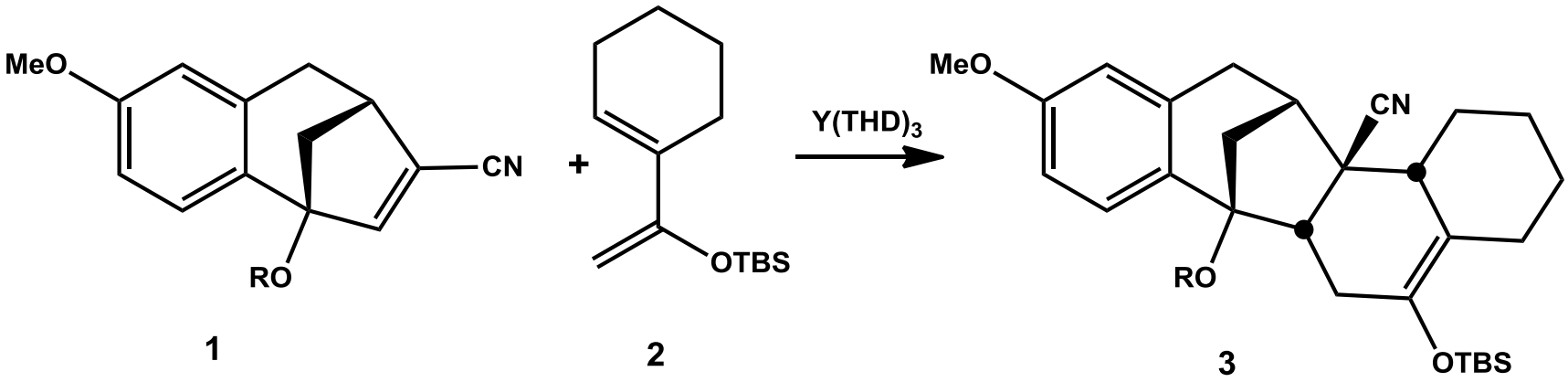


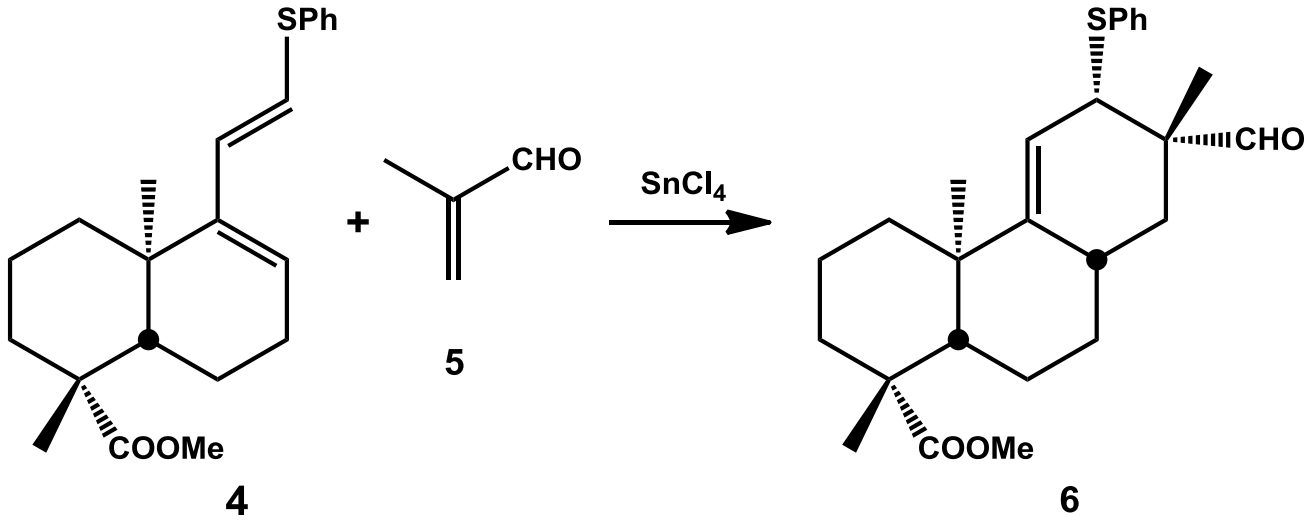
9

Yu, M.; **Danishefsky**, S. J. *J. Am. Chem. Soc.* **2008**, *130*, 2783.
Teo, Y.-C.; **Loh**, T.-P. *Org. Lett.* **2005**, 7, 2539.
Breuning, M.; **Corey**, E. J. *Org. Lett.* **2001**, *3*, 1559.
Stork, G.; Wagle, S. S.; Mukharji, P. C. *J. Am. Chem. Soc.* **1953**, *75*, 3197.
Nazarov, I. N.; Ananchenko, S. N.; Torgov, I. V. *Russ. Chem. B* **1957**, *8*, 84.
Bergmann, E. D.; Becker, A. *J. Am. Chem. Soc.* **1959**, *81*, 221.
Orsini, F.; Pelizzoni, F.; **Pitea**, D.; Abbondanti, E.; Mugnoli, A. *J. Org. Chem.* **1983**, *48*, 2886.
Pitea, D.; Gastaldi, M.; Orsini, F.; Pelizzoni, F.; Mugnoli, A.; Abbondanti, E. *J. Org. Chem.* **1985**, *50*, 1853.
Bergman, Y. E.; Mulder, R.; **Perlmutter**, P. *J. Org. Chem.* **2009**, 74, 2589.
Trost, B. M.; Ippen, J.; Vladuchick, W. C. *J. Am. Chem. Soc.* **1977**, *199*, 8116.
G. Deslongchamps, P. Deslongchamps. *Tetrahedron* **2013**, *69*, 6022-6033.

Reversing Diels-Alder Regioselectivity in Natural Products Synthesis



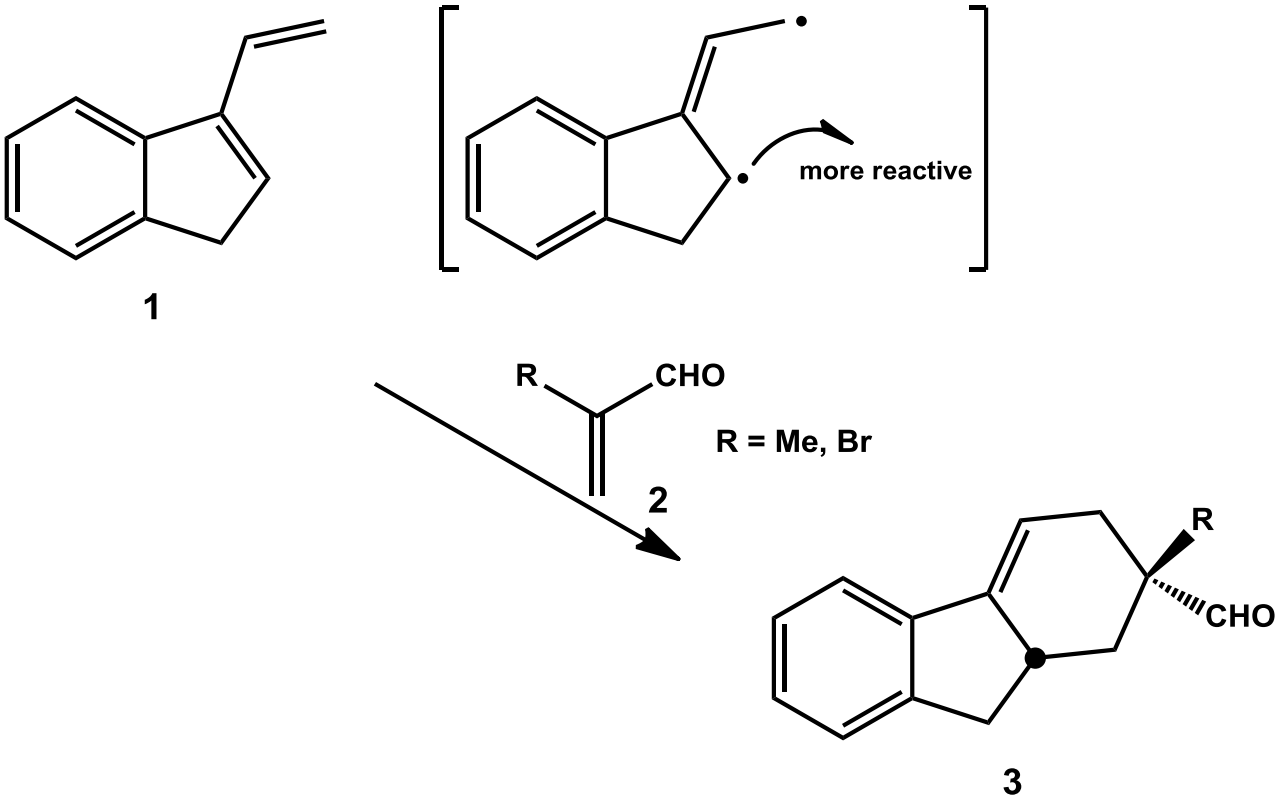
Mander, L. N.; McLachlan, M. M. *J. Am. Chem. Soc.* **2003**, *125*, 2400-2401.



Ling, T.; Chowdhury, C.; Kramer, B. A.; Vong, B. G.; Palladino, M. A.; Theodorakis, E. A. *J. Org. Chem.* **2001**, *66*, 8843-8853.

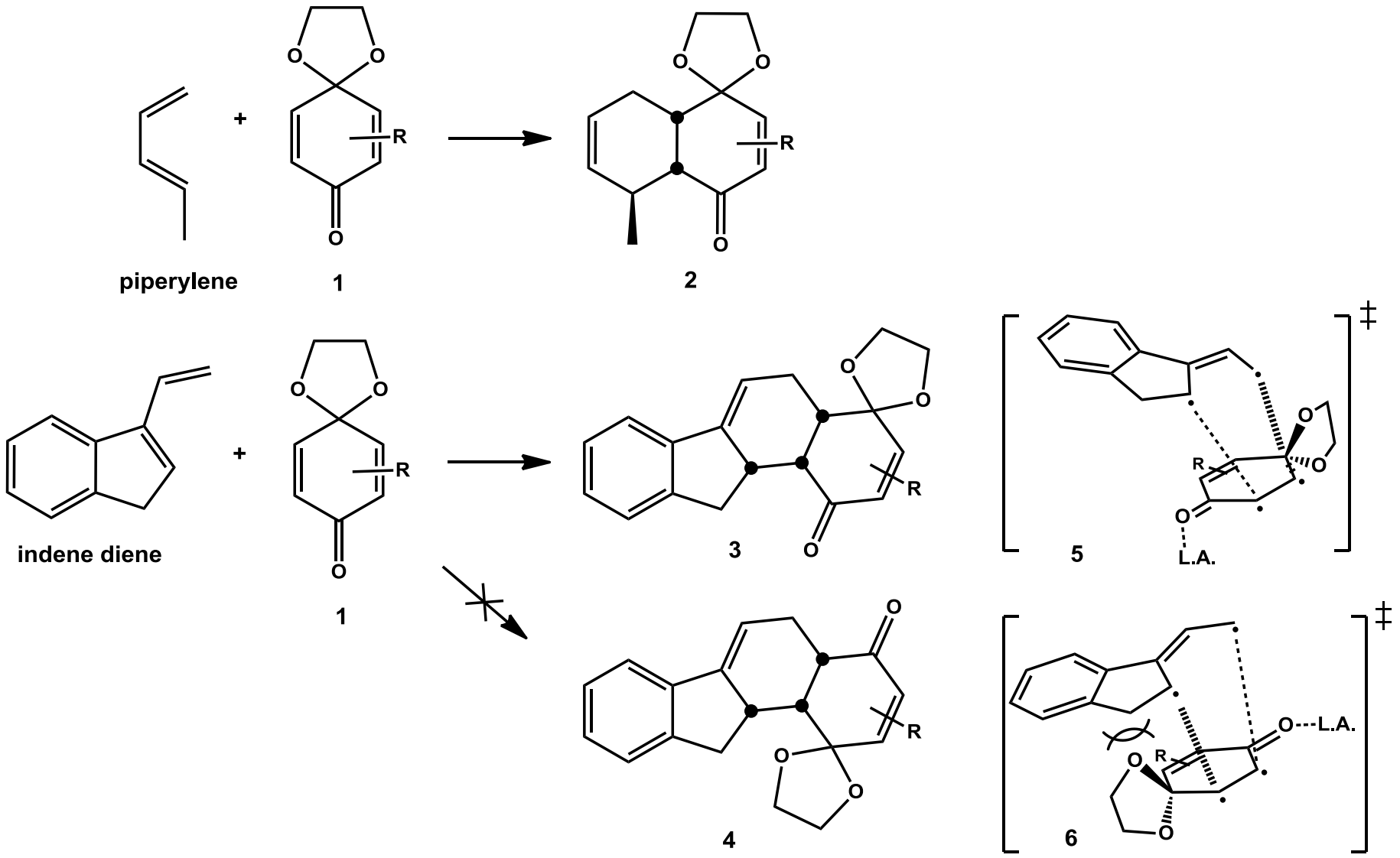
Deslongchamps, G.; Deslongchamps, P. *Tetrahedron* **2013**, *63*, 6022-6033.

Regioselectivity of Indene Diene



Snyder, S. A.; Kontes, F. *J. Am. Chem. Soc*. **2009**, *131*, 1745-1752.
Teo, Y.-C.; Loh, T.-P. *Org. Lett.* **2005**, 7, 2539-2541.
Breuning, M.; Corey, E. J. *Org. Lett.* **2001**, *3*, 1559-1562.
G. Deslongchamps, P. Deslongchamps. *Tetrahedron* **2013**, *69*, 6022-6033.

Regioselectivity of Cycloadditions with *p*-Quinone Monoketal

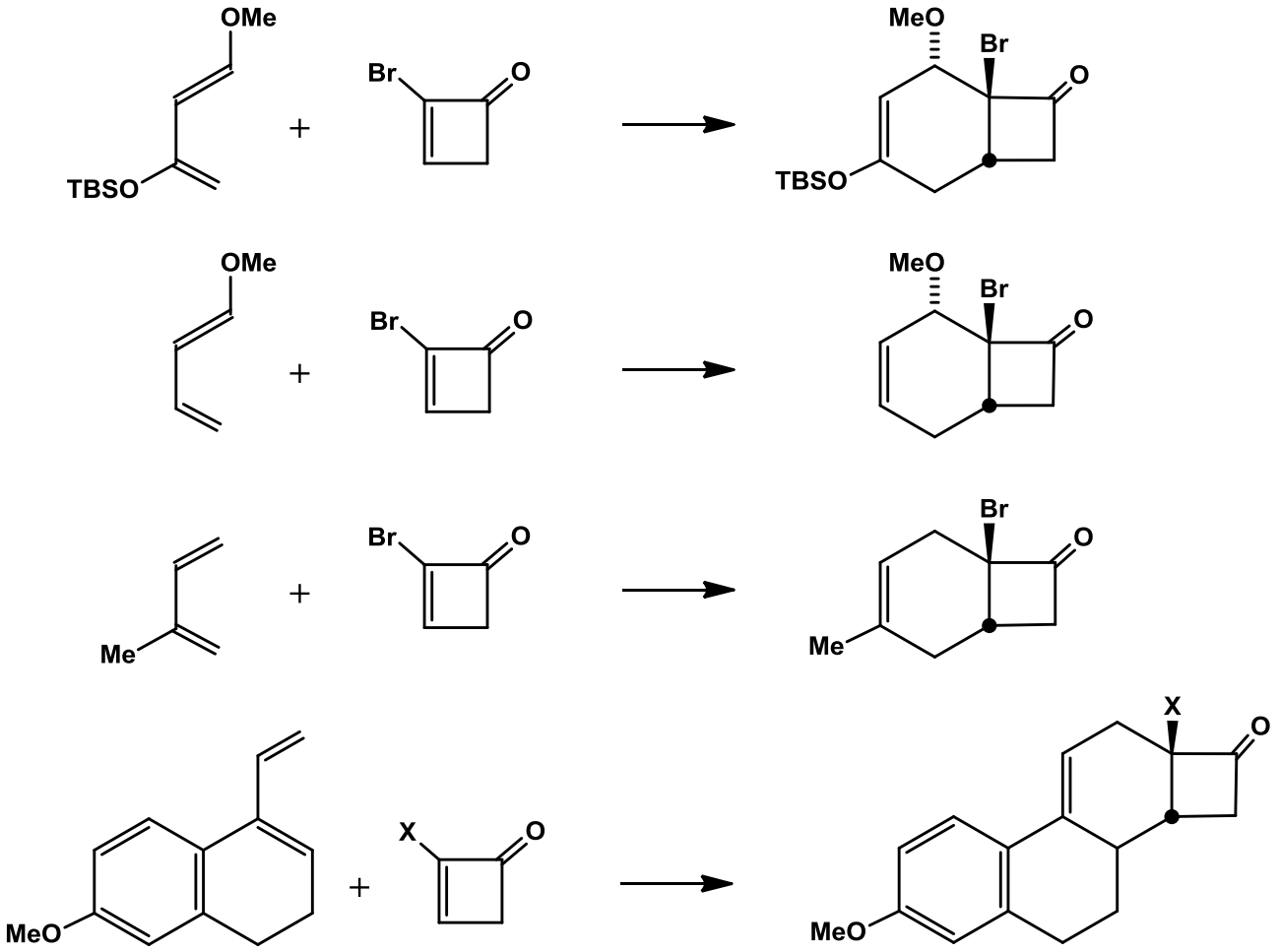


Yu, M.; **Danishefsky**, S. J. *J. Am. Chem. Soc.* **2008**, *130*, 2783-2785.

Hayden, A. E.; DeChancie, J.; George, A. H.; Dai, M.; Yu, M.; **Danishefsky**, S. J.; **Houk**, K. N. *J. Org. Chem.* **2009**, *74*, 6770-6776.

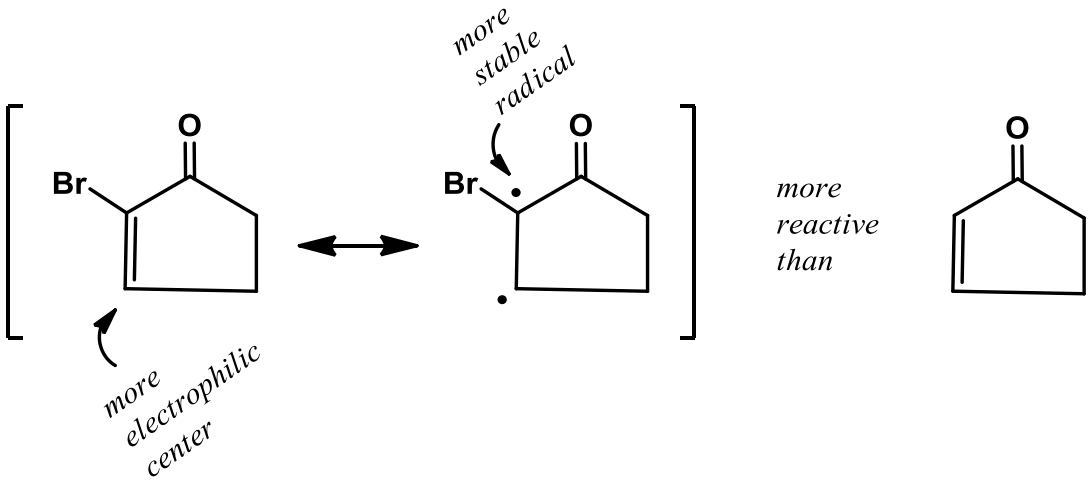
G. Deslongchamps, P. Deslongchamps. *Tetrahedron* **2013**, *69*, 6022-6033.

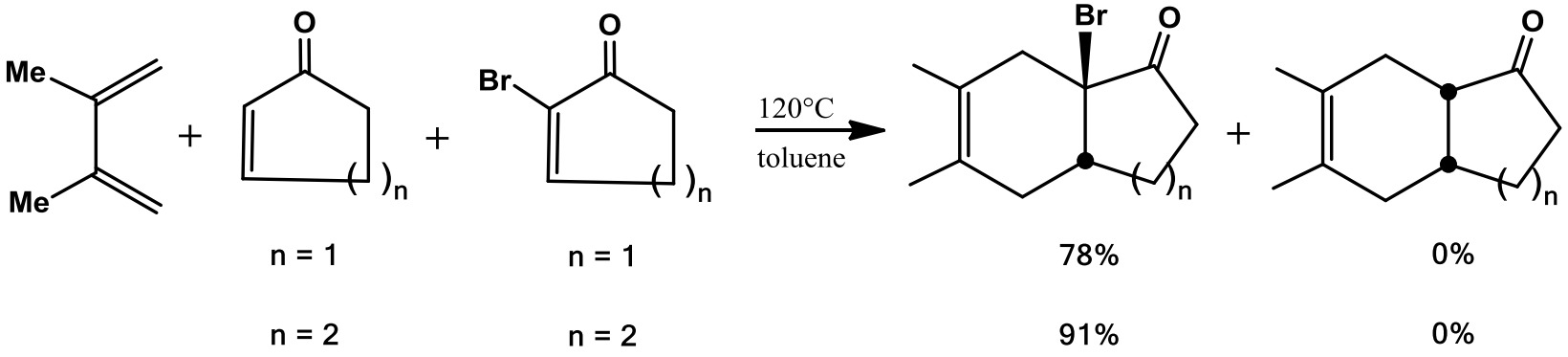
α-Bromo-cyclobutane, a Reactive Dienophile



A. G. Ross, S. D. Townsed, S. Danishefsky.
J. Org. Chem., **2013**, *78*, 204-210.

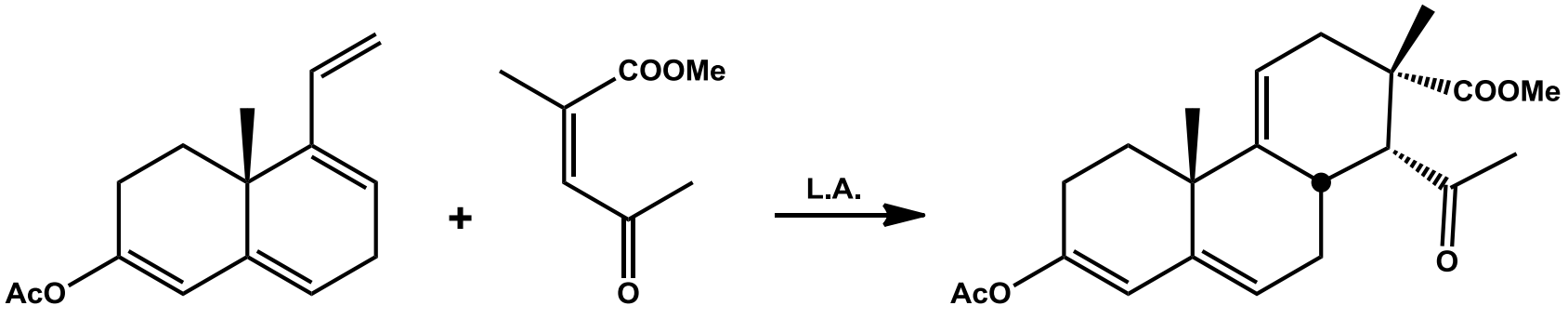
Increasing Reactivity of Dienophile



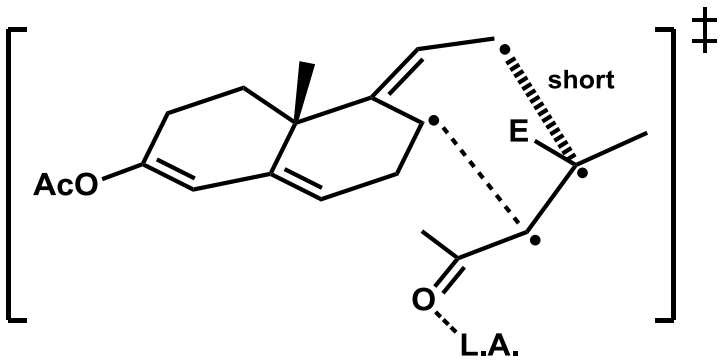


A. G. Ross, S. D. Townsed, S. Danishefsky.
J. Org. Chem., **2013**, *78*, 204-210.

Regioselectivity of Cycloadditions with Valenta diene



1 (Valenta) **2** **3**

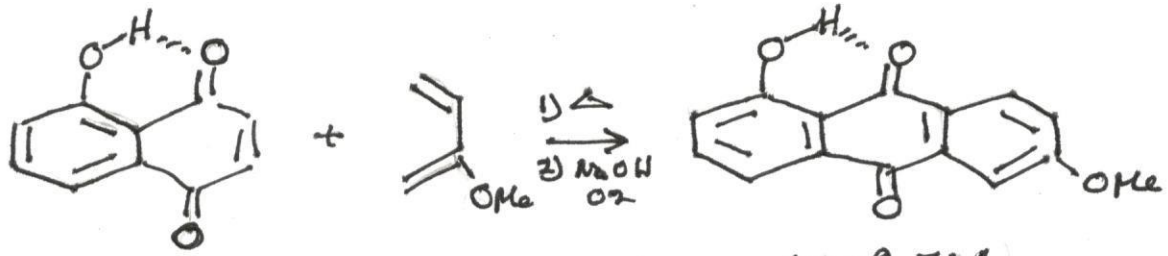


4

Das, J.; Dickinson, R. A.; Kakushima, M.; Kingston, G. M.; Reid, G. R.; Sato, Y.; **Valenta**, Z. *Can. J. Chem.* **1984**, *62*, 1103-1111.

Deslongchamps, G.; Deslongchamps, P. *Tetrahedron* **2013**, *69*, 6022-6033.

Boeckman



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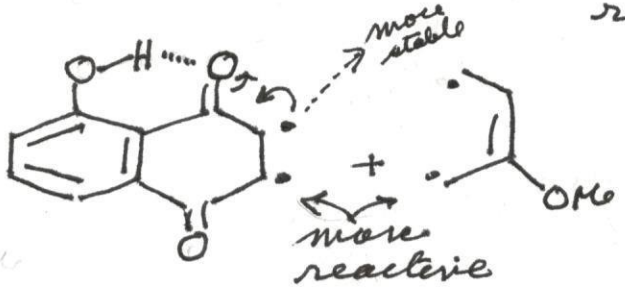

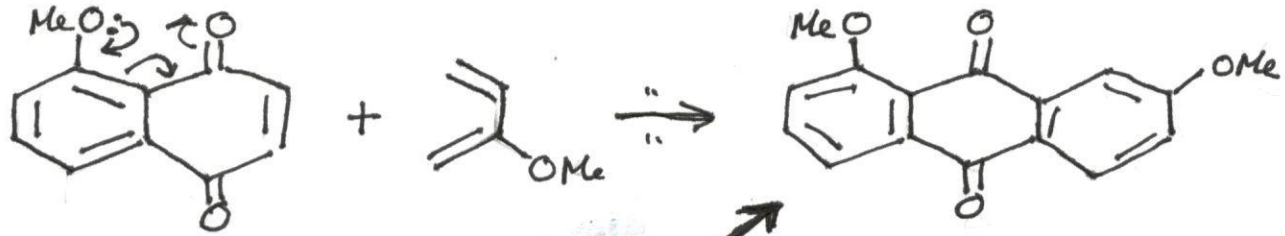

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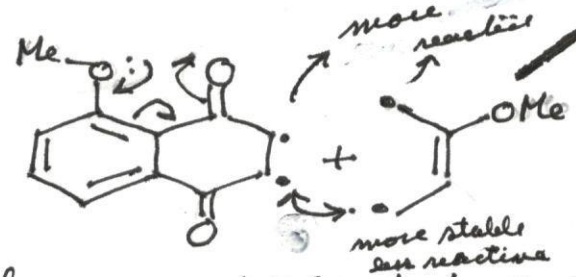
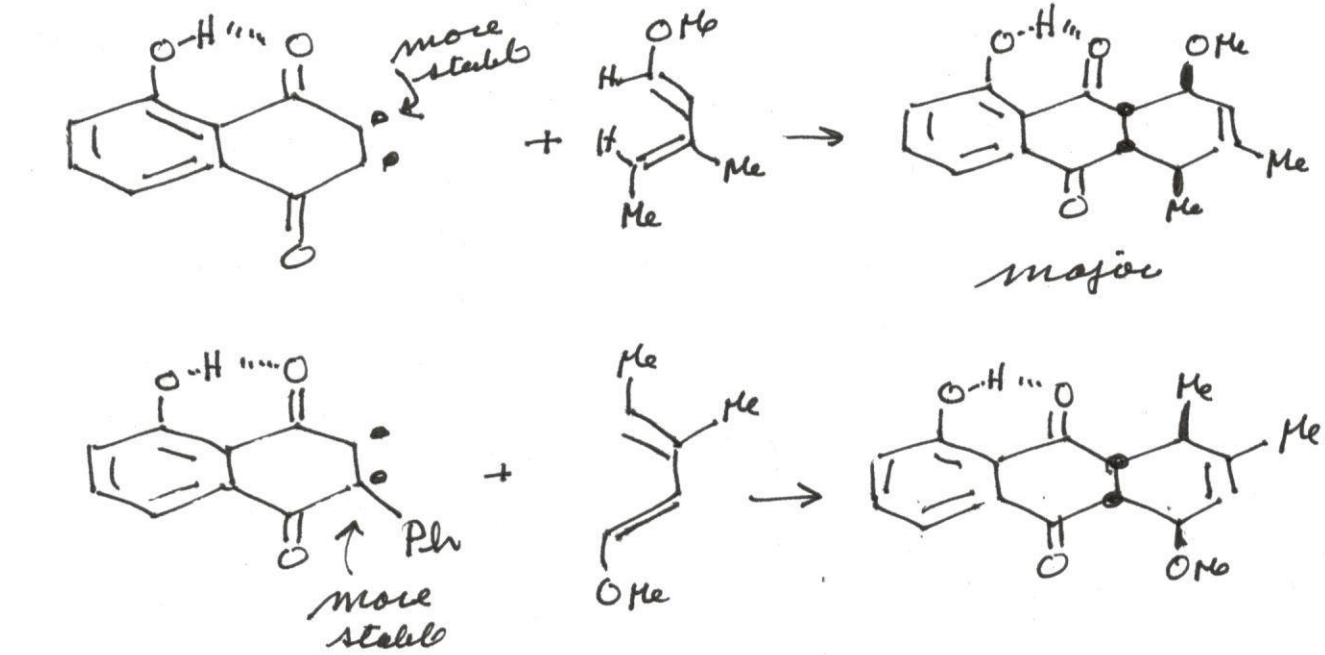
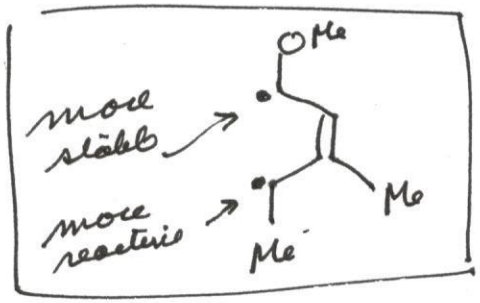


Boeckman et al J.A.C.S 1978, 100, 7098-7100

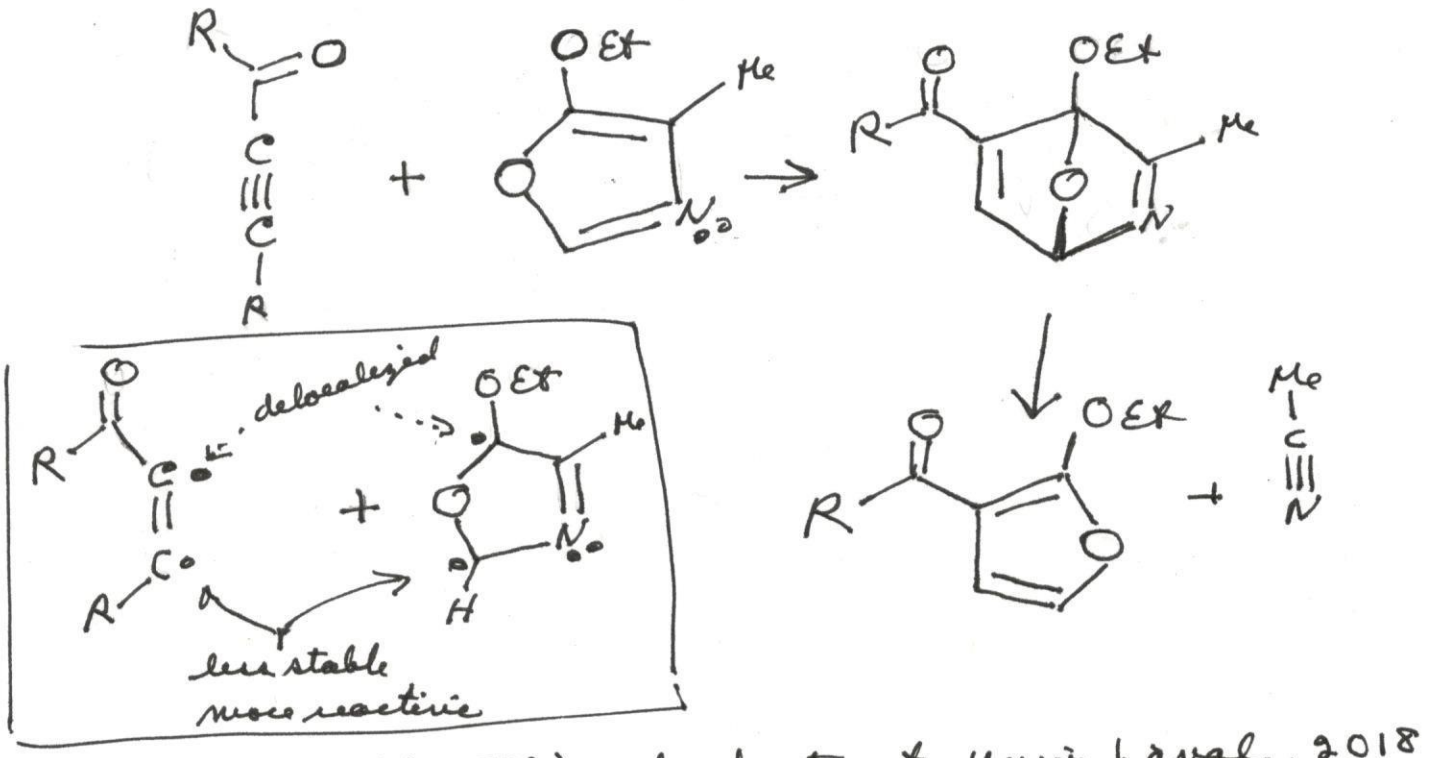
Nicolaou





Nicolaou, Houk et al
J. Org. Chem. 2010, 75, 922

C. Thibault



C. Thibault. Thèse de doctorat, univ. Laval, 2018