

**Applications of
Orbital Symmetry**

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A WORD TO THE USER

ACS AUDIO COURSES are instructional units on subjects of significant interest that are suitable for both individual study and group use.

The ACS AUDIO COURSE on "Applications of Orbital Symmetry," by Gerald L. Goe of the University of Notre Dame, is intended to introduce principles of orbital symmetry and two methods that are useful in predicting organic reaction pathways -- the suprafacial-antarafacial cycloaddition and the Hückel-Möbius methods. No special background, except for the usual undergraduate preparation in general and organic chemistry, is required. The listener need not have any previous acquaintance with quantum mechanics, molecular orbital theory, or formal group theory, although some familiarity with these areas will be helpful.

This volume is the reference manual that is integrated with the audiotape of "Applications of Orbital Symmetry." The two together -- tape and manual -- comprise the ACS AUDIO COURSE; neither is complete without the other. Because the lecturer refers constantly to the manual, each listener should have a copy of the manual as he listens, so he may follow these references.

The manual was not written to be a self-sufficient textbook. It was designed, rather, to be used as a workbook while listening to the tape. The listener is urged to take notes with the expectation that this activity will reinforce the learning process. The product is a personally annotated volume which should serve as an authoritative and up-to-date introduction to the subject.

Your comments and suggestions have proved to be exceptionally valuable guides for improving our educational programs. We hope you will continue to send them to us.

Department of Educational Activities
American Chemical Society

Acknowledgements

The author wishes to thank Prof. Ernest Eliel for suggesting this project, and Prof. Gerhard Binsch for valuable discussion during its early stages.

Outline

Part I - Theory

Section	Subject
1	Nodal and Symmetry Properties of Atomic and Molecular Orbitals
2	Orbital and State Correlation Diagrams
3	The Suprafacial-Antarafacial Cycloaddition Method
4	The Hückel-Möbius Method

Part II - Applications

5	Electrocyclic Reactions
6	Sigmatropic Rearrangements
7	Cycloadditions
8	Other Reactions
a	Bicyclobutane Formation and Destruction
b	The Di- π -methane and Related Rearrangements
c	Formation of Bicyclo[3.1.0]hex-2-ene Derivatives
d	Benzene Photochemistry
e	Hydrogen Transfers
f	Influence of Transition Metals
g	Miscellaneous Reactions
h	Final Problems

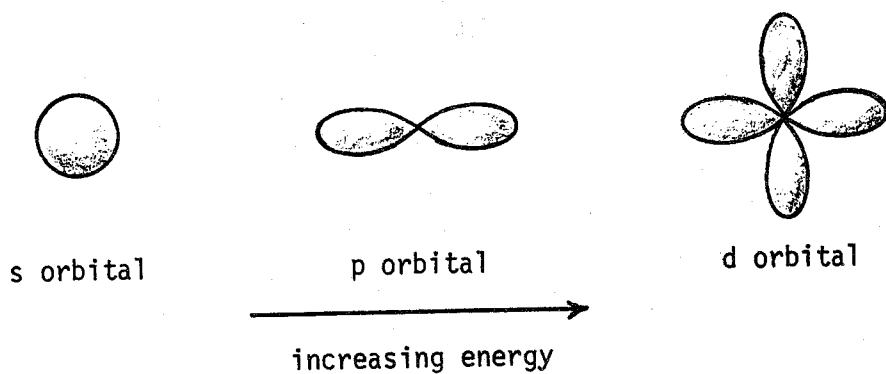
Section 1.

Nodal and Symmetry Properties of Atomic and Molecular Orbitals

Review of atomic orbitals

(I) As the number of nodes in an orbital increases, the energy of the orbital increases.

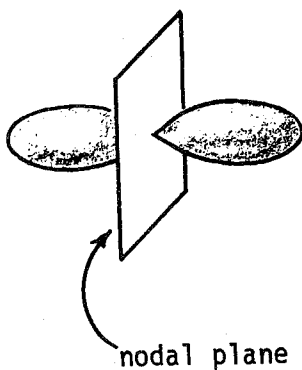
Figure 1-1.



Node: A surface (frequently a plane) of zero electron density separating two volumes of electron density.

Figure 1-2.

p orbital

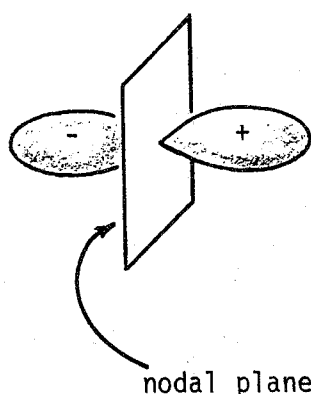


Wave function: Mathematical expression of the probability of occurrence of an electron in a volume of space; electron density = (wave function)².

Wave functions have signs and can be pictured as orbitals with + and - signs.

Figure 1-3.

p orbital wave function



Redefinition:

Node: A surface separating two volumes where the wave function has opposite signs. Wave function has zero value in nodal surface.

Sign of wave function has meaning only relative to other wave function signs; assignment of signs is arbitrary.

(II) Orbitals (wave functions) can be added together.

Hybridization:

Carbon atom: one 2s orbital
three 2p orbitals

Can be added together to make several hybrids:

one s + three p → four sp^3 hybrids

one s + two p → three sp^2 hybrids

one s + one p → two sp hybrids

n orbitals $\xrightarrow{\text{hybridization}}$ n hybrid orbitals

"Linear combinations" of orbitals

$$\phi_{\text{hybrid}} = a\phi_1 + b\phi_2 + c\phi_3 + \dots \quad (1-1)$$

Review:

- (1) More nodes means higher energy
- (2) n orbitals can be combined to form n different orbitals

Molecular orbitals

Outline

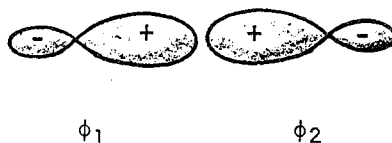
To describe a molecule in terms of molecular orbitals (MO's):

- (1) Start with set of atomic orbitals of constituent atoms of the molecule (basis set)
- (2) Atomic orbitals interact to form molecular orbitals ("linear combination of atomic orbitals" - LCAO). Same number of MO's as AO's in basis set.
- (3) Arrange orbitals in order of energy (more nodes implies higher energy)
- (4) Put required number of electrons in orbitals, filling lowest energy orbitals first (Aufbau principle)

Example: Two carbon atoms interacting to form a single bond

Figure 1-4.

Basis set: Two sp^3 orbitals, ϕ_1 and ϕ_2



Two linear combinations are possible.

Figure 1-5.

(1) $\phi_1 + \phi_2$



A bonding orbital -- signs of wave functions combine to make bonding overlap (+ to +)

Figure 1-6.

(2) $\phi_1 - \phi_2$ [equivalent to $\phi_1 + (-\phi_2)$]



An antibonding orbital -- unfavorable overlap (+ to -)

Notice:

$$(a) \quad \phi_2 - \phi_1 = -(\phi_1 - \phi_2) \quad (1-2)$$

$$(b) \quad \phi_1 + \phi_2 = \phi_1' - \phi_2' \quad (1-3)$$

$$\phi_1 - \phi_2 = \phi_1' + \phi_2' \quad (1-4)$$

Figure 1-7.

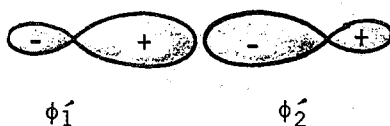
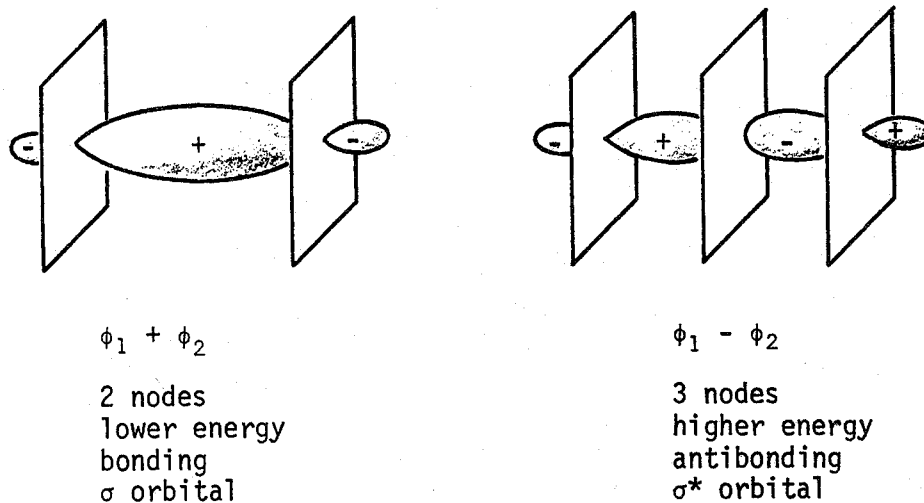


Figure 1-8.



Quantitative definitions:

Bonding: Orbital of lower energy than constituent AO's before interaction (more ++ and -- overlap than +- overlap, in addition to nodes demanded by form of AO's)

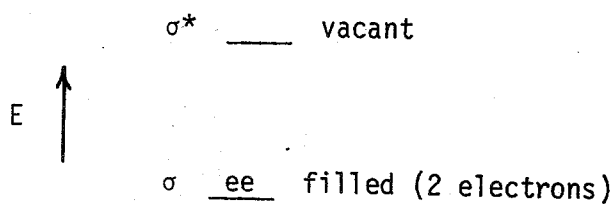
Antibonding: Orbital of higher energy than constituent AO's before interaction

Nonbonding: Orbital of same energy as AO's without interaction

Two electrons to be placed in these MO's (one from each contributing carbon); both go in σ orbital

Figure 1-9.

Energy Level Diagram



Example: Two carbon atoms already joined by a σ bond form a second bond using p orbitals

Figure 1-10.

Basis set (line represents σ bond): Two p orbitals

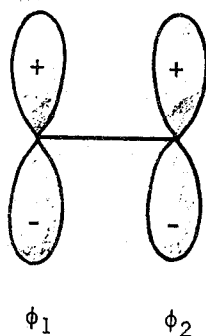
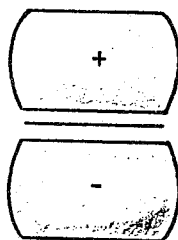


Figure 1-11.

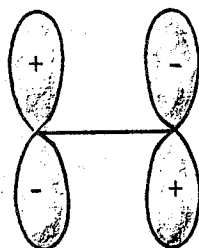
(1) $\phi_1 + \phi_2$



A bonding π orbital (π -- straight line between nuclei is in nodal plane; σ -- straight line between nuclei is in region of maximum value of wave function)

Figure 1-12.

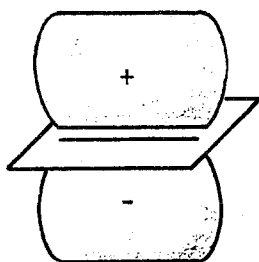
$$(2) \phi_1 - \phi_2$$



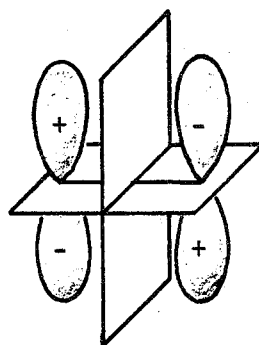
An antibonding π^* orbital

Energy of the orbitals

Figure 1-13.



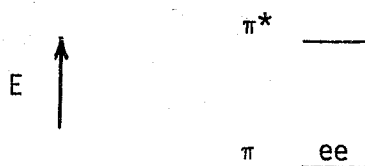
$\phi_1 + \phi_2$
1 node
lower energy
bonding
 π orbital



$\phi_1 - \phi_2$
2 nodes
higher energy
antibonding
 π^* orbital

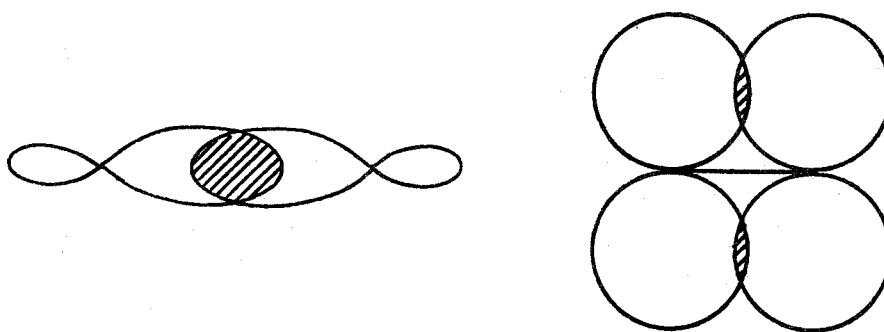
Figure 1-14.

Energy Level Diagram



Note: A σ orbital is of lower energy than a π orbital because the bonding overlap is better.

Figure 1-15.



A σ^* orbital is of higher energy than a π^* orbital.

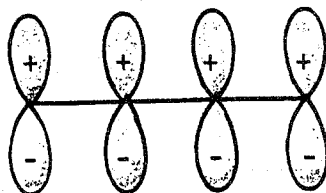
Larger molecules; delocalized molecular orbitals

Butadiene $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$

" π -electron approximation" -- Presume framework of normal σ bonds between sp^2 carbons and hydrogens; generate orbitals from basis set of p orbitals.

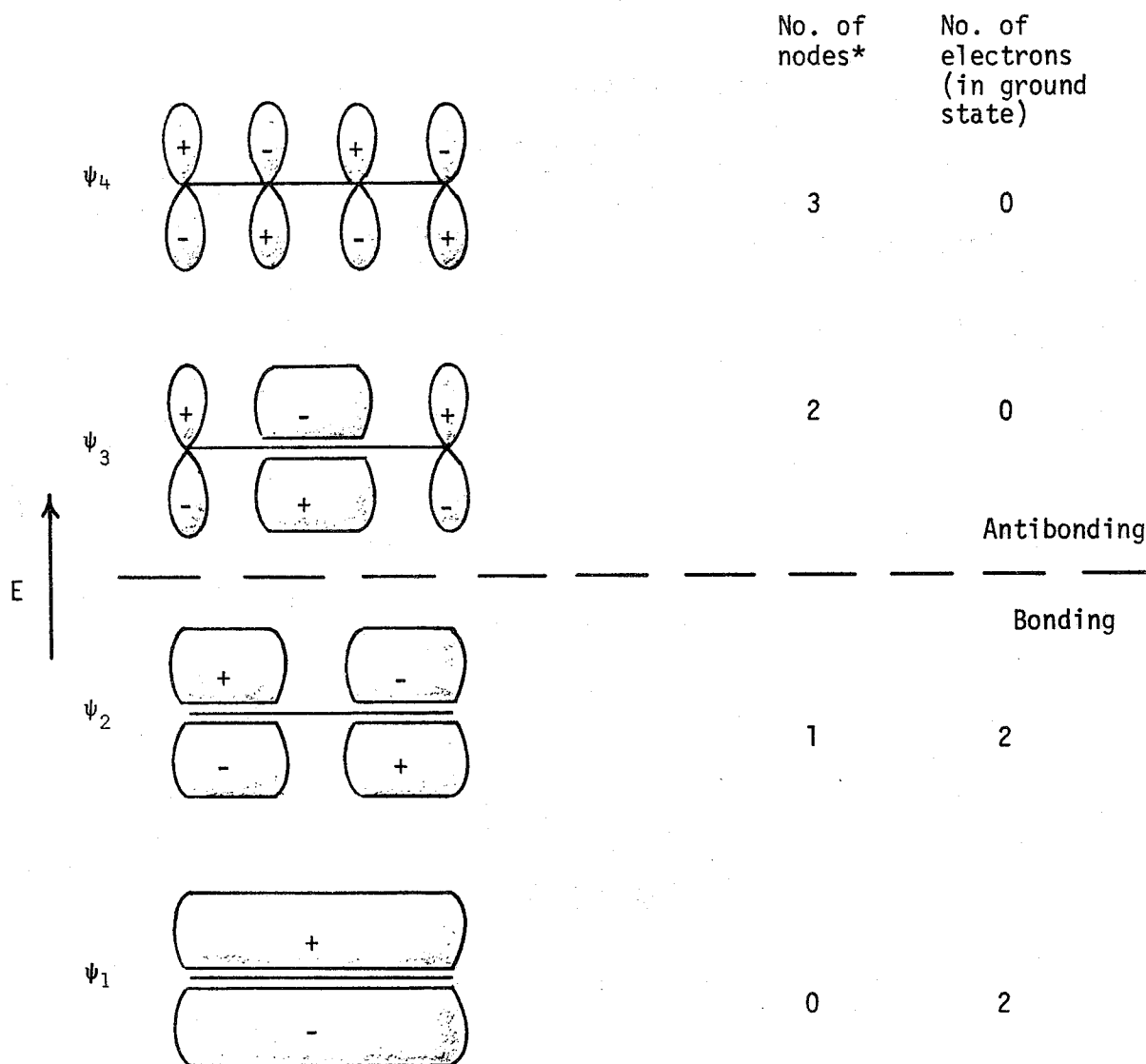
Figure 1-16.

Basis set



Four π -MO's; plane of carbon nuclei is a nodal plane in all the orbitals.

Figure 1-17.



* in addition to the nodal plane of the p orbitals

Not considered yet:

(1) Magnitude of contribution from each AO to each MO (coefficients). The signs and the nodes do not depend on the calculation method.

In the Hückel approximation:

$$\psi_2 = 0.602 \phi_1 + 0.372 \phi_2 - 0.372 \phi_3 - 0.602 \phi_4 \quad (1-5)$$

In the Pople-Pariser-Parr approximation:

$$\psi_2 = 0.583 \phi_1 + 0.400 \phi_2 - 0.400 \phi_3 - 0.583 \phi_4 \quad (1-6)$$

Use of orbital symmetry does not depend on the values of the coefficients.

(2) Normalization

$$\int_{-\infty}^{+\infty} \int \int \psi_i^2 dx dy dz = 1 \quad (1-7)$$

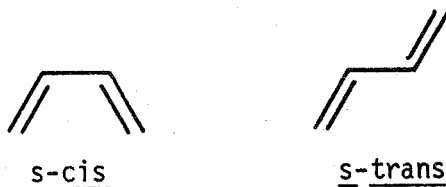
(3) Orthogonality

$$\int_{-\infty}^{+\infty} \int \int \psi_i \psi_j dx dy dz = 0 \quad (1-8)$$

(4) Symmetry.

Figure 1-18.

Conformations of Butadiene

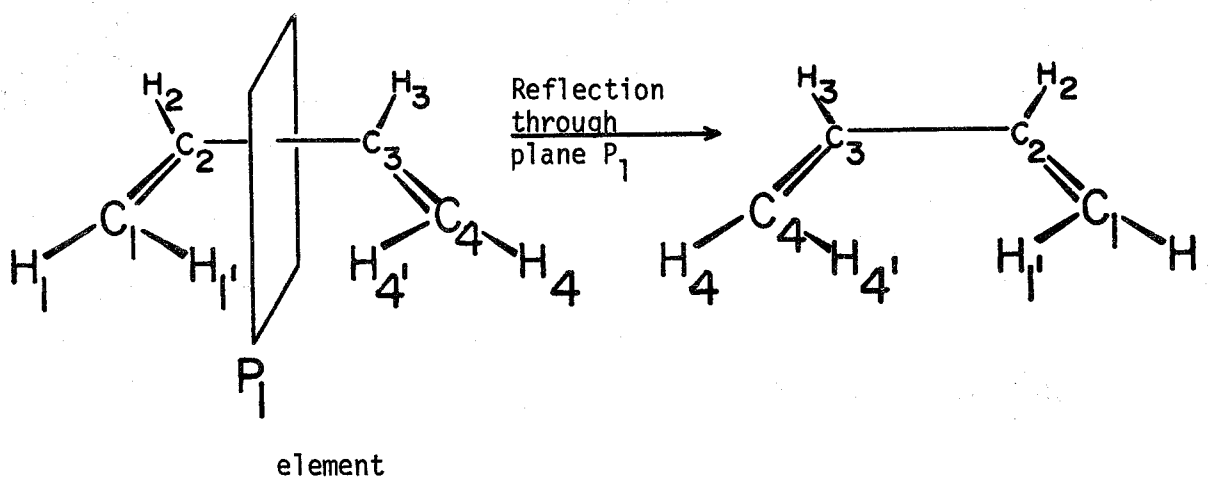


Symmetry elements and operations

Plane of symmetry

Element: Plane

Operation: reflection



Reflection: Atom on one side of plane moves to other side and same distance away along line perpendicular to the plane.

Operation of reflection through plane P_1 gives a molecule indistinguishable from the first except for labels; P_1 is a symmetry element of the molecule.

Not considered yet:

Axis of symmetry

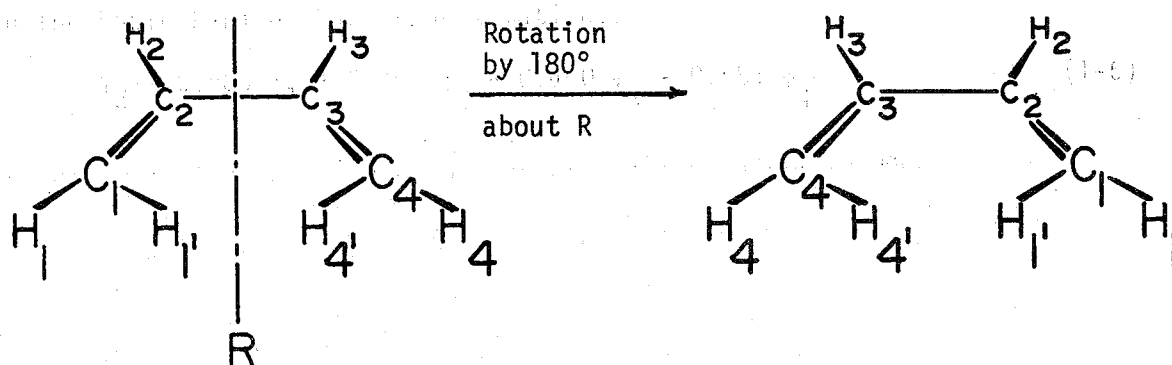
Element: axis (line)

Operation: rotation

(The coefficients of the MOs are not the same as in the calculation method, and the nodes do not depend on the calculation method.)

Figure 1-20.

(1-5)



Twofold rotation: rotation by $\frac{360^\circ}{2}$. Smaller rotations are possible.

(There are other symmetry elements -- the inversion center and the improper axis -- not required here.)

Figure 1-21.

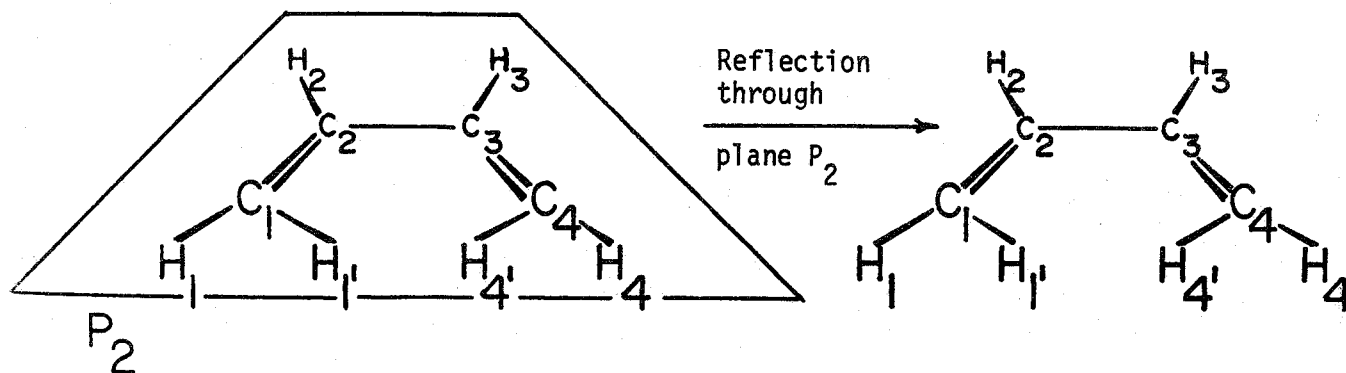
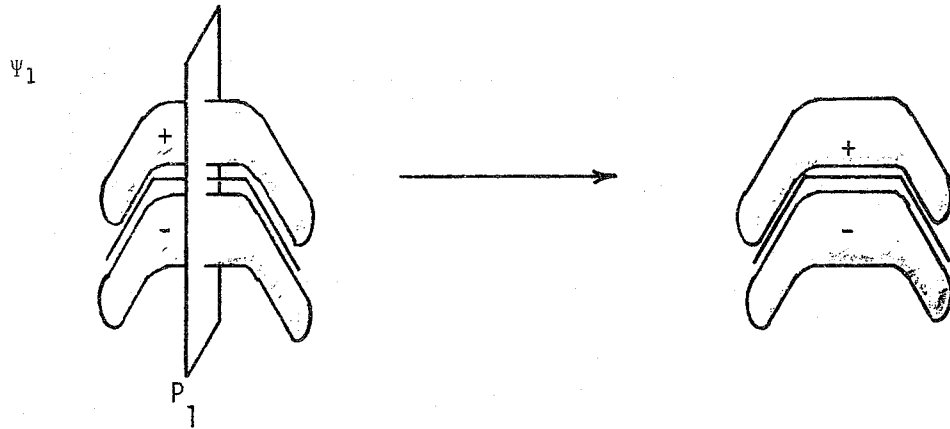
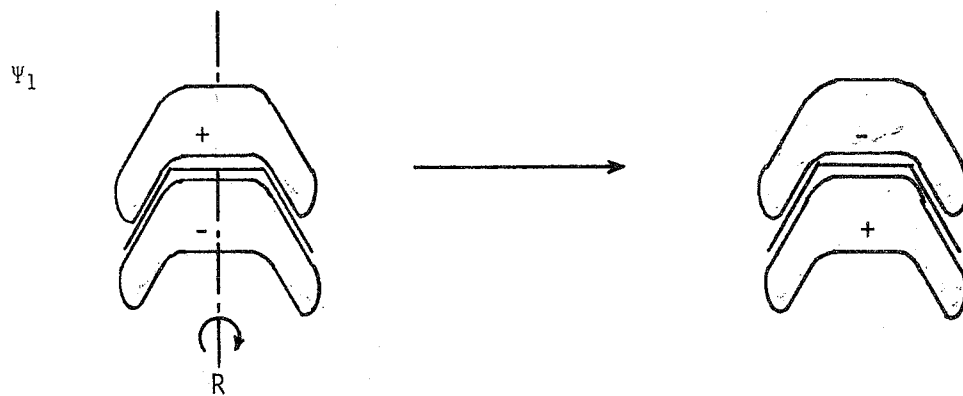


Figure 1-22.



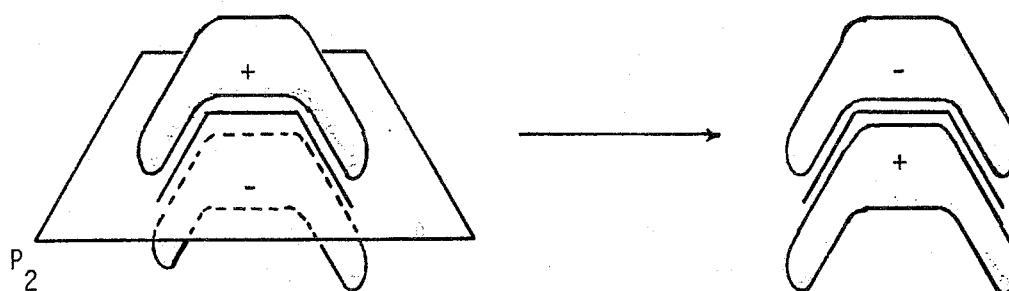
Ψ_1 is the same after reflection through plane P_1 ; " Ψ_1 is symmetric (S) with respect to P_1 ."

Figure 1-23.



Ψ_1 is the same but with the signs reversed; it is transformed into the negative of itself by rotation about R ; " Ψ_1 is antisymmetric (A) with respect to R ."

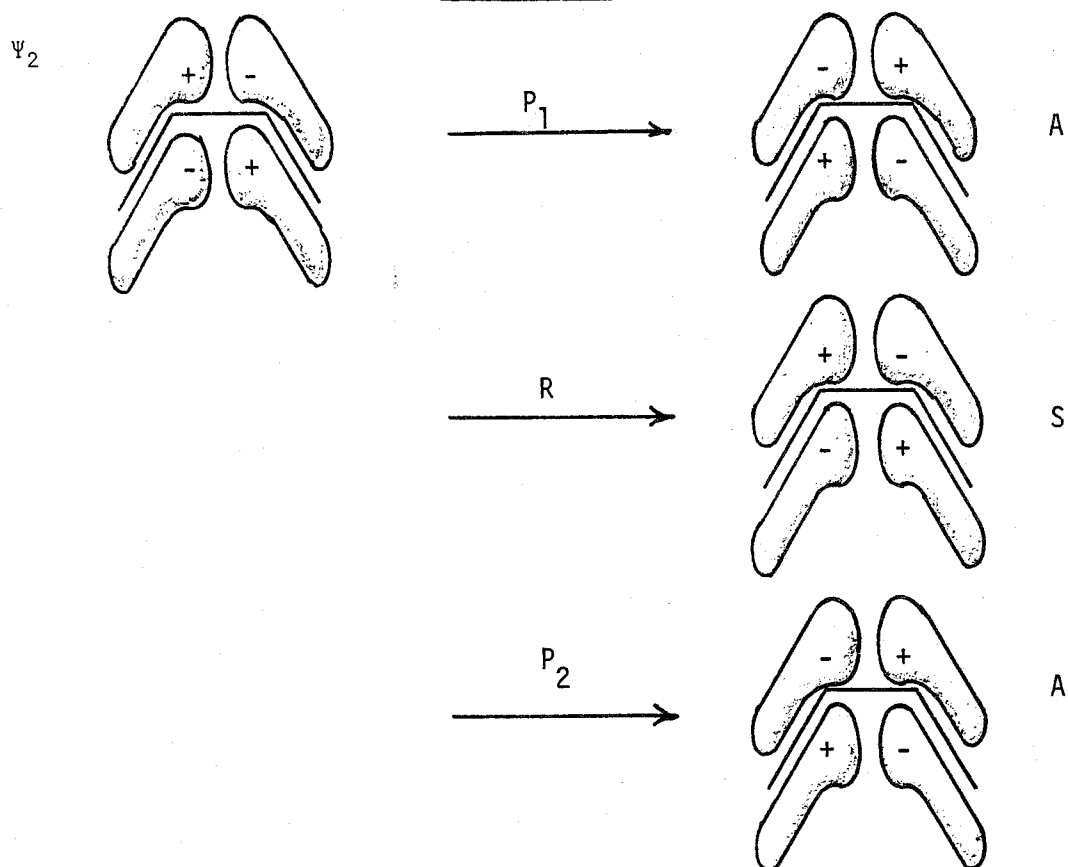
Figure 1-24



ψ_1 is antisymmetric with respect to P_2 .

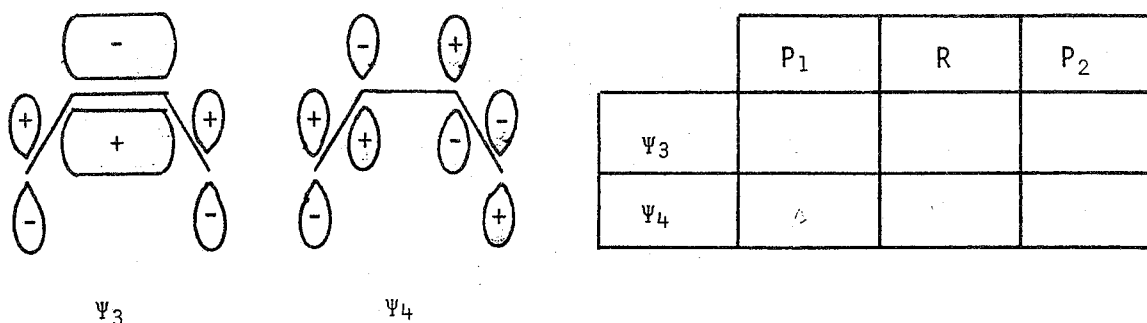
Note π -type orbitals are always A with respect to the plane of the carbon nuclei.

Figure 1-25.



Problem 1-1.

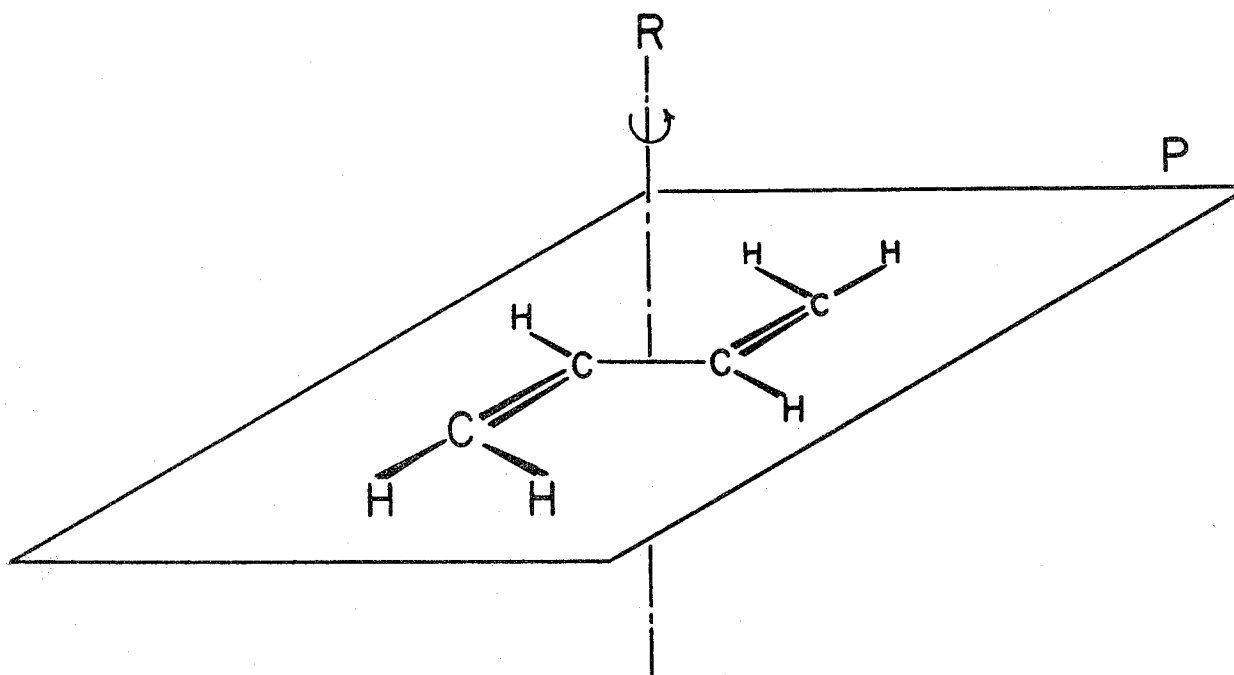
Classify Ψ_3 and Ψ_4 of butadiene with respect to the three symmetry elements of s-cis butadiene.



Classification of orbitals depends on shape of molecule and symmetry elements present.

Figure 1-26.

s-trans-Butadiene



Problem 1-2.

Classify the four MO's of butadiene (Figure 1-17) with respect to the two symmetry elements of s-trans butadiene.

	R	P
Ψ_1		
Ψ_2		
Ψ_3		
Ψ_4		

Figure 1-27.

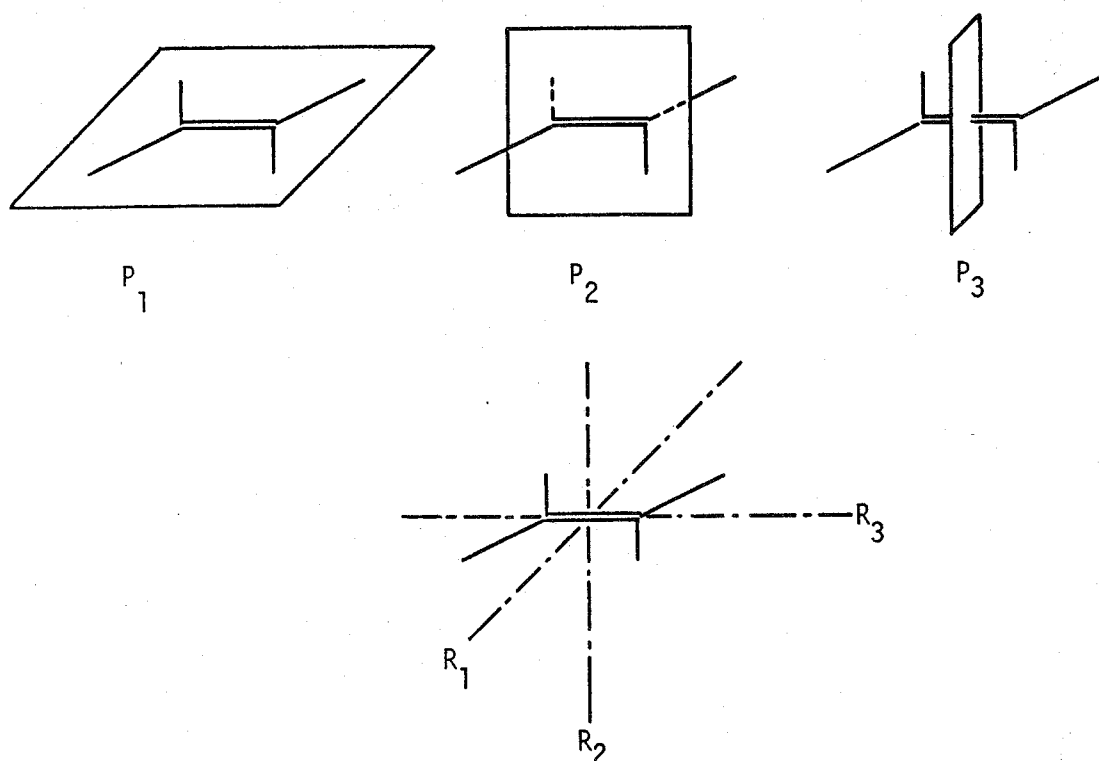
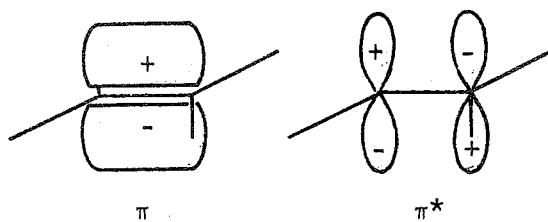


Figure 1-28.



Problem 1-3.

Classify the two π -MO's of ethylene with respect to the six symmetry elements.

	P_1	P_2	P_3	R_1	R_2	R_3
π						
π^*						

Rule:

A molecular orbital must be either symmetric or antisymmetric to each symmetry element of the molecule. (Exception: axes more than twofold.)

Figure 1-29.

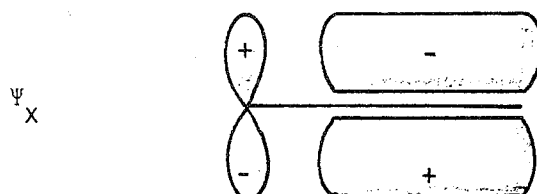
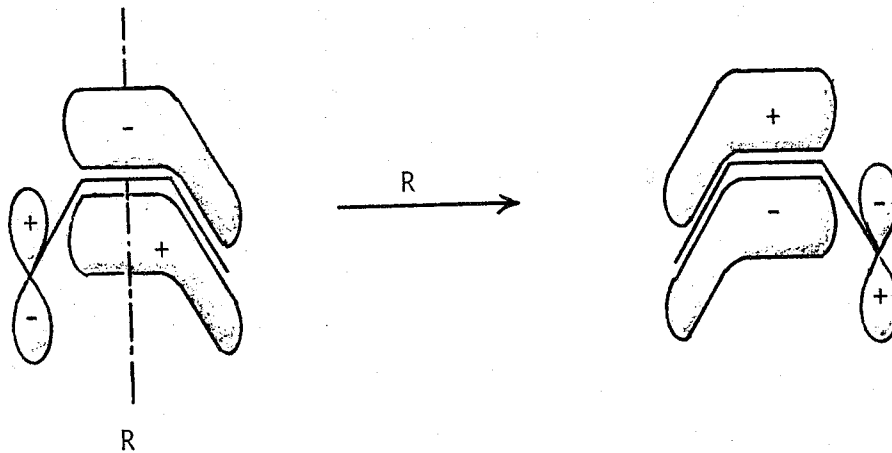
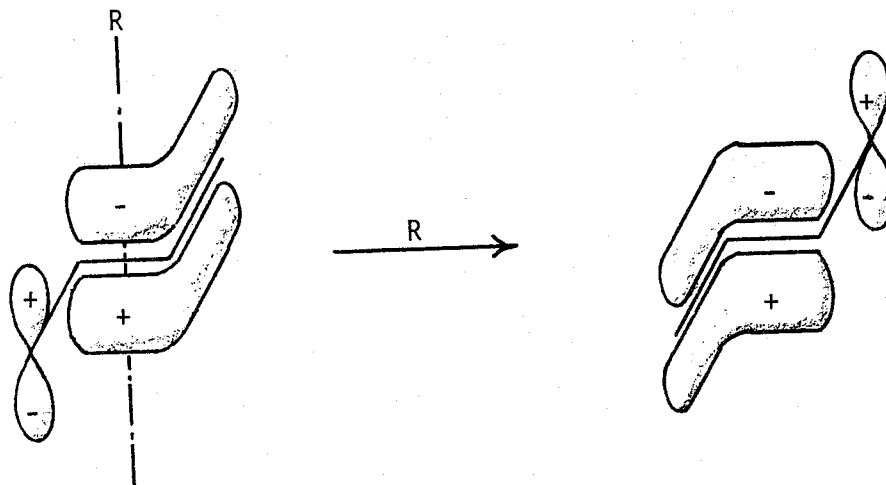


Figure 1-30.



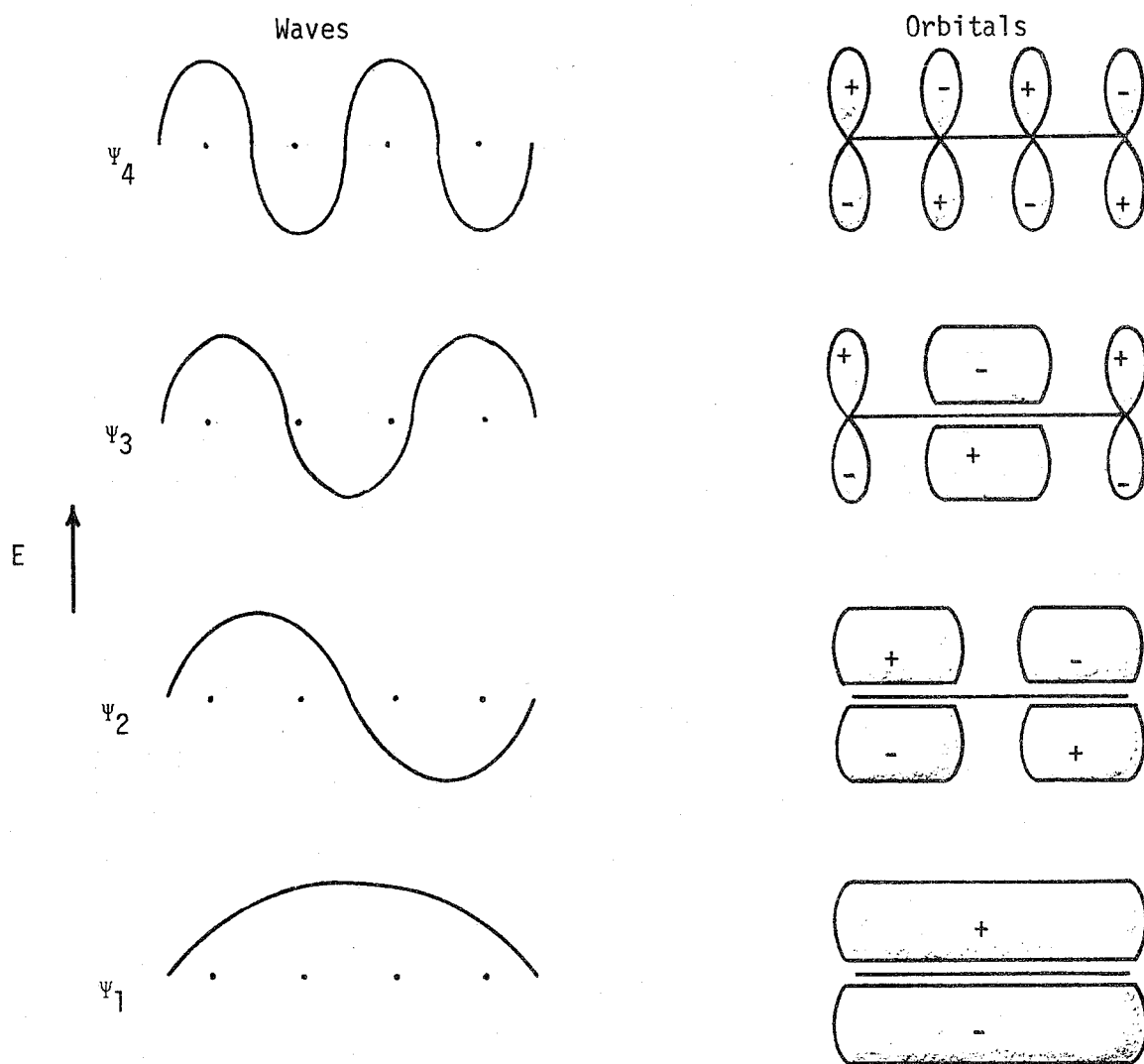
ψ is not transformed into itself, and not transformed into its negative; it is neither A nor S.

Figure 1-31.



To make MO's for linear conjugated polyene; MO's resemble the standing waves of a vibrating string.

Figure 1-32.



Summary

To describe a molecule in terms of π -MO's:

- (1) Start with σ -bonded framework and basis set of p orbitals
 - (2) No. of π -MO's to be formed = no. of p orbitals
 - (3) Write waves to set up pattern of nodes; write orbitals
 - (4) Check for symmetry correctness
 - (5) Put required number of electrons in orbitals
-

Problem 1-4.

Make a set of π -MO's for allyl cation $\text{CH}_2=\text{CH}-\text{CH}_2^+$; designate the symmetry of each MO with respect to the symmetry elements present.

(A hint is given.)

Ground and excited states.

Ground state: Molecule with electrons in electron configuration of lowest energy. Electron configuration predicted by Aufbau principle (and Pauli principle and Hund's rule).

(Electronically) Excited state: Molecule in any other electron configuration.

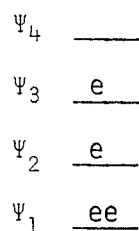
Figure 1-33.

Butadiene Ground State

Ψ_4	_____
Ψ_3	_____
Ψ_2	<u>ee</u>
Ψ_1	<u>ee</u>

Figure 1-34.

Lowest-energy Excited State of Butadiene

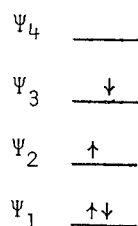


Multiplicity = Number of unpaired electrons + 1

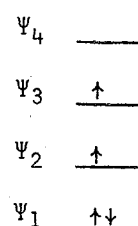
Singlet: No unpaired electrons

Triplet: Two unpaired electrons

Figure 1-35.



Lowest-energy
singlet excited
state



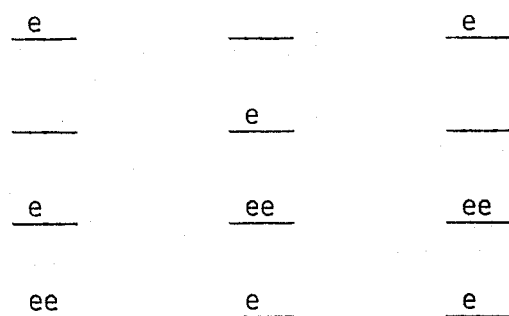
Lowest-energy
triplet excited
state

A triplet state is lower in energy than a singlet state of the same electron configuration (Hund's rule).

Figure 1-36.

Higher-energy Excited States

Singly-excited states:



Doubly-excited states:

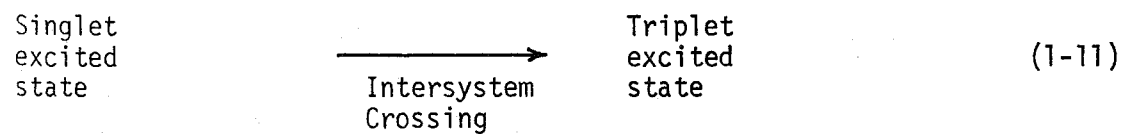
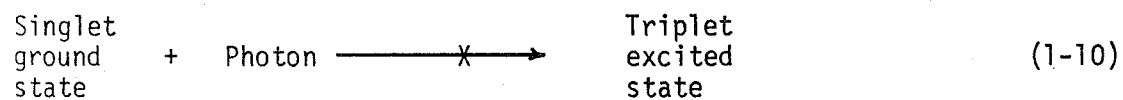
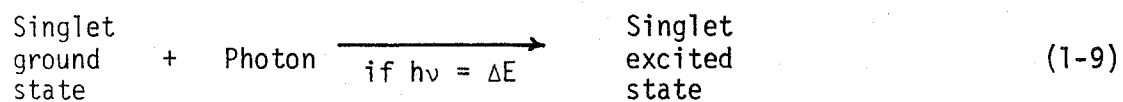
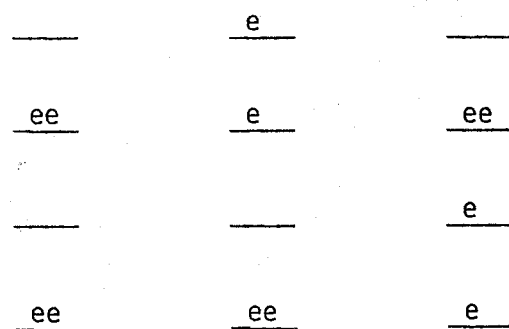
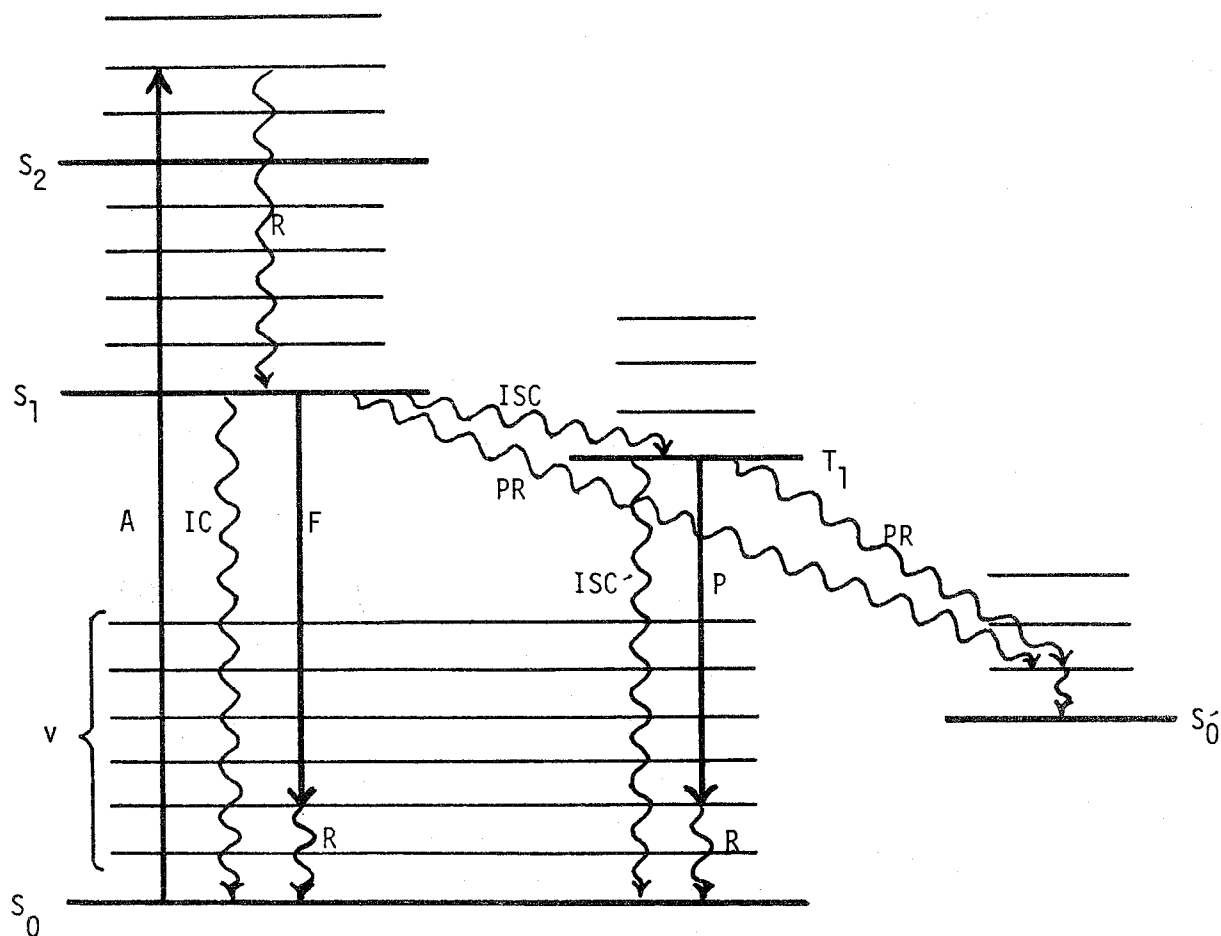


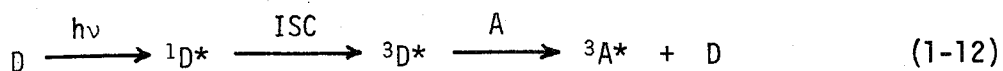
Figure 1-37.

Jablonski Diagram



- | | |
|--------------------|---|
| \longrightarrow | Radiative process (absorption or emission) |
| \rightsquigarrow | Radiationless process |
| S_0 | Singlet ground state |
| S_1 | Lowest singlet excited state |
| S_2 | Higher singlet excited state |
| T_1 | Lowest triplet excited state |
| v | Vibrational levels |
| A | Absorption |
| R | Vibrational relaxation |
| F | Fluorescence |
| IC | Internal conversion |
| ISC, ISC' | Intersystem crossing |
| P | Phosphorescence |
| PR | Photochemical reaction |
| S'_0 | Singlet ground state of photochemical product |

Photosensitization



General references: C. A. Coulson, "Valence," 2nd ed., Oxford University Press, London, 1961.

M. Orchin and H. H. Jaffé, "Symmetry, Orbitals, and Spectra," Interscience, New York, N. Y., 1971.

J. D. Roberts, "Notes on Molecular Orbital Calculations," W. A. Benjamin, New York, N. Y., 1961.

F. A. Cotton, "Chemical Applications of Group Theory," 2nd ed., Interscience, New York, N. Y., 1971.

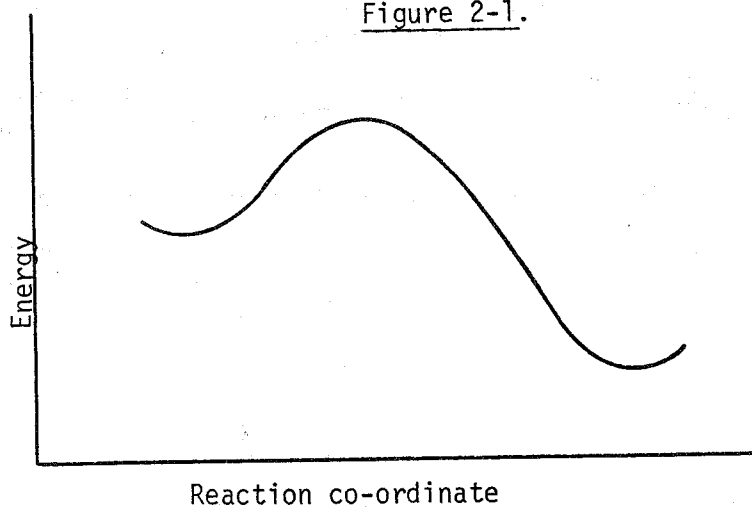
C. H. DePuy and O. L. Chapman, "Molecular Reactions and Photochemistry," Prentice-Hall, Englewood Cliffs, N. J., 1972.

Section 2.

Orbital and State Correlation Diagrams

Concerted reaction: One step, no intermediates (Example: S_N2 displacement)

Figure 2-1.



Non-concerted reaction: More than one step, one or more intermediates involved (Example: S_N1 displacement, intermediate carbonium ion)

Figure 2-2.

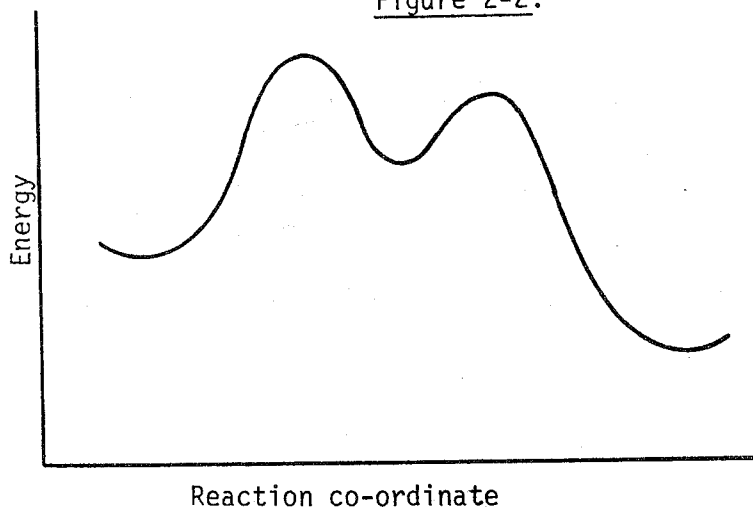
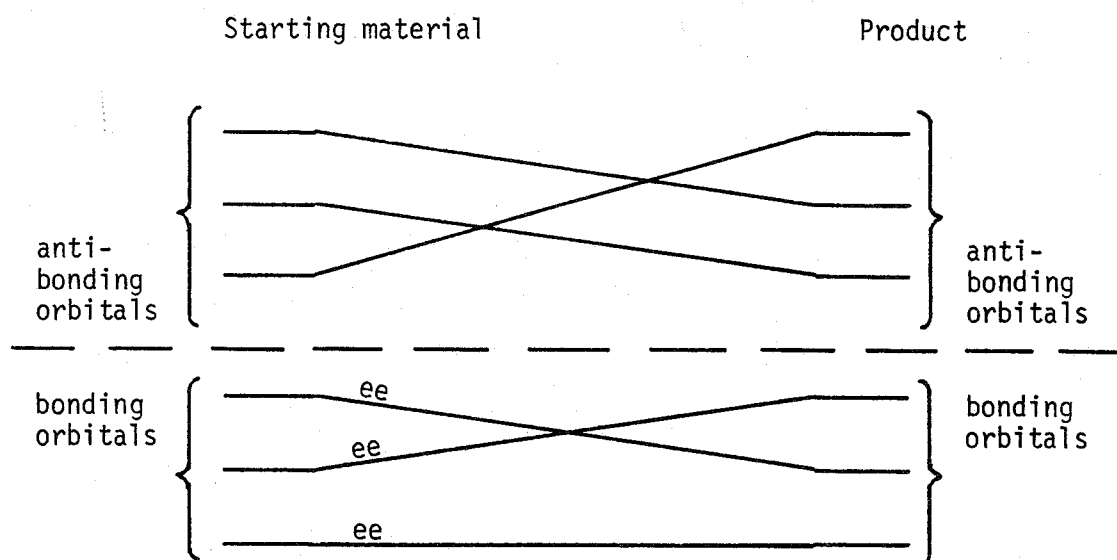


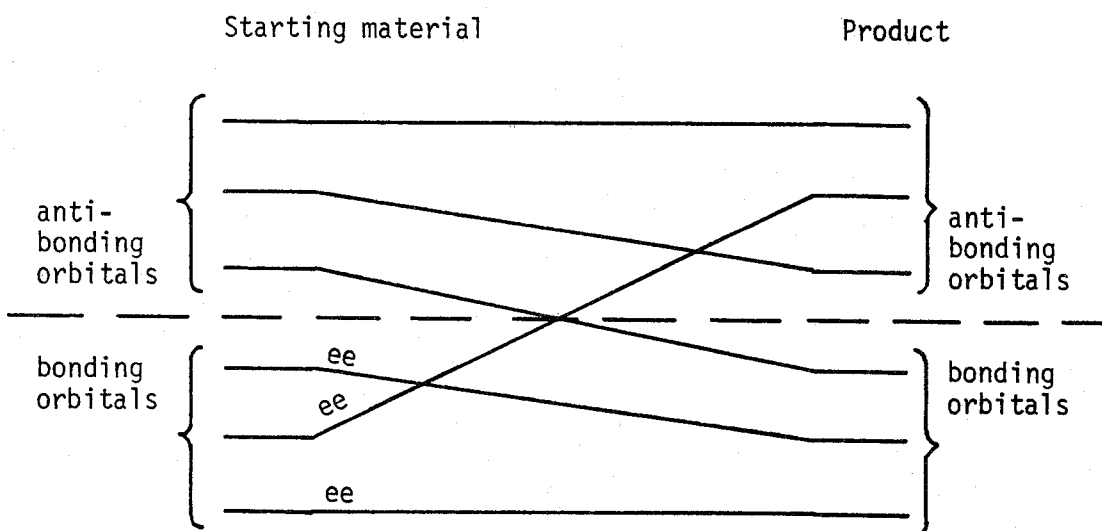
Figure 2-3.

Orbital Correlation Diagram



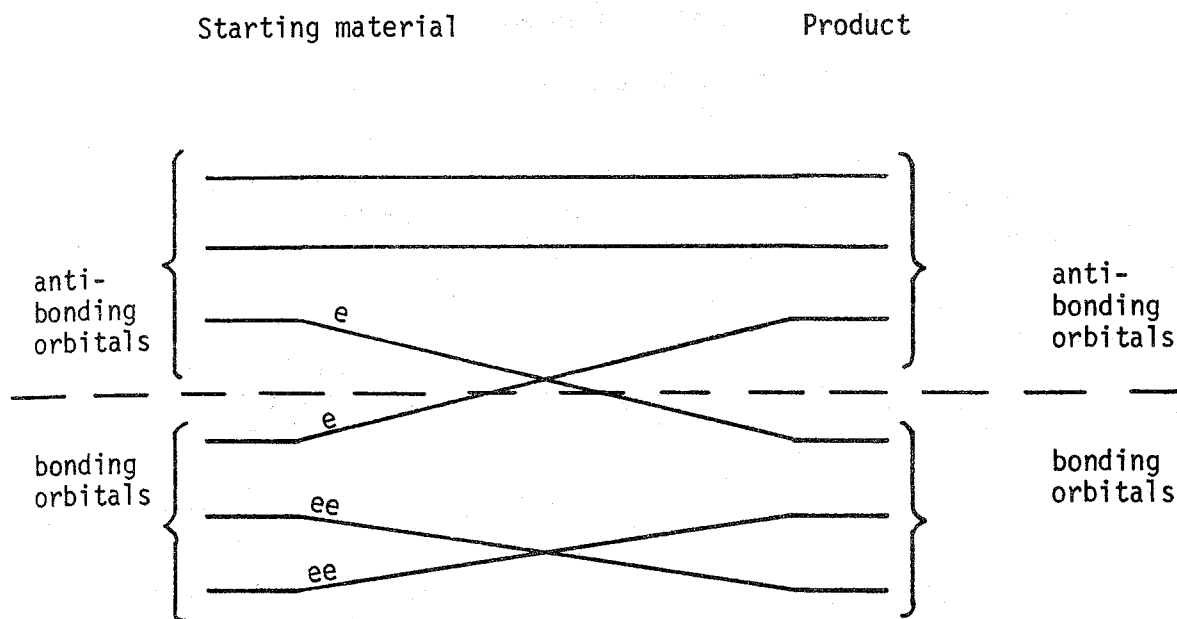
Reaction allowed in the ground state (thermal reaction is allowed).

Figure 2-4.



Reaction forbidden in the ground state.

Figure 2-5.



Reaction allowed in the lowest excited state (photochemical reaction allowed).

The Conservation of orbital symmetry:

Orbitals in the starting material correlate with orbitals of the same symmetry in the product

Outline

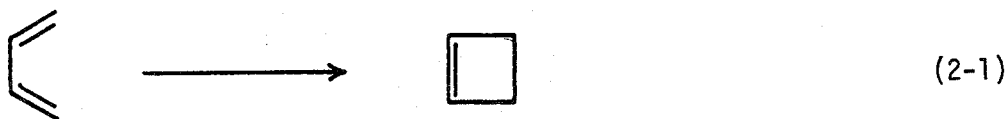
To construct an orbital correlation diagram:

- (1) Draw necessary orbitals of starting material and product on rough energy scale.
 - (2) Classify necessary orbitals of starting material and product with respect to one or more useful symmetry elements that are preserved during the reaction.
 - (3) Join orbitals of like symmetry.
 - (4) Place electrons in appropriate orbitals of starting material and allow them to flow into the correlating orbitals of the product; find if product is formed in ground state.
-

Thermal concerted reactions: Microscopic reversibility applies, examine reaction in whichever direction is convenient.

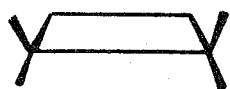
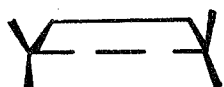
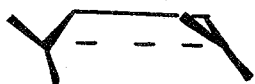
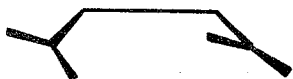
Photochemical reactions: Treat same way (artificial treatment).

Reaction:

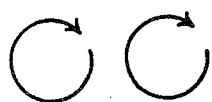


Two stereochemically different ways this reaction can occur

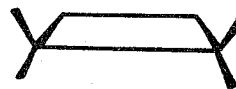
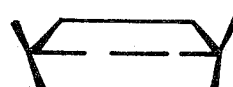
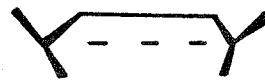
Figure 2-6.



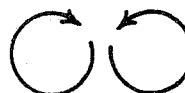
conrotatory



groups turning
in the same
direction



disrotatory

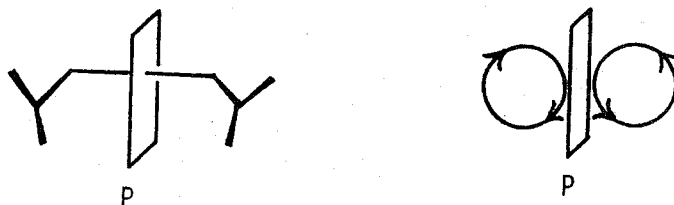


groups turning
in opposite
directions

Starting material and product are the same in each case if there are no labels, but the symmetry preserved during the reaction is different.

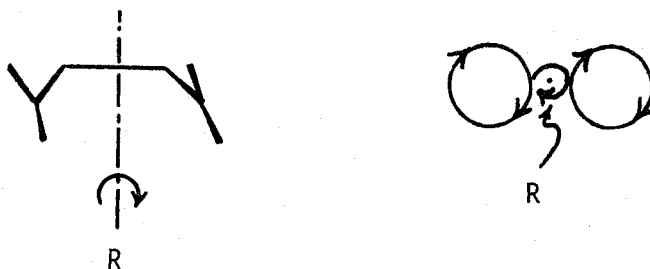
Disrotatory: One symmetry element present during reaction
-- a plane.

Figure 2-7.

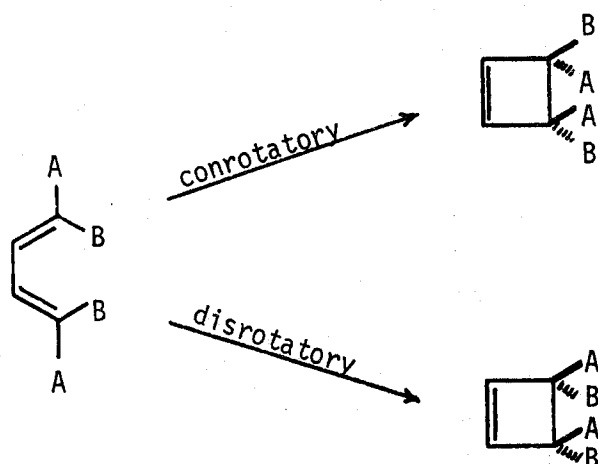


Conrotatory: One symmetry element present during reaction
-- a twofold axis.

Figure 2-8.



With labels, the two paths are different.



(2-2)

Constructing an orbital correlation diagram for the conrotatory reaction.

Selecting necessary orbitals: Use arrows



Starting material (butadiene): use four π -MO's; C-C and C-H σ bonds don't change.

In the product these form:

π and π^* orbitals of C=C
 σ and σ^* orbitals of new C-C

The other single bonds are present in the starting material.

Note same number of orbitals in each molecule are considered.

Classify necessary orbitals with respect to twofold axis preserved during reaction.

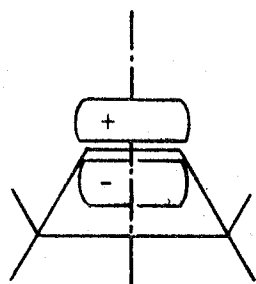
Table 2-1

Butadiene:		R
	Ψ_4	S
	Ψ_3	A
	Ψ_2	S
	Ψ_1	A

Figure 2-9.

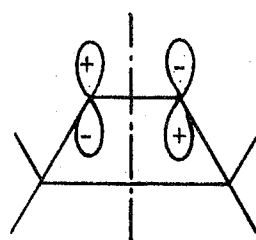
Cyclobutene Orbital

Symmetry
with respect to R



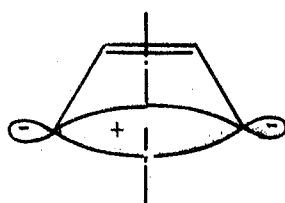
π

A



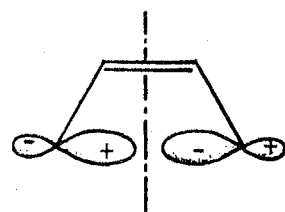
π^*

S



σ

S

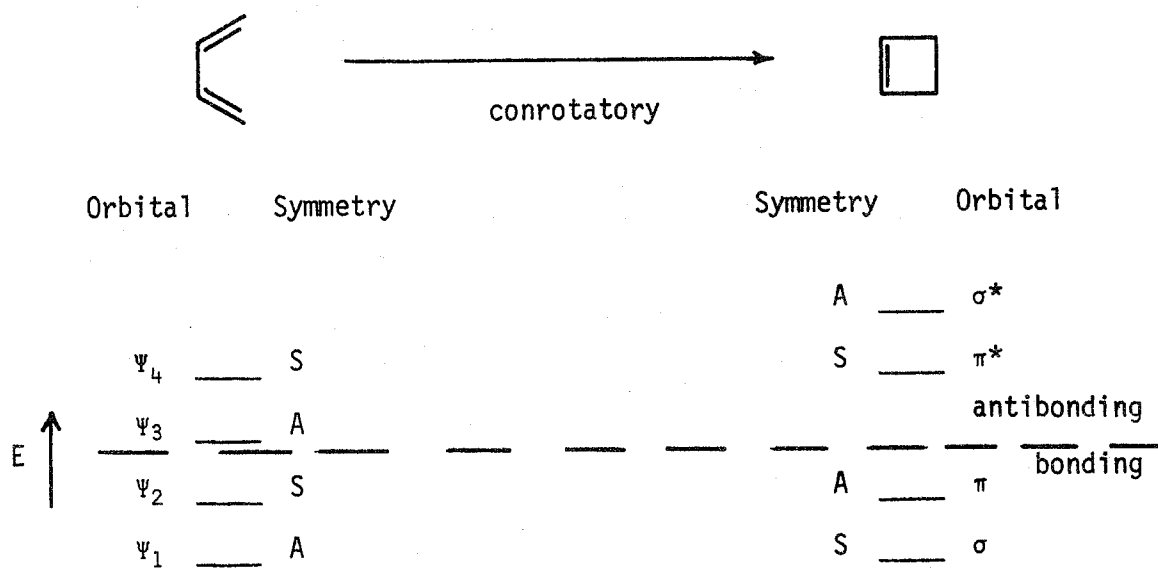


σ^*

A

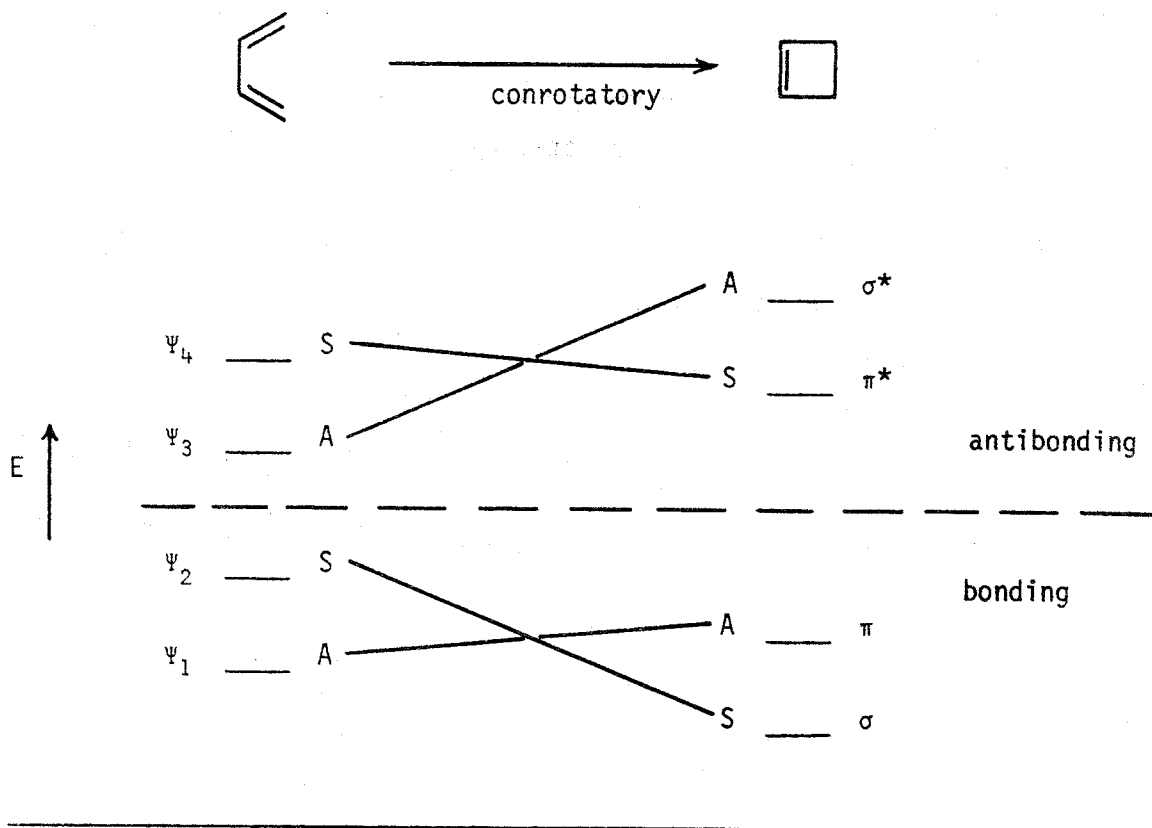
Figure 2-10.

Energy Level Diagram



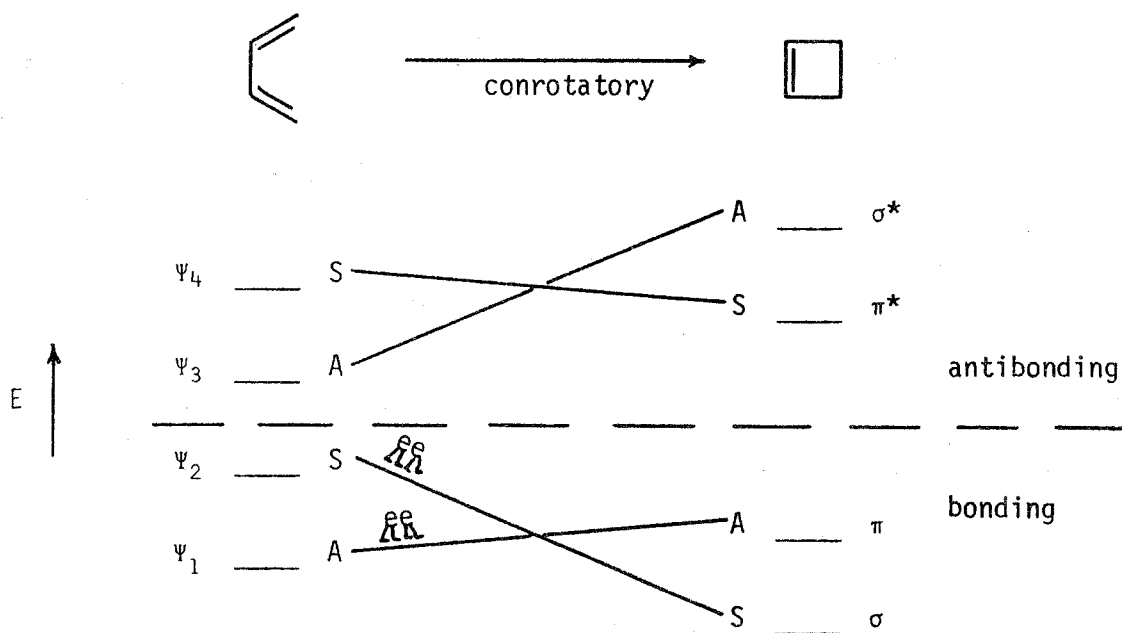
Join orbitals of like symmetry on left and right

Figure 2-11.



Electron occupation: Butadiene, $\Psi_1^2\Psi_2^2$ in ground state.

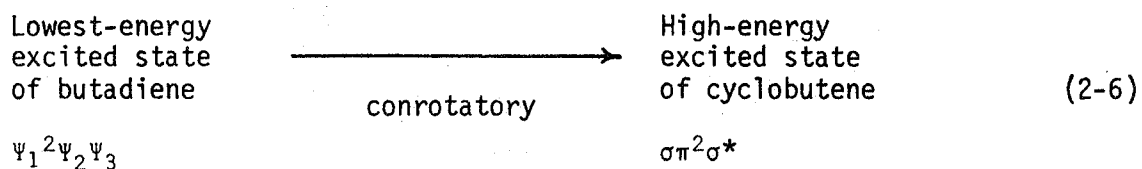
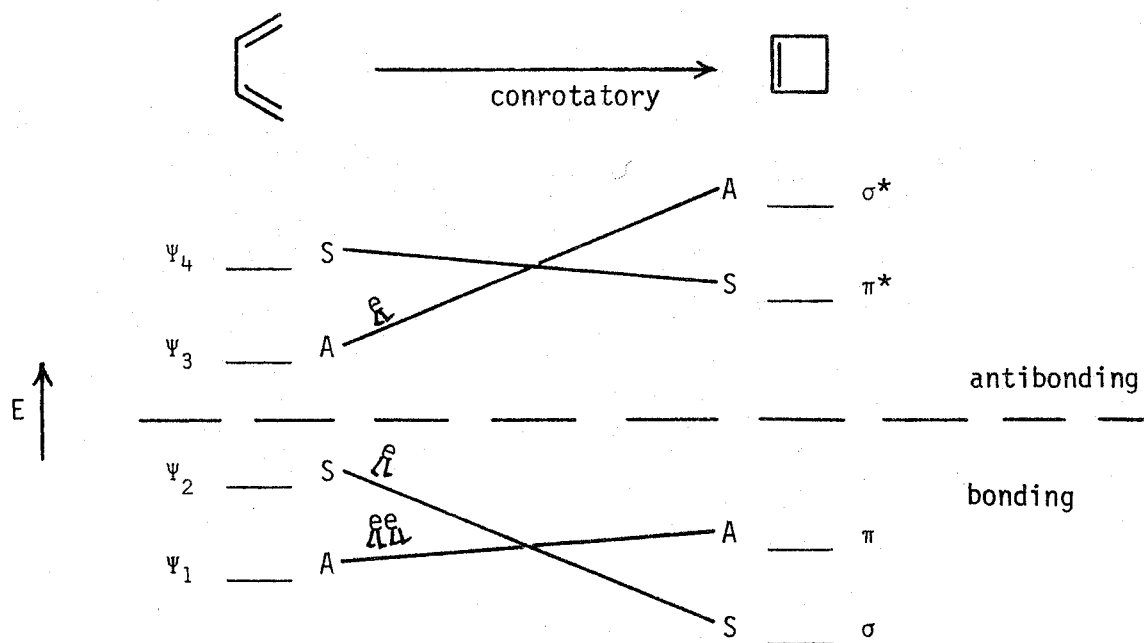
Figure 2-12.



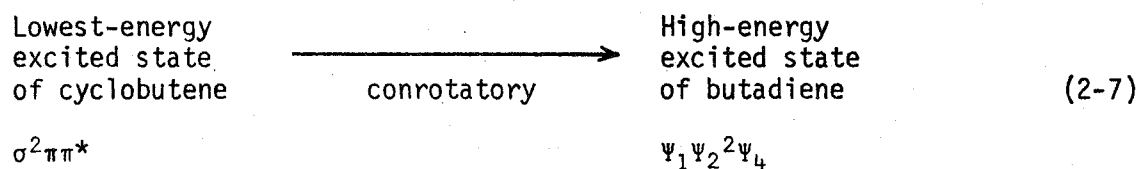
Conrotatory reaction is allowed in the ground state, in either direction.

Start in lowest excited state of butadiene.

Figure 2-13.



Reverse reaction:



Photochemical conrotatory reaction is forbidden.

State correlation diagrams

Ground and excited states of starting material and product placed on rough energy scale. Correlation between states is obtained from the orbital correlation diagram.

Only ground and lowest excited states, and the states they correlate with, are shown here.

Figure 2-14.

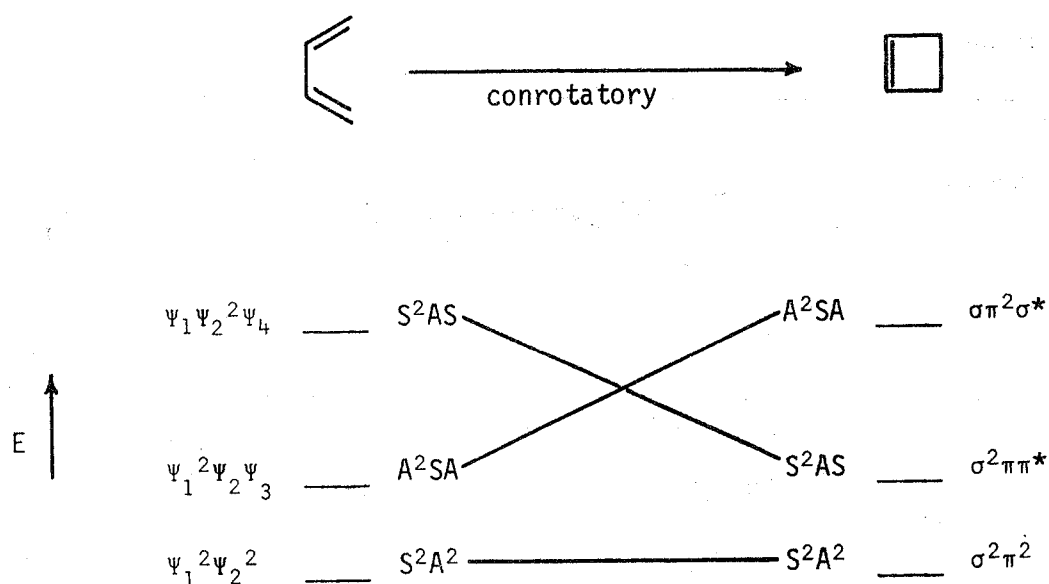
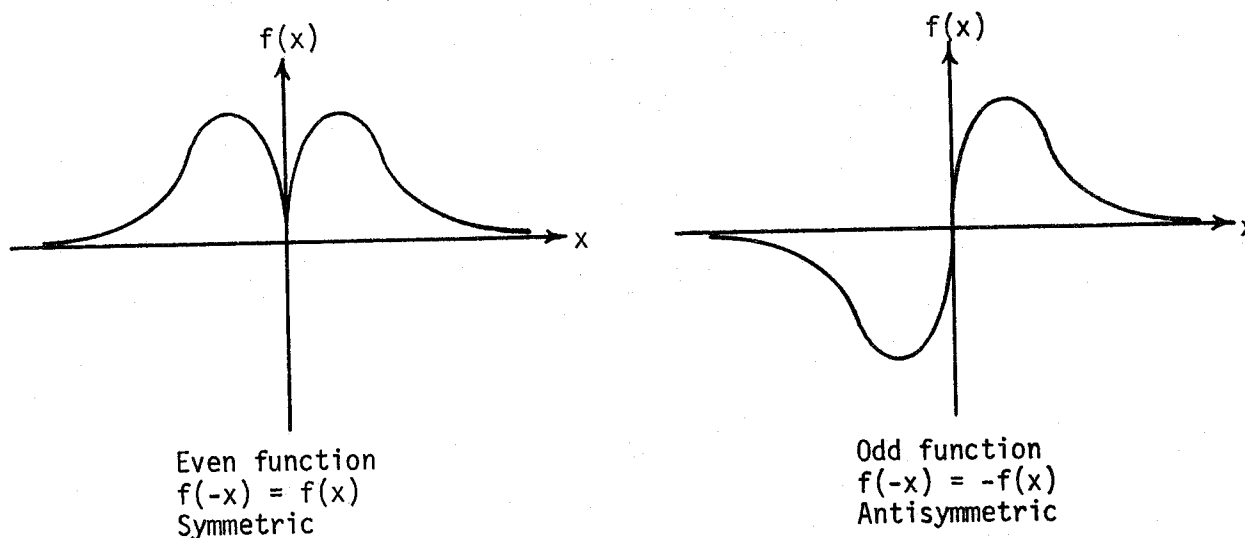


Figure 2-15.



(even function) x (even function) = (even function)

(odd function) x (odd function) = (even function)

(even function) x (odd function) = (odd function)

$$S \times S = S$$

$$A \times A = S$$

$$S \times A = A$$

State symmetry from orbital symmetry:

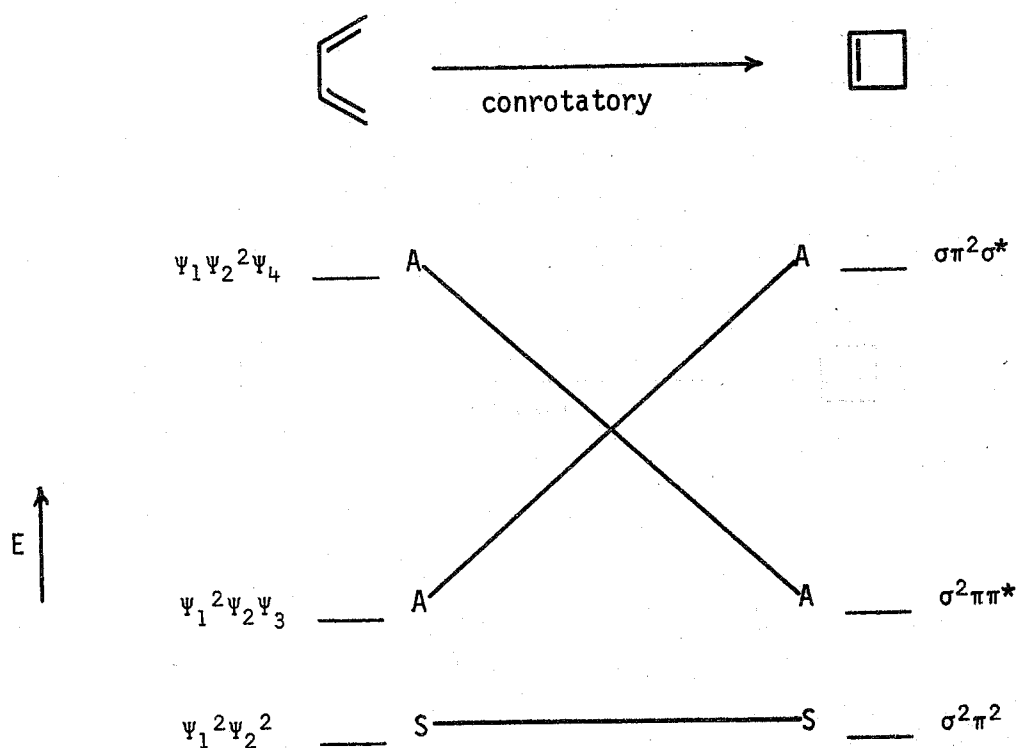
State symmetry is product of orbital symmetries (in group theory, the direct product)

$$S^2 A^2 = S$$

$$S^2 A S = A^2 S A = A$$

Figure 2-16.

State correlation diagram with correct state symmetry



Lines correlating states of the same symmetry cannot cross.

Configuration interaction

Two states of the same symmetry interact by forming linear combinations between themselves to form two new states, one of higher energy than the high energy unmixed state, and one of lower energy than the unmixed low energy state.

The amount of mixing is inversely proportional to the difference in energy between the unmixed states.

Figure 2-17.

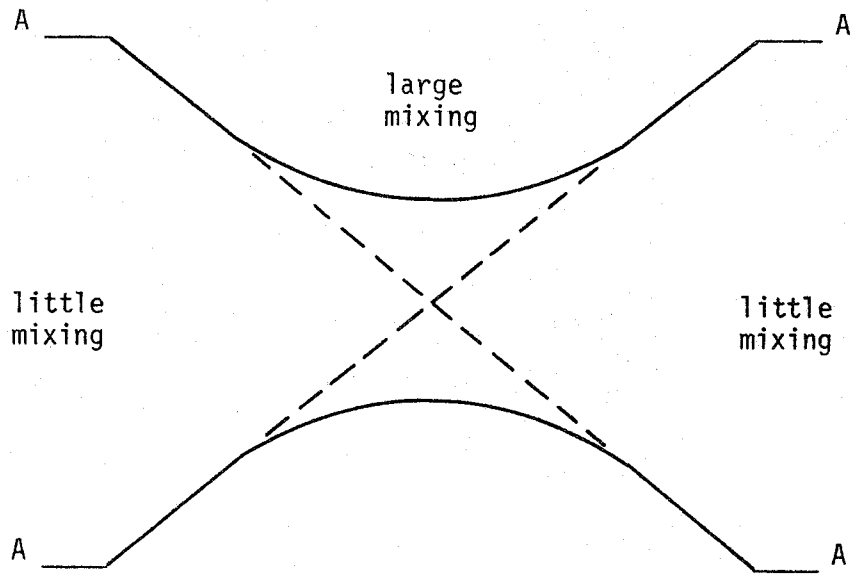
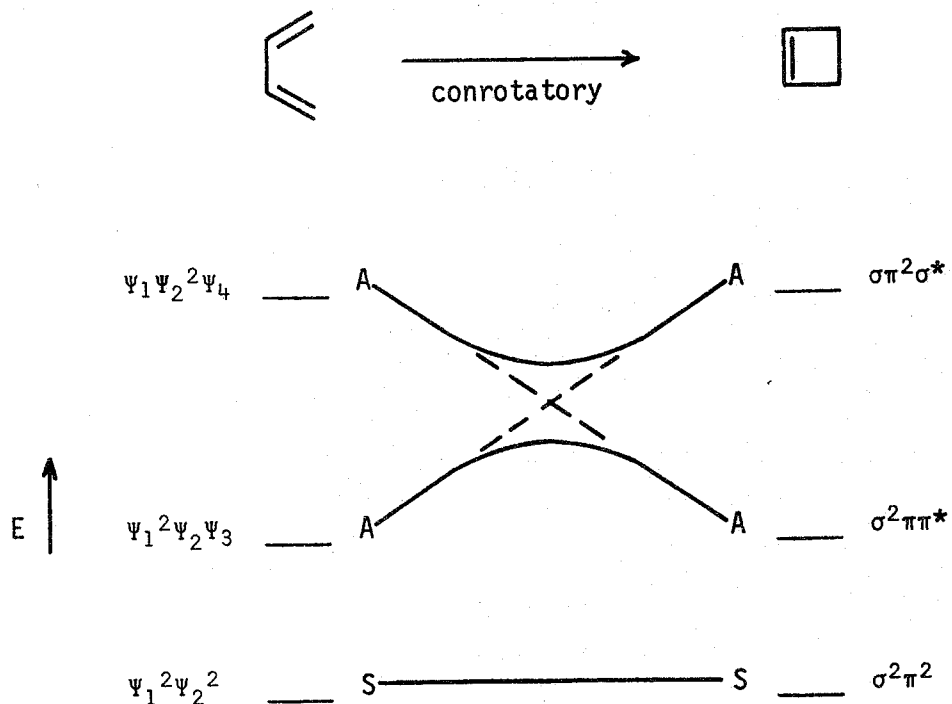


Figure 2-18.

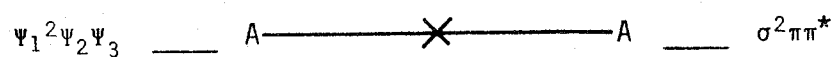
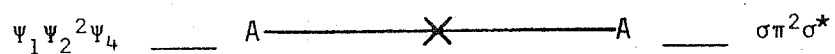
Correct state correlation diagram



The reaction is allowed in the ground state (either direction), forbidden in the lowest excited state (either direction).

Incorrect to correlate lowest excited states of A symmetry directly because the orbitals do not correlate (from the orbital correlation diagram).

Figure 2-19.



Disrotatory reaction path -- plane of symmetry preserved

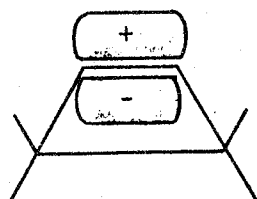
Table 2-2

Butadiene:	P_1
ψ_4	A
ψ_3	S
ψ_2	A
ψ_1	S

Figure 2-20.

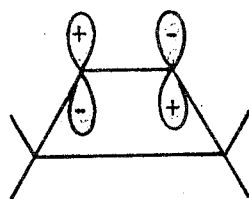
Cyclobutene orbitals

Symmetry with
respect to P_1



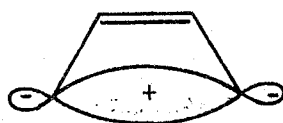
π

S



π^*

A



σ

S



σ^*

A

Figure 2-21.

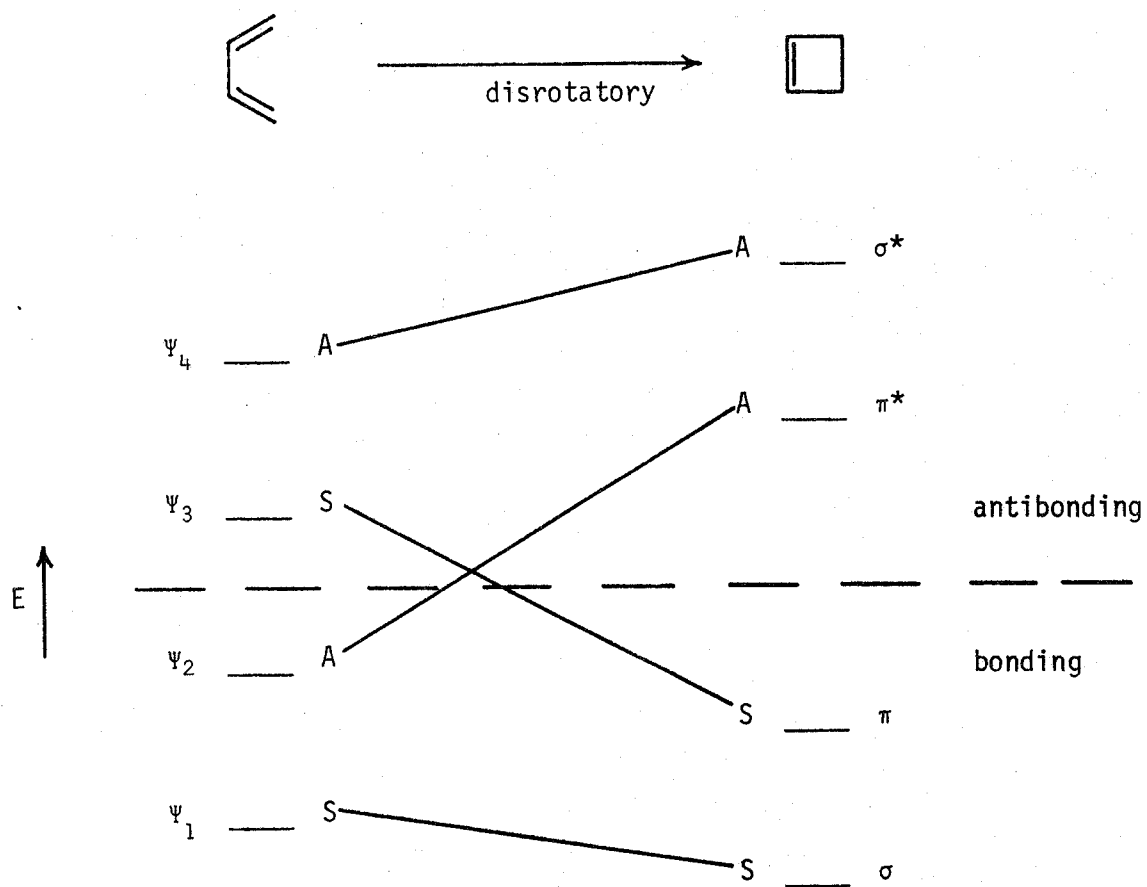
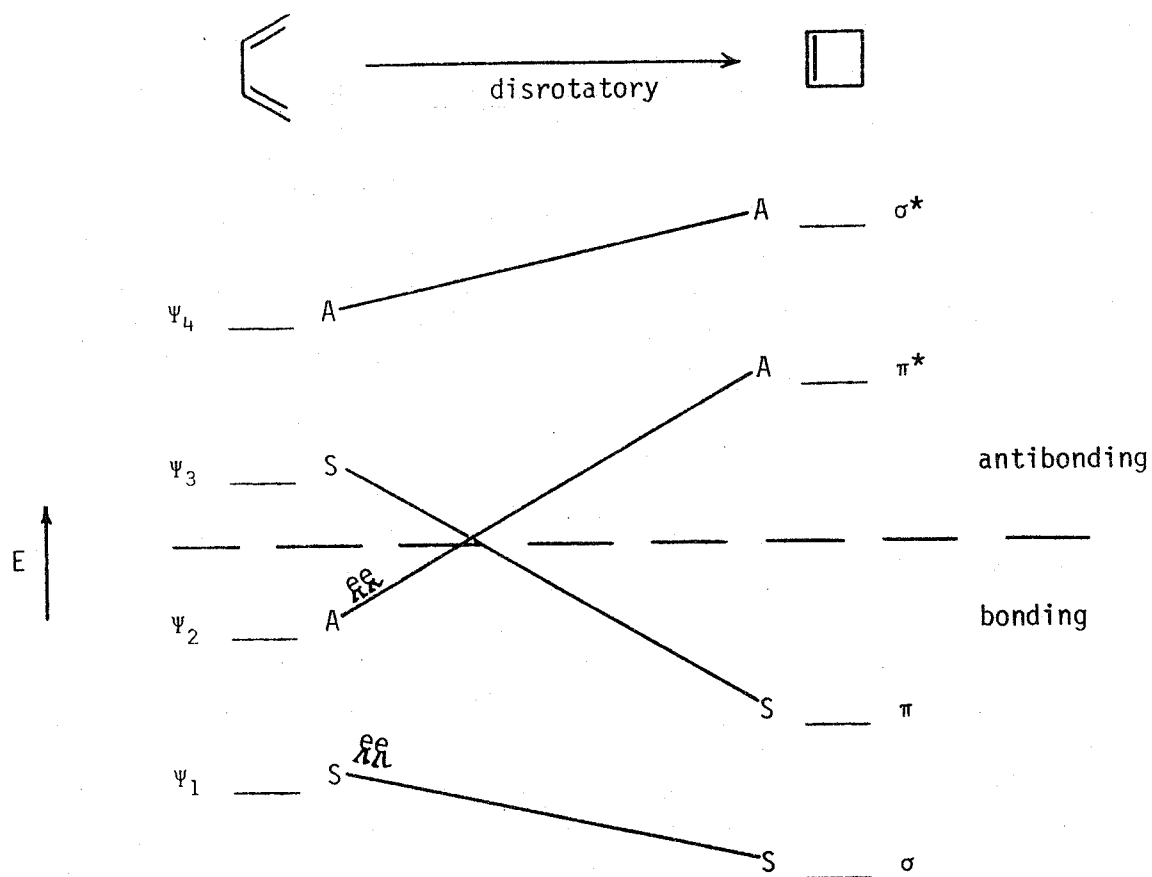


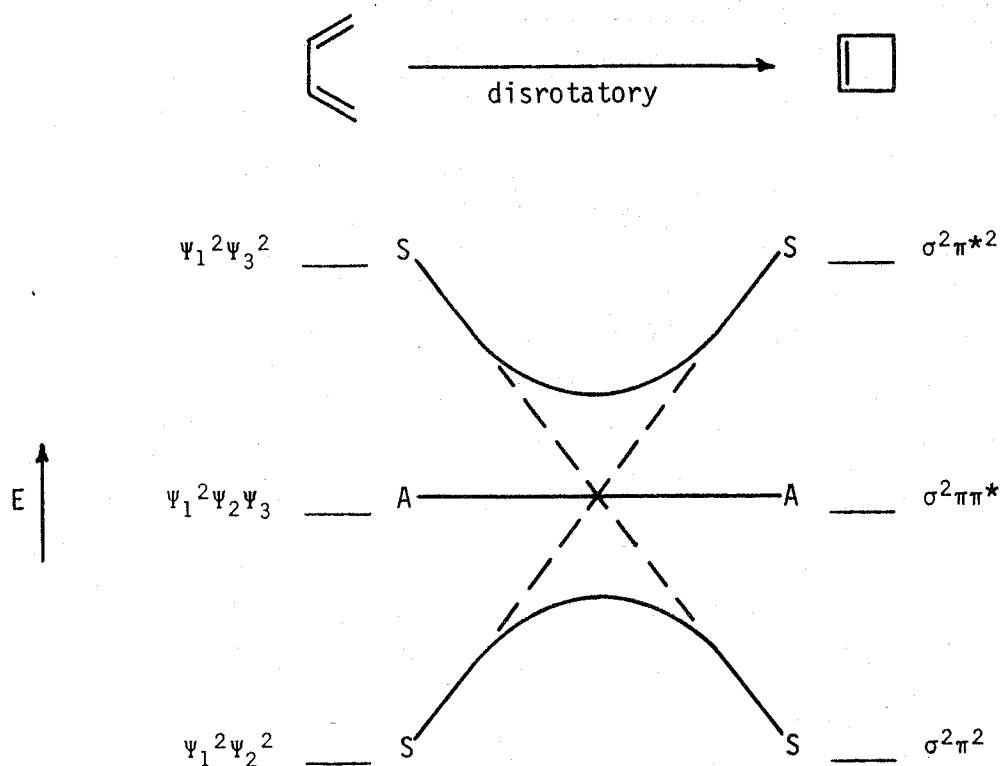
Figure 2-22.



Reaction is forbidden in ground state -- correlation with high energy excited state.

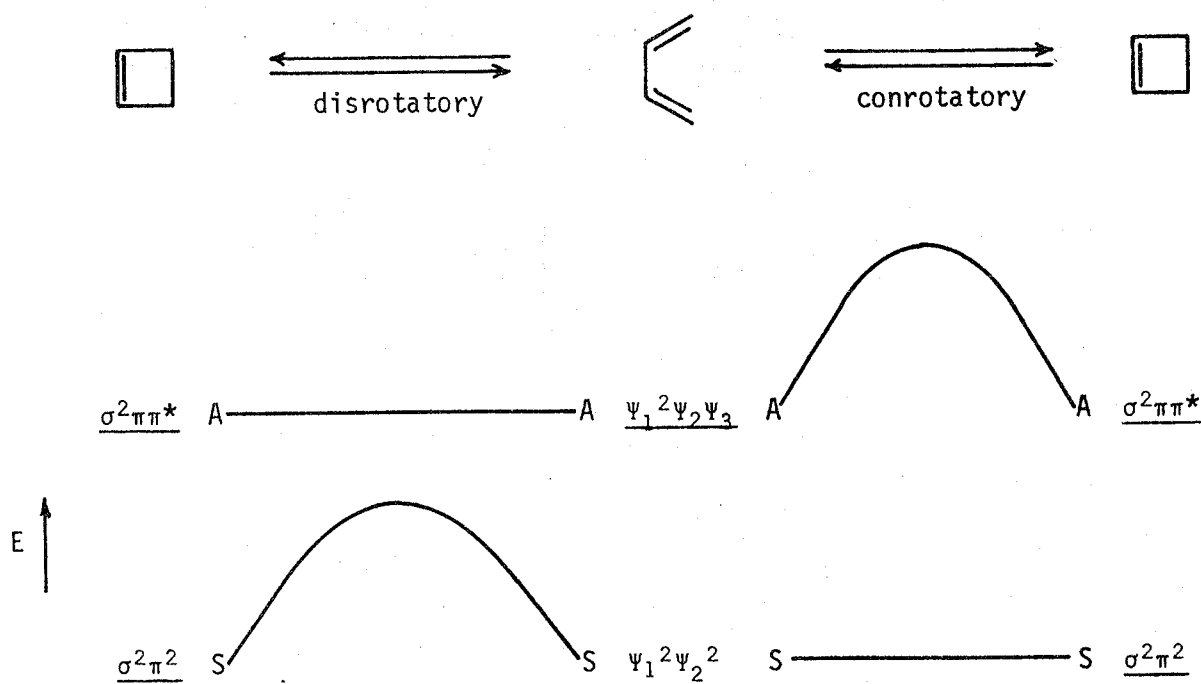
Figure 2-23.

State correlation diagram



Disrotatory reaction allowed in lowest excited state. Disrotatory reaction forbidden in ground state because of barrier imposed by intended correlation with high energy excited state.

Figure 2-24.



Correlation diagram does not include:

Difference in energy between states of different compounds (ΔG for reaction - determines direction of ground state reaction)

Activation energy for allowed process

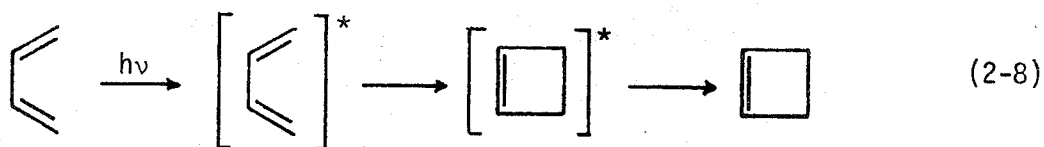
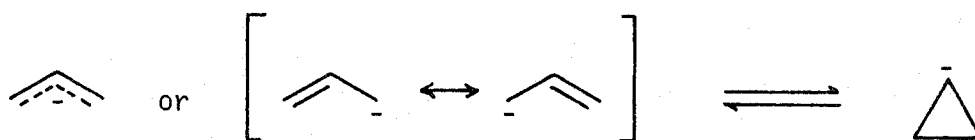
Difference in activation energies of allowed and forbidden processes

Note "forbidden" reaction path not really forbidden -- disfavored compared to allowed process by additional activation energy barrier, caused by intended correlation with high energy excited state.

Problem 2-1.

Draw correlation diagrams for the conrotatory and disrotatory closures of allyl anion to cyclopropyl anion.

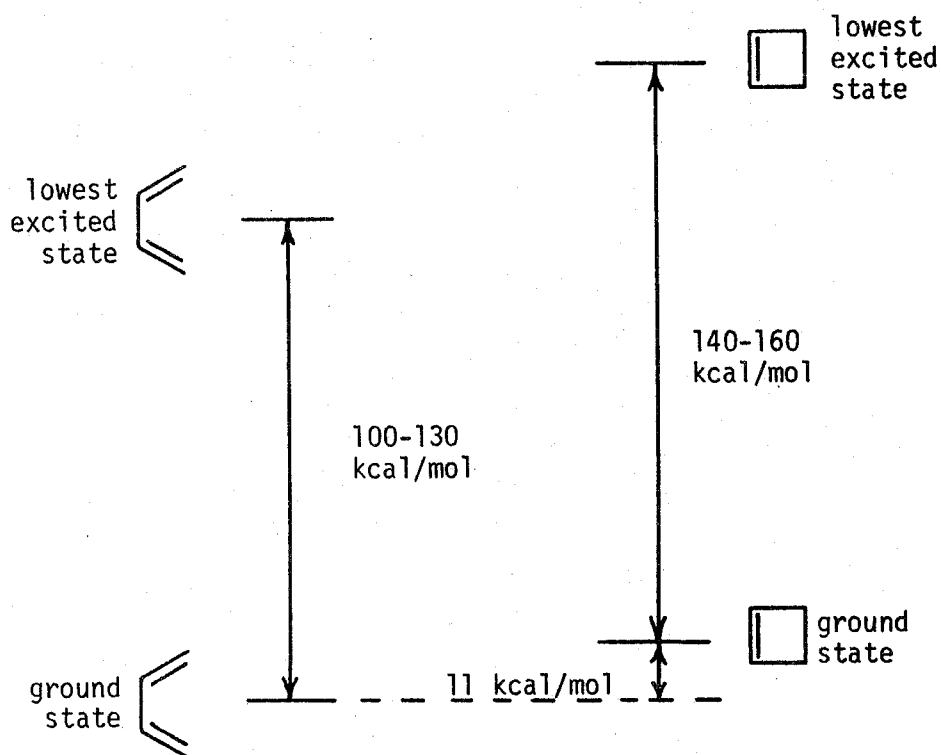
(A hint is given.)



Photochemical reaction occurs in this direction, not in this manner.

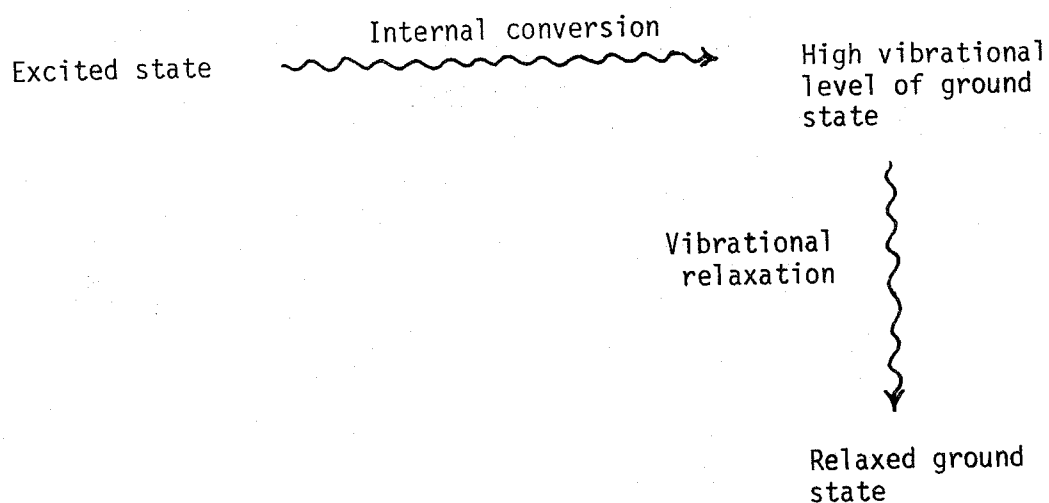
(1) Energetically unreasonable; (butadiene)* \rightarrow (cyclobutene)* is endothermic by about 45 kcal/mol.

Figure 2-25.



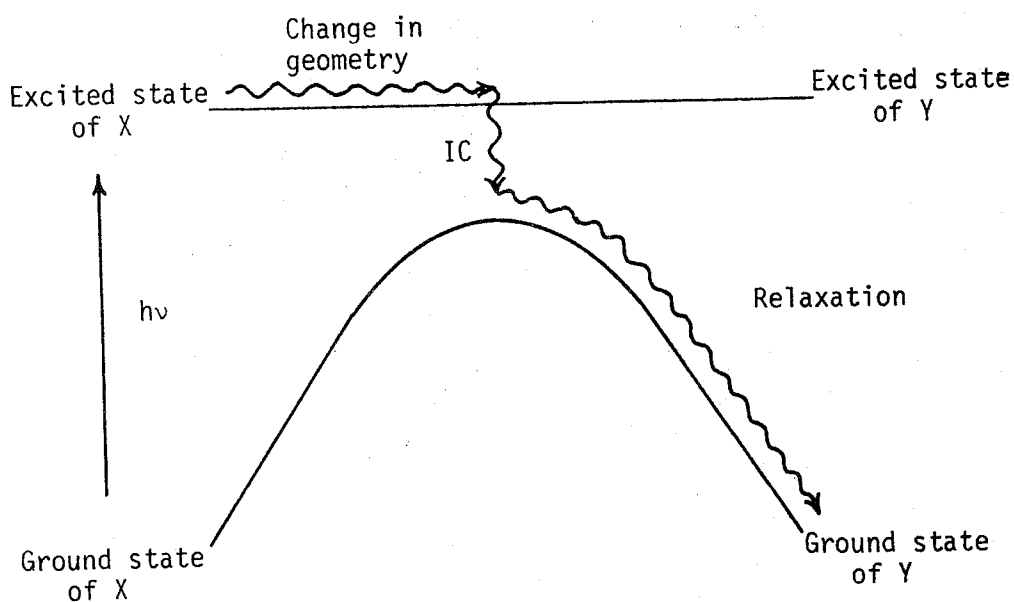
(2) Most photochemical reactions follow a different kind of path.

Figure 2-26.

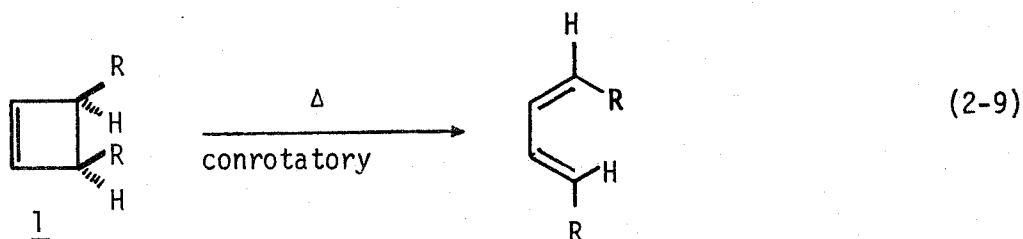


Probability of internal conversion is inversely proportional to difference in energy between excited and ground states.

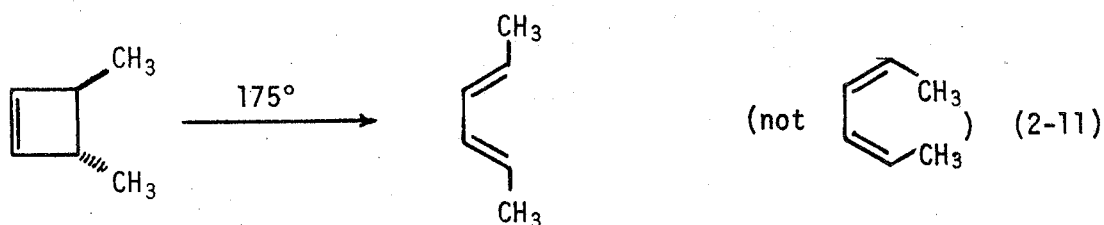
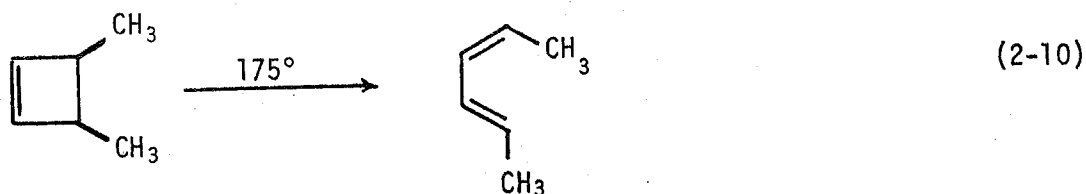
Figure 2-27.



References: G. S. Hammond in "Advances in Photochemistry," Vol. 7, J. N. Pitts, Jr., G. S. Hammond, and A. W. Noyes, Jr., Eds., Interscience, New York, N. Y., 1969, p 373; W. Th. A. M. van der Lugt and L. J. Oosterhoff, *J. Amer. Chem. Soc.*, 91, 6042 (1969); R. C. Dougherty, *ibid.*, 93, 7187 (1971).



Local symmetry: The bonds and orbitals that change in this reaction still have almost the same symmetry used to derive the correlation diagrams; the substituents are only a small perturbation, and shouldn't affect the result.



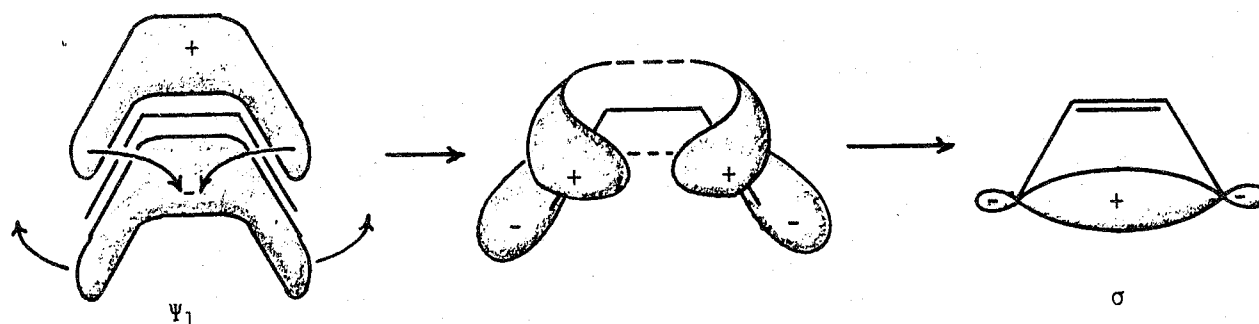
References: R. E. K. Winter, *Tetrahedron Lett.*, 1207 (1965); J. I. Brauman and W. C. Archie, Jr., *J. Amer. Chem. Soc.*, 94, 4262 (1972).

"Local symmetry" works because the generalizations of the orbital symmetry method are dependent on the nodal relationships in the molecular orbitals, not just on the symmetry present.

Disrotatory

Ψ_1 can close to give σ , allowing wave function to disappear at C_2 and C_3 .

Figure 2-28.



Ψ_2 can close smoothly only to σ^* or π^* .

Figure 2-29.

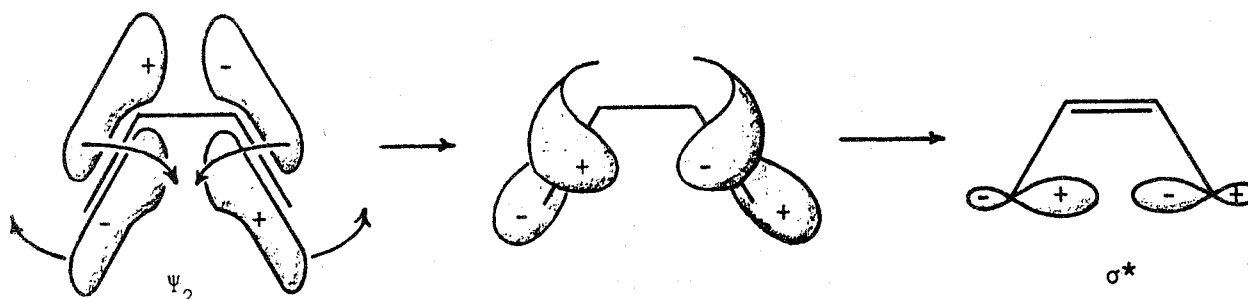
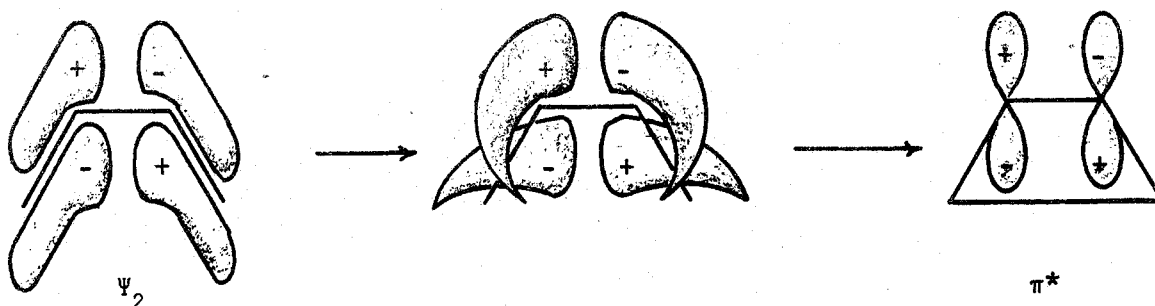


Figure 2-30.



A filled bonding orbital is transformed into an antibonding orbital of the product; the reaction is forbidden in the ground state -- without using symmetry.

Conrotatory

Figure 2-31.

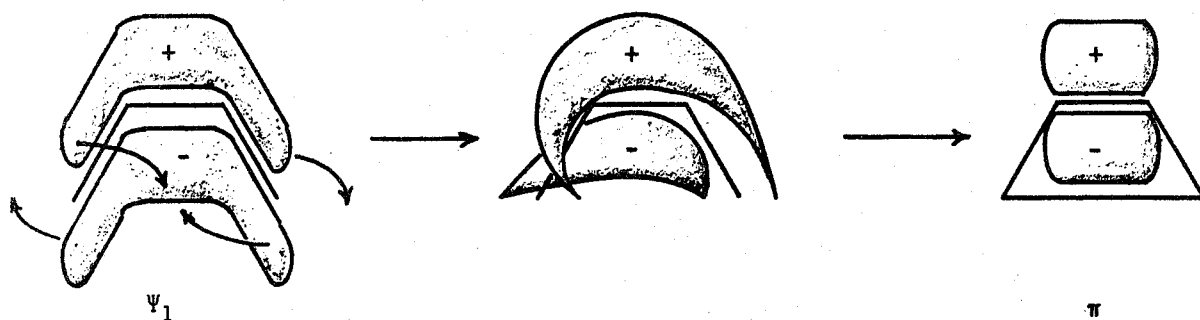
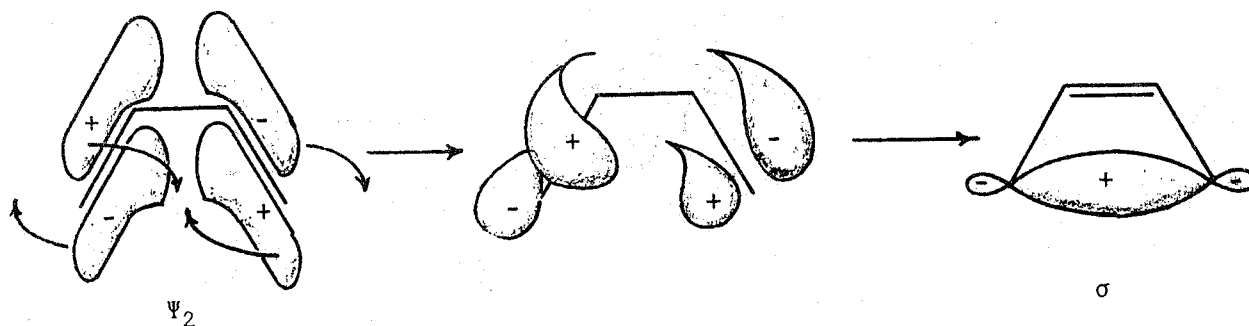
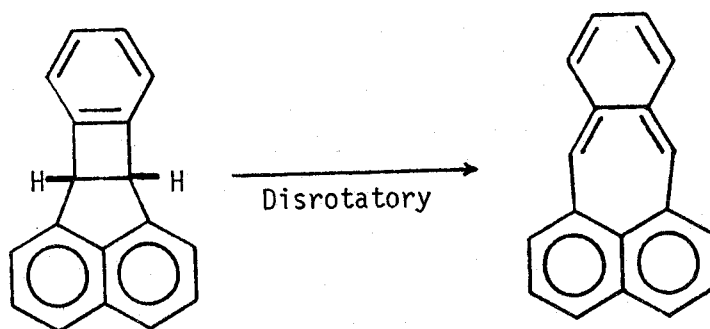


Figure 2-32.



In the conrotatory closure, filled bonding levels of the starting material are transformed smoothly into bonding levels of the product; the reaction is allowed in the ground state -- without using symmetry.



(2-12)

Neither ground states nor lowest excited states correlate; second excited states correlate.

Reaction occurs photochemically on irradiation into the second absorption band.

Reference: J. Michl, J. Amer. Chem. Soc., 93, 523 (1971).

Figure 2-33.

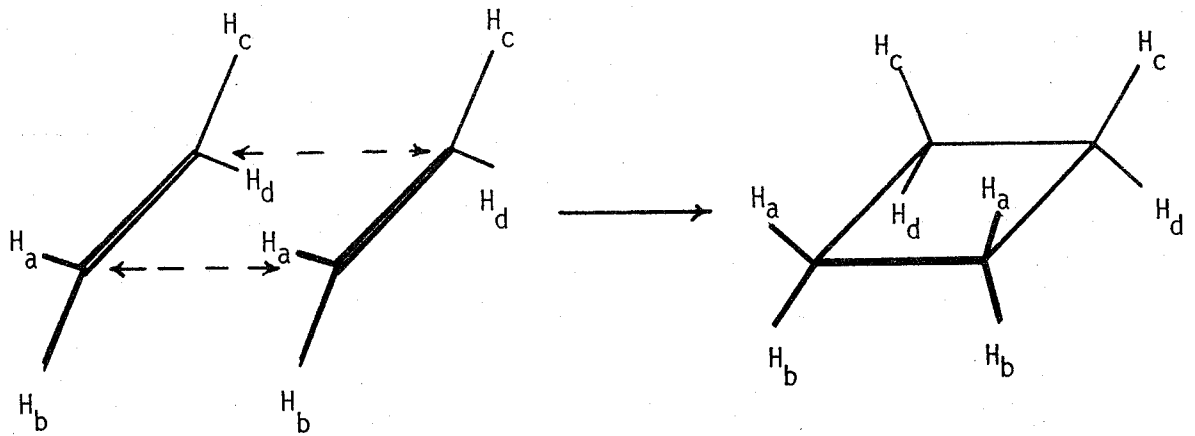


Figure 2-34.

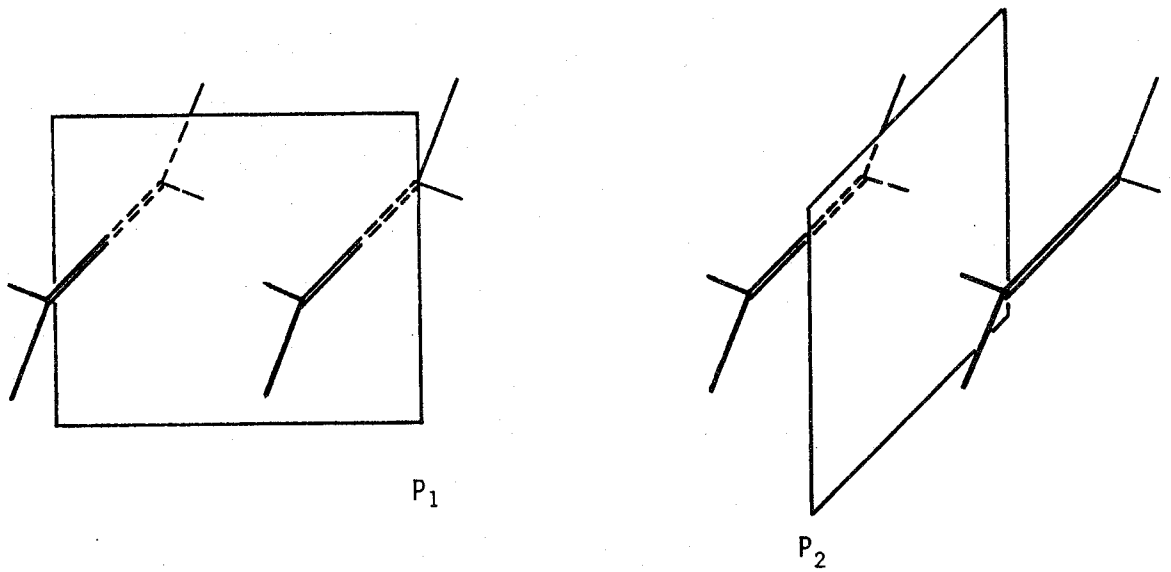


Figure 2-35.

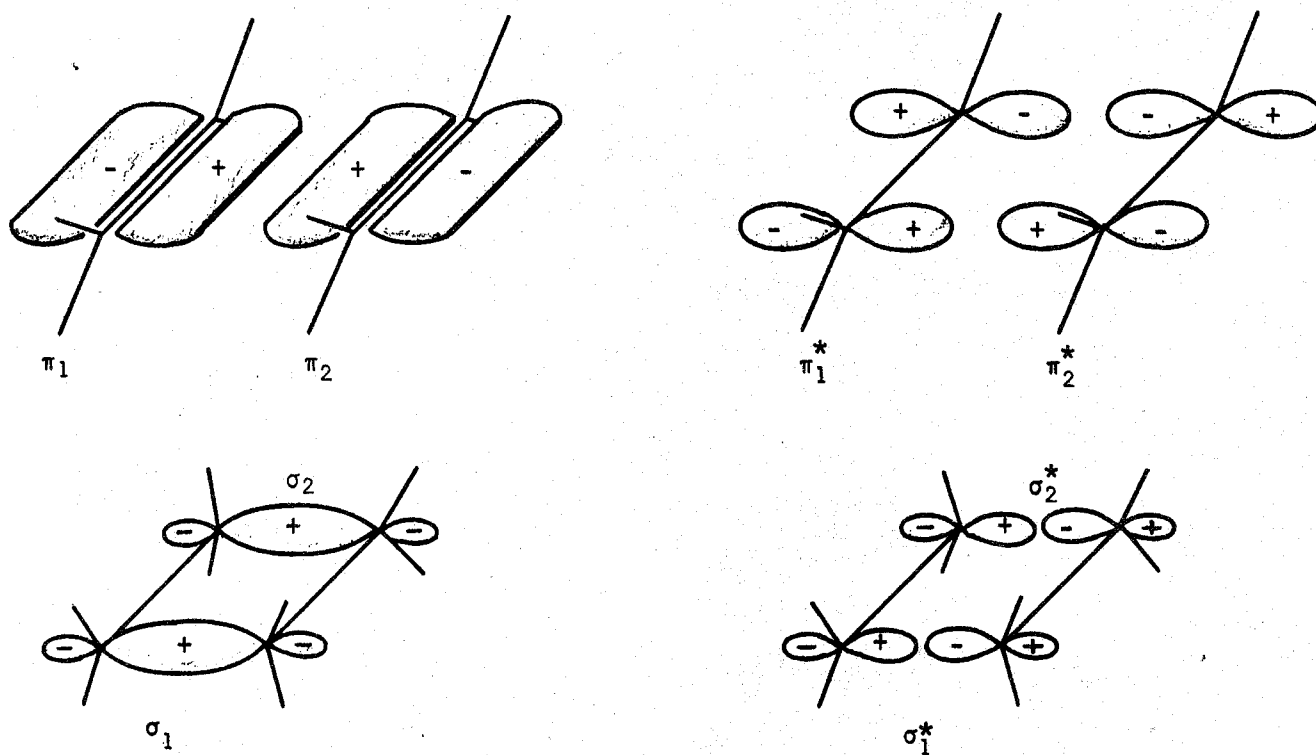
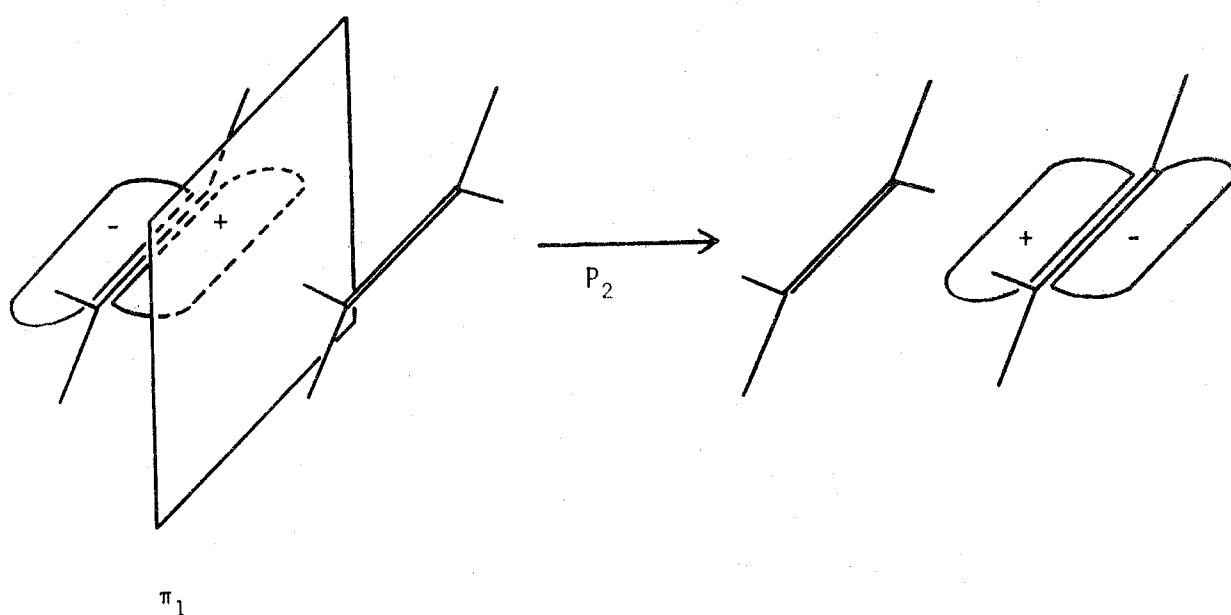


Figure 2-36.



Two linear combinations of π_1 and π_2 , and of π_1^* and π_2^*

Figure 2-37.



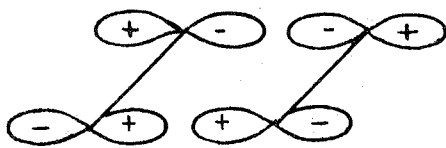
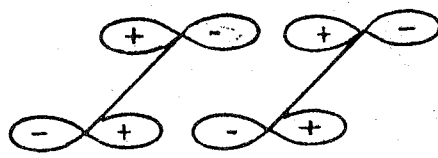
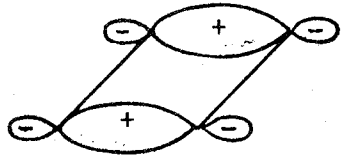
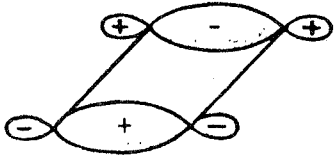
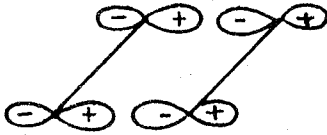
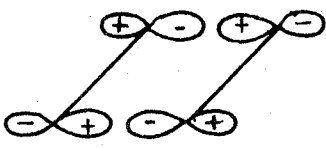
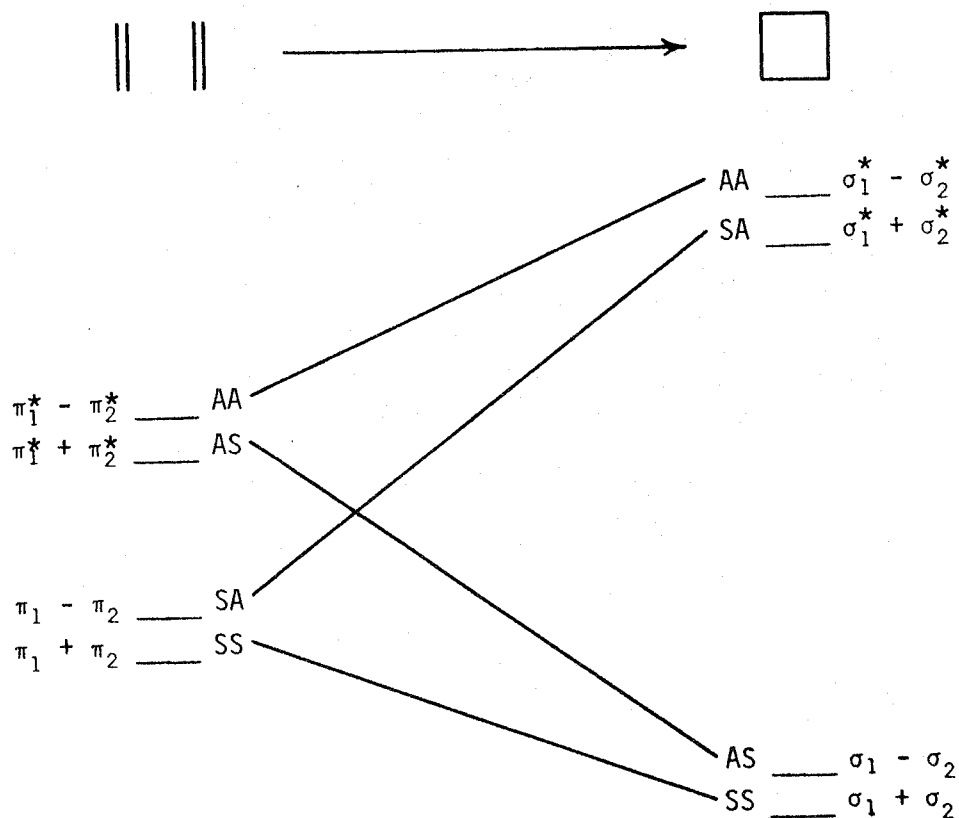
		P_1	P_2
	$\pi_1 + \pi_2$	S	S
	$\pi_1 - \pi_2$	S	A
	$\pi_1^* + \pi_2^*$	A	S
	$\pi_1^* - \pi_2^*$	A	A
	$\sigma_1 + \sigma_2$	S	S
	$\sigma_1 - \sigma_2$	A	S
	$\sigma_1^* + \sigma_2^*$	S	A
	$\sigma_1^* - \sigma_2^*$	A	A

Figure 2-38.



Reaction is forbidden in ground state, allowed in lowest excited state. (See Appendix I for group theory treatment.)

Figure 2-39.

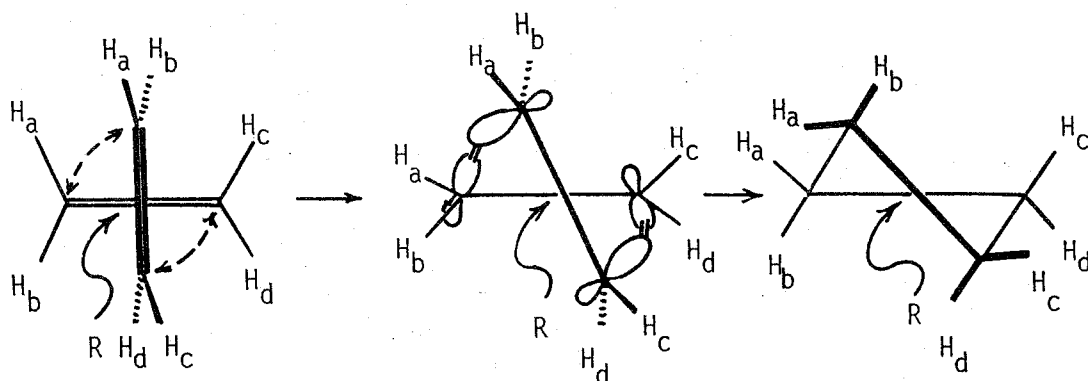


Figure 2-40.

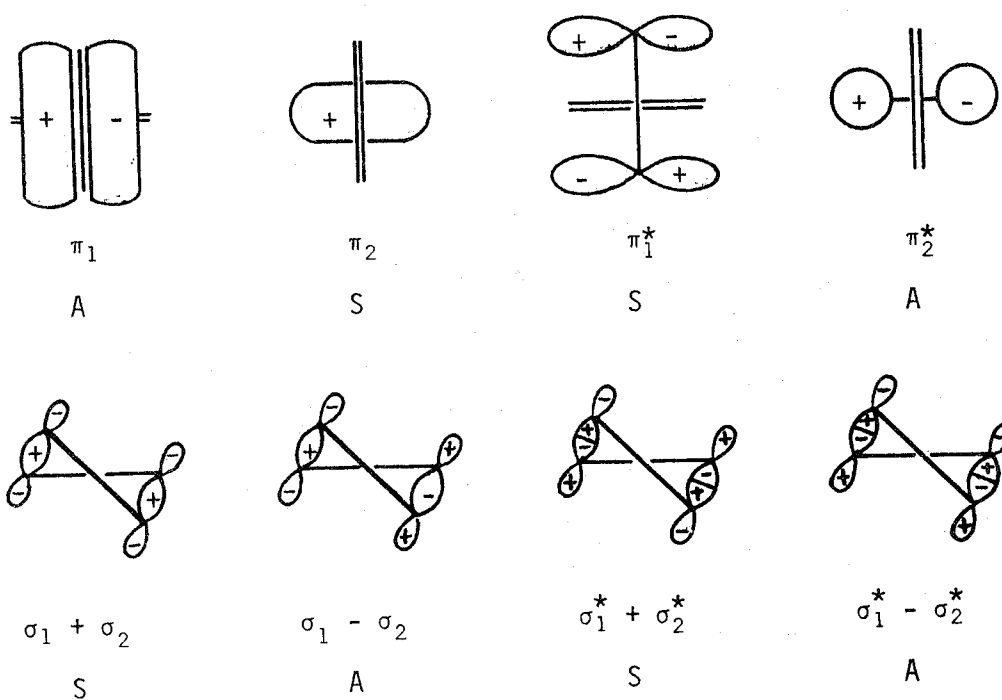
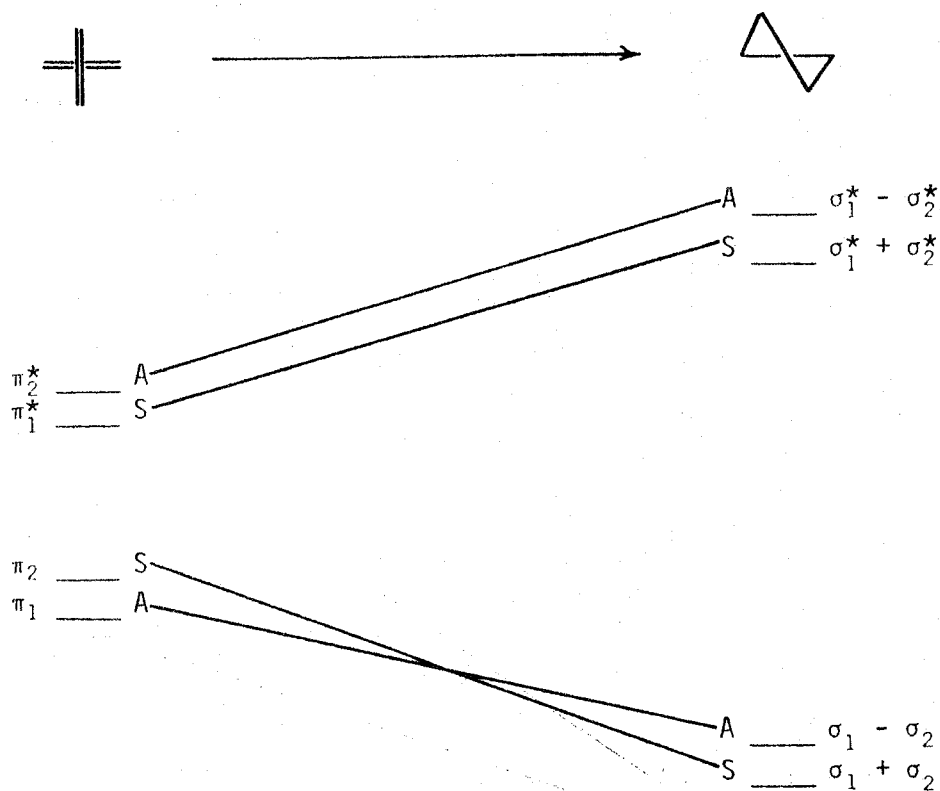


Figure 2-41.



Reaction is allowed in the ground state.

Figure 2-42.

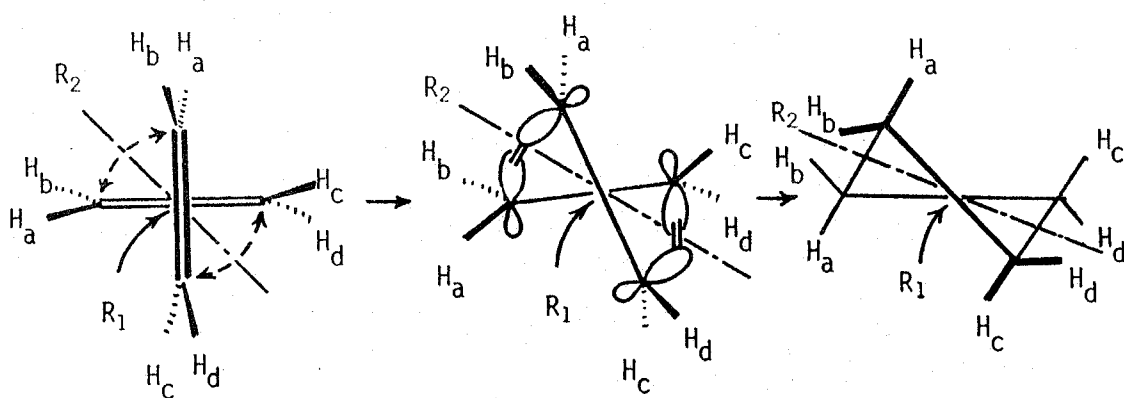
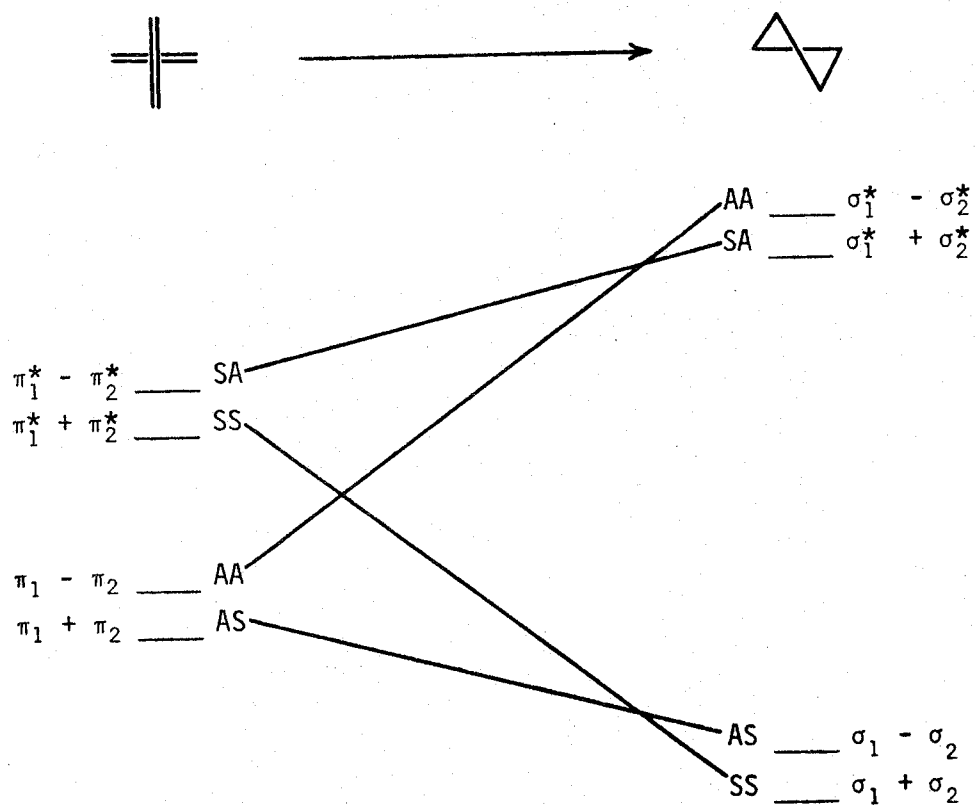


Figure 2-43.

		R_1	R_2
	$\pi_1 + \pi_2$	A	S
	$\pi_1 - \pi_2$	A	A
	$\pi_1^* + \pi_2^*$	S	S
	$\pi_1^* - \pi_2^*$	S	A
	$\sigma_1 + \sigma_2$	S	S
	$\sigma_1 - \sigma_2$	A	S
	$\sigma_1^* + \sigma_2^*$	S	A
	$\sigma_1^* - \sigma_2^*$	A	A

Figure 2-44.



Reaction is forbidden in the ground state.

Summary

Orbital correlation diagrams

- (1) Select necessary orbitals (orbitals undergoing change) of starting material and product, and useful symmetry element(s) present during reaction.
- (2) Classify orbitals with respect to the symmetry element(s); make linear combinations as necessary.
- (3) Arrange orbitals on a rough energy scale and join orbitals of like symmetry to make an orbital correlation diagram.
- (4) Assign electronic configuration of ground state of starting material and allow electrons to flow along correlation lines to form the product; if the product is formed in its ground state, the reaction is allowed in the ground state. Proceed similarly for the lowest excited state.

State correlation diagrams

- (1) Arrange necessary states on a rough energy scale and classify states as to symmetry.
- (2) Correlation lines between states come from the orbital correlation diagram. Lines joining states of like symmetry cannot cross.
- (3) If ground states correlate without a barrier (caused by intended correlation with a high energy state) the reaction is allowed in the ground state; if the lowest excited states correlate without a barrier, the photochemical reaction is allowed.

Construction of correlation diagrams for unusual reactions should be attempted only with great care.

References: R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N.Y., 1971; Angew. Chem. Int. Ed. Engl., 8, 781 (1969) (hereinafter referred to as "op. cit."); R. B. Woodward in "Aromaticity," Special Publication No. 21, The Chemical Society, London, 1967.
H. C. Longuet-Higgins and E. W. Abrahamson, J. Amer. Chem. Soc., 87, 2045 (1965).

Related references: N. D. Epiotis, J. Amer. Chem. Soc., 94, 1924, 1935, 1941, 1949 (1972).

K. Fukui and H. Fujimoto in "Mechanisms of Molecular Migrations," Vol. 2, B. S. Thyagarajan, Ed., Interscience, New York, N. Y. 1969, pp 118-190; K. Fukui, Fortschr. Chem. Forsch., 15, 1 (1970); Accounts Chem. Research, 4, 57 (1971).

W. C. Herndon, Chem. Rev., 72, 157 (1972).

J. Langlet and J.-P. Malrieu, J. Amer. Chem. Soc., 94, 7254 (1972).

L. Salem, Chem. Brit., 5, 449 (1969), and references cited therein; A. Devaquet and L. Salem, J. Amer. Chem. Soc., 91, 3793 (1969).

E. C. W. Scheuneman and W. G. Laidlaw, ibid., 93, 5731 (1971).

C. Trindle, ibid., 3251, 3255 (1970); Theor. Chim. Acta, 18, 261 (1970).

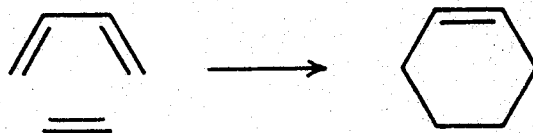
R. G. Pearson, J. Amer. Chem. Soc., 94, 8287 (1972).

Other references cited in Section 4.

Problem 2-2.

Construct an orbital correlation diagram for the Diels-Alder reaction of butadiene plus ethylene.

(A hint is given.)



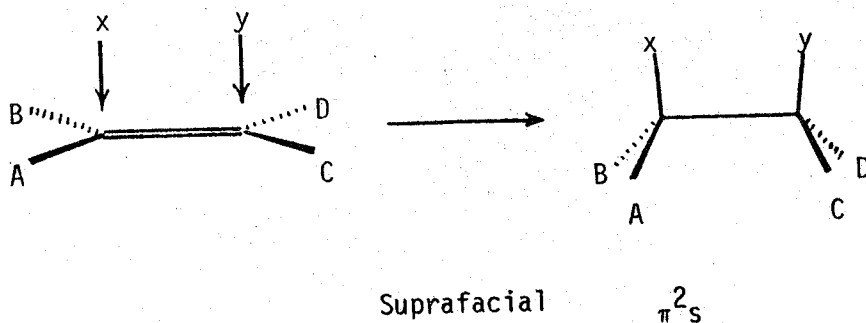
Section 3

The Suprafacial - Antarafacial (S-A) Cycloaddition Method

Definitions

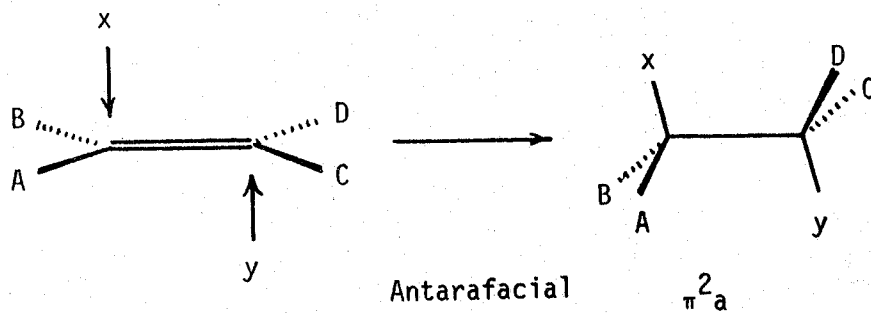
Suprafacial addition to a double bond: new substituents become attached to same face of C=C

Figure 3-1.



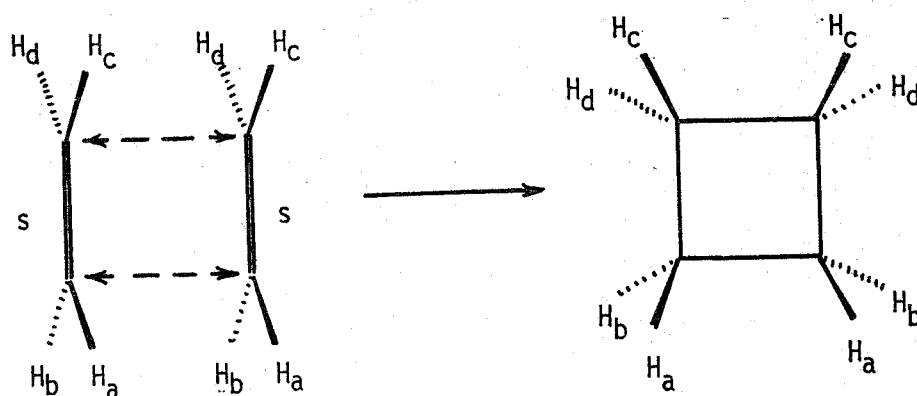
Antarafacial addition -- substituents become attached to opposite faces

Figure 3-2.



Ethylene + ethylene \rightarrow cyclobutane: 2 + 2 cycloaddition

Figure 3-3.

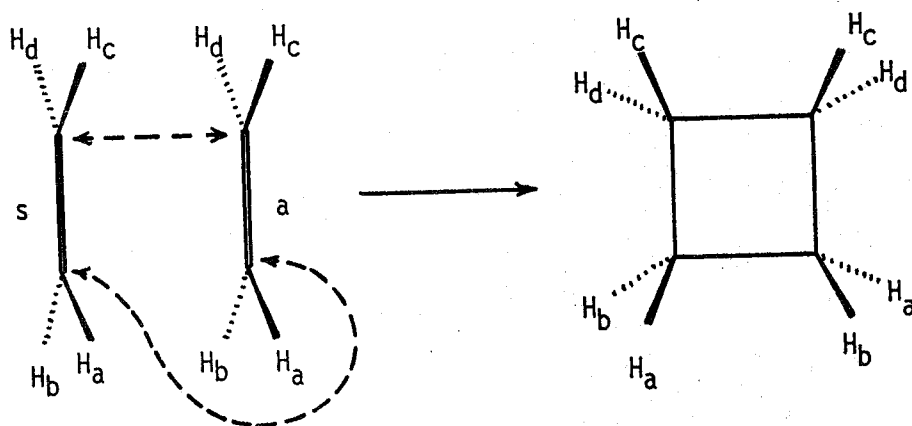


$\pi^2_s + \pi^2_s$ cycloaddition

Δ forbidden, $h\nu$ allowed

(compare Figures 2-33 to 2-38)

Figure 3-4.

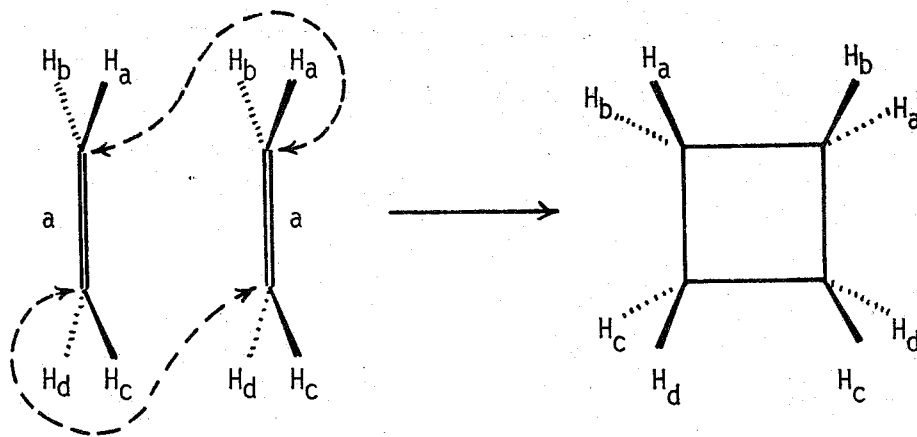


$\pi^2_s + \pi^2_a$

Δ allowed

(compare Figures 2-39 to 2-41)

Figure 3-5.



$$\pi^2_a + \pi^2_a$$

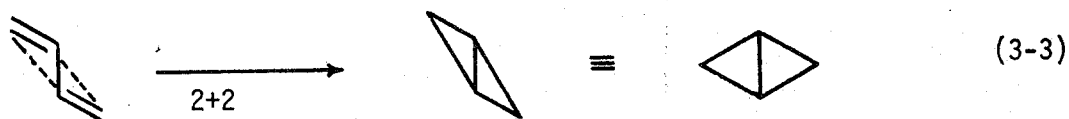
Δ forbidden, $h\nu$ allowed

(compare Figures 2-42 to 2-44)

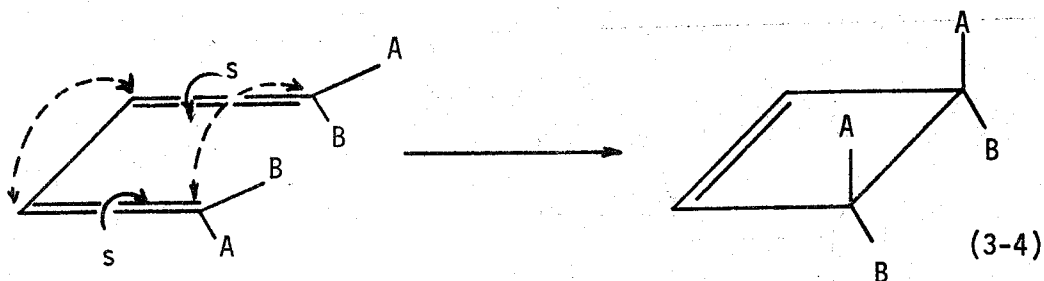
These rules may be derived without the use of symmetry.

Most concerted reactions can be thought of as 2 + 2 (or 2 + 2 + 2 +) cycloadditions.

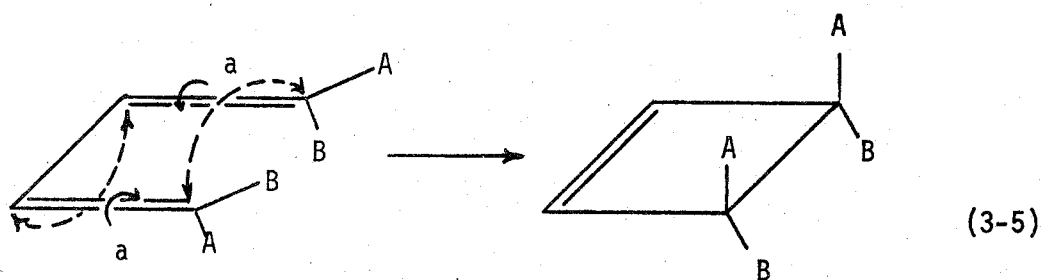
Examples (without stereochemistry); dotted line = new bond:



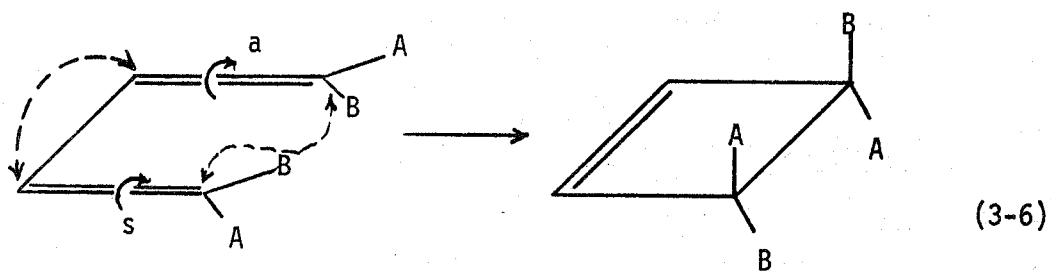
Butadiene-cyclobutene as a cycloaddition.



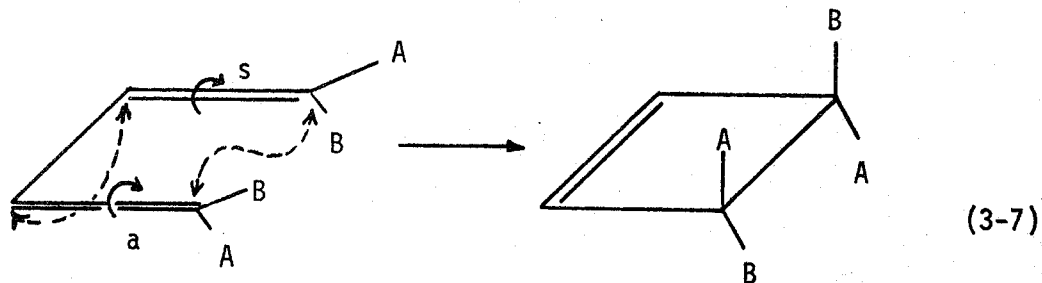
Disrotatory: $2_s + 2_s$: Δ forbidden, $h\nu$ allowed
 Δ forbidden, $h\nu$ allowed



$2_a + 2_a$: Δ forbidden, $h\nu$ allowed

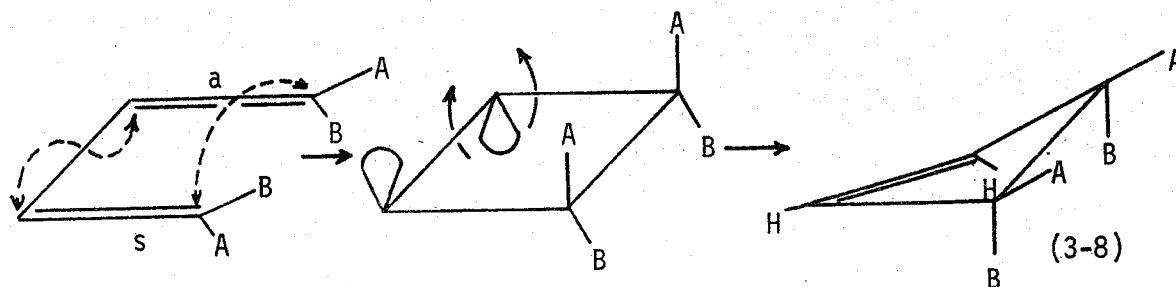


conrotatory: $2_s + 2_a$: Δ allowed
 Δ allowed



$2_s + 2_a$: Δ allowed

Notice that addition resulting in a π bond only gives half of the π bond; the halves must line up.



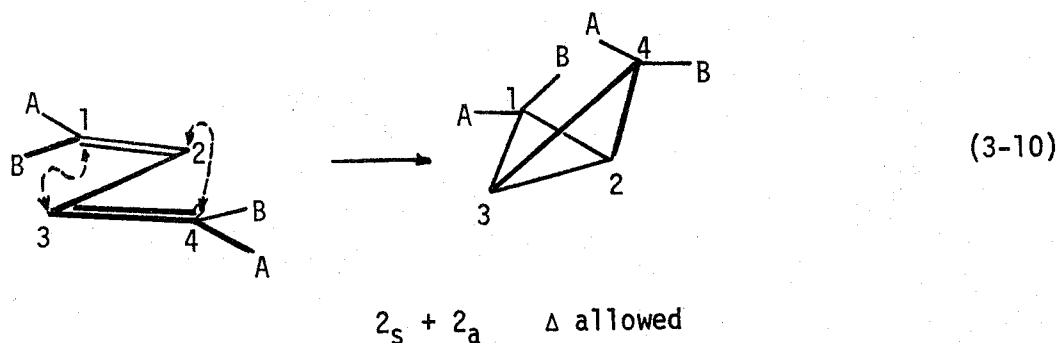
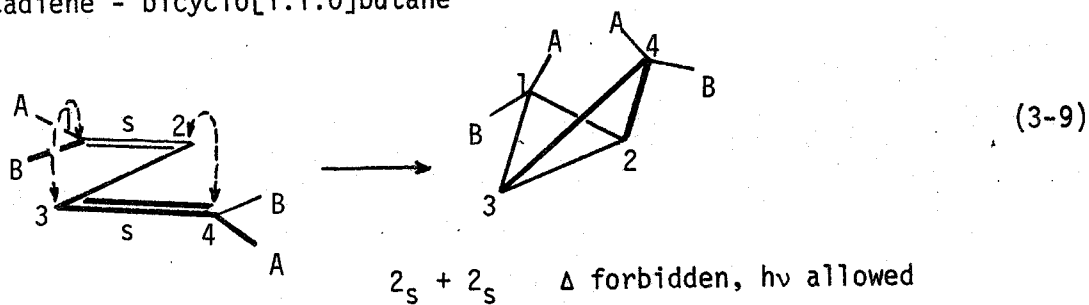
trans-cyclobutene

unrealistic treatment - overlap to make concerted reaction possible is not present

Problem 3-1.

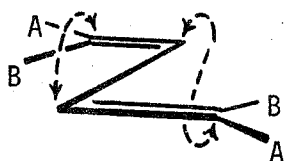
Show one way in addition to equations 3-6 and 3-7 in which the conrotatory closure of butadiene to cyclobutene is shown to be thermally allowed.

Butadiene - bicyclo[1.1.0]butane



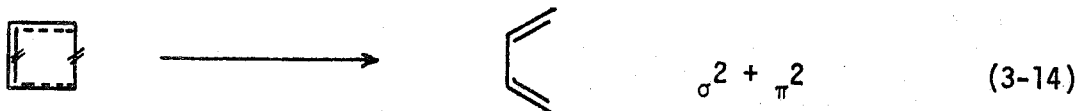
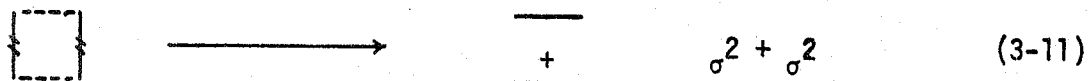
Problem 3-2.

Draw the expected product from the cycloaddition shown below. Is the reaction thermally allowed or forbidden?



Reverse reactions (cycloreversions) treated as cycloadditions to σ bonds.

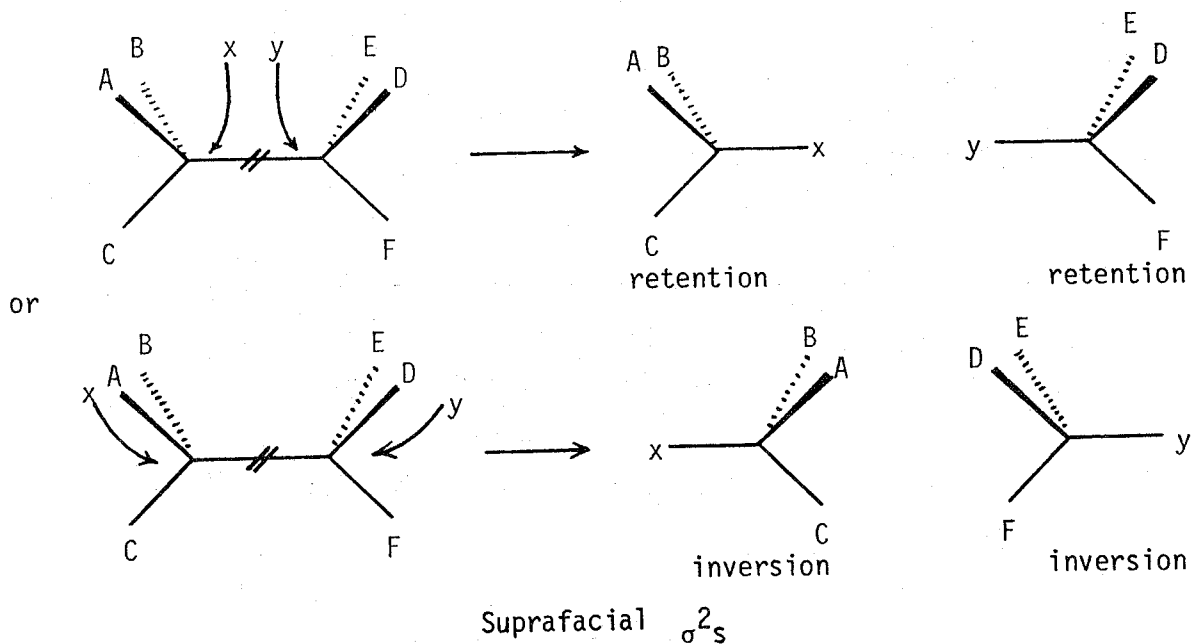
Examples (dotted line = new bond; ~~—~~ = old bond broken):



Stereochemistry

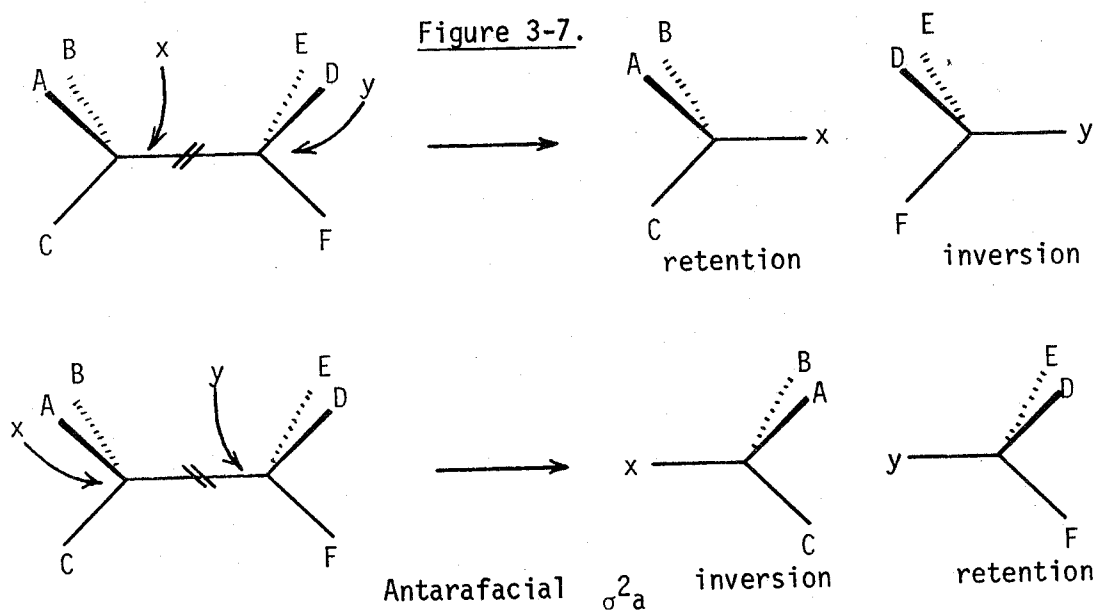
Suprafacial addition to a σ bond: retention of configuration at both ends, or inversion at both ends.

Figure 3-6.

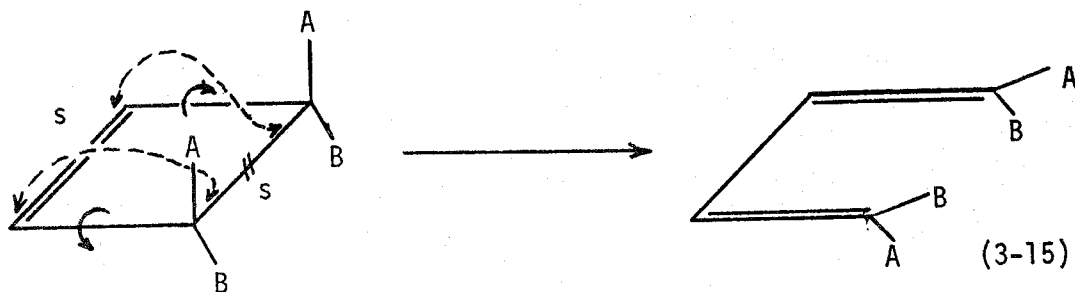


Antarafacial addition to a σ bond: inversion at one end and retention at the other.

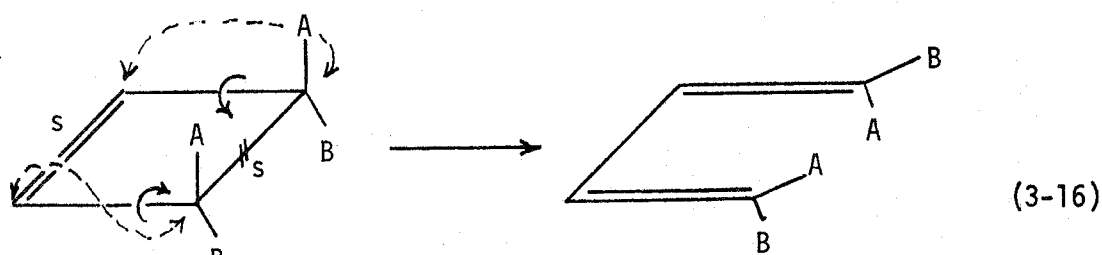
Figure 3-7.



Cyclobutene - butadiene

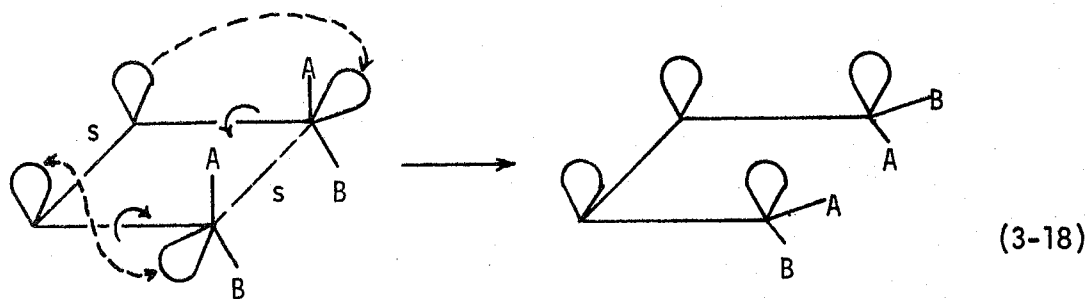
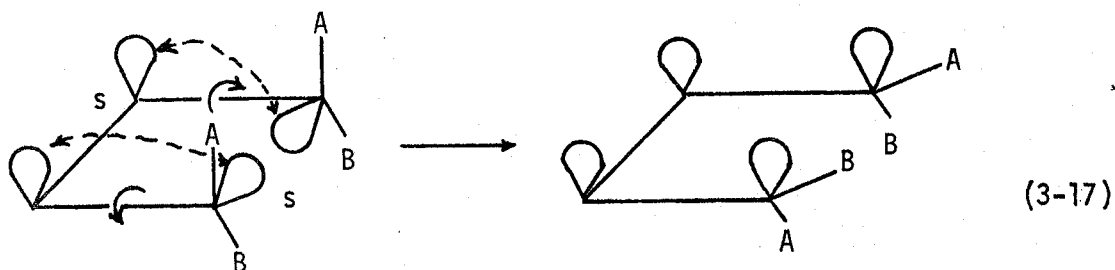


$\pi^2_s + \sigma^2_s$ Δ forbidden
disrotatory

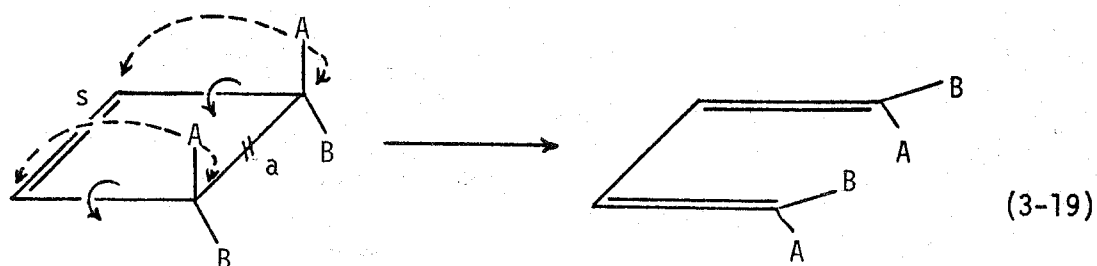


$\pi^2_s + \sigma^2_s$ Δ forbidden

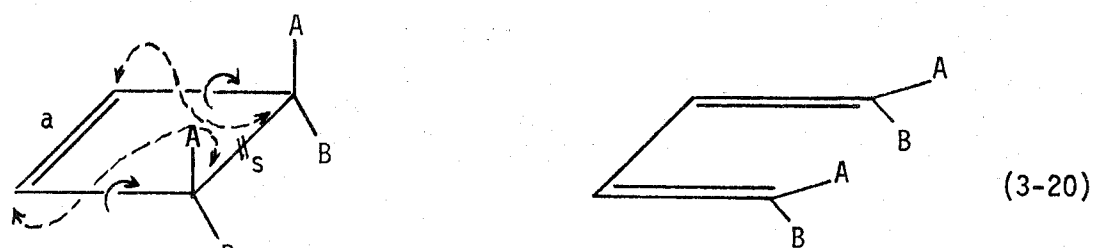
Objective: to make half-bonds line up



Conrotatory



$$\pi^2_s + \sigma^2_a \quad \Delta \text{ allowed}$$

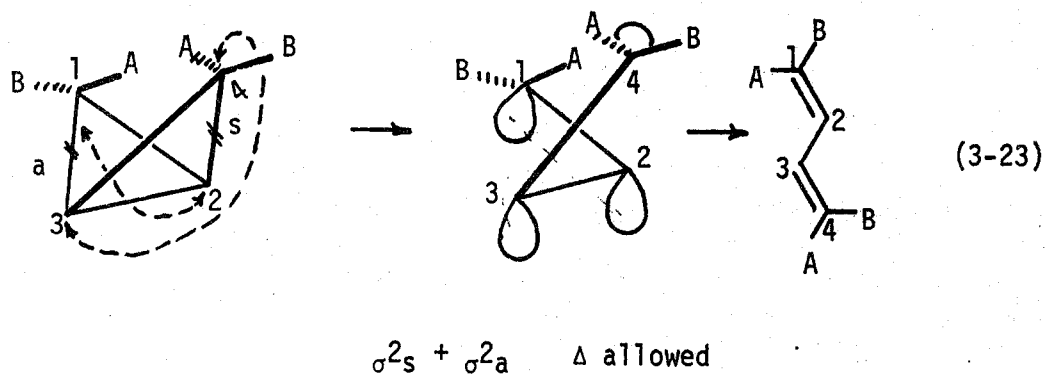
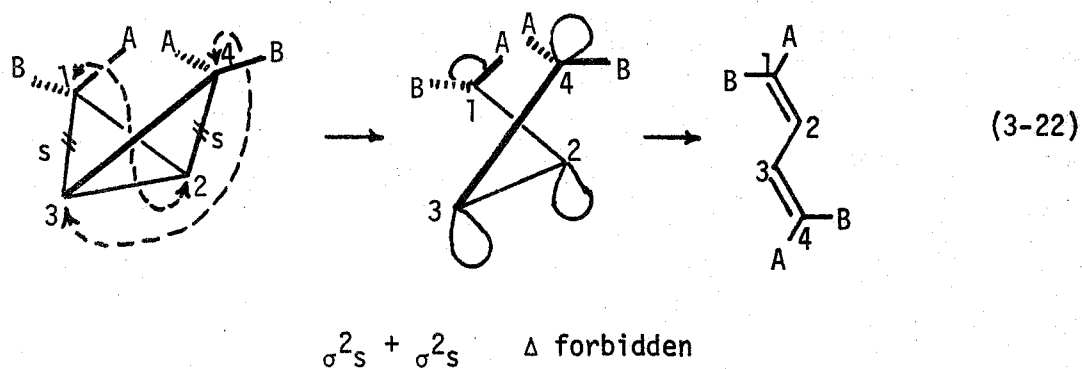
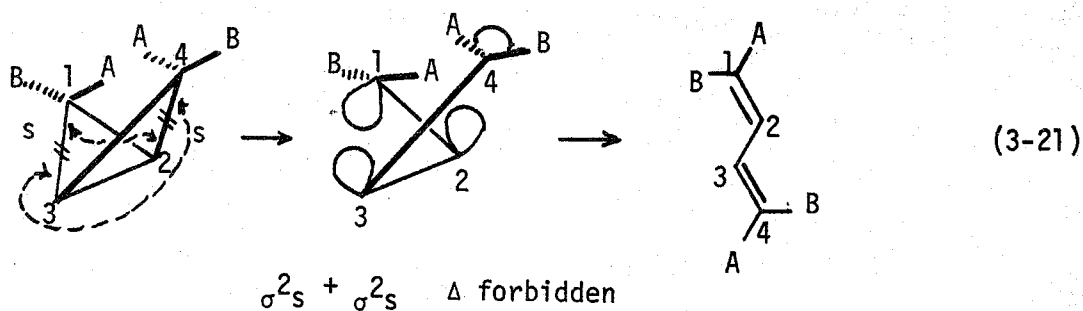


$$\pi^2_a + \sigma^2_s \quad \Delta \text{ allowed}$$

Problem 3-3.

Show one other way in which the conrotatory ring opening of cyclobutene can be shown to be thermally allowed.

Bicyclo[1.1.0]butane - butadiene

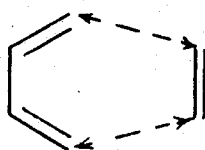


Problem 3-4.

Draw this reaction as a $\sigma^2_s + \sigma^2_a$ reaction, with retention-retention on the σ^2_s component.

Larger reactions

Figure 3-8.



Diels-Alder reaction - $\pi 4_s + \pi 2_s$, Δ allowed

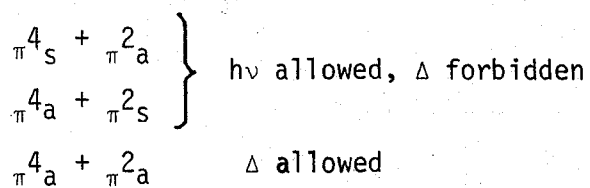


Figure 3-9.

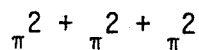
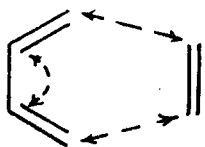
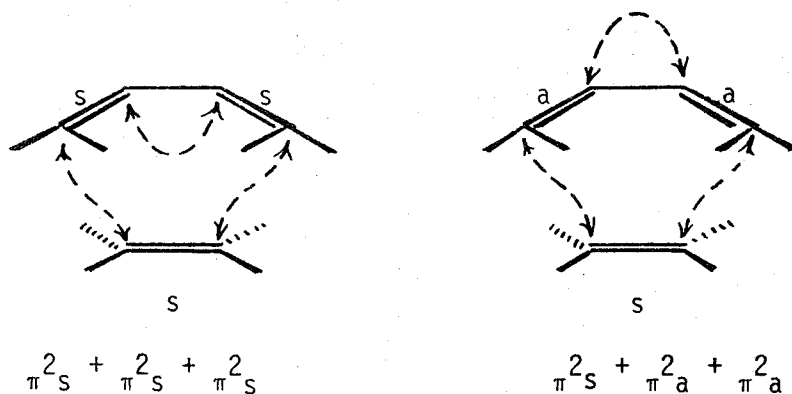
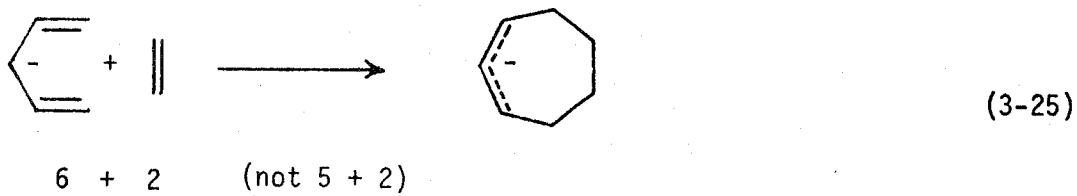
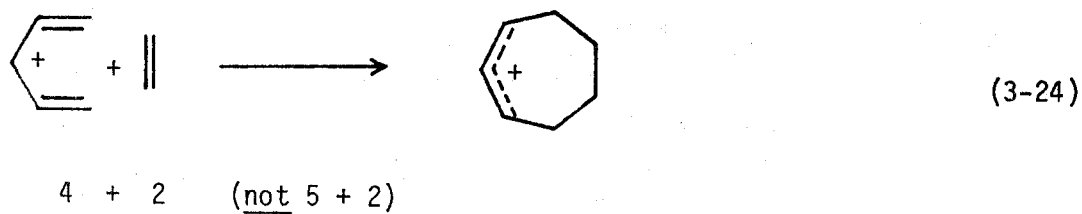


Figure 3-10.



Both same net stereochemical result ($\pi^4_s + \pi^2_s$); both thermally allowed.

The numbers in the description of a reaction as a cycloaddition refer to the number of electrons in the bonds undergoing cycloaddition, not the number of atoms. Changing the number of electrons by two changes a reaction from allowed to forbidden (or vice versa).



Any reaction that can be considered a cycloaddition will have two or more of these components:

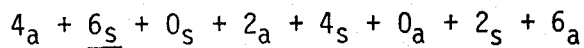
$(4j + 2)_s$	e.g., 2_s , 6_s , 10_s , etc.
$(4k)_s$	e.g., 0_s , 4_s , 8_s , etc.
$(4m + 2)_a$	e.g., 2_a , 6_a , 10_a , etc.
$(4n)_a$	e.g., 0_a , 4_a , 8_a , etc.

The rule:

A concerted reaction is thermally allowed if the total number of $(4j + 2)_s$ and $(4n)_a$ components is ODD.

Note that $(4k)_s$ and $(4m + 2)_a$ components don't count.

Example (countable components underlined):



Thermal reaction forbidden.

Problem 3-5.

Which of the following cycloadditions are thermally allowed?

- | | |
|-----------------|-----------------------------|
| (a) $2_s + 2_s$ | (e) $12_s + 2_s + 6_a$ |
| (b) $2_s + 2_a$ | (f) $14_a + 2_s$ |
| (c) $2_a + 2_a$ | (g) $2_s + 2_s + 2_s + 2_a$ |
| (d) $4_s + 2_a$ | (h) $0_a + 2_s + 2_s$ |

Simpler rule useful in most situations (exception: positively charged species)

The reaction is first factored into 2_s and 2_a components.

The thermal reaction is allowed if there is an ODD of 2_s components.

Justification:

Any $(4k)_s$ can be divided into an even number of 2_s components.

Any $(4j + 2)_s$ can be factored into an odd number of 2_s components.

Any $(4m + 2)_a$ can be factored into a 2_a component and an even number of 2_s components.

Any $(4n)_a$ except 0_a can be factored into a 2_a component and an odd number of 2_s components.

The two rules are identical unless there is a 0_a component.

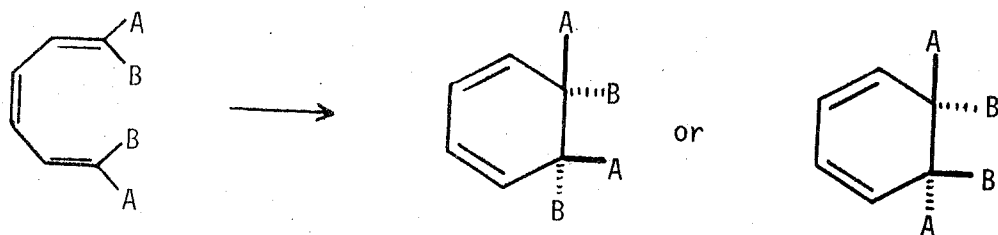
Although dividing a reaction into smaller components can be done in many different ways, the prediction is always the same for a particular reaction.

Reference: R. B. Woodward and R. Hoffmann, op. cit.

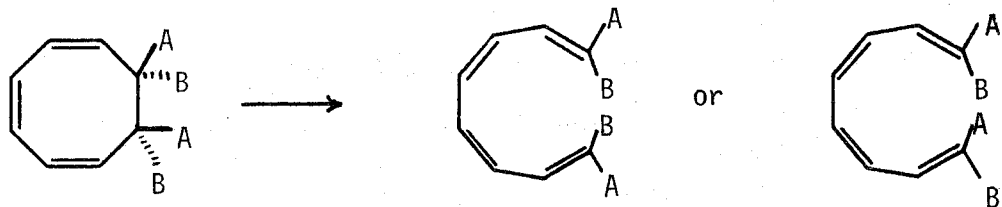
Problems

For each of the following reactions, which stereochemical result is thermally allowed?

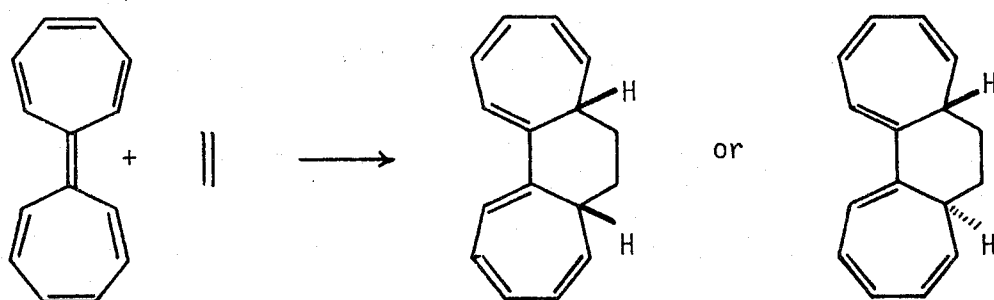
3-6



3-7



3-8



(presume suprafacial addition to ethylene)

Section 4

The Hückel - Möbius (H-M) Method

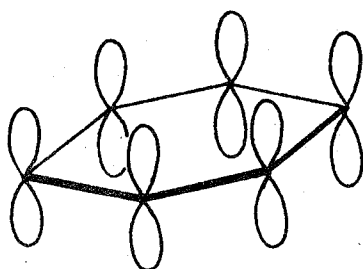
Benzene (and related compounds): $4n + 2 \pi$ electrons, unusual stability (aromaticity)

Cyclobutadiene, cyclooctatetraene: $4n \pi$ electrons, lack of stability, tendency to avoid complete delocalization (antiaromaticity?)

Molecular orbitals of cyclic polyene

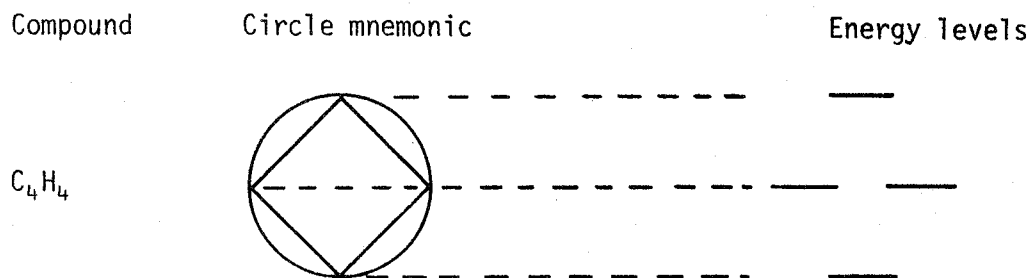
Basis set: p orbitals arranged in a regular polygon

Figure 4-1.



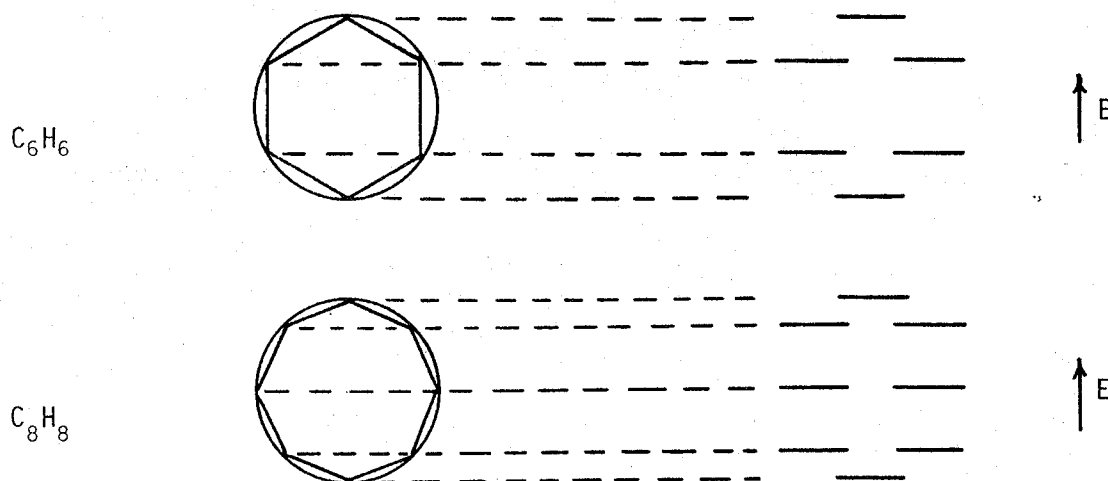
Energies of the LCAO π -MO's: Inscribe polygon in circle, point down; each corner represents an energy level.

Figure 4-2.



↑ E

continued



Arrangement of energy levels leads to stabilization if occupied by $4n + 2$ electrons - "Hückel-aromatic."

With $4n$ electrons, expect triplet ground states (Hund's rule).

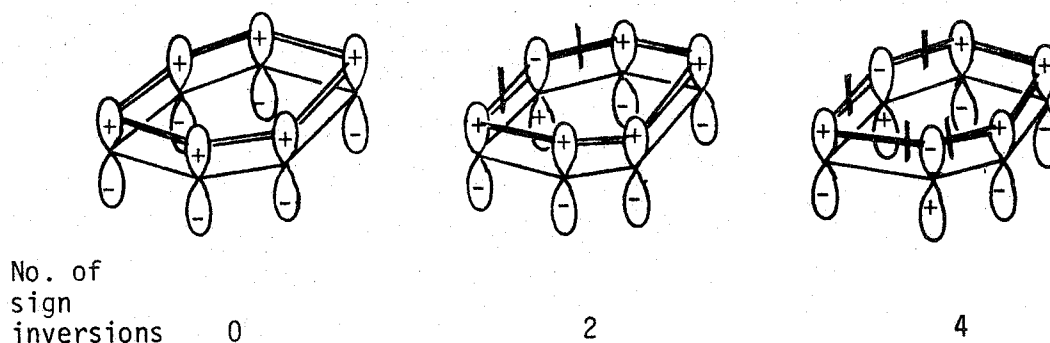
Figure 4-3.



$4n$ systems more stable if regular polygon geometry lost; cyclic system with complete delocalization and $4n$ electrons is "Hückel-antiaromatic."

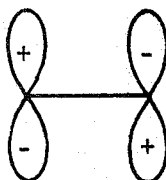
Reconsider basis set with signs: Always zero or an even number of sign inversions(=+).

Figure 4-4.



Count one side of plane only -- actually counting one inversion for

Figure 4-5.

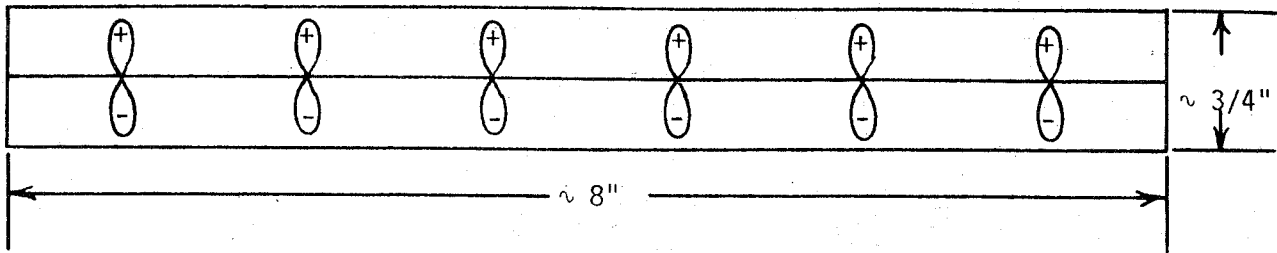


An even number of sign inversions in the basis set gives the same energy levels, although the LCAO-MO's would have different signs for the contributions of the atomic orbitals.

Such systems have "Hückel geometry."

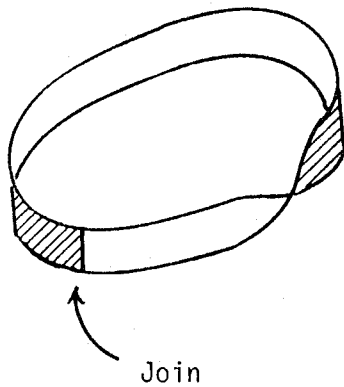
Another way to arrange basis orbitals in a ring.

Figure 4-6.



Make a paper strip as shown in Figure 4-6. Repeat the markings on the back of the strip, making sure the signs match, front and back. Give the strip a half-twist and join the ends (Figure 4-7).

Figure 4-7.

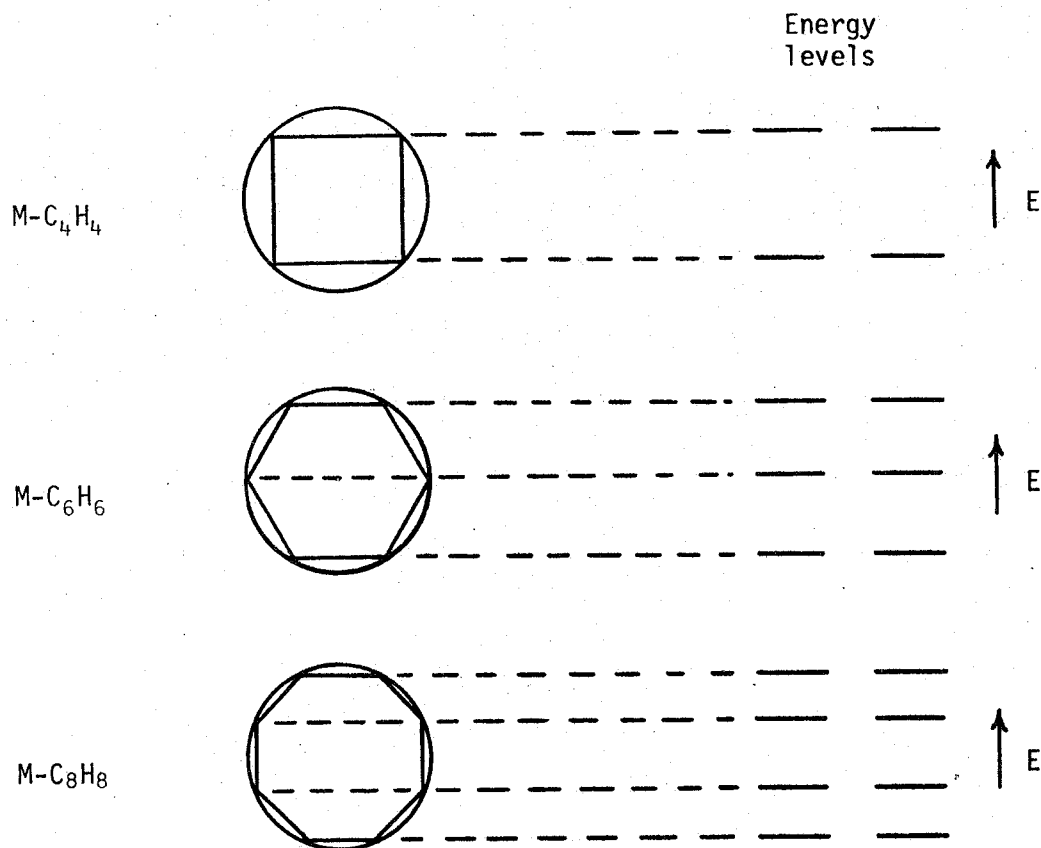


A Möbius Strip

A Möbius basis set always has an odd number of sign inversions.

The energy levels derived from a Möbius basis set can be found by inscribing a polygon in a circle edge down.

Figure 4-8.

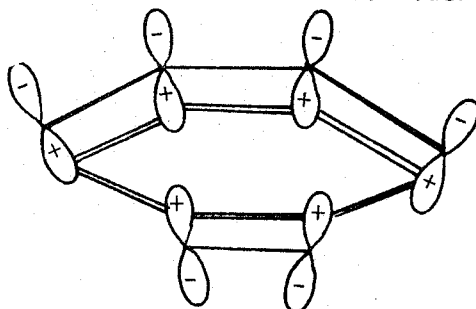


With a Möbius basis set, the energy levels are arranged so that occupation by $4n$ electrons gives an aromatic stabilization, and $4n + 2$ electrons gives a system that is antiaromatic.

These rules are not dependent on the actual geometry or symmetry of the compound, or on equal overlap around the ring. Based on topology -- the connectivity of the basis set in terms of the number of sign inversions.

Figure 4-9.

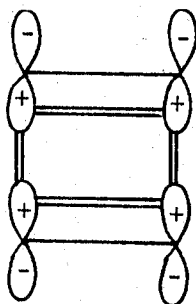
The transition state of the Diels-Alder reaction



The basis set has an even number of sign inversions (Hückel); occupation by $4n + 2$ electrons should lead to special stability (aromatic).

Figure 4-10.

A $\pi^2_s + \pi^2_s$ cycloaddition

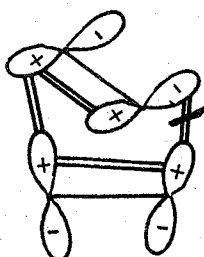


No sign inversions (or an even number) - Hückel

$4n$ electrons - antiaromatic (destabilized)

Figure 4-11.

A $\pi^2_s + \pi^2_a$ cycloaddition



one sign inversion - Möbius

4n electrons - aromatic (stabilized)

The change in sign on going from one lobe of a p orbital (or sp, sp², or sp³) to the other lobe of the same orbital does not count as a sign inversion; normal part of the basis set.

The Hückel-Möbius method

(1) Draw a rough transition state for the reaction, showing lobes of atomic orbitals in breaking and forming bonds. Put signs in the lobes in a convenient manner. (Make sure that opposite lobes on the same atom have opposite signs.)

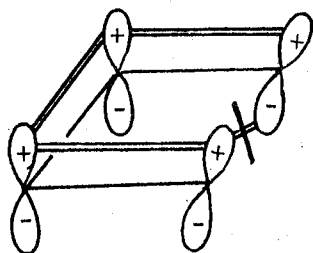
(2) Connect the orbital lobes in a cyclic fashion, showing bonds forming and bonds being broken.

(3) Count the sign inversions, count the electrons.

Rules	Δ allowed	Δ forbidden (h ν allowed)
Even sign inversions (Hückel)	4n + 2 e	4n e
Odd sign inversions (Möbius)	4n e	4n + 2 e

Examples
Butadiene - cyclobutene; conrotatory

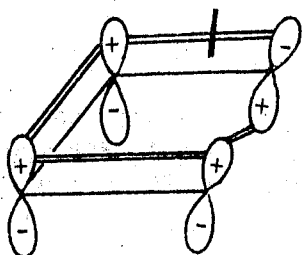
Figure 4-12.



one inversion, 4 e
 Δ allowed

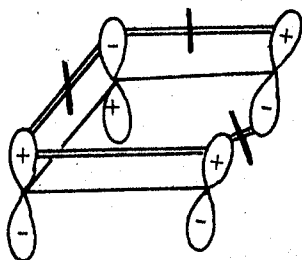
Other ways to set up

Figure 4-13.



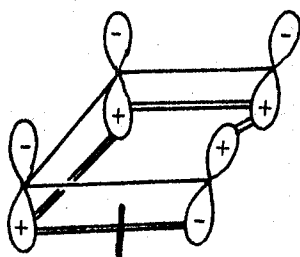
one inversion

Figure 4-14.



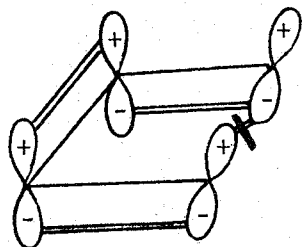
three inversions

Figure 4-15.



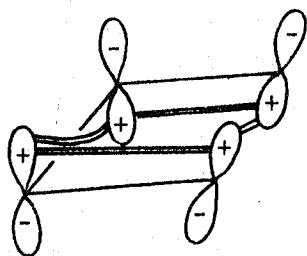
one inversion

Figure 4-16.



one inversion

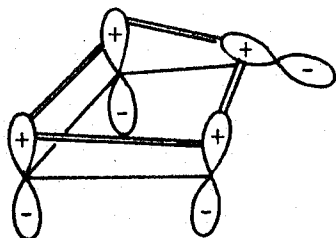
Figure 4-17.



Incorrect! Overlap is not that way in concerted reaction basis set. (Compare Figure 3-8)

Disrotatory reaction

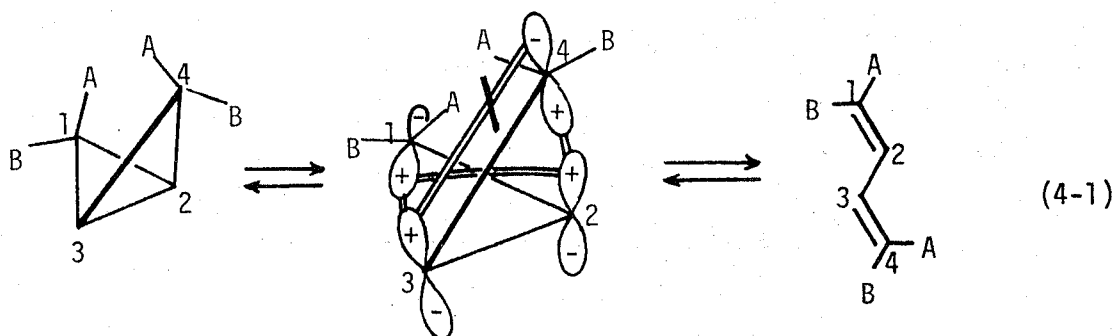
Figure 4-18.



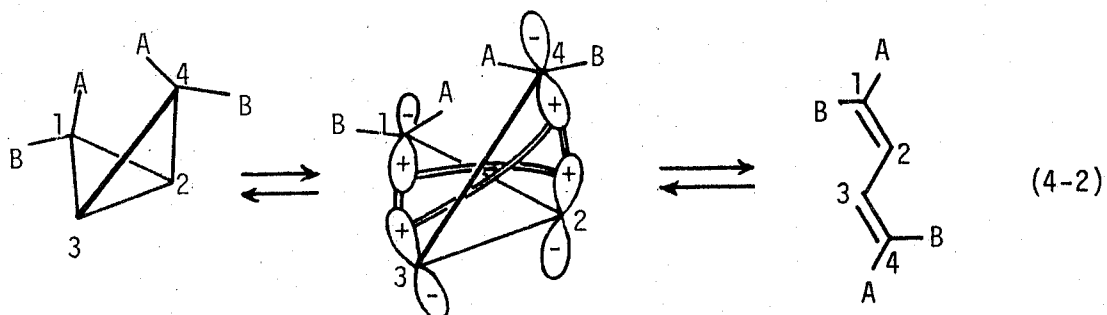
no inversions, 4 e
 Δ forbidden (hv allowed)

Reverse reactions: Same transition states

Butadiene - bicyclo[1.1.0]butane



one inversion, 4 e: Δ allowed



no inversions, 4 e: Δ forbidden
hv allowed

Pericyclic reaction: reaction with a cyclic transition state; can be treated by S-A or H-M.

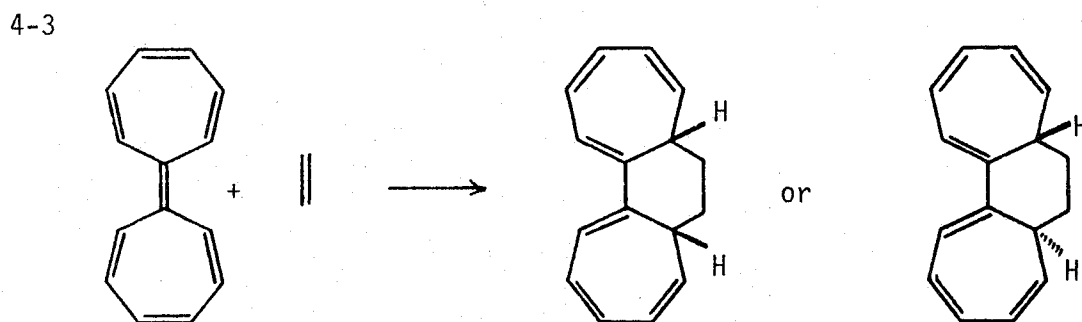
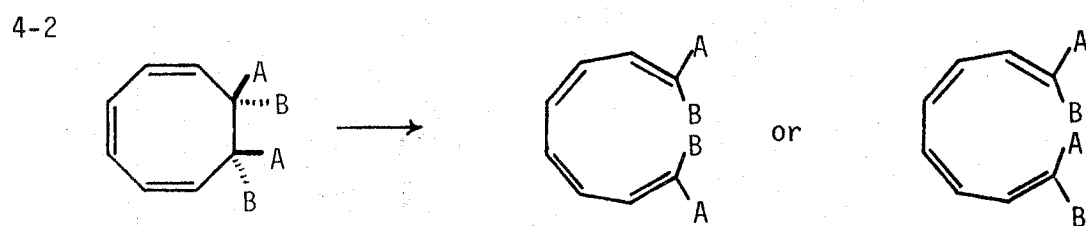
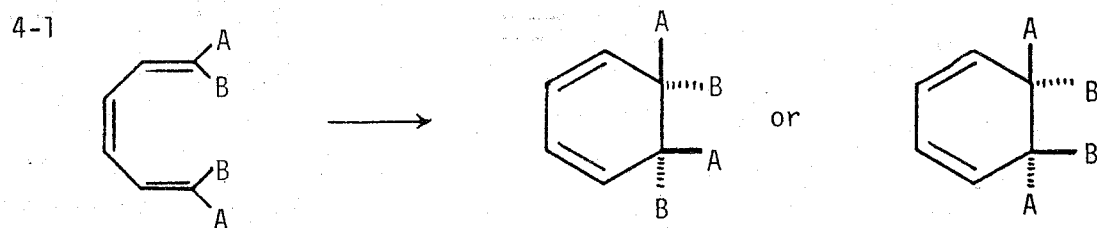
References: H. E. Zimmerman, Accounts Chem. Research, **4**, 272 (1971);
Angew. Chem., Int. Ed. Engl., **8**, 1 (1969).

M. J. S. Dewar, Angew. Chem., Int. Ed. Engl., **10**, 761 (1971).

C. L. Perrin, Chem. Brit., **8**, 193 (1972).

Problems

Predict the stereochemistry of the products of each of the following thermal reactions, using the H-M method.



Section 5
Electrocyclic Reactions

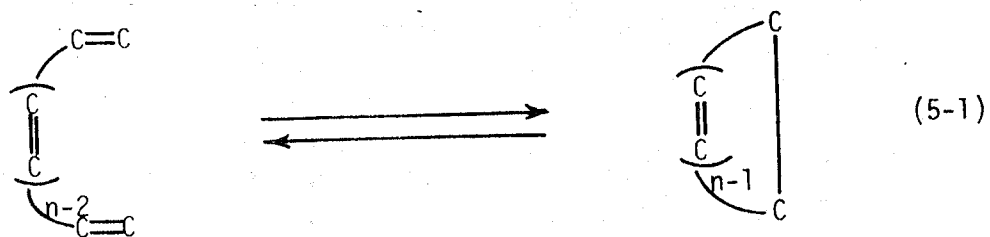
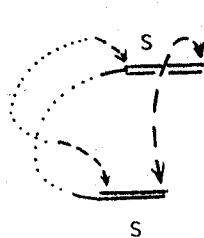
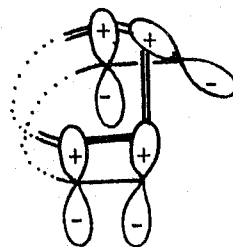


Figure 5-1.

Disrotatory



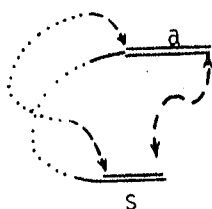
all $\pi 2_s$



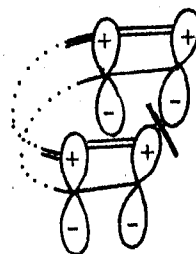
no sign inversions

Figure 5-2.

Conrotatory



one $\pi 2_a$, rest $\pi 2_s$



one sign inversion

Table 5-1

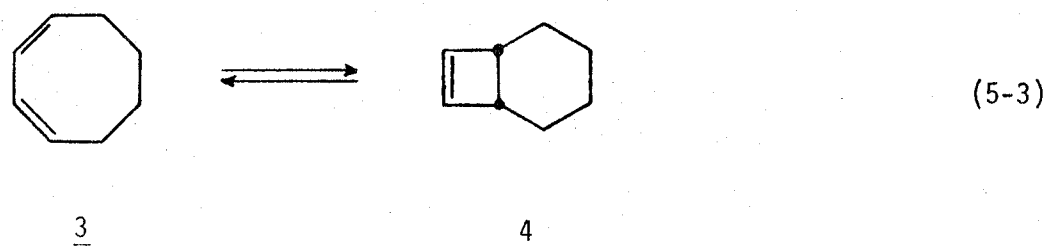
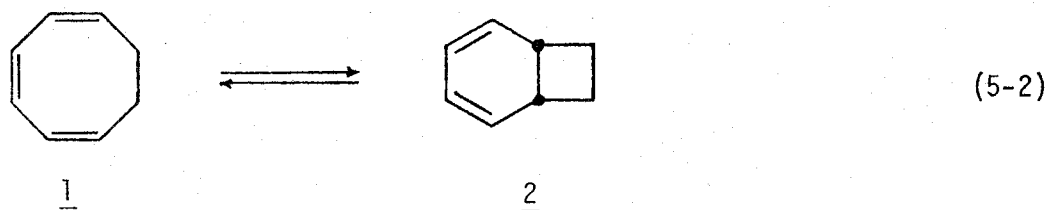
No. of electrons	Δ	$h\nu$
$4m$	conrotatory	disrotatory
$4m + 2$	disrotatory	conrotatory

Consequences

Acyclic compounds: Stereochemistry determined

Cyclic compounds: Stereochemistry already fixed, ease of reaction determined

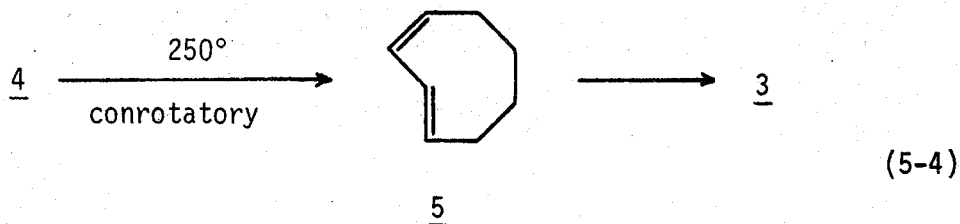
Compare:



1 - 2 disrotatory, 6 e, Δ allowed. 1 and 2 are in rapid equilibrium at 60° (valence tautomerism).

Review: R. Huisgen, Angew. Chem., Int. Ed. Engl., 9, 751 (1970).

3 - 4 disrotatory, 4 e, Δ forbidden, $h\nu$ allowed. 4 has only end absorption in uv; 3 \rightarrow 4 in good yield photochemically.



Reference: J. S. McConaghy, Jr. and J. J. Bloomfield, Tetrahedron Lett., 3719 (1969).

Why do reactions go in one direction?

Photochemical reactions:

- (1) One compound absorbs light, other doesn't
- (2) Other reasons

Thermal reactions:

$$K = e^{-\Delta G/RT} \quad (5-5)$$

$$\Delta G = \Delta H - T\Delta S \quad (5-6)$$

$T\Delta S$: Very important at higher temperatures

ΔH : Two single C-C bonds are lower in energy than one double C=C bond by 20 kcal/mole

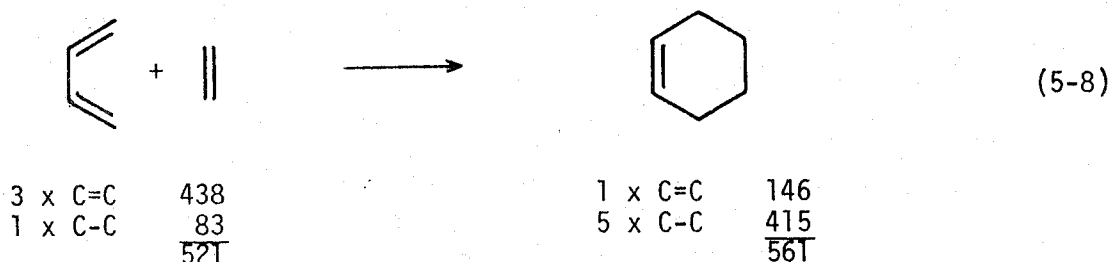


$$-\Delta H = \Delta H_{\text{atom'n}}$$

Bond energy: Contribution of bond to $\Delta H_{\text{atom'n}}$ such that sum of bond energies = $\Delta H_{\text{atom'n}}$ (different from bond dissociation energy).

Table 5-2

Bond	Bond energy (25°)
C-C	83 kcal/mole
C=C	146



$$\Delta H \approx -40 \text{ kcal/mole (exothermic)}$$

Neglecting:

Entropy
 Conformation
 Conjugation
 Change in C-H bonds

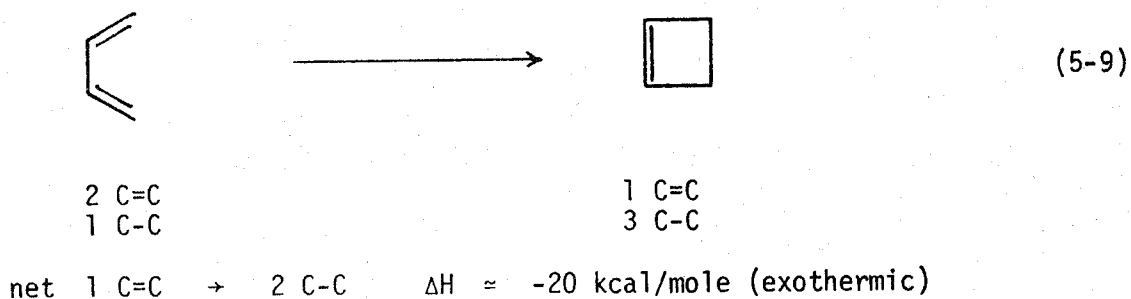






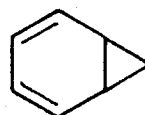
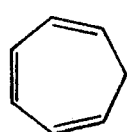
Table 5-3
Ring Strain Energies

	27.5 kcal/mole
	52
	26
	28.5

$$\Delta H \approx -20 + 28.5 = + 8.5 \text{ kcal/mole (endothermic)}$$

$$\text{Found: } \Delta H = + 11.5 \text{ kcal/mole}$$

Reference: K. B. Wiberg and R. A. Fenoglio, J. Amer. Chem. Soc., 90, 3395 (1968), and references cited therein.



(5-10)

norcaradiene

disrotatory, Δ allowed

$$\Delta H \approx -20 + 27 = + 7 \text{ kcal/mole}$$

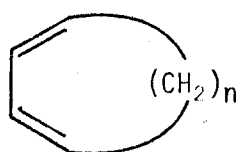
Review: G. Maier, Angew. Chem., Int. Ed. Engl., 6, 402 (1967).

References: Estimation of ΔG :

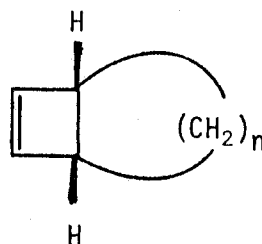
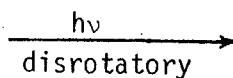
R. O. C. Norman, "Principles of Organic Synthesis," Methuen, London, 1968, pp 5-27.

K. B. Wiberg, "Physical Organic Chemistry," Wiley, New York, N. Y., 1964, pp 228-248.

Cyclic dienes

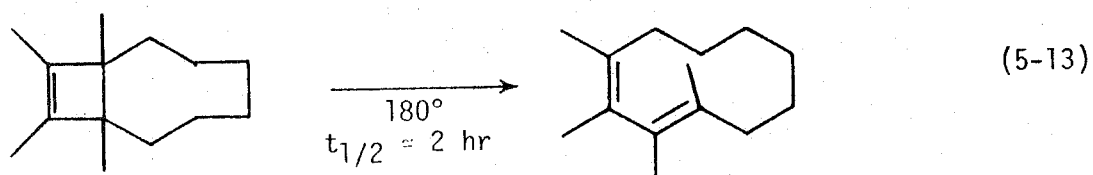
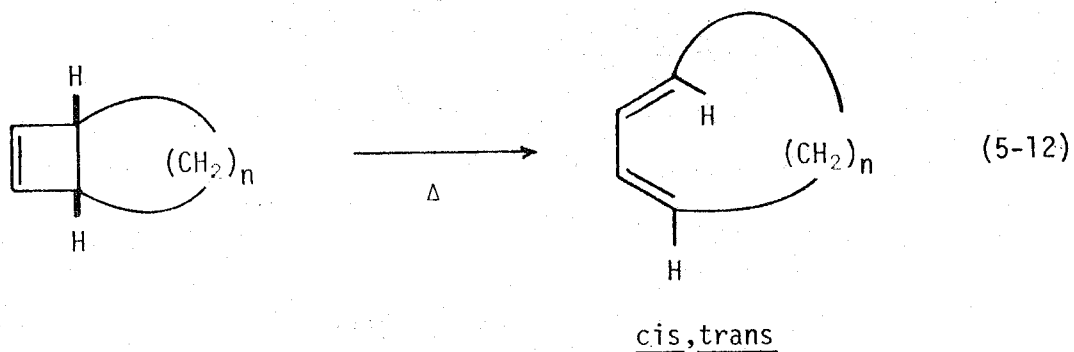


cis,cis



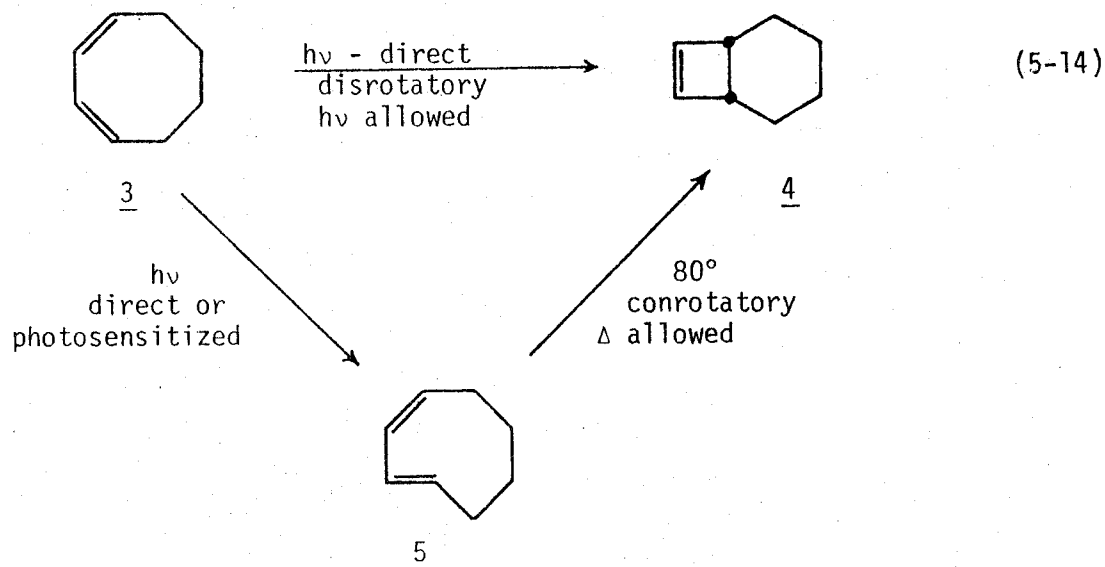
(5-11)

Δ allowed ring opening is conrotatory

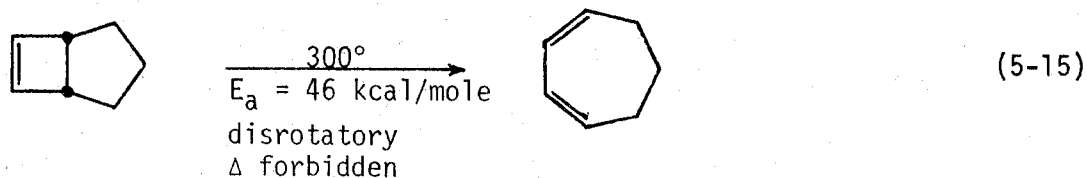


Reference: R. Criegee, G. Bolz, and R. Askani, Chem. Ber., 102, 275 (1969).

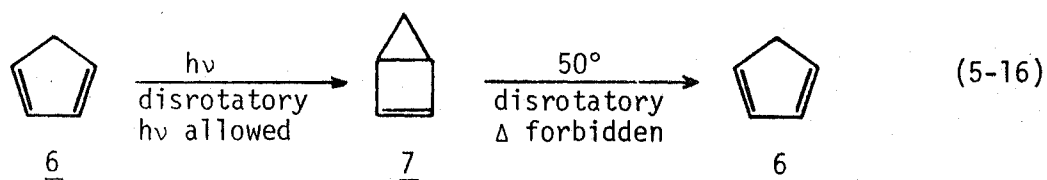
Complications



References: R. S. H. Liu, J. Amer. Chem. Soc., 89, 112 (1967).
W. J. Nebe and G. J. Fonken, ibid., 91, 1249 (1969).



Reference: G. R. Branton, H. M. Frey, D. C. Montague, and I. D. R. Stevens, Trans. Faraday Soc., 62, 659 (1966).



Reference: E. E. van Tamelen, J. I. Brauman, and L. E. Ellis, J. Amer. Chem. Soc., 93, 6145 (1971).

Possibilities:

(1) Relief of ring strain lowers activation energy of non-concerted reaction - homolytic C-C cleavage.

(2) Correlation diagrams imply forbidden reactions only higher ΔG^\ddagger ; ring strain might raise $\Delta G^\ddagger_{\text{allowed}}$ and lower $\Delta G^\ddagger_{\text{forbidden}}$ to allow reaction.

Predictions of general $\Delta\Delta G^\ddagger$: 10-15 kcal/mole

References: J. I. Brauman and D. M. Golden, J. Amer. Chem. Soc., 90, 1920 (1968); E. C. Lupton, Tetrahedron Lett., 4209 (1968).

(3) This reaction might be occurring by a completely different (allowed) mechanism.

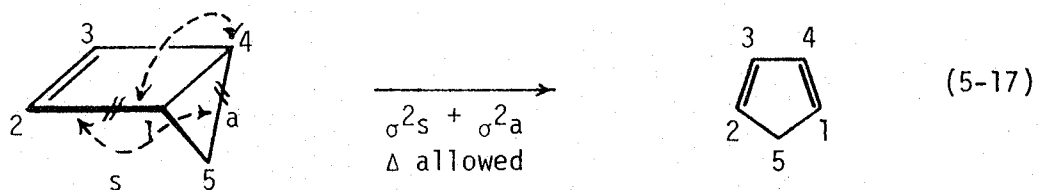
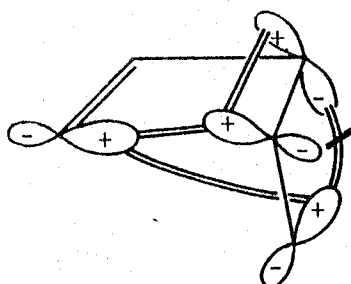
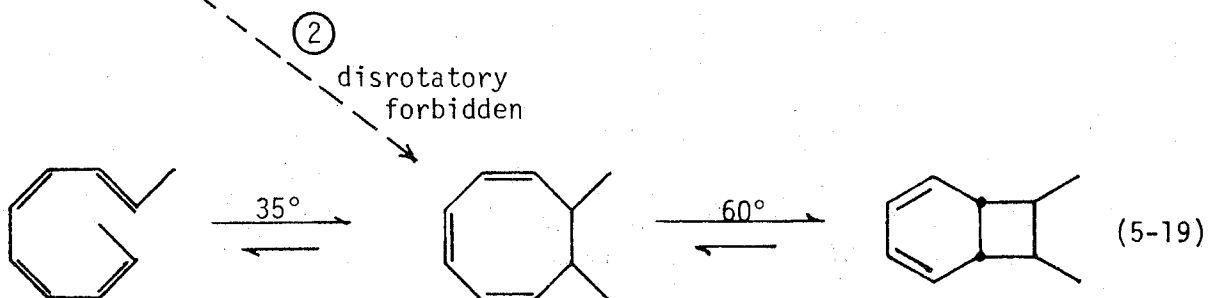
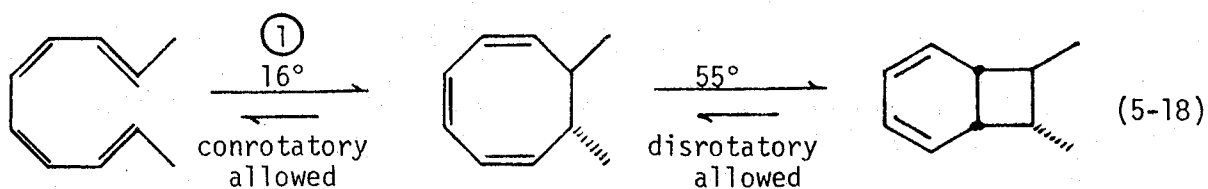


Figure 5-3.



one inversion, 4e
 Δ allowed

Reference: J. E. Baldwin and G. D. Andrews, J. Amer. Chem. Soc., 94, 1775 (1972). However, see M. C. Flowers and H. M. Frey, J. Amer. Chem. Soc., 94, 8636 (1972).



From relative rates of 1 and 2 at elevated temperature:

$$\Delta\Delta G^\ddagger = 11 \text{ kcal/mole}$$

Reference: R. Huisgen, A. Dahmen, and H. Huber, *Tetrahedron Lett.*, 1461 (1969); A. Dahmen and R. Huisgen, *ibid.*, 1469 (1969).

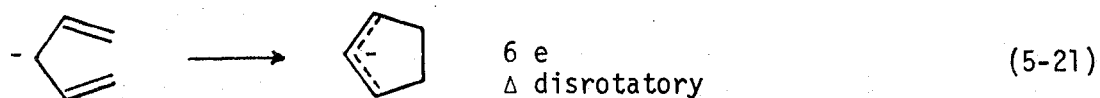
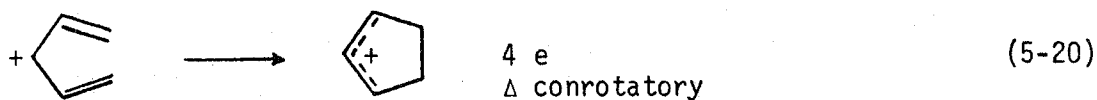
Related experiments:

$\Delta\Delta G^\ddagger > 7.3 \text{ kcal/mole}$: see Problem 5-4.

$\Delta\Delta G^\ddagger \geq 15 \text{ kcal/mole}$: J. I. Brauman and W. C. Archie, Jr., *J. Amer. Chem. Soc.*, **94**, 4262 (1972).

Charged species

Selection rule depends on number of electrons



Treatment by H-M: Number of electrons used explicitly.

Treatment by S-A:

Addition to one carbon (p orbital)

Figure 5-4.

Suprafacial addition

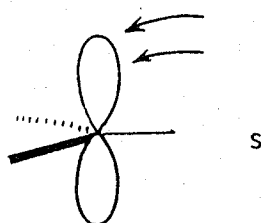
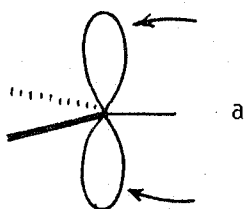


Figure 5-5.

Antarafacial addition



If carbon has two electrons (carbanion):

$${}_w 2_s \text{ or } {}_w 2_a$$

If carbon has no electrons (carbonium ion):

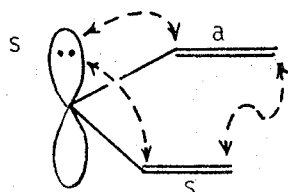
$${}_w 0_s \text{ or } {}_w 0_a$$

Remember ${}_w 0_a$ is a $(4n)_a$ component and must be counted in counting even or odd.

Application to pentadienyl anion

Conrotatory

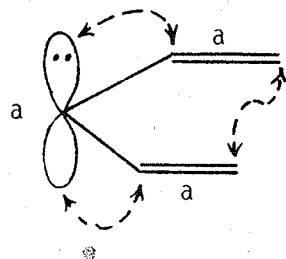
Figure 5-6.



$$\pi^2_S + \omega^2_S + \pi^2_a$$

Δ forbidden

Figure 5-7.

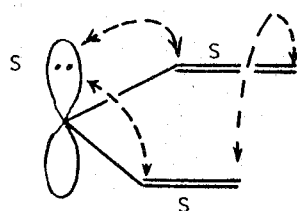


$$\pi^2_a + \omega^2_a + \pi^2_a$$

Δ forbidden

Disrotatory

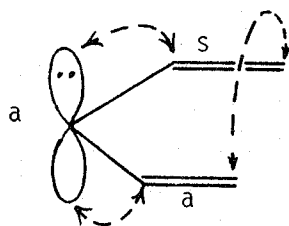
Figure 5-8.



$$\pi^2_S + \omega^2_S + \pi^2_S$$

Δ allowed

Figure 5-9.



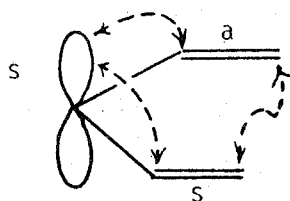
$$\pi^2_S + \omega^2_a + \pi^2_a$$

Δ allowed

Application to pentadienyl cation

Conrotatory

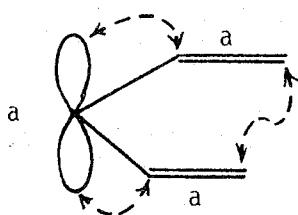
Figure 5-10.



$$\frac{\pi^2_s}{\omega^0_s} + \frac{\pi^2_a}{\omega^0_a} + \frac{\pi^2_s}{\omega^0_s}$$

Δ allowed

Figure 5-11.

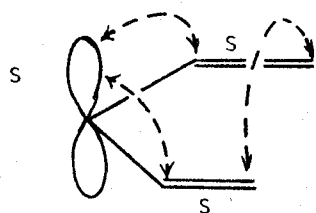


$$\frac{\pi^2_a}{\omega^0_a} + \frac{\pi^2_a}{\omega^0_a} + \frac{\pi^2_a}{\omega^0_a}$$

Δ allowed

Disrotatory

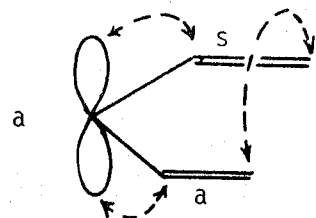
Figure 5-12.



$$\frac{\pi^2_s}{\omega^0_s} + \frac{\pi^2_s}{\omega^0_s} + \frac{\pi^2_s}{\omega^0_s}$$

Δ forbidden

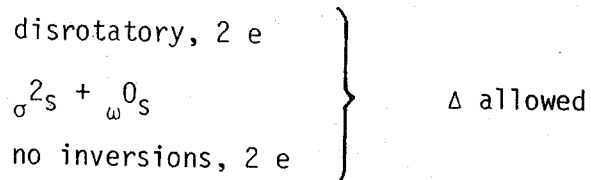
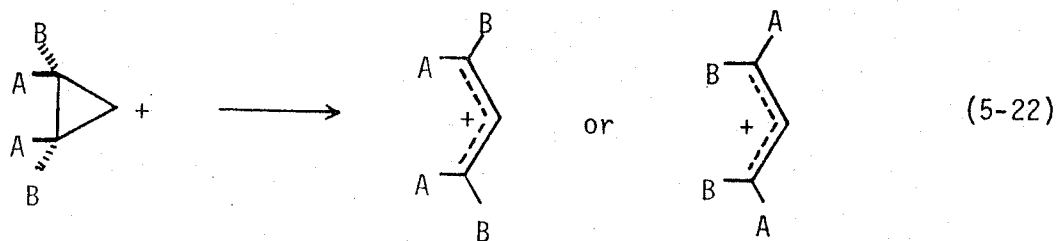
Figure 5-13.



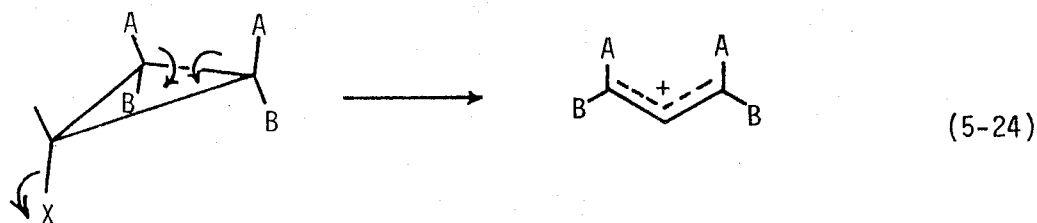
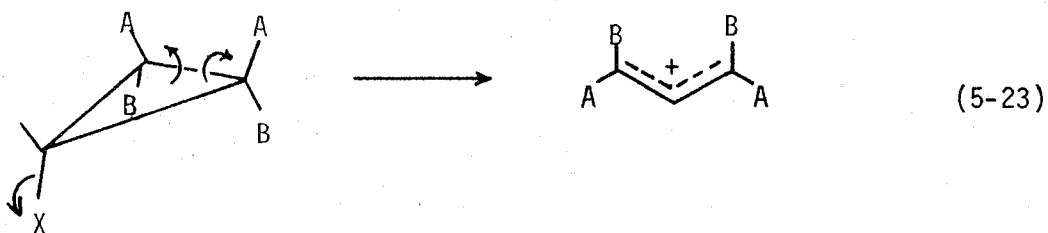
$$\frac{\pi^2_s}{\omega^0_s} + \frac{\pi^2_a}{\omega^0_a} + \frac{\pi^2_s}{\omega^0_s}$$

Δ forbidden

Cyclopropyl cation -- allyl cation

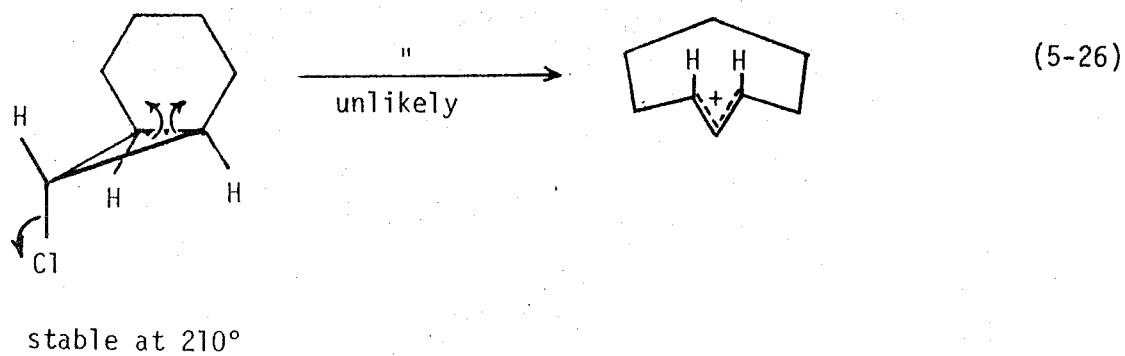
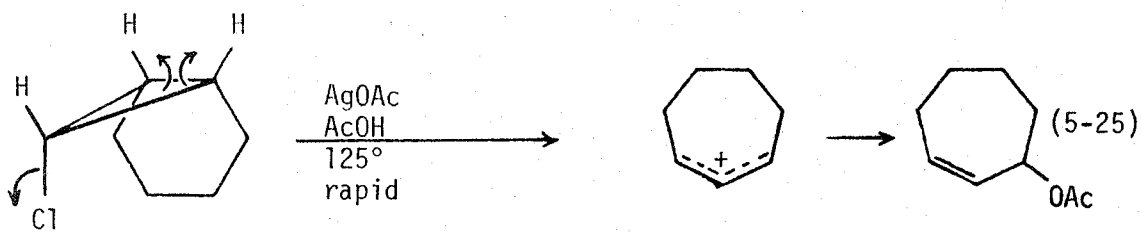
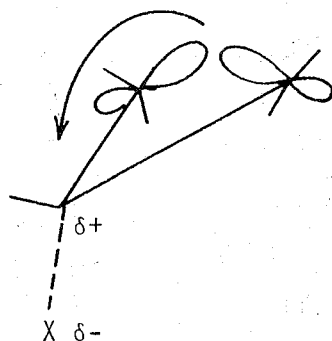


If loss of leaving group is synchronous with ring opening, reactions are internally different.



In first case electron density from breaking σ bond stabilizes developing positive charge; preferred.

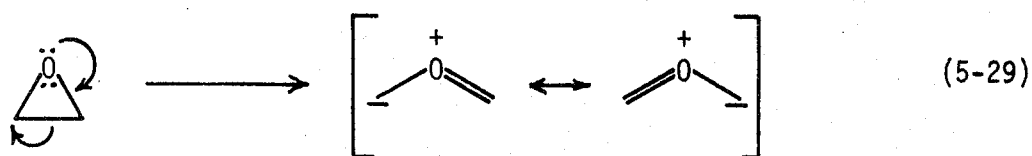
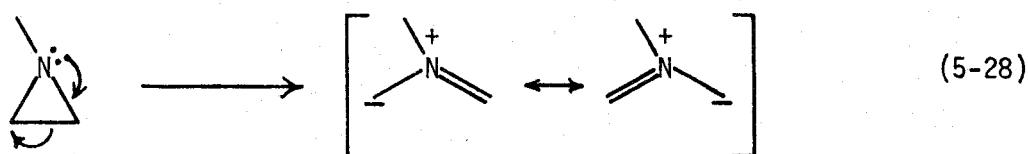
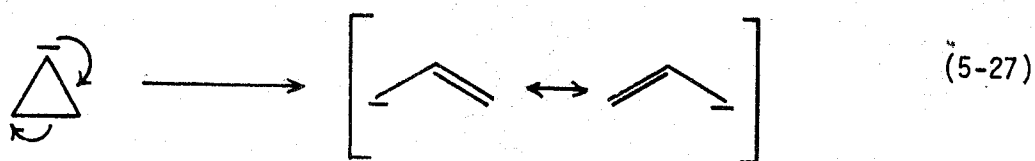
Figure 5-14.



Review: C. H. DePuy, Accounts Chem. Research, **1**, 33 (1968).

Heterocycles

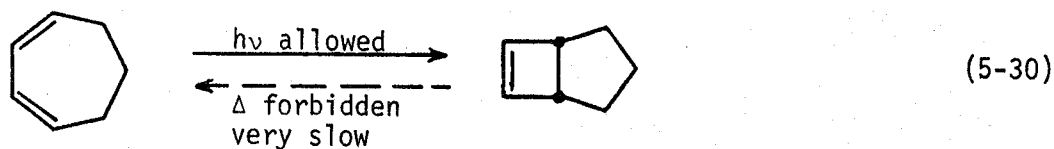
$\text{-}\ddot{\text{N}}\text{-}$ and $\text{-}\ddot{\text{O}}\text{-}$ are isoelectronic with $\text{-}\ddot{\text{C}}\text{-}$.



Same stereochemistry (see Problems 6-10 and 7-5).

Convenient mnemonic for electrocyclic reactions:

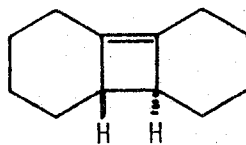
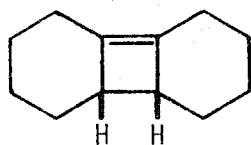
Remember one example with easily recognizable stereochemistry.



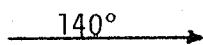
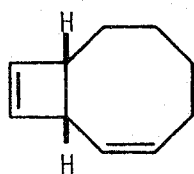
The allowed stereochemistry is reversed on addition or removal of two electrons (or one C=C double bond).

Problems

- 5-1 Of the following two compounds, one rearranges rapidly to a substituted butadiene, and the other slowly. Which should be faster?

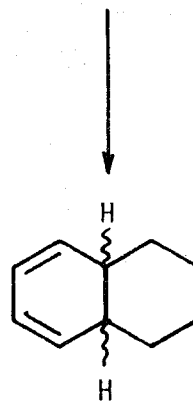


- 5-2 What should be the stereochemistry of 1 and 2?



1,3,5-cyclodecatriene 1

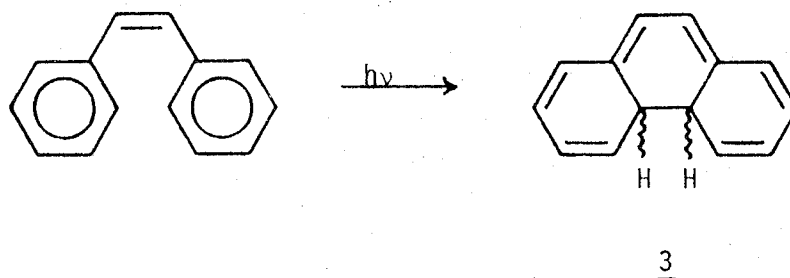
220°



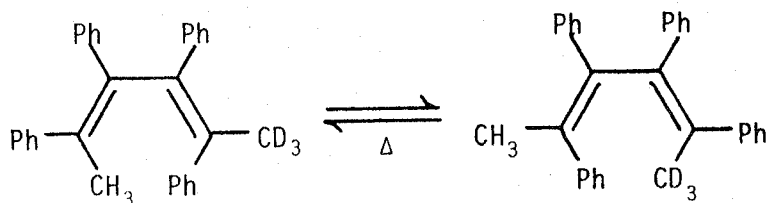
(A hint is given.)

2

5-3 What should be the stereochemistry of 3?

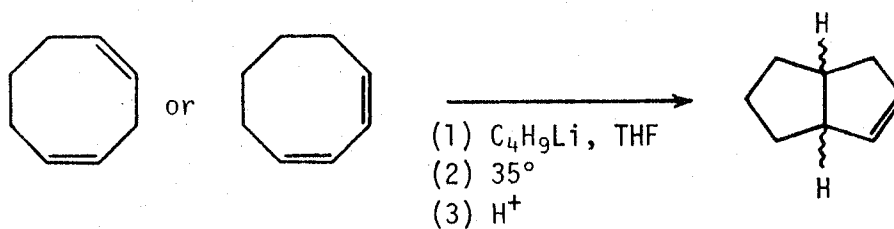


5-4 Suggest a mechanism for the interconversion



(A hint is given.)

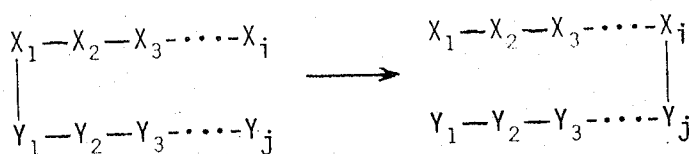
5-5 What should be the stereochemistry of the product?



Section 6
Sigmatropic Rearrangements

Figure 6-1.

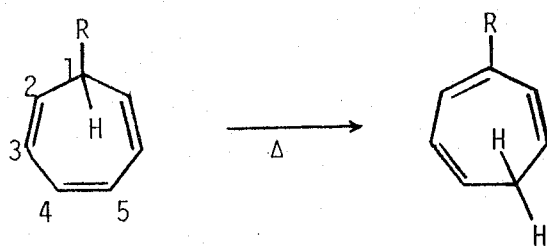
Sigmatropic rearrangement of order $[i,j]$



double bonds or charges as required

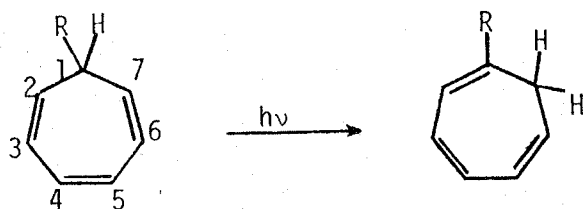
Figure 6-2.

[1,5] Hydrogen shift



(6-1)

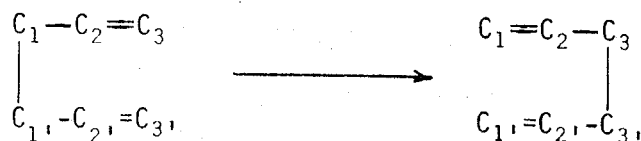
[1,7] Hydrogen shift



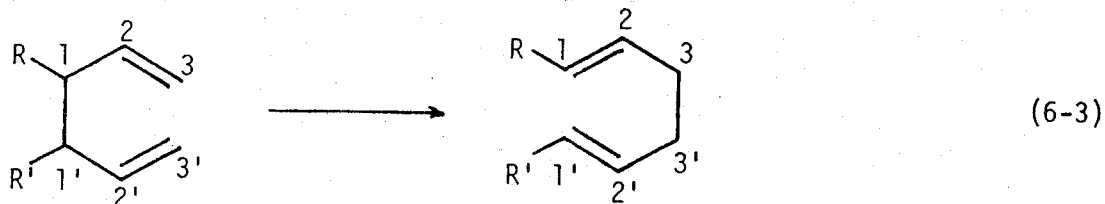
(6-2)

Figure 6-3.

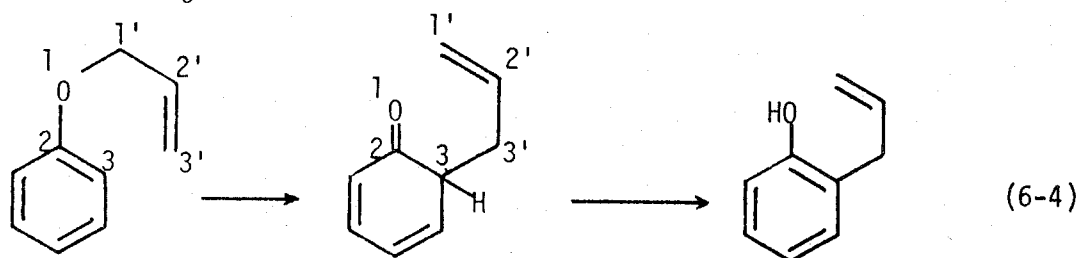
[3,3] Sigmatropic rearrangement



Cope rearrangement



Claisen rearrangement

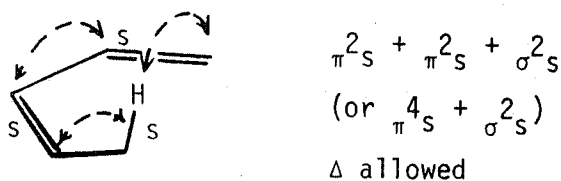


Reviews: K. Mackenzie in "Chemistry of Alkenes," Vol. 2, J. Zabicky, Ed., Interscience, New York, N. Y., 1970, p 115, and references cited therein; S. J. Rhoads in "Molecular Rearrangements," Vol. 2, P. de Mayo, Ed., Interscience, New York, N. Y., 1964, p 655.

Treatment by S-A

Figure 6-4.

[1,5] Hydrogen shift



Notice that there cannot be inversion at H in addition to a C-H bond; there is no node there.

Figure 6-5.

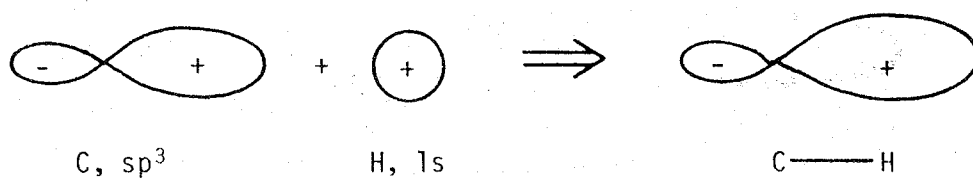
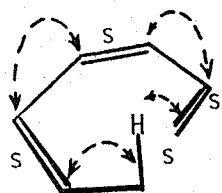


Figure 6-6.

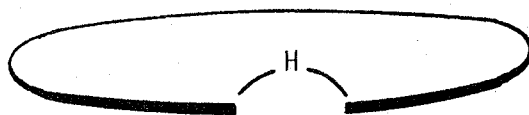
[1,7] Hydrogen shift



$\pi^2_s + \pi^2_s + \pi^2_s + \sigma^2_s$
 Δ forbidden, $h\nu$ allowed

Overall stereochemistry suprafacial.

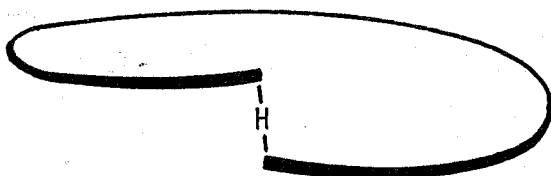
Figure 6-7.



Another stereochemistry

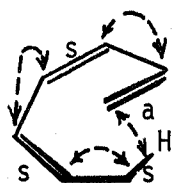
antarafacial

Figure 6-8.



Overall stereochemistry antarafacial.

Figure 6-9.



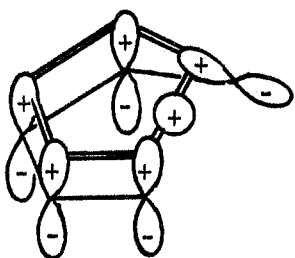
$$\pi^2_s + \pi^2_s + \pi^2_a + \sigma^2_s$$

Δ allowed

H-M Treatment

Figure 6-10.

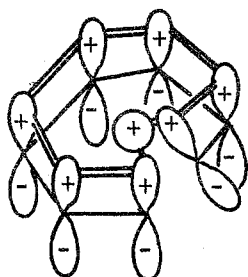
[1,5] Hydrogen shift - suprafacial



no sign inversions, 6 e
 Δ allowed

Figure 6-11.

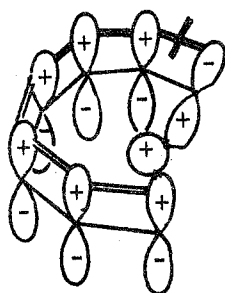
[1,7] Hydrogen shift - suprafacial



no sign inversions, 8 e
 Δ forbidden, hv allowed

Figure 6-12.

[1,7] Hydrogen shift - antarafacial

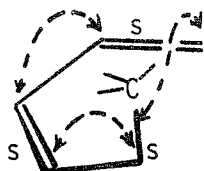


one sign inversion, 8 e
 Δ allowed

Carbon can also migrate.

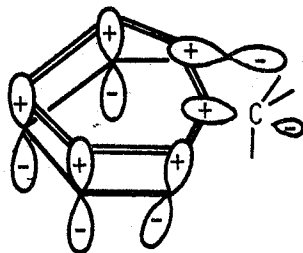
[1,5] alkyl shift - suprafacial

Figure 6-13.



$\pi^2_s + \pi^2_s + \sigma^2_s$
 Δ allowed

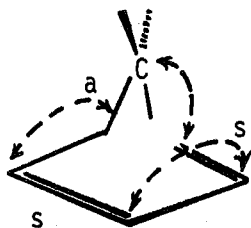
Figure 6-14.



no sign inversions, 6 e
 Δ allowed

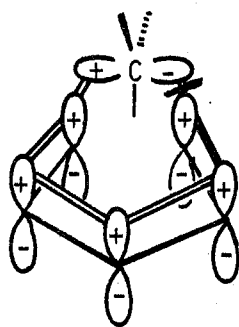
Configuration of migrating carbon can invert.
 Suprafacial [1,5] alkyl shifts with inversion.

Figure 6-15.



$\pi^2_s + \pi^2_s + \sigma^2_a$
 Δ forbidden

Figure 6-16.



one inversion, 6 e
 Δ forbidden

Table 6-1

Allowed [1,n] Sigmatropic Rearrangements

Thermal Reactions

	Without inversion at migrating center	With inversion at migrating center
[1,3]	antarafacial	suprafacial
[1,5]	suprafacial	antarafacial
[1,7]	antarafacial	suprafacial
[1,9]	suprafacial	antarafacial

Table would be reversed for photochemical reactions.

Note ease of remembering one reaction; stereochemical result is reversed on changing the number of electrons by two (adding or removing one double bond).

Larger reactions.

Figure 6-17.

Cope rearrangement [3,3]

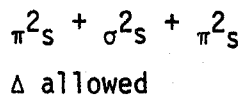
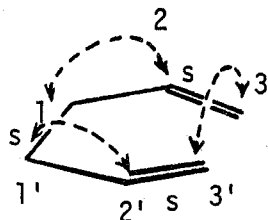
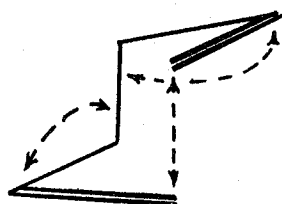
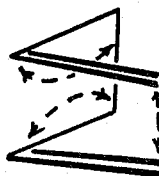


Figure 6-18.

Stereochemistry



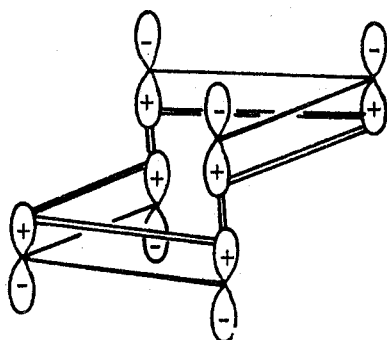
chair-like
(preferred)



boat-like

Reference: M. J. Goldstein and M. S. Benzon, *J. Amer. Chem. Soc.*, **94**, 7147, 7149 (1972), and references cited therein.

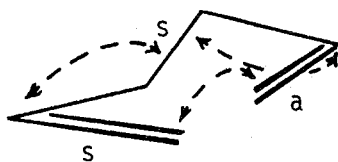
Figure 6-19.



no inversions, 6 e
 Δ allowed

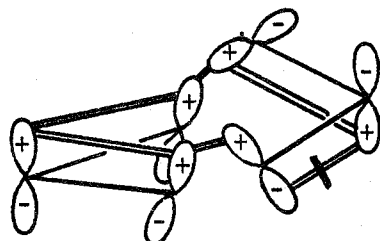
Suprafacial with respect to each three-atom component. [3,3] is forbidden if supra-antara.

Figure 6-20.



$\pi^2_s + \sigma^2_s + \pi^2_a$
 Δ forbidden

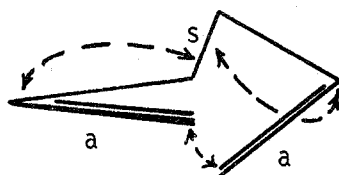
Figure 6-21.



one inversion, 6e
 Δ forbidden

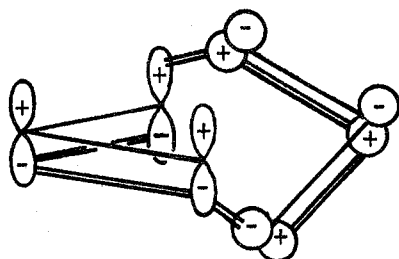
Figure 6-22.

Antara-antara [3,3] sigmatropic rearrangement

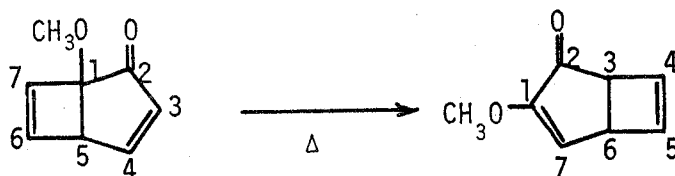


$\sigma^2_s + \pi^2_a + \pi^2_a$
 Δ allowed

Figure 6-23.



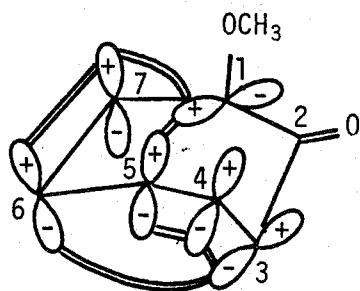
no inversions, 6 e
 Δ allowed



(6-5)

Treatment in S-A: see Appendix II

Figure 6-24.



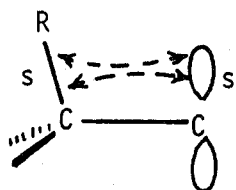
no inversions, 6 e
 Δ allowed

Reference: T. Miyashi, M. Nitta, and T. Mukai, *J. Amer. Chem. Soc.*, **93**, 3441 (1971); however, see J. E. Baldwin and M. S. Kaplan, *ibid.*, **94**, 668 (1972) and references cited therein.

Sigmatropic rearrangements in charged systems

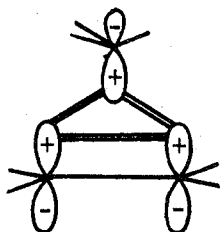
[1,2] shift in carbonium ions

Figure 6-25.



$\sigma^2_s + \omega^0_s$
 Δ allowed

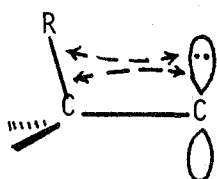
Figure 6-26.



no inversions, 2 e
 Δ allowed

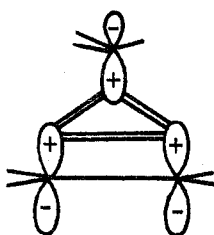
[1,2] shift in a carbanion without inversion is forbidden.

Figure 6-27.



$\sigma^2_s + \omega^2_s$
 Δ forbidden

Figure 6-28.



no inversions, 4 e
 Δ forbidden

Problem 6-1.

Show that the [1,4] alkyl shift is thermally allowed suprafacially, without inversion, for a carbanion, and with inversion for a cation.

Sigmatropic rearrangements of zwitterions

Sommelet-Hauser rearrangement; a [2,3] sigmatropic rearrangement.

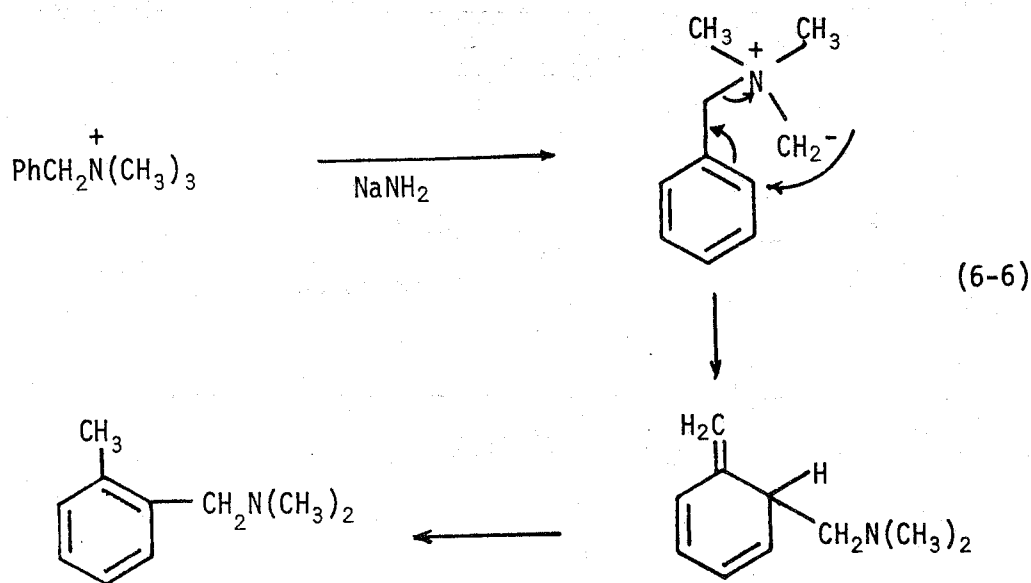


Figure 6-29.

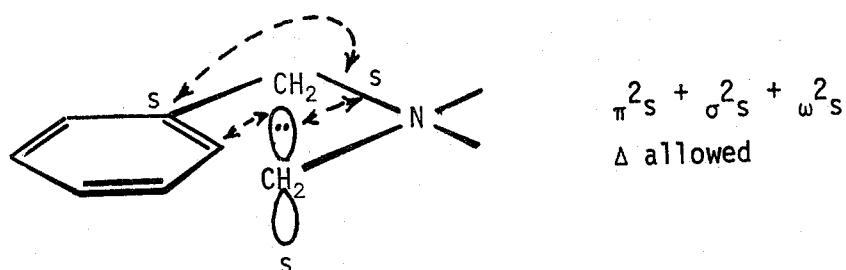
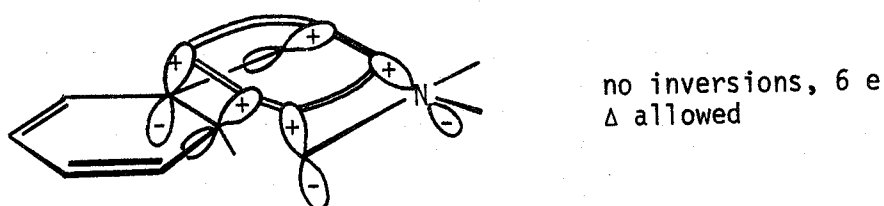
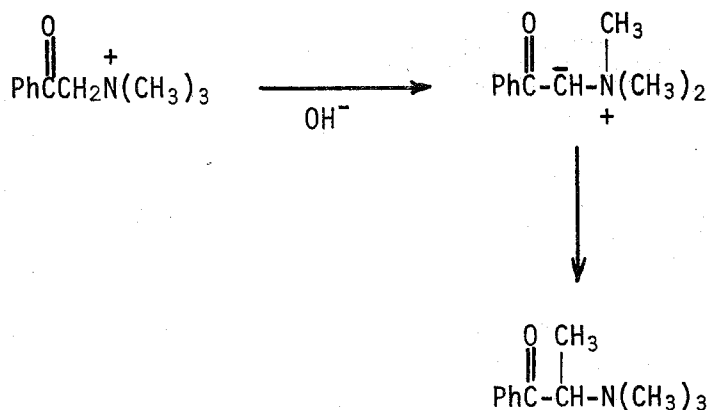


Figure 6-30.



Stevens rearrangement; a [1,2] sigmatropic rearrangement



(6-7)

Migrating group retains configuration.

Figure 6-31.

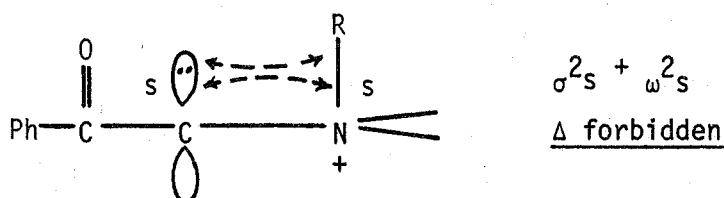
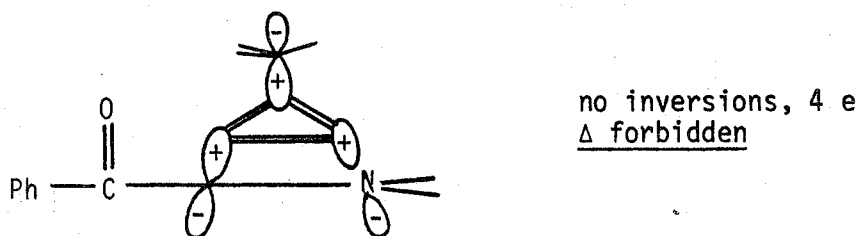


Figure 6-32.



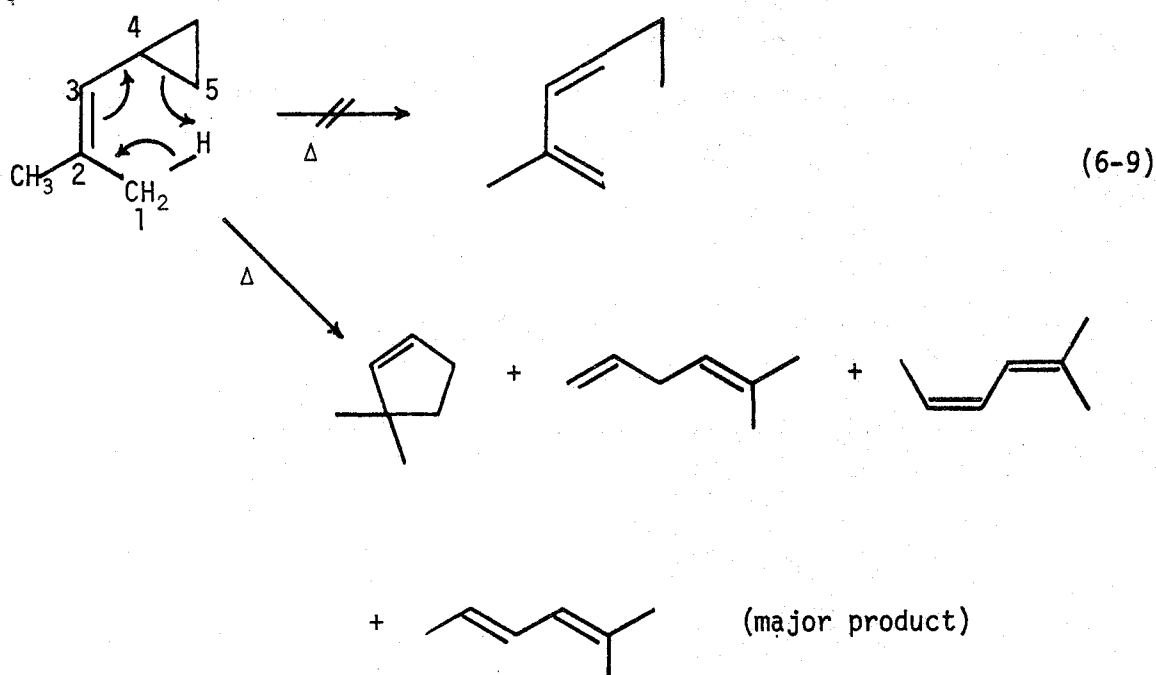
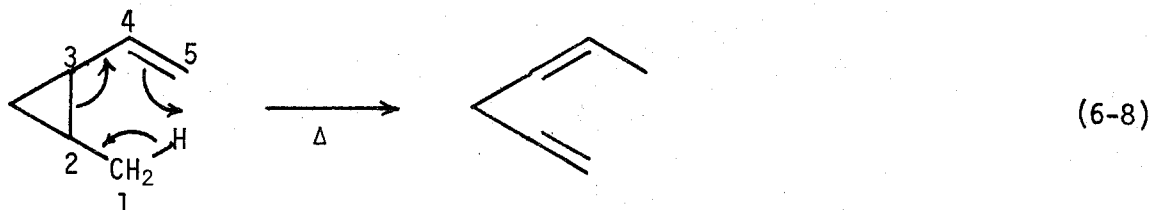
Evidence for radical intermediates in both reactions.

Review: S. H. Pine, Org. Reactions, **18**, 403 (1970).

06.12 A cyclopropane ring is similar to a C=C double bond in many of its reactions.

Review: M. Charton in "The Chemistry of Alkenes," Vol. 2, J. Zabicky, Ed., Interscience, New York, N. Y., 1970, p 511.

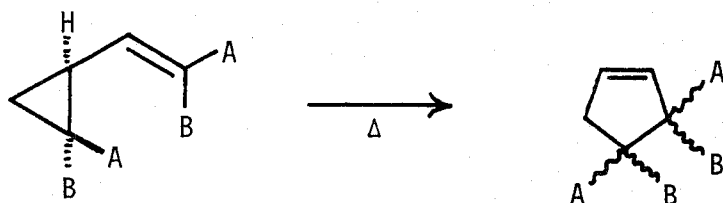
"Homodienyl 1,5-hydrogen shift"



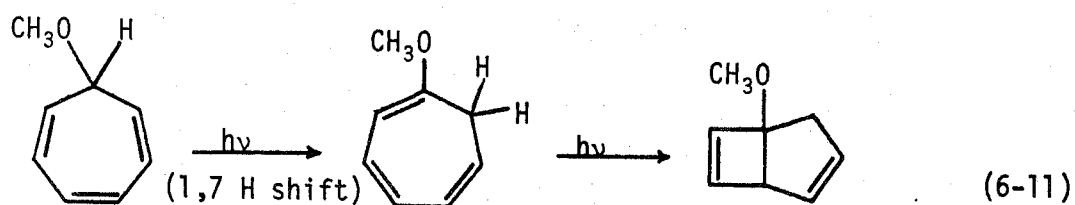
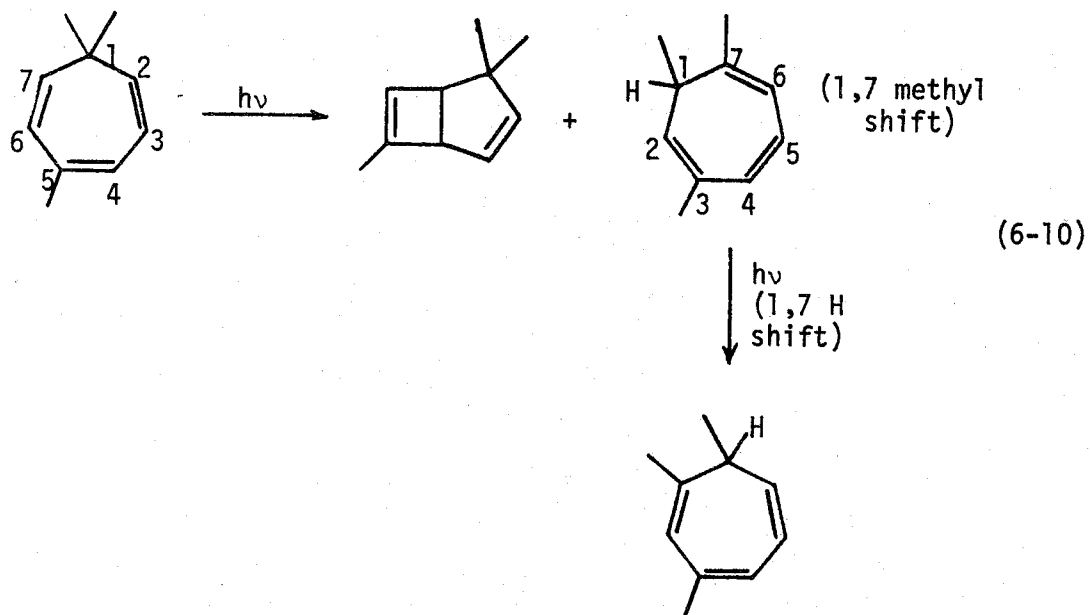
Review: H. M. Frey and R. Walsh, Chem. Rev., **69**, 103 (1969).

Problem 6-2.

Predict the stereochemistry of the vinylcyclopropane \rightarrow cyclopentene rearrangement.



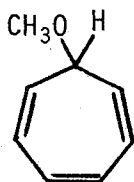
Photochemical sigmatropic rearrangements



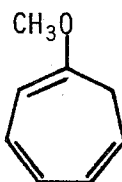
Review: L. B. Jones and V. K. Jones, Fortschr. Chem. Forsch., **13**, 307 (1969).

Problems

- 6-3 What are the allowed photochemical sigmatropic and electrocyclic reactions of 1? Of 2?



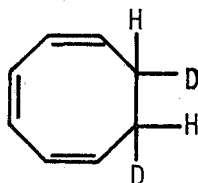
1



2

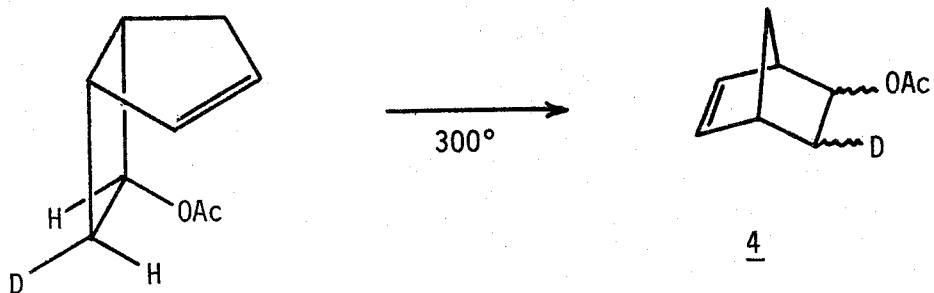
(A hint is given.)

- 6-4 Heating 1,3,5-cyclooctatriene gives some 1,3,6-cyclooctatriene, reversibly. What isotopic labeling would be expected in the 1,3,5-cyclooctatriene recovered after heating 3 for an extended time?



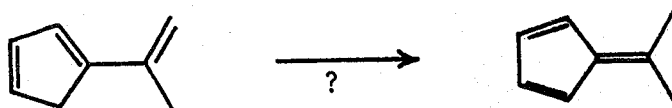
3

6-5 What should be the stereochemistry of 4?

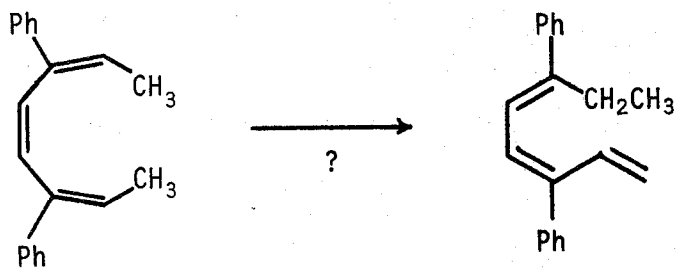


(A hint is given.)

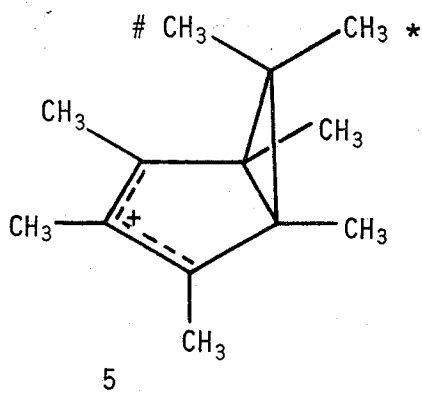
6-6 Should this reaction be thermal or photochemical? (Check models.)



6-7 Should this reaction be thermal or photochemical? (Check models.)

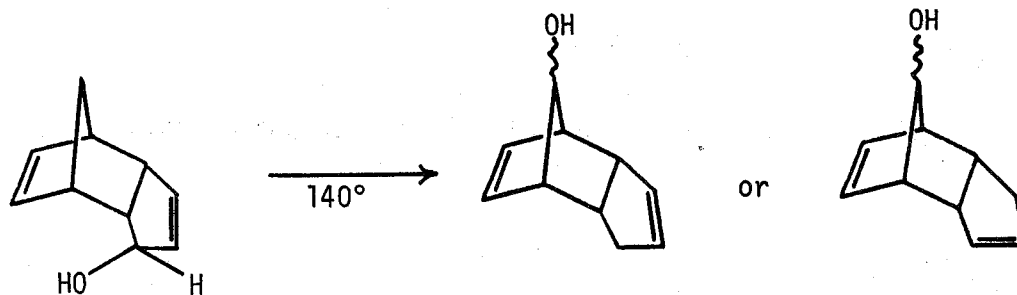


6-8 Cation 5 at high temperatures undergoes sigmatropic rearrangement so rapidly that all five methyl groups on the five-membered ring become equivalent (on the nmr time scale). Should the gem-methyl groups (* and #) become equivalent also?



(A hint is given.)

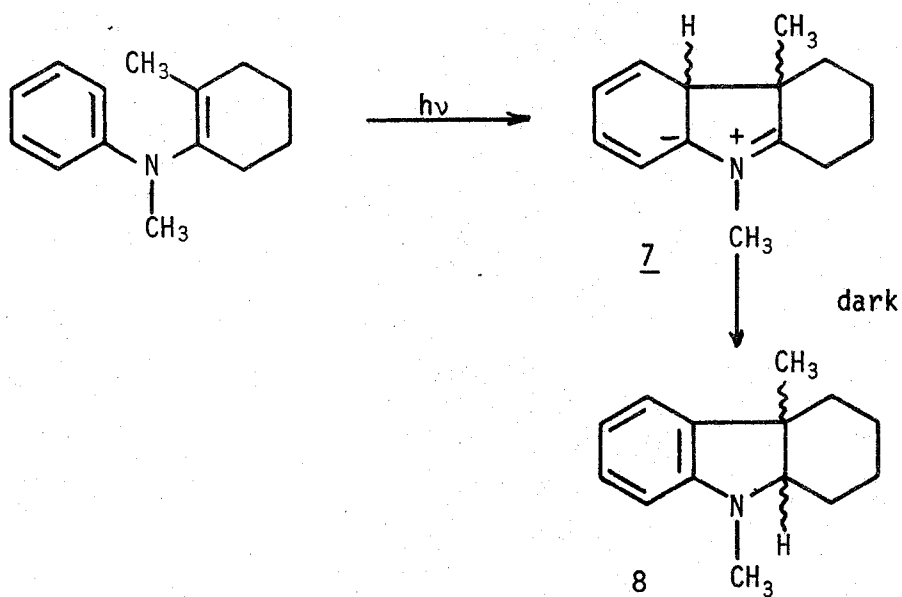
6-9 Predict the stereochemistry of 6.



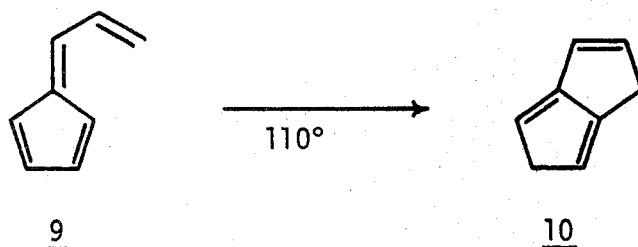
(optically active)

6

6-10 Predict the stereochemistry of 7 and 8.

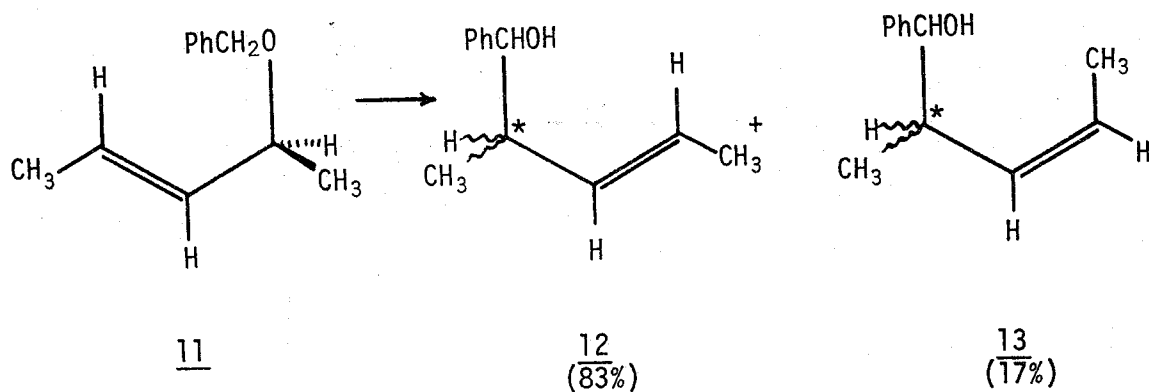


6-11 Postulate two intermediates to get from 9 to 10 via thermally allowed reactions.



(A hint is given.)

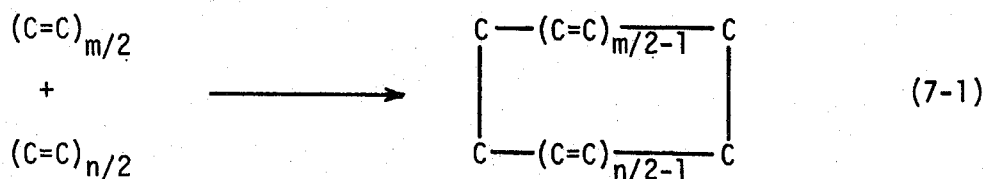
6-12 Treatment of optically active ether 11 with base gives alcohols 12 and 13. Predict the absolute configurations of the alcohols at the labelled centers.



Ede 13

Section 7
Cycloadditions

All-carbon cycloadditions - (m+n)



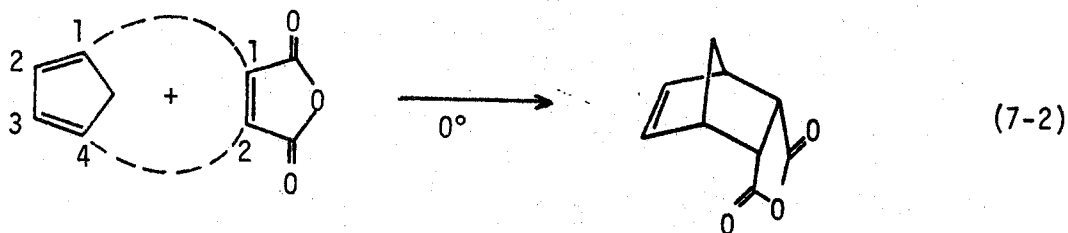
All-suprafacial reaction thermally allowed if $(m+n) = 4q + 2$

Proof: $(4q+2) = (2q+1) 2_s$ cycloadditions

no sign inversions, requires $4n+2$ electrons

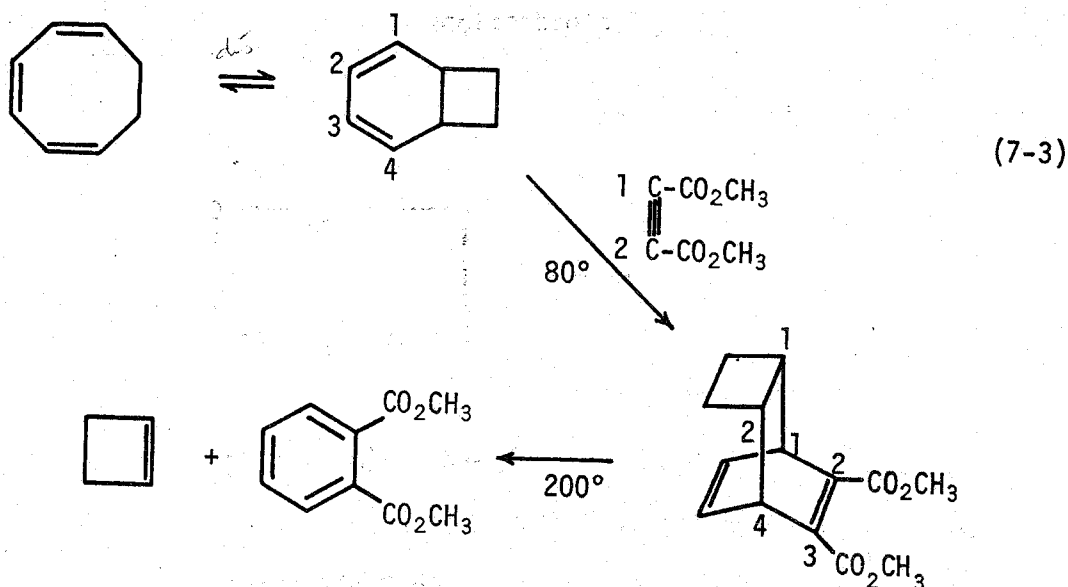
Examples

4+2 (Diels-Alder reaction)



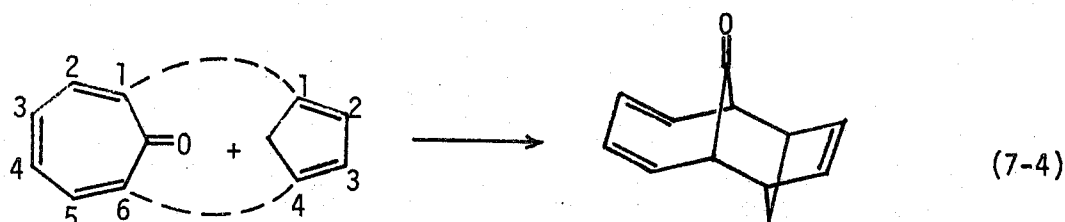
Reviews: R. Huisgen, R. Grashey, and J. Sauer, in "The Chemistry of Alkenes," Vol. 1, S. Patai, Ed., Interscience, New York, N. Y., 1964, p 739; S. Seltzer, in "Advances in Alicyclic Chemistry," Vol. 2, H. Hart and G. J. Karabatsos, Eds., Academic Press, New York, N. Y., 1968, p 1.

Reverse reaction (cycloreversion)

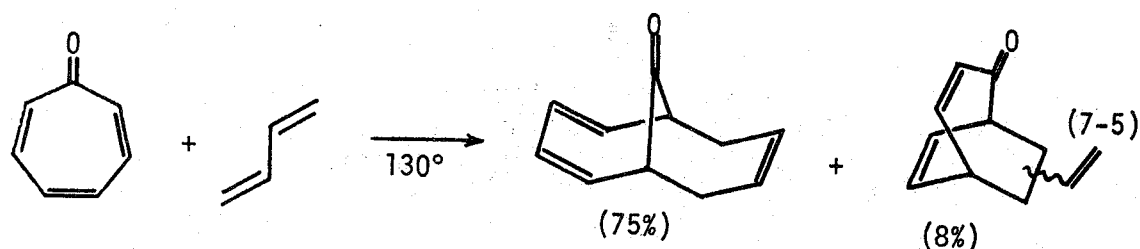


Review: H. Kwart and K. King, Chem. Rev., **68**, 415 (1968).

6+4

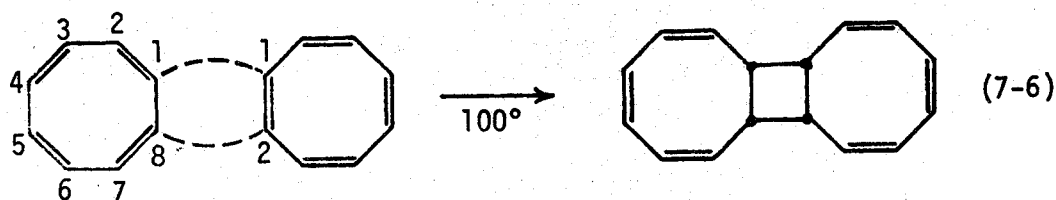


Reference: R. C. Cookson, B. V. Drake, J. Hudec, and A. Morrison, Chem. Commun., **15** (1966).



Reference: S. Itô, H. Ohtani, S. Narita, and H. Houma, Tetrahedron Lett., **2223** (1972).

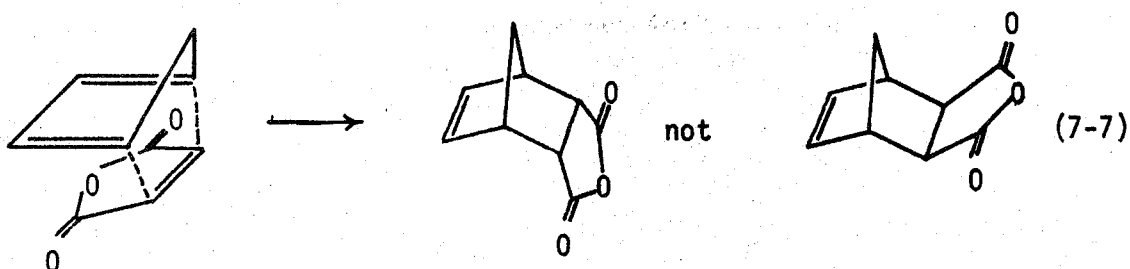
8+2



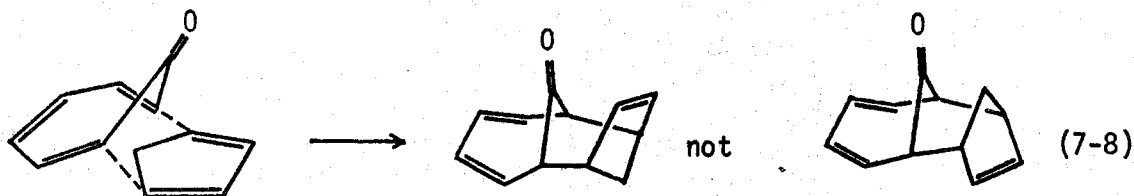
Reference: G. Schröder and W. Martin, Angew. Chem., Int. Ed. Engl., 5, 130 (1966).

Secondary stereochemistry.

4+2: endo (Alder endo rule)



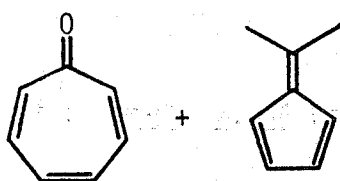
6+4: exo



References: R. B. Woodward and R. Hoffmann, op. cit., pp 145-147.
 L. Salem, J. Amer. Chem. Soc., 90, 553 (1968).
 R. Sustmann and G. Binsch, Mol. Phys., 20, 1, 9 (1971).
 K. N. Houk, Tetrahedron Lett., 2621 (1970), footnote 6.
 W. C. Herndon, Chem. Rev., 72, 157 (1972).

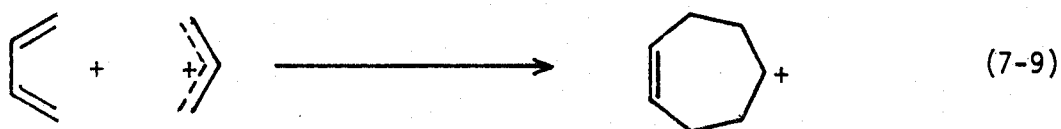
Problem 7-1.

Predict all possible cycloadducts, with the expected stereochemistry, for the reaction



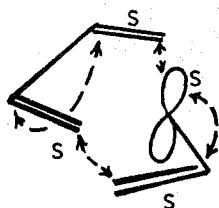
(A hint is given.)

Cycloadditions with charged species.



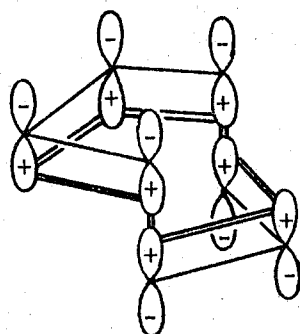
$\pi^4_s + \pi^2_s$ cycloaddition, Δ allowed

Figure 7-1.

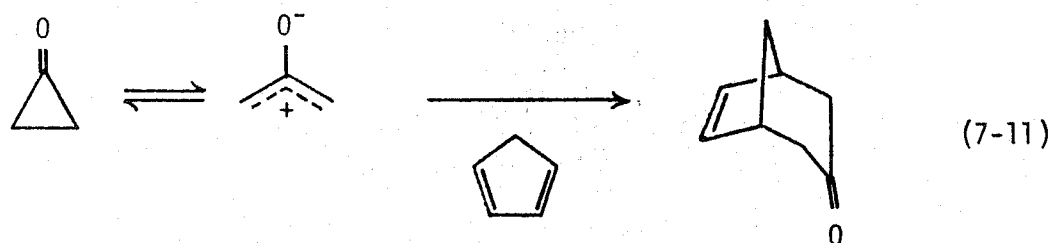
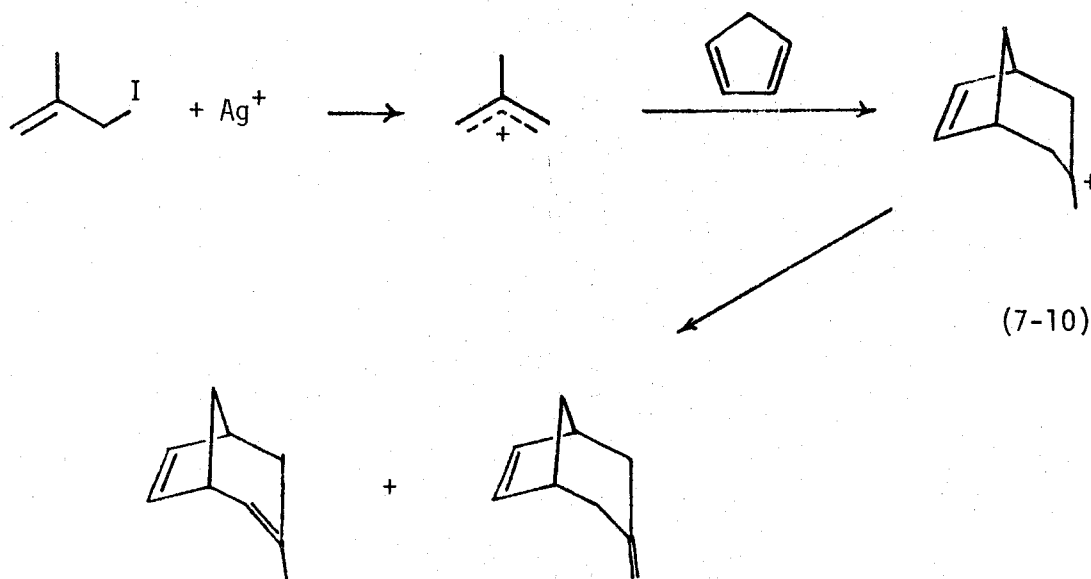


$\pi^2_s + \pi^2_s + \pi^2_s + \omega^0_s$
 Δ allowed

Figure 7-2.



no inversions, 6 e
 Δ allowed



Reference: H. M. R. Hoffmann, K. E. Clemens, and R. H. Smithers, J. Amer. Chem. Soc., 94, 3940 (1972), and references cited therein.

Problem 7-2.

Predict the products of the following all-suprafacial cycloadditions, and whether the reaction should be thermally allowed.

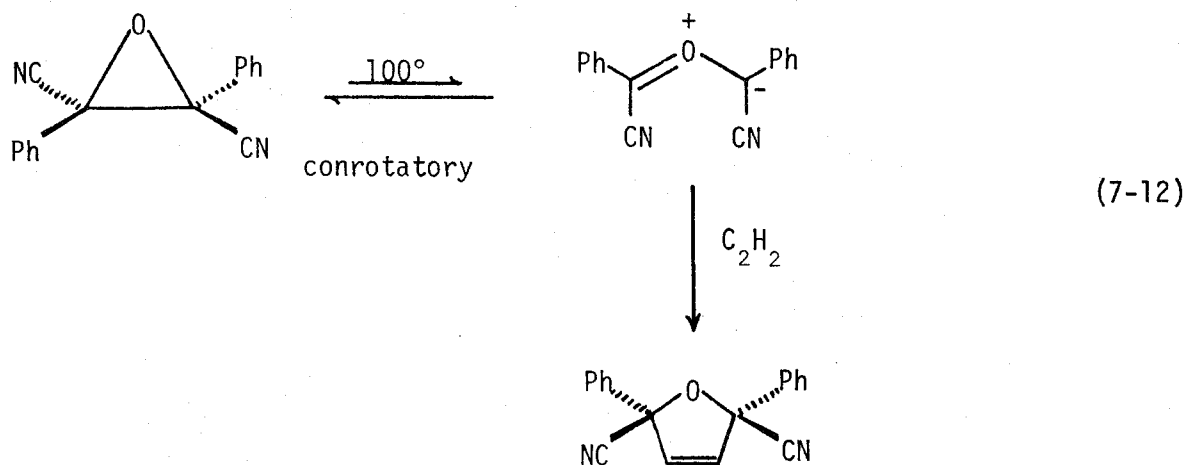
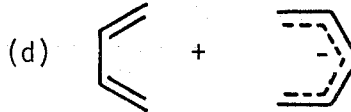
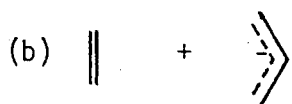
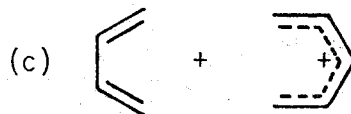
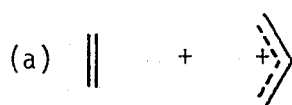
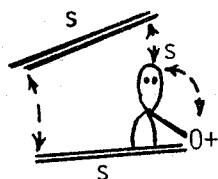


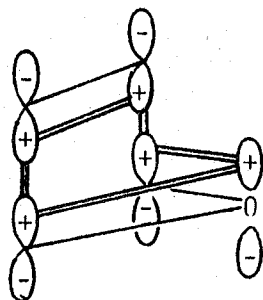
Figure 7-3.



$$\pi^2_S + \pi^2_S + \omega^2_S$$

Δ allowed

Figure 7-4.



no inversions, 6 e
Δ allowed

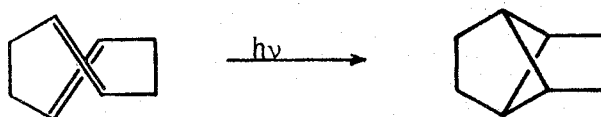
Review: G. W. Griffin, *Angew. Chem., Int. Ed. Engl.*, **10**, 537 (1971).

Photochemical 2+2 cycloadditions

Problem 7-3.

What dimeric products should be expected from irradiation of cis-2-butene? Of trans-2-butene?

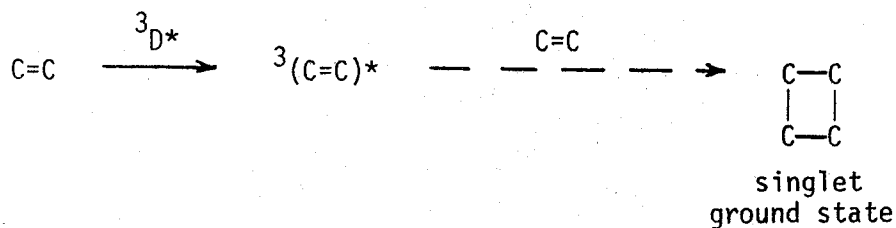
(A hint is given.)



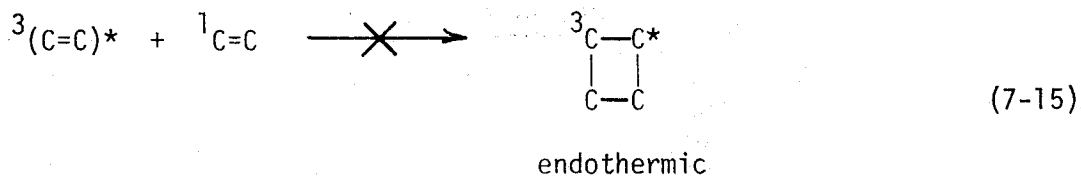
(7-13)

Reference: G. M. Whitesides, G. L. Goe, and A. C. Cope, *J. Amer. Chem. Soc.*, **91**, 2608 (1969).

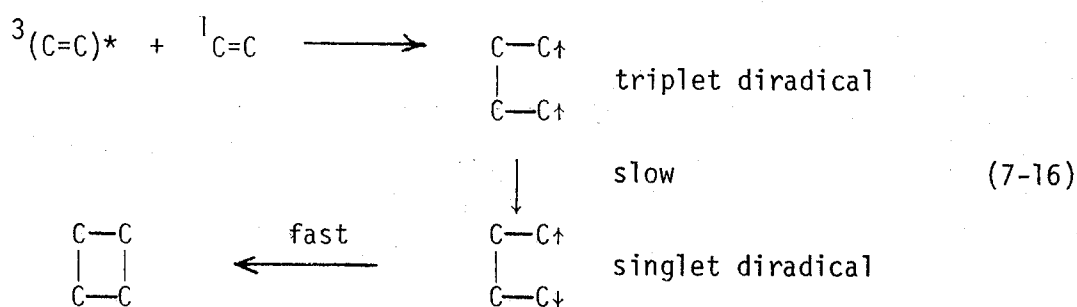
Many photosensitized cycloadditions



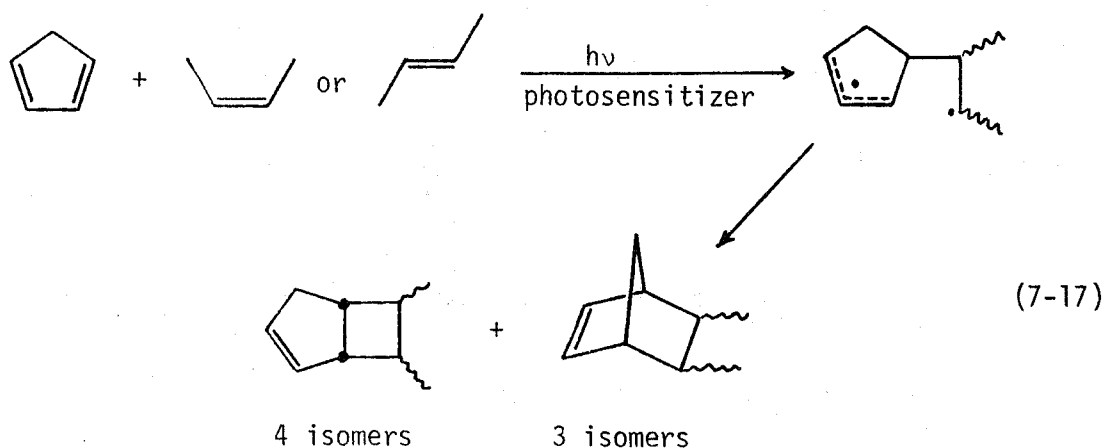
(7-14)



Non-concerted reactions via triplet diradical

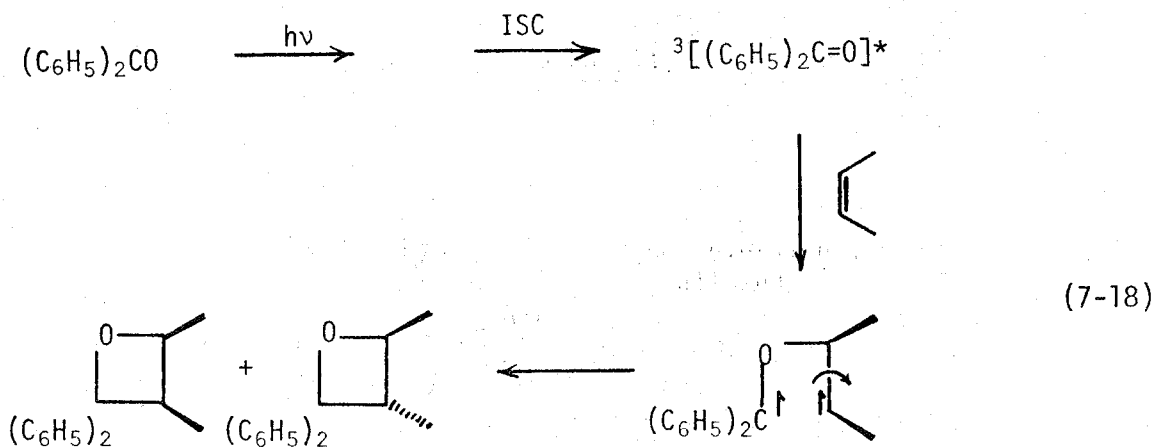


Reference: (Electronic properties of diradicals) L. Salem and C. Rowland, Angew. Chem., Int. Ed. Engl., 11, 92 (1972).

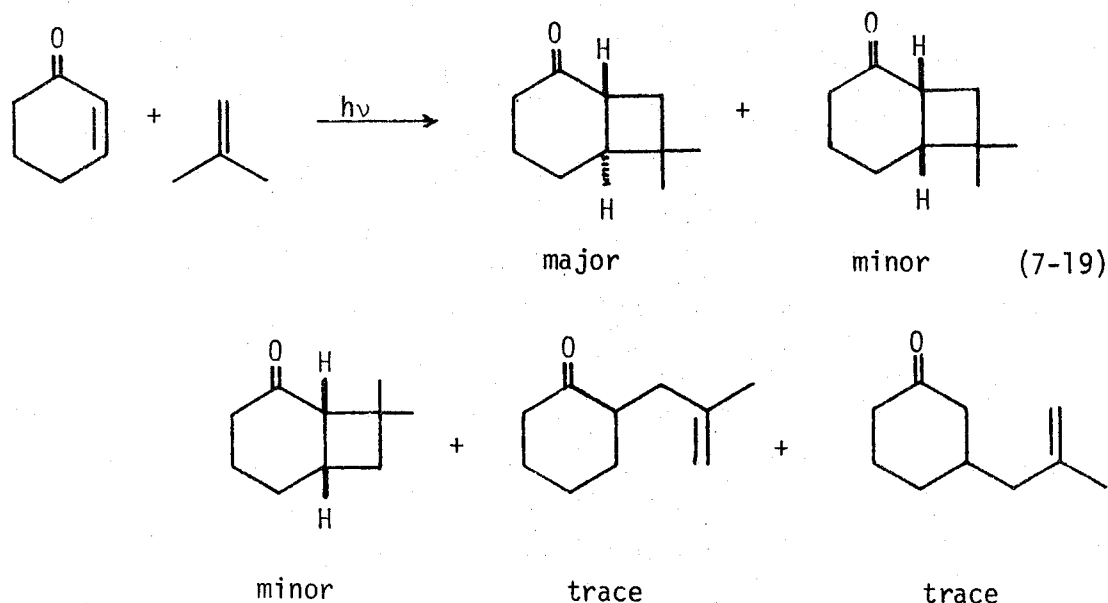


Reference: B. D. Kramer and P. D. Bartlett, J. Amer. Chem. Soc., 94, 3934 (1972).

Review: W. L. Dilling, Chem. Rev., 69, 845 (1969).



Review: D. R. Arnold, in "Advances in Photochemistry," Vol. 6, A. W. Noyes, Jr., G. S. Hammond, and J. N. Pitts, Jr., Eds., Interscience, New York, N. Y., 1968, p 301.

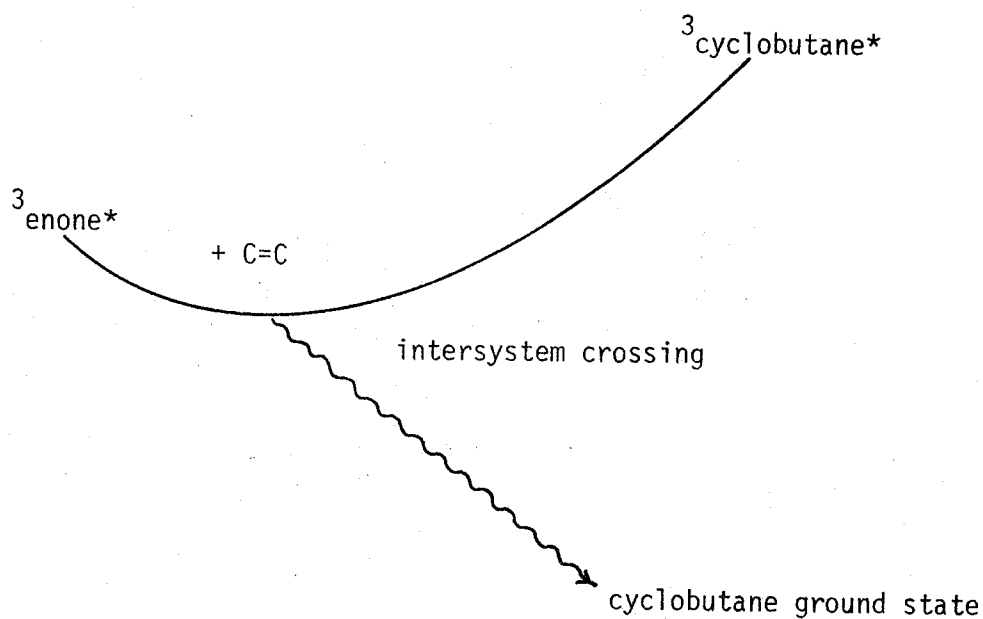


Reviews: P. de Mayo, *Accounts Chem. Research*, 4, 41 (1971), and references cited therein; O. L. Chapman and G. Lenz, in "Organic Photochemistry," Vol. 1, O. L. Chapman, Ed., Marcel Dekker, New York, N. Y., 1967, p 283; D. J. Trecker, *ibid.*, Vol. 2, 1969, p 63; P. G. Sammes, *Quart. Rev.* (London), 24, 37 (1970); P. G. Bauslaugh, *Synthesis*, 287 (1970).

Reaction occurs from triplet state of enone.
 Reaction is stereoselective for overall $\pi^2_s + \pi^2_a$.

Concerted reactions can occur from triplet states.

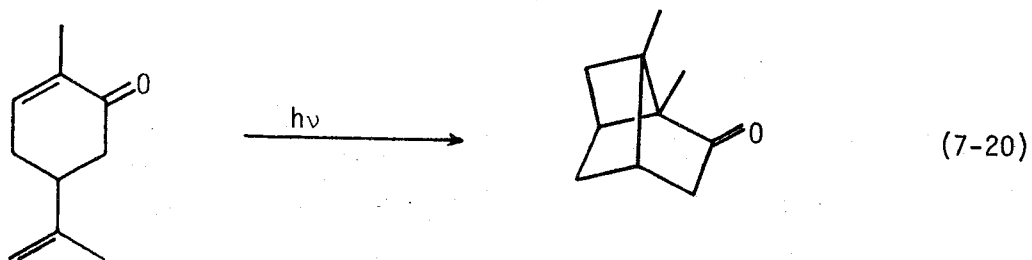
Figure 7-5.



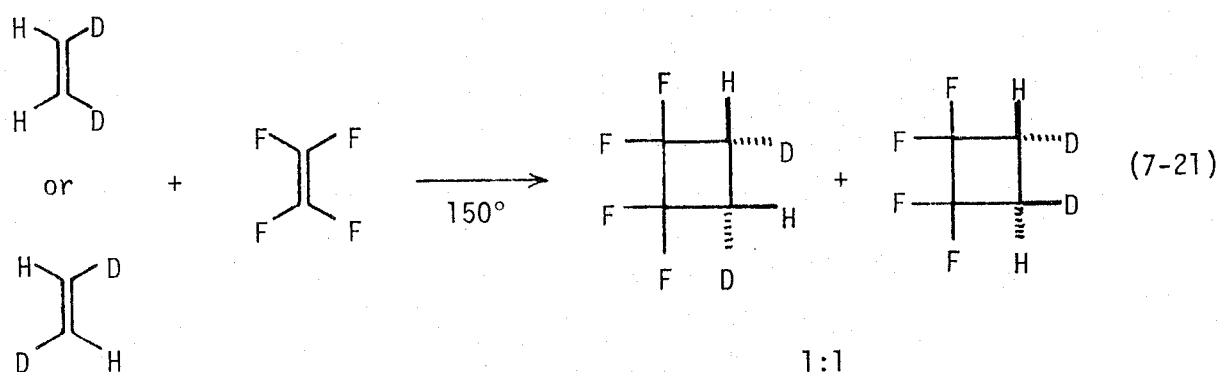
References: R. B. Woodward and R. Hoffmann, *op. cit.*, p 100.
A. Devaquet and L. Salem, *J. Amer. Chem. Soc.*, **91**, 3793 (1969).

Possibly two excited states of different geometry.

Reference: A. Devaquet, *J. Amer. Chem. Soc.*, **94**, 5160 (1972); *cf.*
R. R. Birge and P. A. Leermakers, *ibid.*, **94**, 8105 (1972).



Thermal non-stereospecific 2+2 cycloadditions with diradical intermediates.

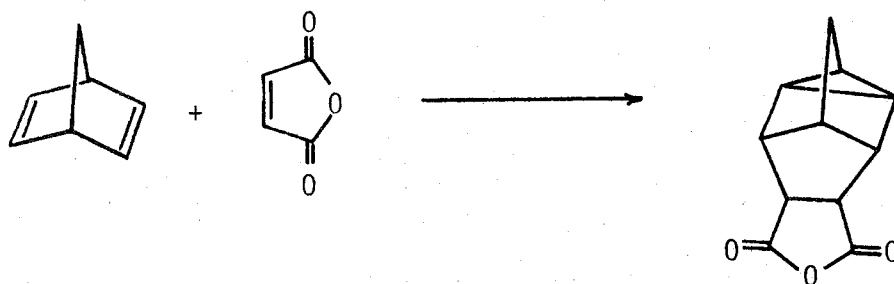


Reference: P. D. Bartlett, G. M. Cohen, S. P. Elliott, K. Hummel, R. A. Minns, C. M. Sharts, and J. Y. Fukunaga, J. Amer. Chem. Soc., **94**, 2899 (1972).

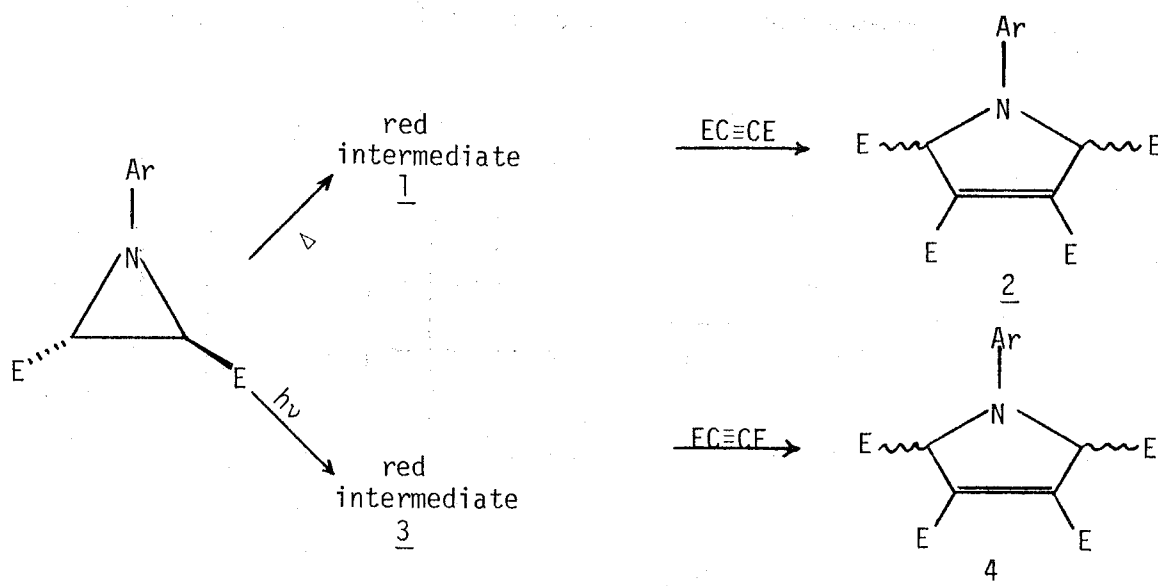
Reviews: J. D. Roberts and C. M. Sharts, Org. Reactions, **12**, 1 (1962).
 P. D. Bartlett, Quart. Rev. (London), **24**, 473 (1970).

Problems

7-4 Should this reaction be thermal or photochemical?

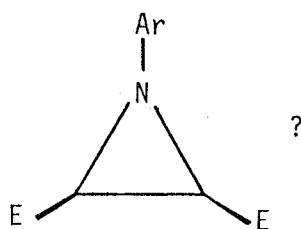


7-5 Predict the stereochemistry of intermediates and products.



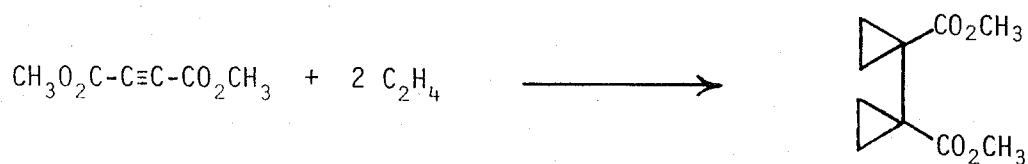
Ar = $p\text{-CH}_3\text{OC}_6\text{H}_4\text{-}$, E = $-\text{CO}_2\text{CH}_3$

How could 2 and 4 be prepared from



7-6

Should the following reaction be thermal or photochemical?

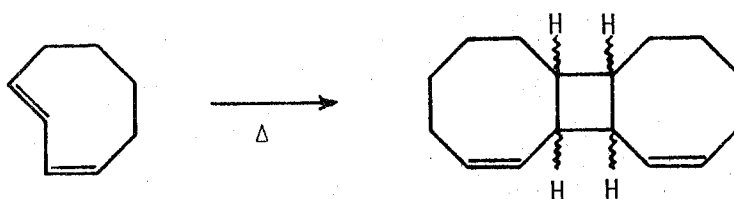


- 7-7 Predict all possible cycloadducts for the reaction



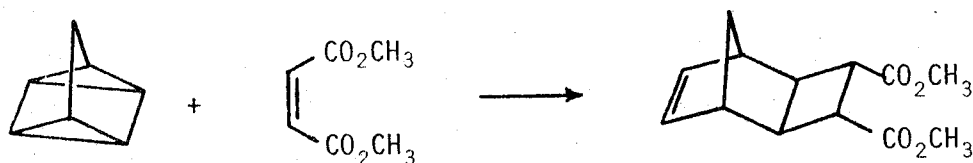
(A hint is given.)

- 7-8 What should be the stereochemistry of the product?



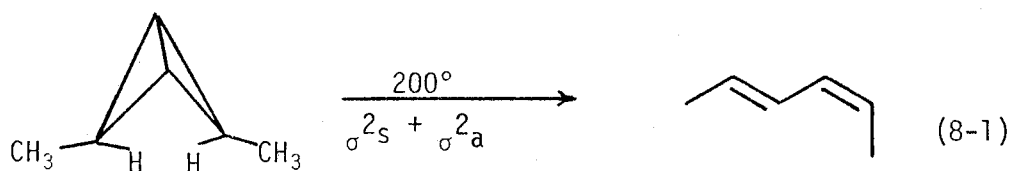
(A hint is given.)

- 7-9 Should the following reaction be thermal or photochemical?



Section 8
Other Reactions

Part a. Bicyclobutane formation and rearrangement



Reference: G. L. Closs and P. E. Pfeffer, J. Amer. Chem. Soc., **90**, 2452 (1968).

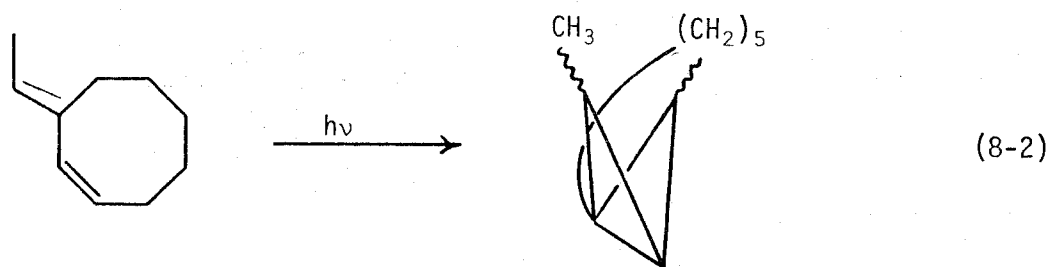


Figure 8-1.

Predicted Products

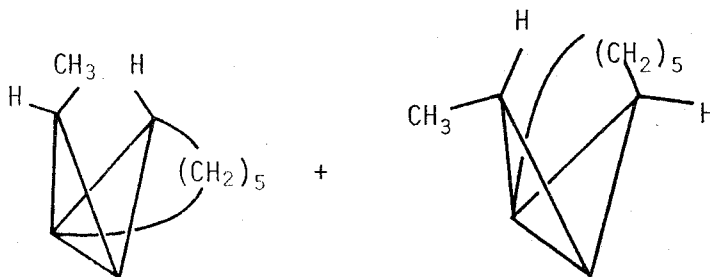
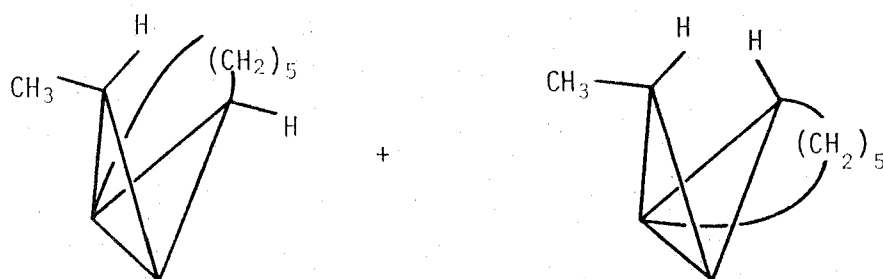


Figure 8-2.

Observed Products



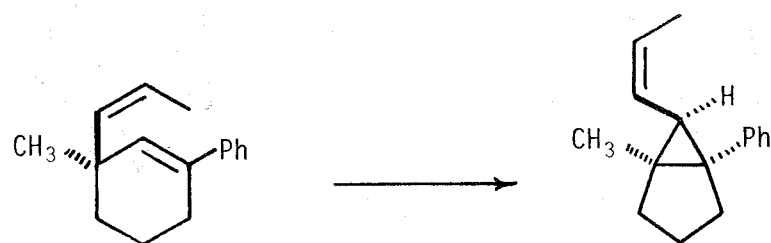
Orbital symmetry argument based on structure of relaxed excited state.

Reference: W. G. Dauben and J. S. Ritscher, J. Amer. Chem. Soc., 92, 2925 (1970).

Part b. Di- π -methane and related rearrangements

Problem 8-1.

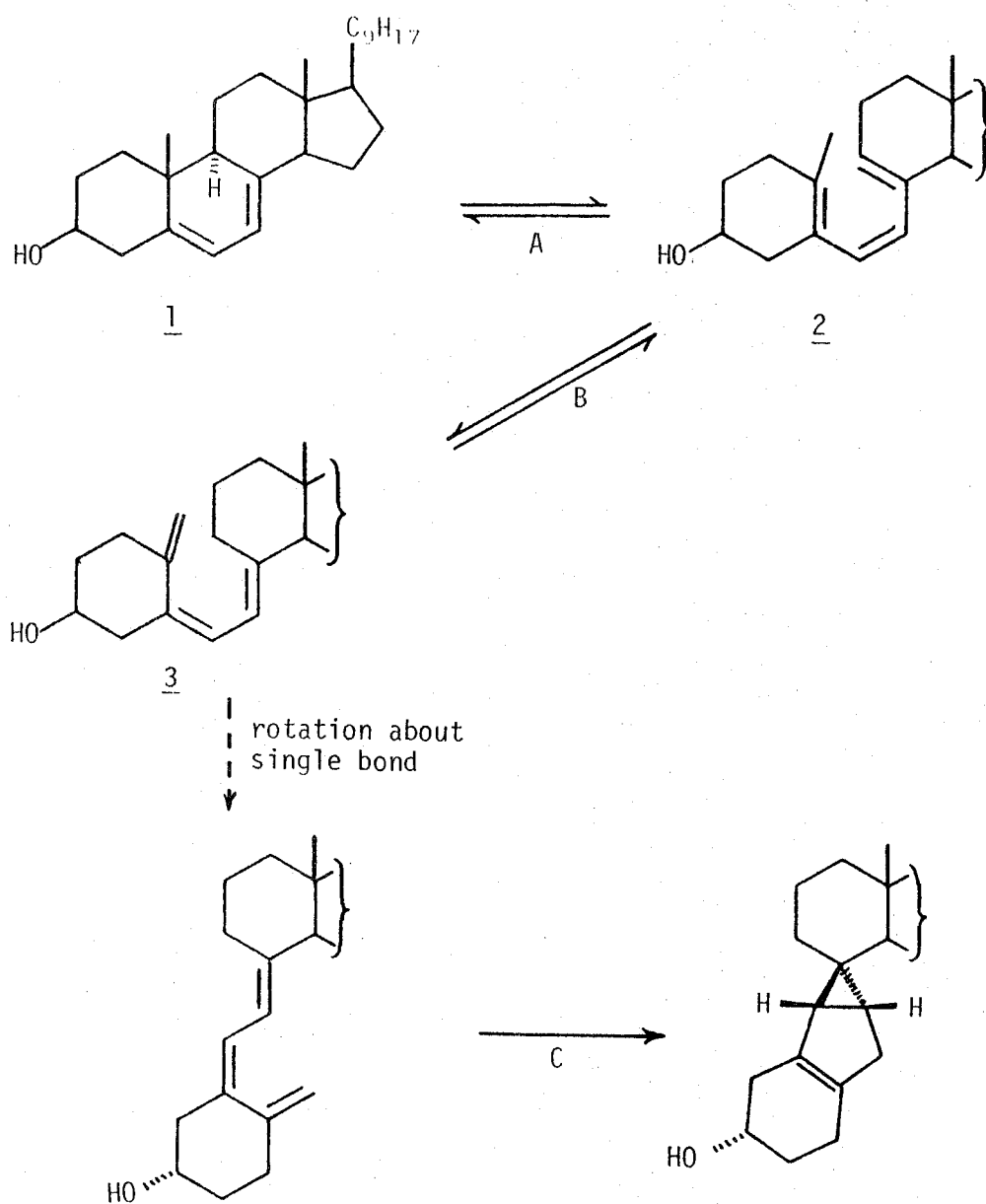
Should this reaction be thermal or photochemical?



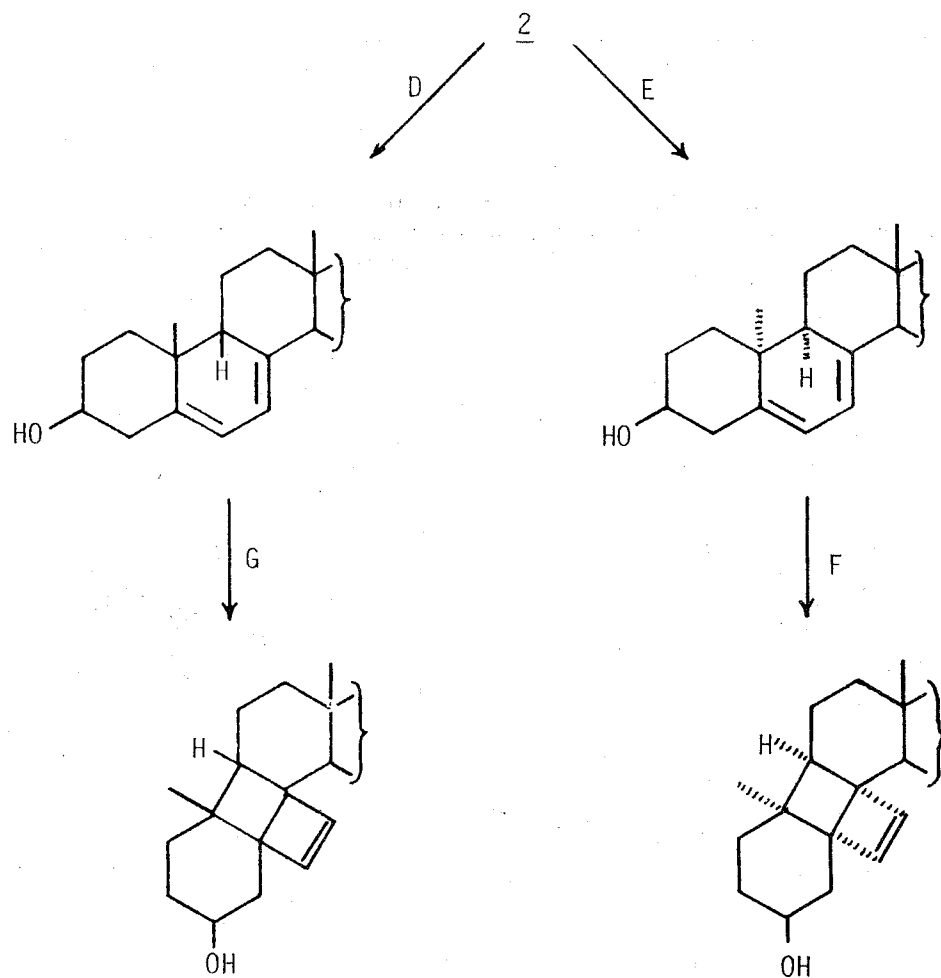
Part c. Formation of bicyclo[3.1.0]hexene derivatives

Problem 8-2.

Ergosterol (1), on heating and irradiation, undergoes several transformations, including the formation of vitamin D₂ (3). Which of the following reactions should be thermal, and which photochemical? (Suggestion: use models.)

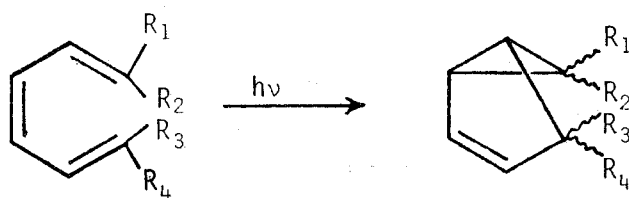


(continued)



Problem 8-3.

Predict the stereochemistry of the product.

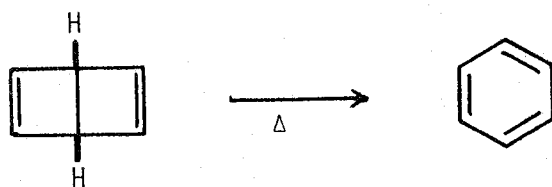


(A hint is given.)

Part d. Benzene

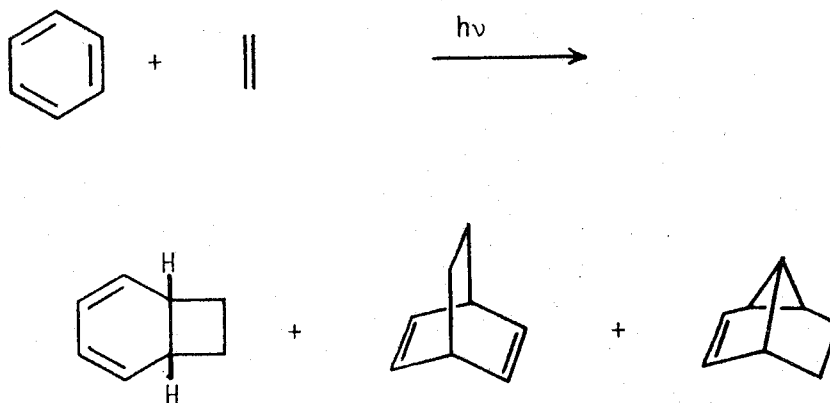
Problem 8-4.

Is this reaction allowed?



Problem 8-5.

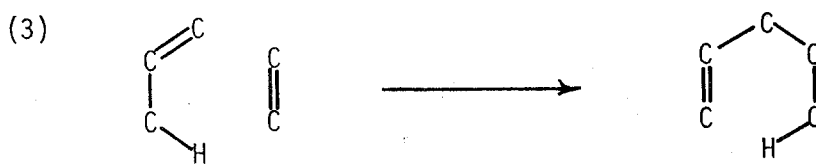
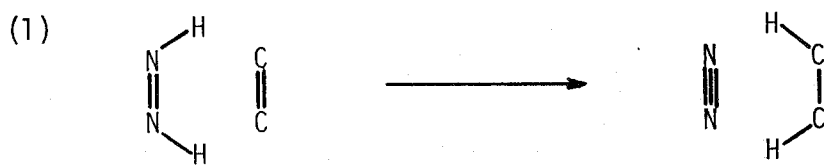
Which of the following reactions are photochemically allowed (suprafacial addition to olefin)?



Part e. Hydrogen transfers

Problem 8-6.

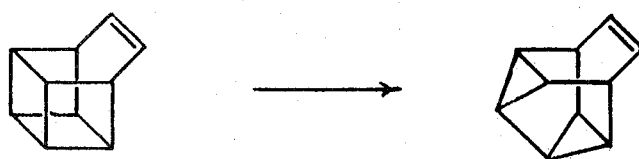
Which of the following reactions are thermally allowed (all-suprafacial stereochemistry)?



Part f. Influence of transition metals

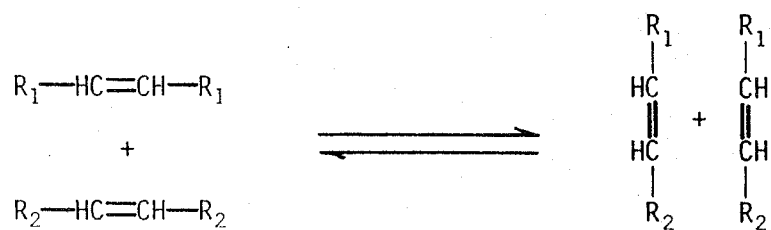
Problem 8-7.

Should the following reaction be thermally allowed?



Problem 8-8.

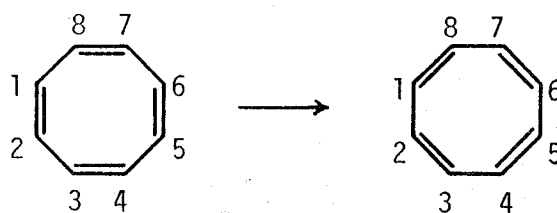
Should the following reaction be thermally allowed?



Part g. Miscellaneous reactions

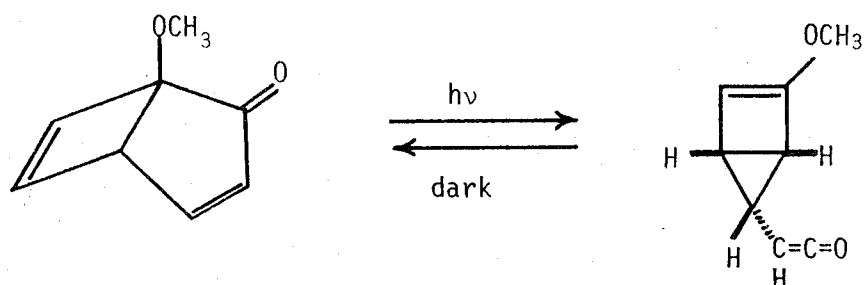
Problem 8-9.

Should the following reaction be thermally allowed?



Problem 8-10.

The following reaction occurs photochemically in the forward direction and thermally in the reverse direction. What are the stereochemical consequences?

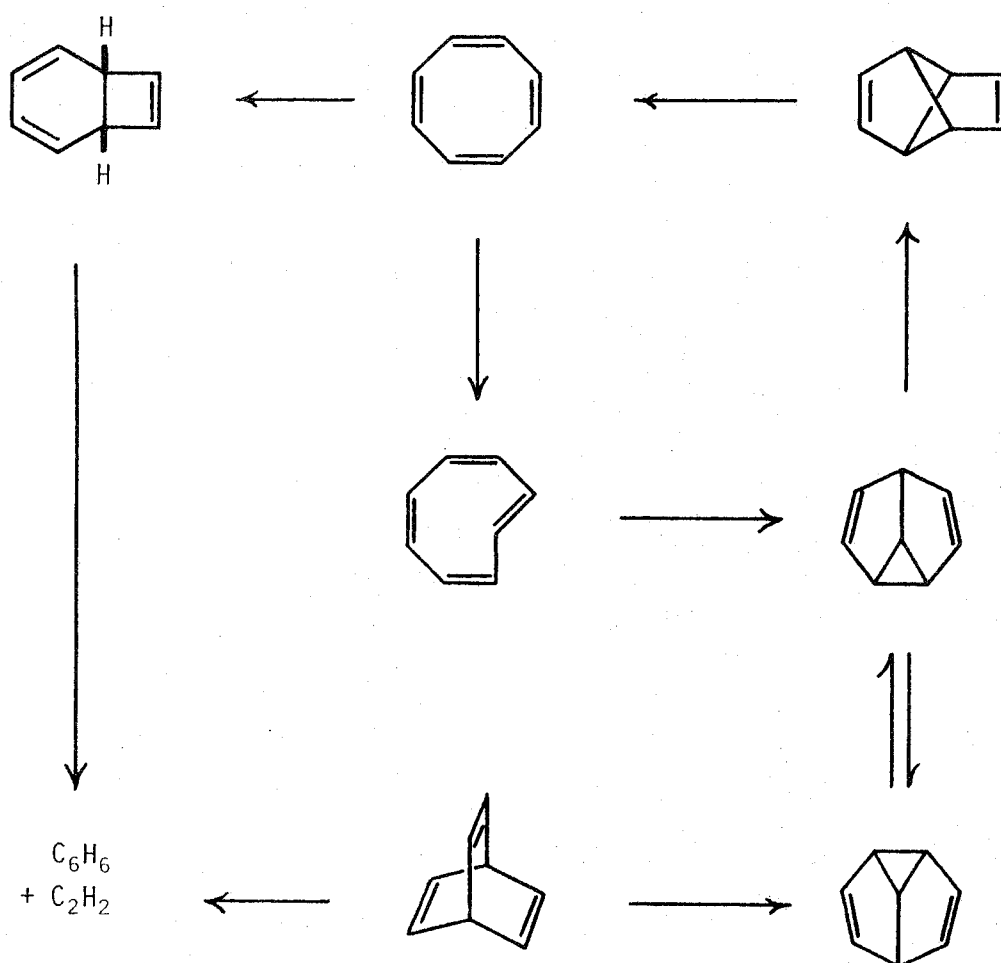


Part h. Final problems

Answers are not given. Not all the reactions can be treated by orbital symmetry; in some cases, the orbital symmetry treatment is not justified by experiment.

Problem 8-11.

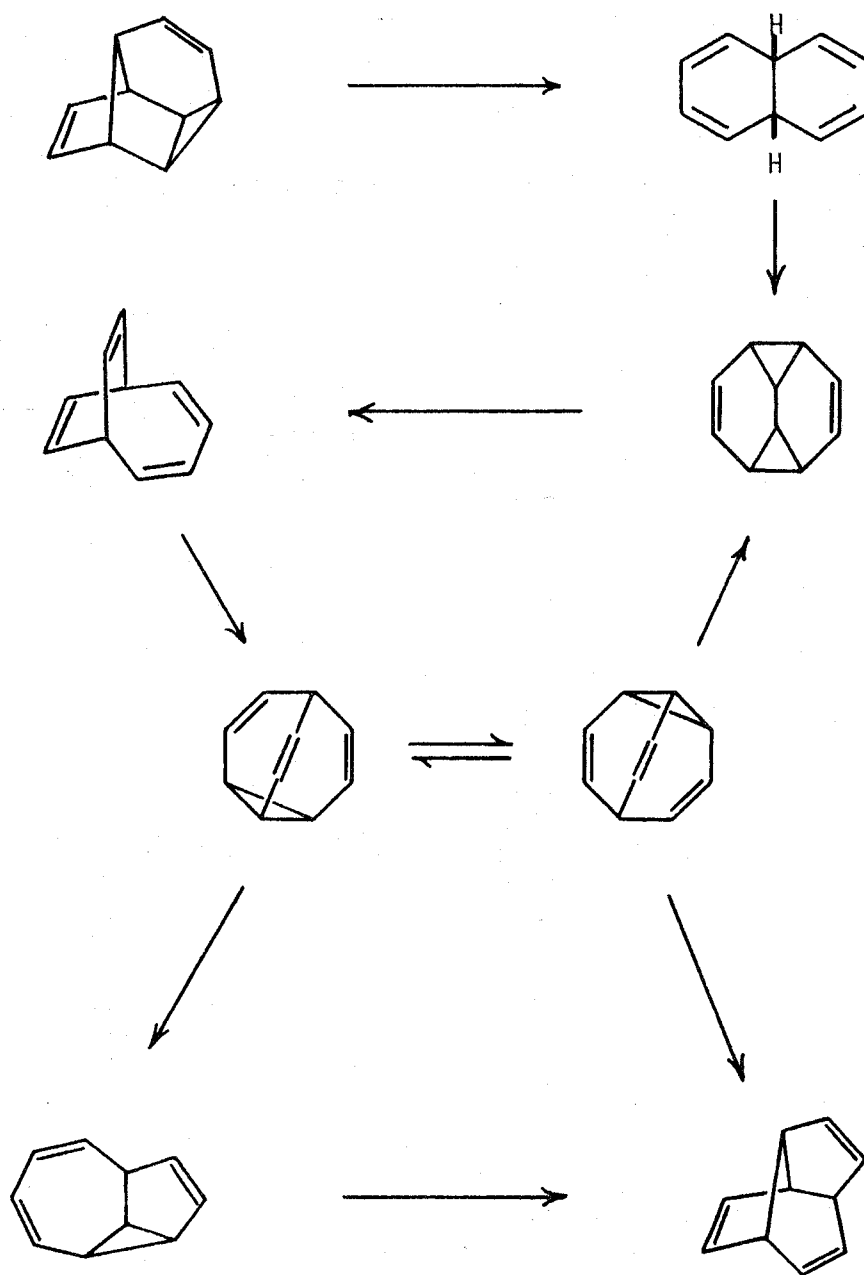
Which of the following interconversions should be thermal, and which photochemical?



Reference: L. T. Scott and M. Jones, Jr., Chem. Rev., 72, 181 (1972).

Problem 8-12.

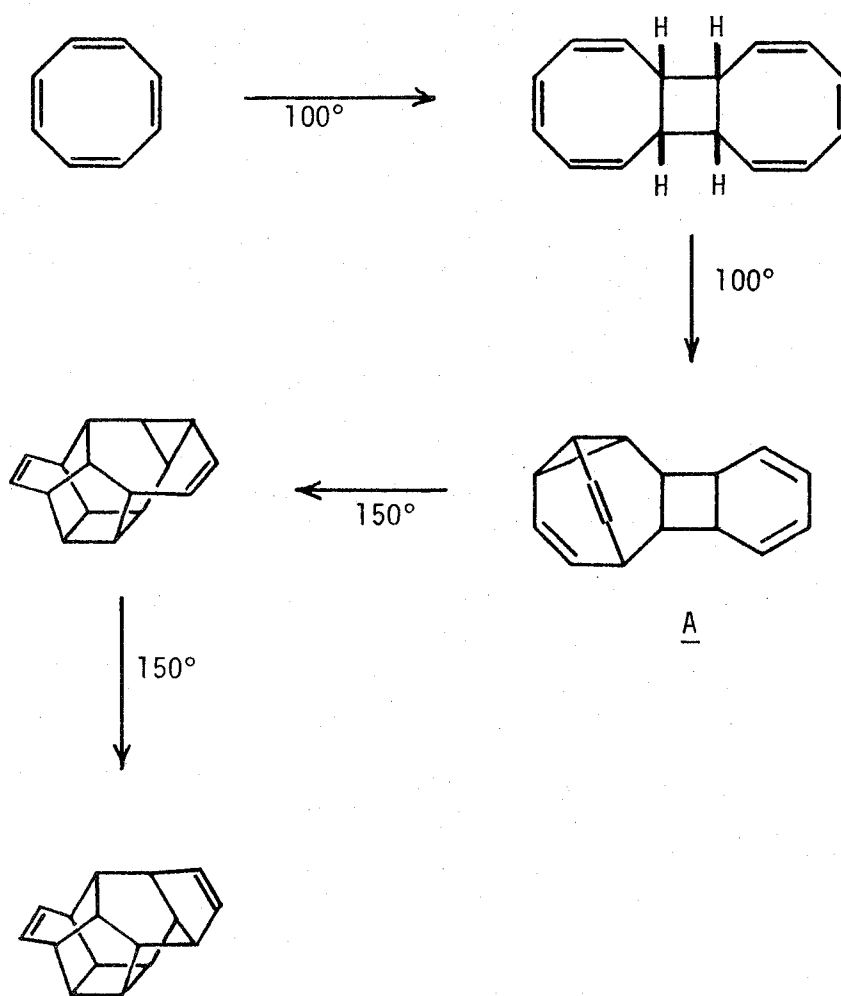
Which of the following reactions should be thermal, and which photochemical?



References: L. T. Scott and M. Jones, Jr., Chem. Rev., **72**, 181 (1972).
 S. Masamune and N. Darby, Accounts Chem. Research, **5**, 272 (1972).

Problem 8-13.

Explain this reaction sequence in terms of orbital symmetry, wherever possible. Hints: there are four undetected intermediates; all compounds prior to compound A have a plane of symmetry.



References: G. Schröder, "Cyclooctatetraen," Verlag Chemie, Weinheim, Germany, 1965, pp 60-63, and references cited therein.

G. Schröder and W. Martin, Angew. Chem., Int. Ed. Engl., 5, 130 (1966).

Hints for Problems

1-4

The basis set is three p orbitals, so there are three MO's. The symmetry elements are two planes and a twofold axis.

2-1

There are three orbitals on each side of the correlation diagram: ψ_1 , ψ_2 , and ψ_3 of the allyl fragment (see problem 1-4), and σ , σ^* , and the doubly occupied p orbital on C2 in the cyclopropyl anion.

2-2

The necessary orbitals are the four π -MO's of butadiene and the π and π^* orbitals of ethylene, for the starting materials, and the two σ and two σ^* orbitals, and the π and π^* orbitals of the product. The symmetry element is a plane. Linear combinations of the σ orbitals, and of the σ^* orbitals, must be made.

5-2

Triene 1 can be formed in two different stereoisomers, but only one can cyclize to give 2.

5-4

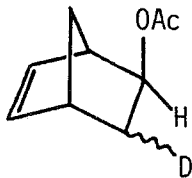
There is a cyclic intermediate.

6-3

There are three possible photoproducts from 1, and four from 2.

6-5

The reaction is a [1,3] sigmatropic rearrangement to give



6-8

Are the labelled methyl groups interconverted during the sigmatropic rearrangement?

6-11

The reaction involves one electrocyclic and two sigmatropic steps.

6-12

The products arise from different conformations of 11; a benzylic proton is removed by base.

7-1

There are nine stereochemically reasonable allowed cycloadducts.

7-3

There are two allowed products from each isomer.

7-7

There are three stereochemically reasonable allowed cycloadducts.

7-8

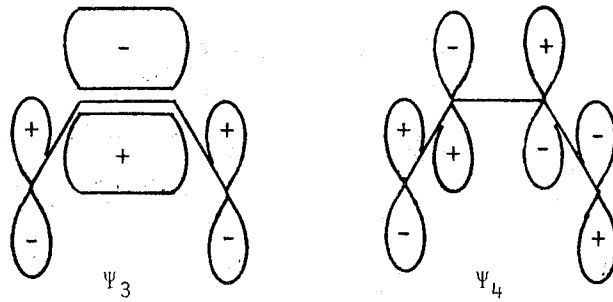
Two stereochemically different products are allowed.

8-3

Two stereochemically different products are allowed.

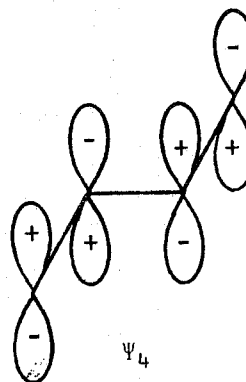
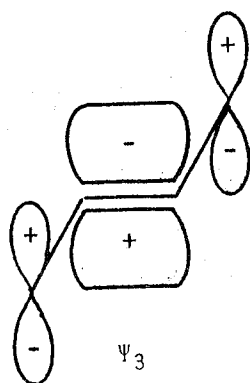
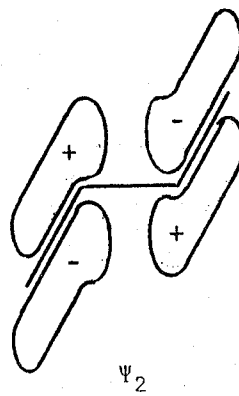
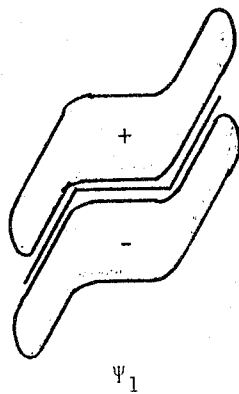
Answers to Problems

1-1



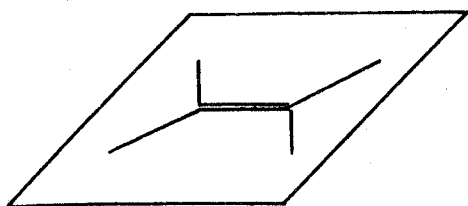
	P_1	R	P_2
Ψ_3	S	A	A
Ψ_4	A	S	A

1-2

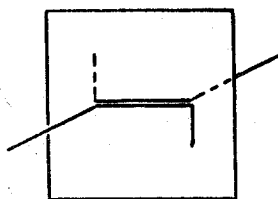


	R	P
Ψ_1	S	A
Ψ_2	A	A
Ψ_3	S	A
Ψ_4	A	A

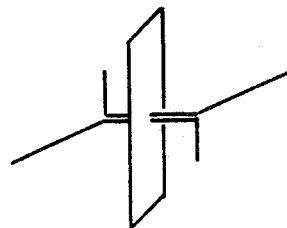
1-3



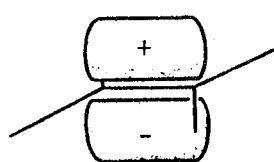
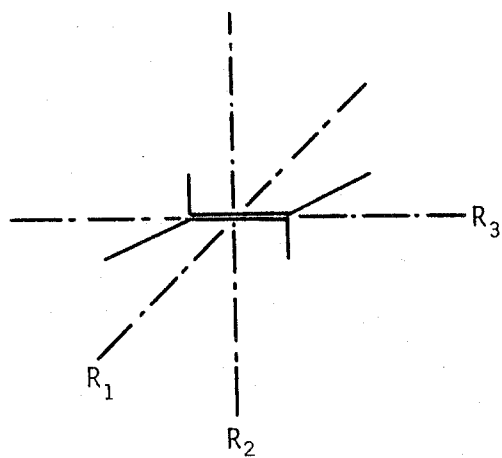
P_1



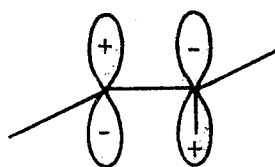
P_2



P_3



π



π^*

	P_1	P_2	P_3	R_1	R_2	R_3
π	A	S	S	A	S	A
π^*	A	S	A	S	A	A

1-4

Figure 1-4A.

Symmetry elements

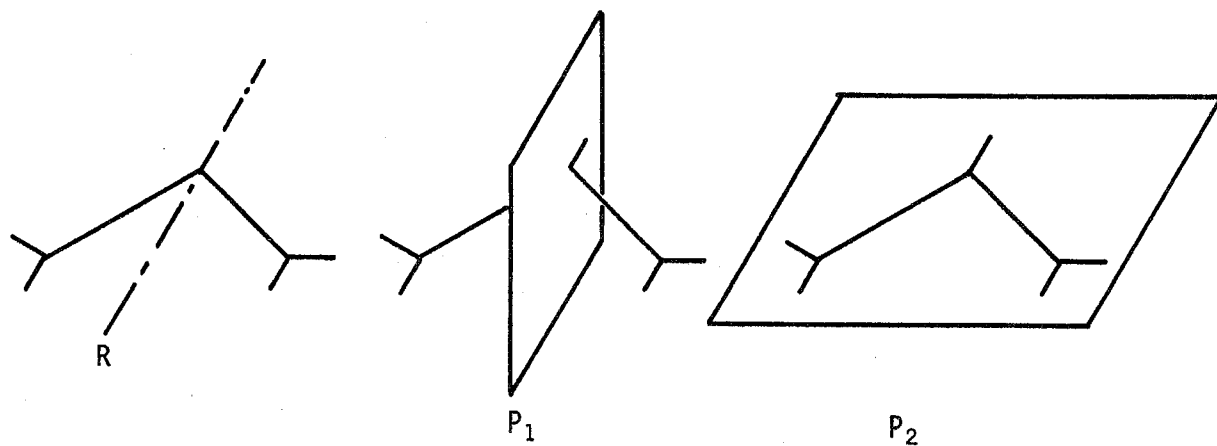


Figure 1-4B.

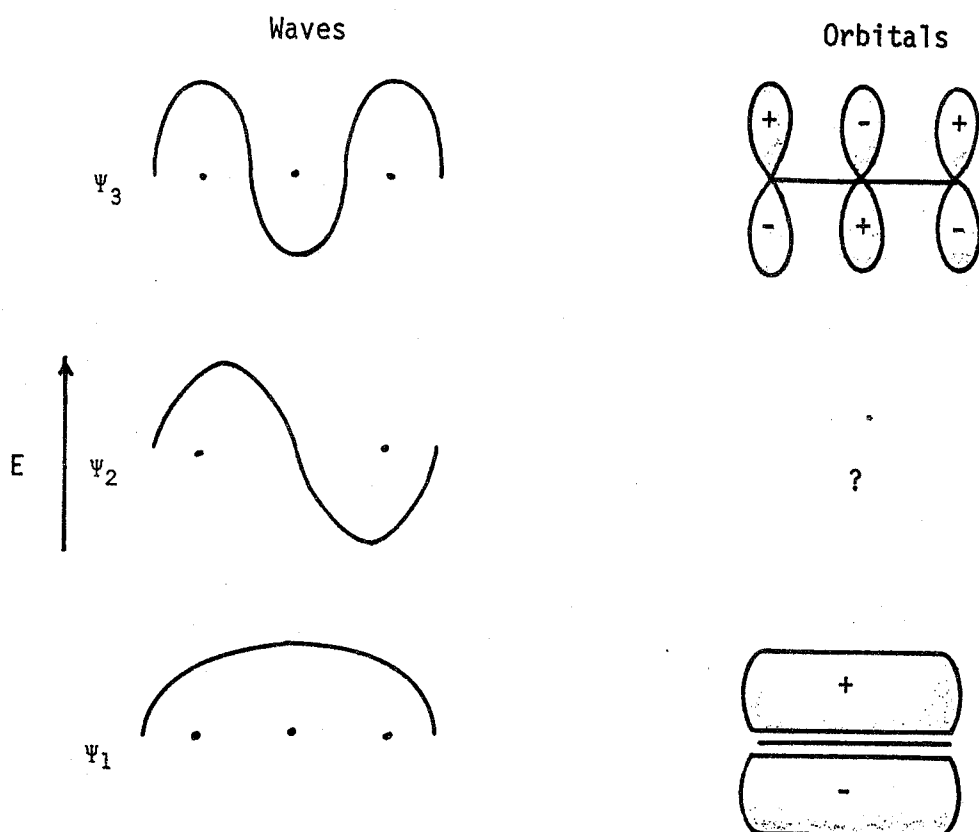


Figure 1-4C.

Trial solution for ψ_2 with one node:

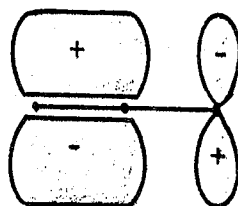
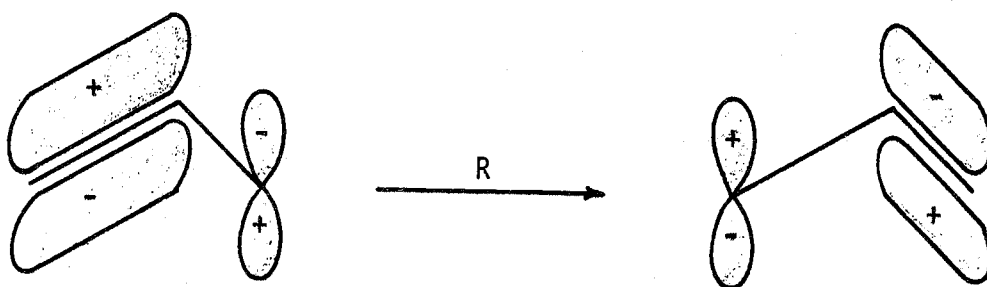


Figure 1-4D.

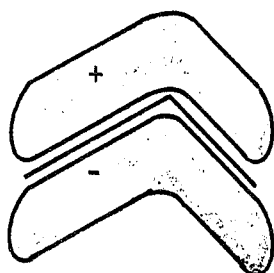


Not S, not A; not valid MO.

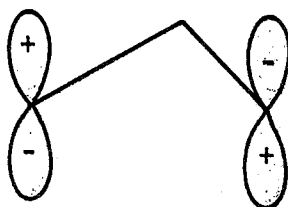
Only way to get ψ_2 with one node and correct symmetry is to have node at C_2 ; P_1 is identical with nodal plane.

Figure 1-4E.

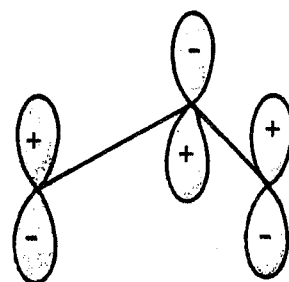
Correct solutions:



ψ_1
Bonding



ψ_2
Nonbonding



ψ_3
Antibonding

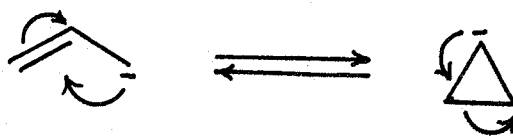
	R	P ₁	P ₂
Ψ_1	A	S	A
Ψ_2	S	A	A
Ψ_3	A	S	A

Electron configuration of cation: Ψ_1^2

Figure 1-4F.



2-1



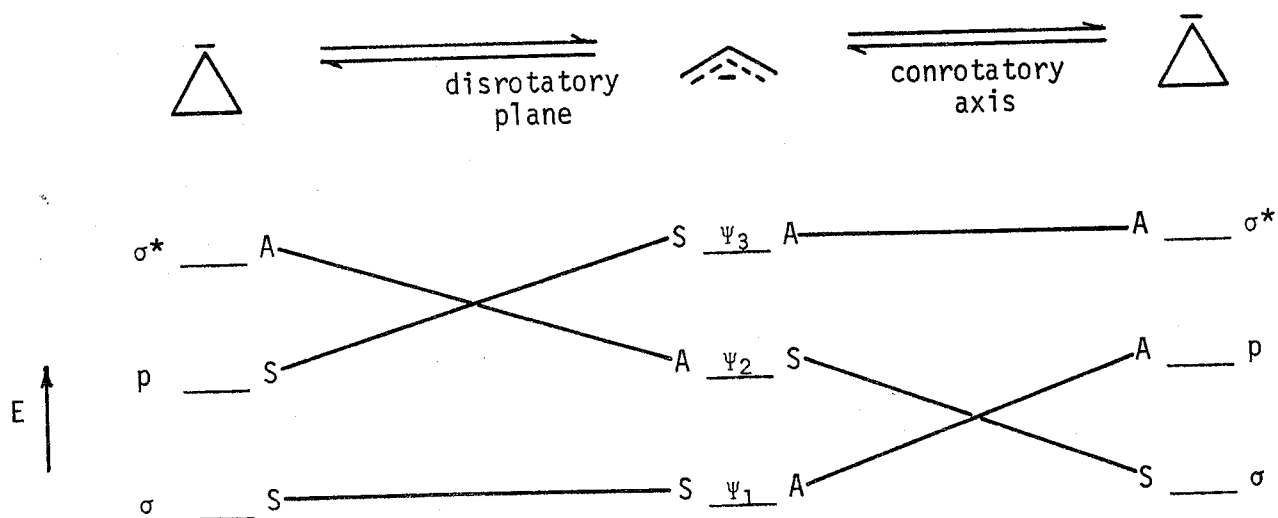
(2-1A)

Figure 2-1A.

	Orbitals	Plane	Symmetry with respect to Axis
Allyl			
Ψ_3		S	A
Ψ_2		A	S
Ψ_1		S	A
Cyclopropyl			
p		S	A
σ		S	S
σ^*		A	A

Figure 2-1B.

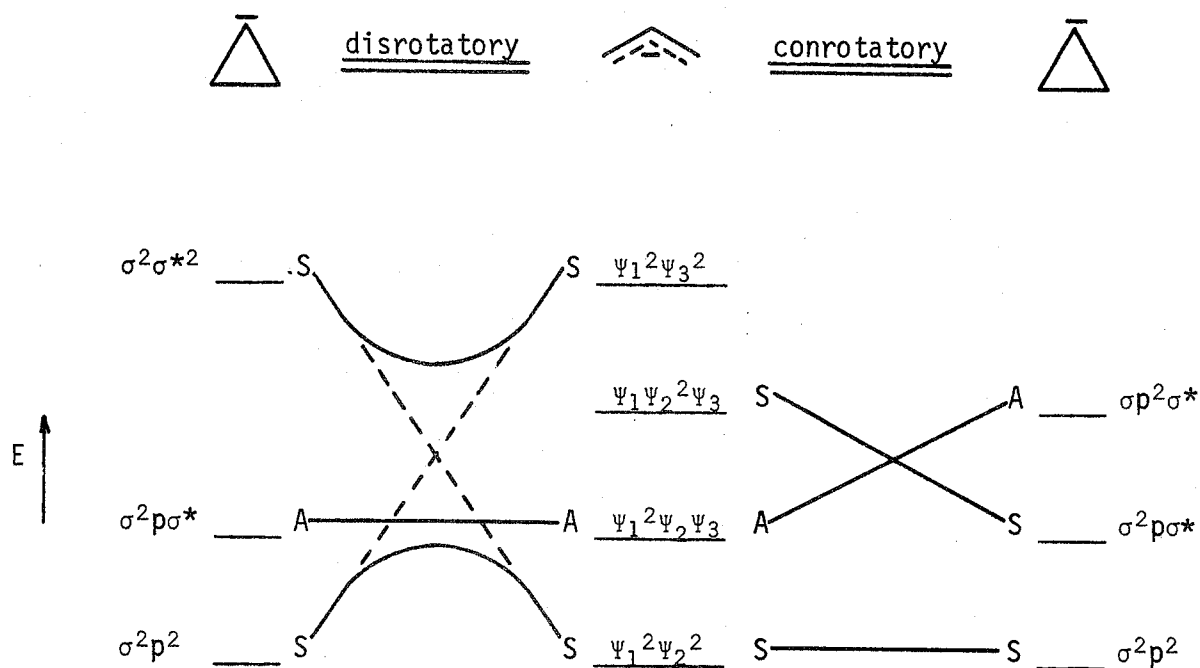
Orbital correlation diagrams



Four π electrons in the ion. Reaction should be conrotatory in the ground state and disrotatory in the lowest excited state.

Figure 2-1C.

State correlation diagrams



2-2

Figure 2-2A.

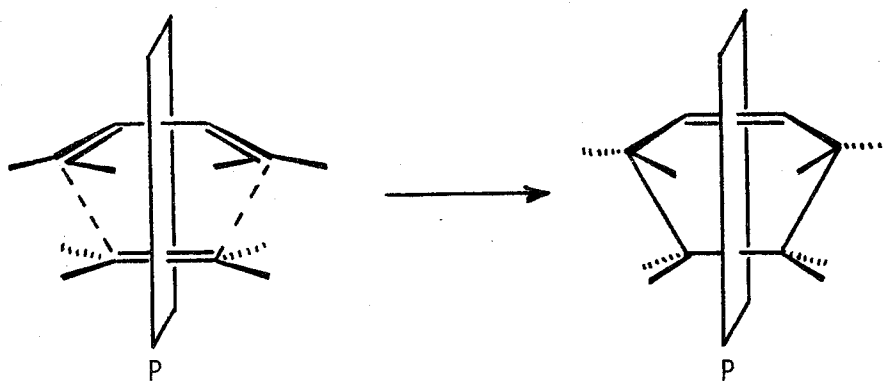


Table 2-2A.

Butadiene	Ψ_4	A	Cyclohexene	π^*	A
	Ψ_3	S		π	S
	Ψ_2	A		σ_1	?
	Ψ_1	S		σ_2	?
Ethylene	π^*	A		σ_1^*	?
	π	S		σ_2^*	?

Figure 2-2B.

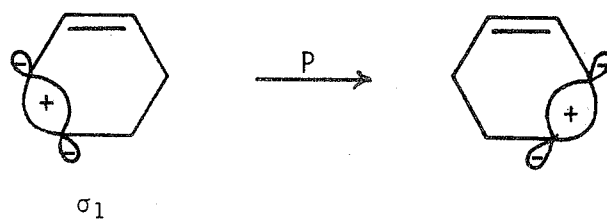


Figure 2-2C.

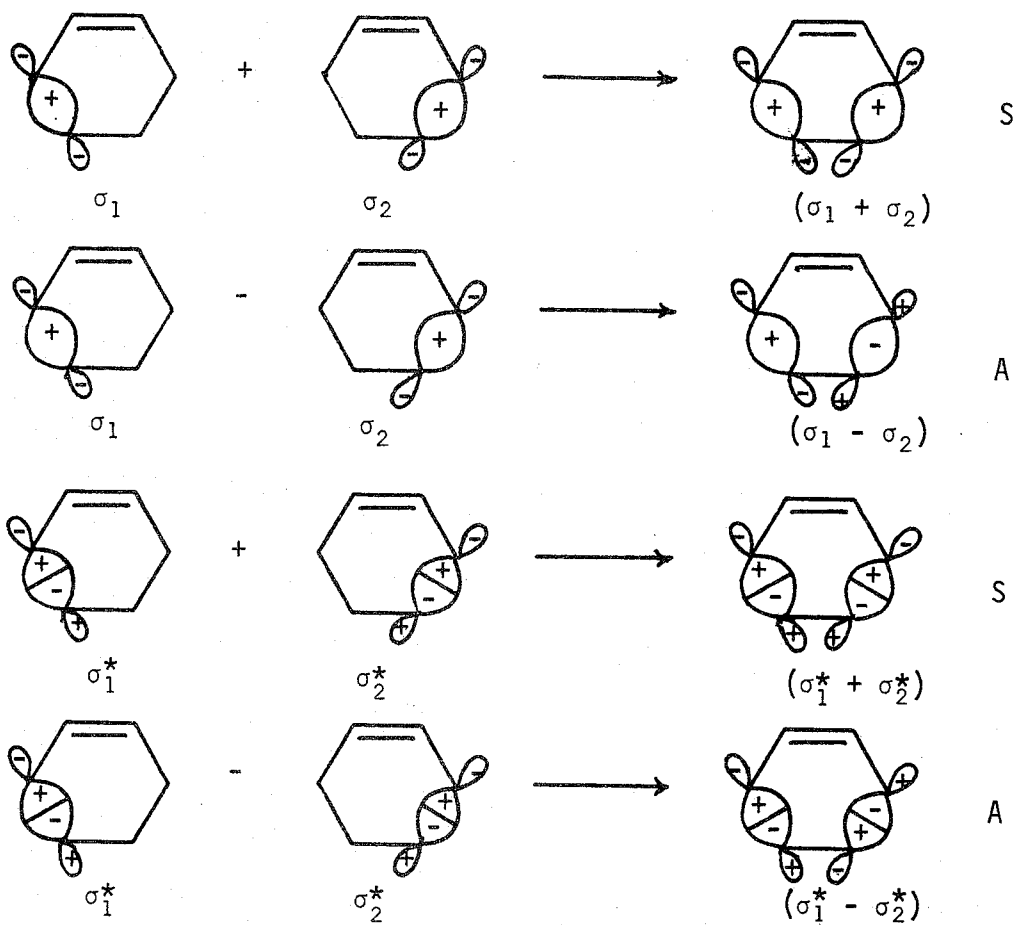
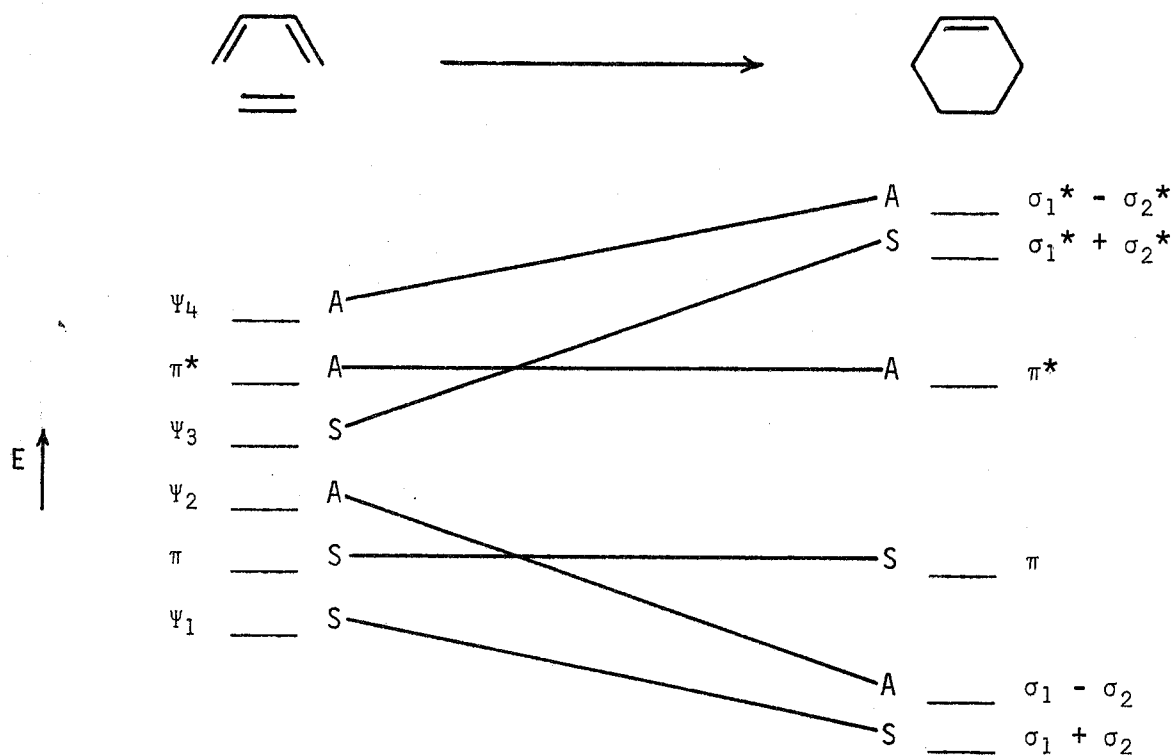


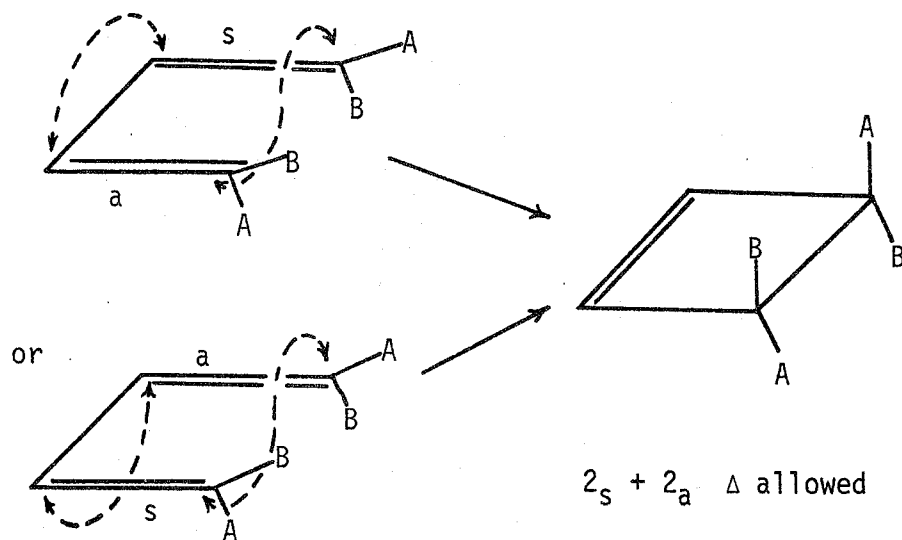
Figure 2-2D.

Orbital correlation diagram

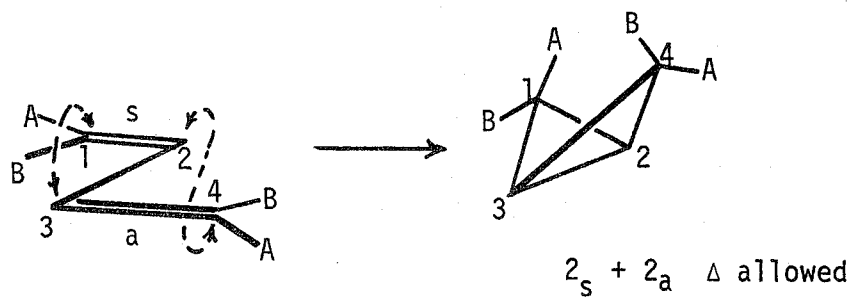


Reaction is allowed in ground state, forbidden in lowest excited state.

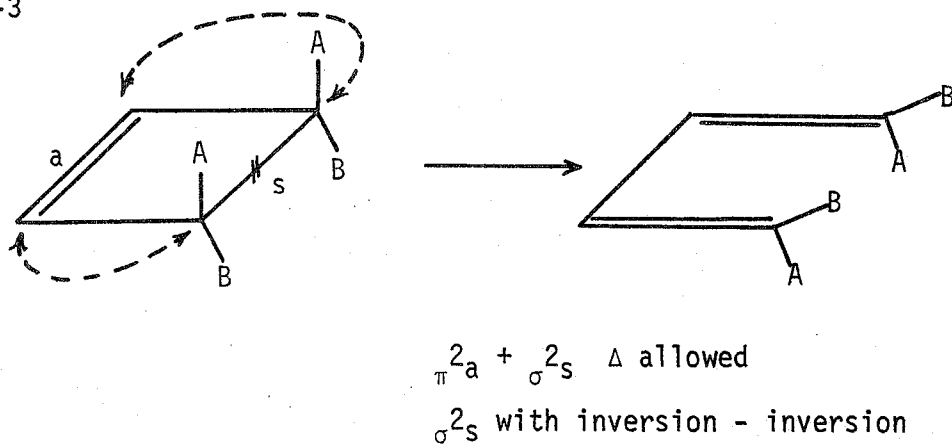
3-1



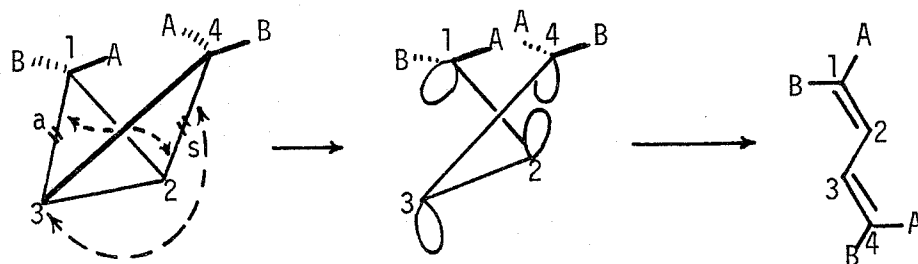
3-2



3-3



3-4

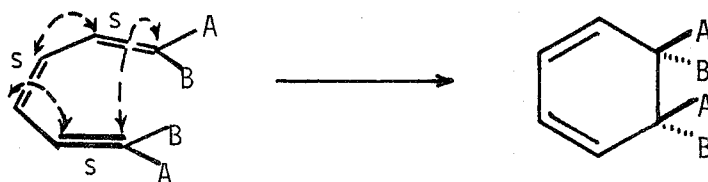


3-5

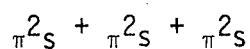
Underlined components are counted.

- (a) $\underline{2_s} + \underline{2_s}$ forbidden
- (b) $\underline{2_s} + 2_a$ allowed
- (c) $2_a + 2_a$ forbidden (zero is even)
- (d) $4_s + 2_a$ forbidden
- (e) $12_s + \underline{2_s} + 6_a$ allowed
- (f) $14_a + \underline{2_s}$ allowed
- (g) $\underline{2_s} + \underline{2_s} + \underline{2_s} + 2_a$ allowed
- (h) $\underline{0_a} + \underline{2_s} + \underline{2_s}$ allowed (0 is $4n$ where $n = 0$)

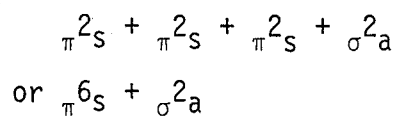
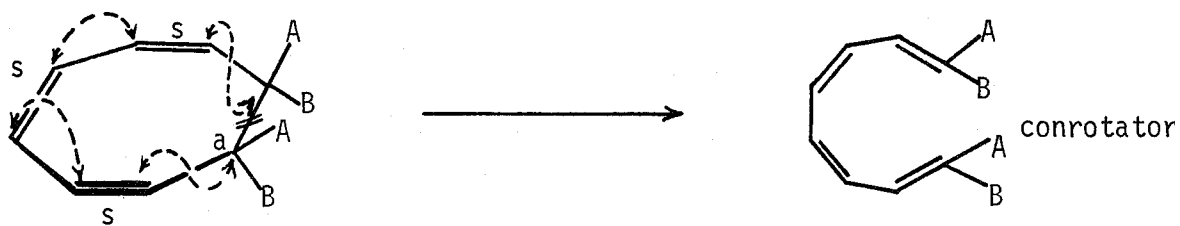
3-6



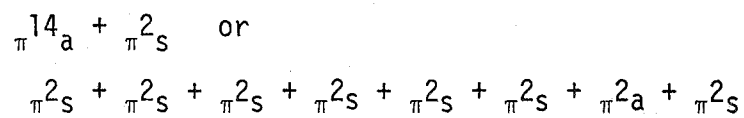
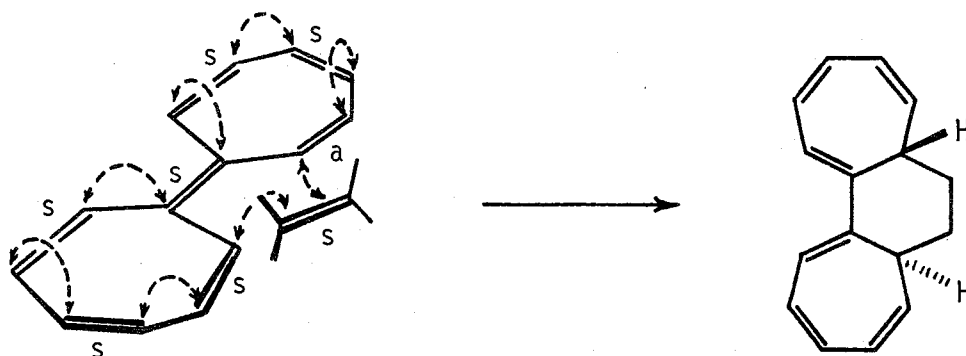
disrotatory



3-7

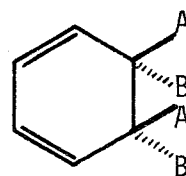
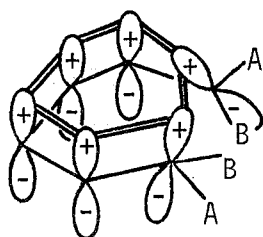


3-8



Reference: W. v. E. Doering, private communication quoted in R. B. Woodward and R. Hoffmann, op. cit., p 85.

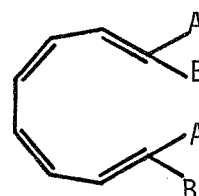
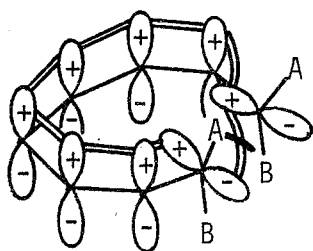
4-1



disrotatory

no inversions, 6 e: Δ allowed

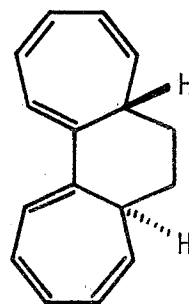
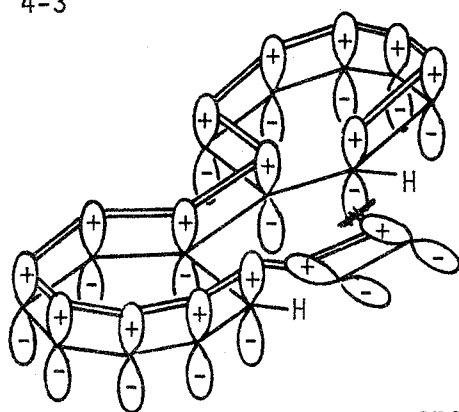
4-2



conrotatory

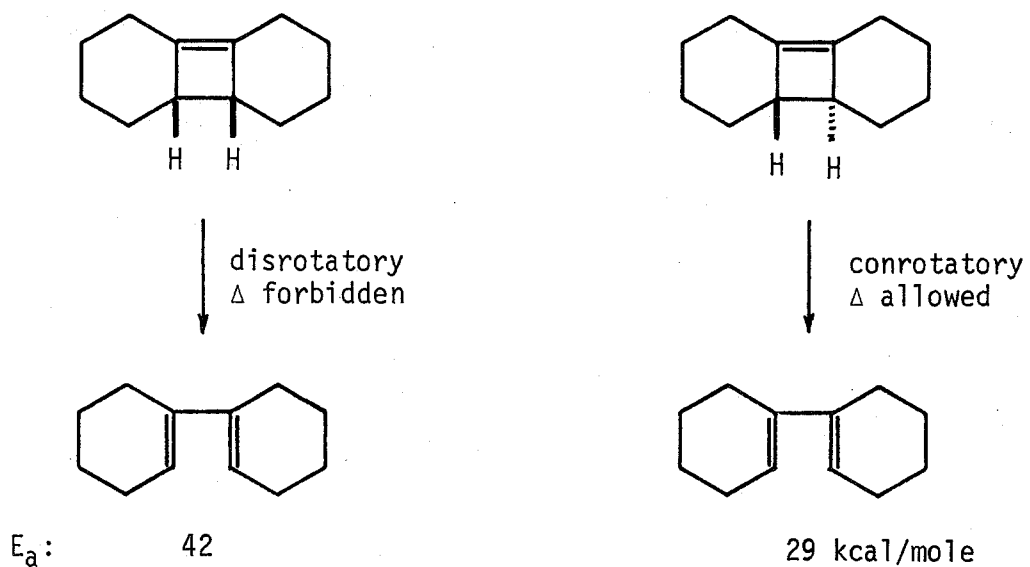
one inversion, 8 e: Δ allowed

4-3



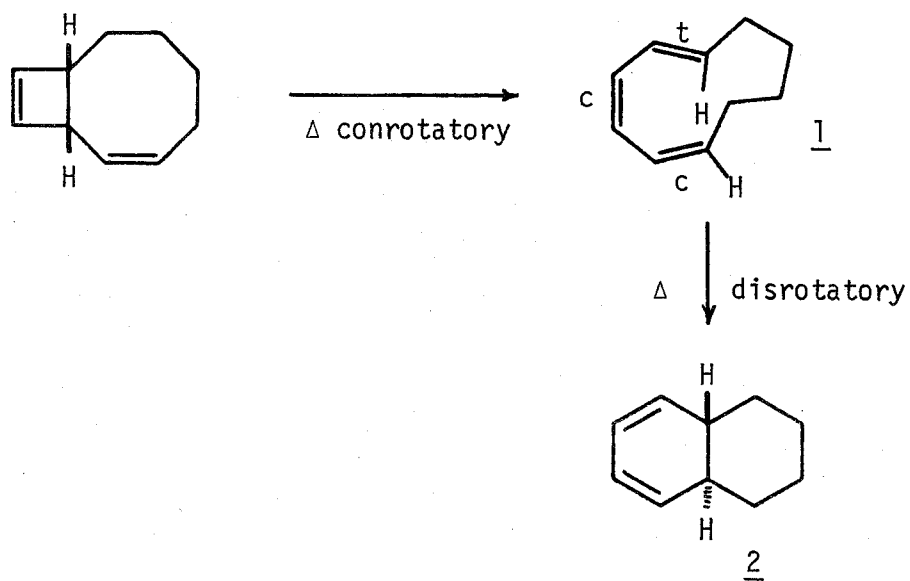
one inversion, 16 e: Δ allowed

5-1



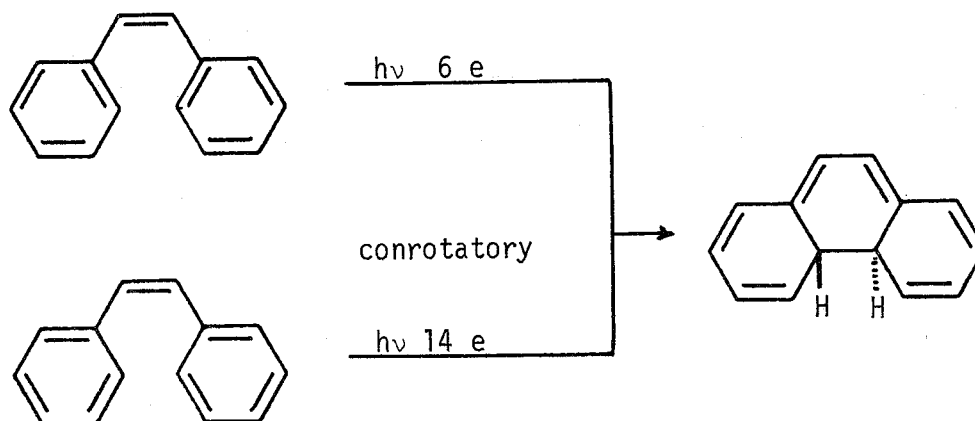
Reference: R. Criegee and H. G. Reinhardt, Chem. Ber., 101, 102 (1968).

5-2



Reference: P. Radlick and W. Fenical, Tetrahedron Lett., 4901 (1967).

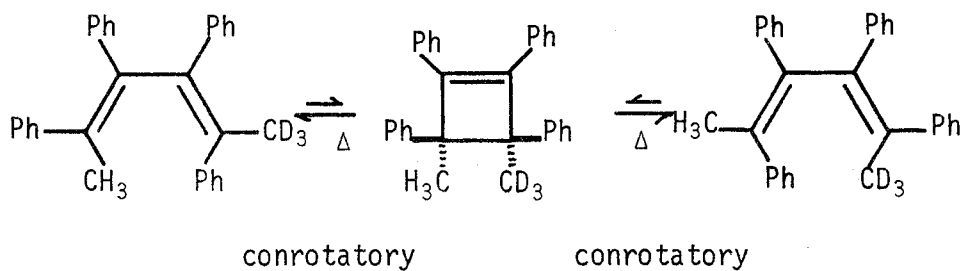
5-3



Reference: Th. J. H. M. Cuppen and W. H. Laarhoven, J. Amer. Chem. Soc., 94, 5914 (1972).

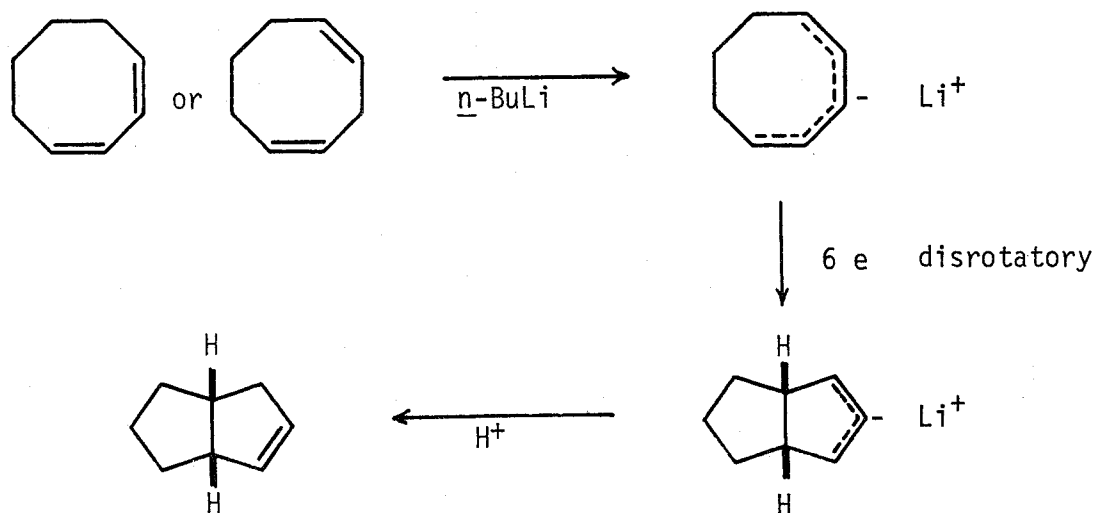
Review: F. R. Stermitz in "Organic Photochemistry," Vol. 1, O. L. Chapman, Ed., Marcel Dekker, New York, N. Y., 1967, p 247.

5-4



Reference: G. A. Doorakian and H. H. Freedman, J. Amer. Chem. Soc., 90, 5310, 6896 (1968); L. M. Stephenson, R. V. Gemmer, and J. I. Brauman, ibid., 94, 8620 (1972).

5-5



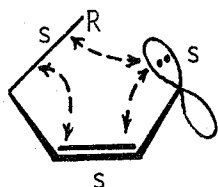
Reference: R. B. Bates and D. A. McCombs, Tetrahedron Lett., 977 (1969).

6-1

suprafacial [1,4] shift in anion, without inversion



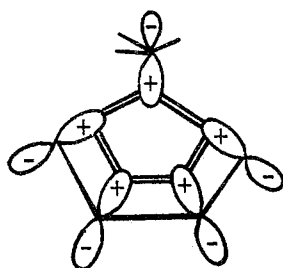
in S-A



$$\sigma^2_s + \pi^2_s + \omega^2_s$$

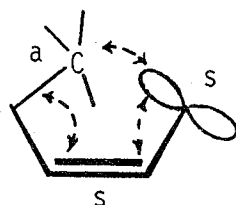
Δ allowed

in H-M



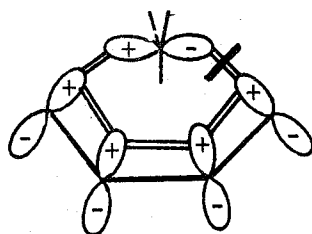
no inversions, 6 e
 Δ allowed

Suprafacial [1,4] shift in cation, with inversion



$$\sigma^2_a + \pi^2_s + \omega^0_s$$

Δ allowed

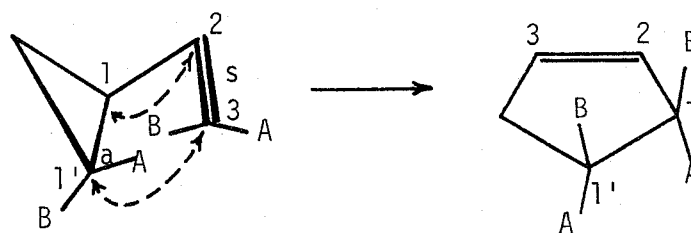


one inversion, 4 e
 Δ Allowed

6-2

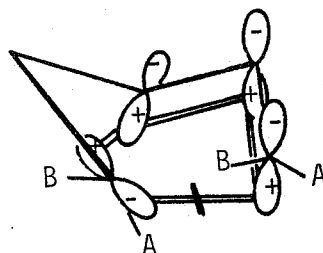
The reaction is a [1,3] sigmatropic rearrangement and should have one inversion, or be antarafacial.

in S-A



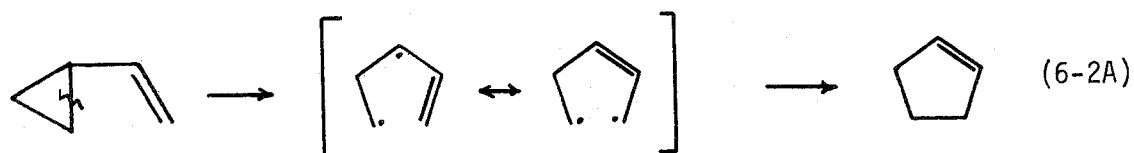
$\pi^2_s + \sigma^2_a \Delta$ allowed
(may also be written $\pi^2_a + \sigma^2_s$)

in H-M



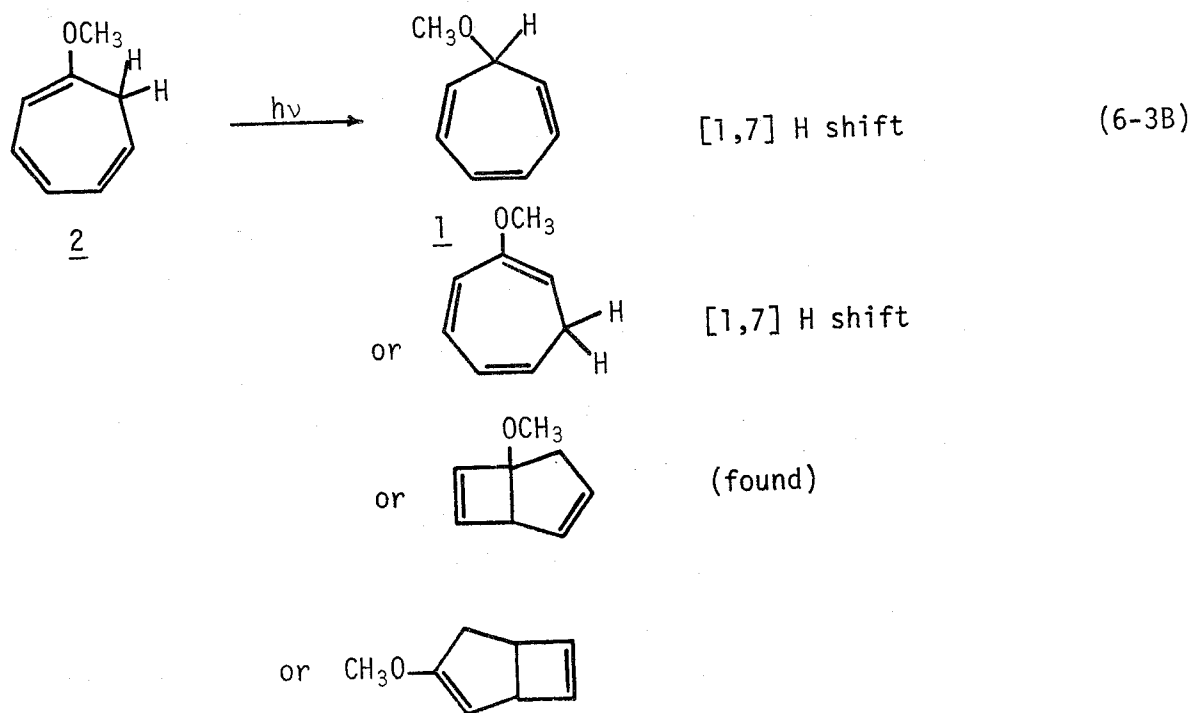
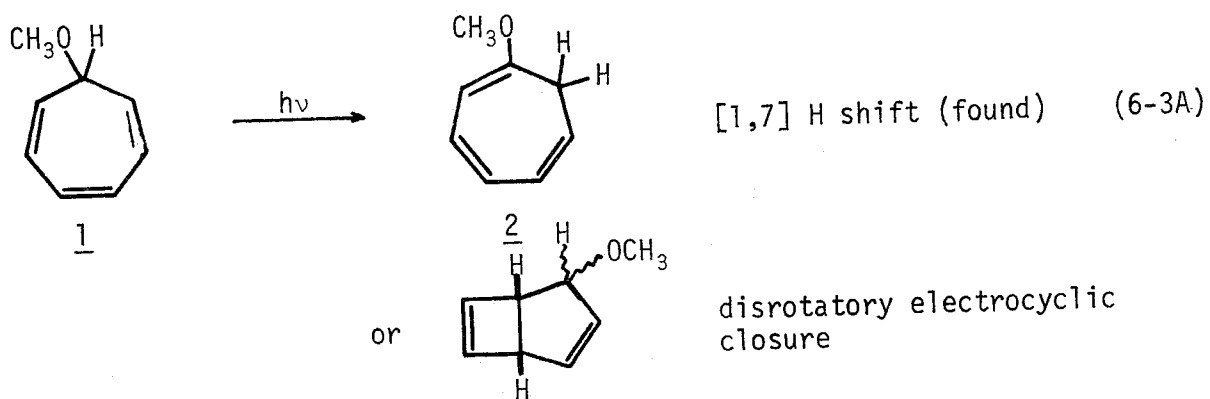
one inversion, 4 e
 Δ allowed

Available evidence is consistent with a non-concerted mechanism.

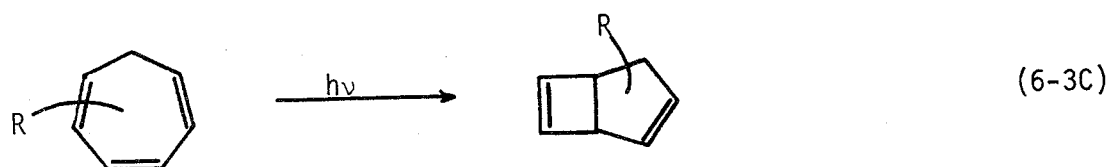


Reference: H. M. Frey and R. Walsh, Chem. Rev., 69, 103 (1969).

6-3

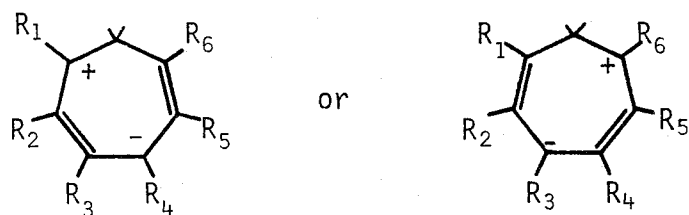


Selection among allowed reaction paths (periselectivity)

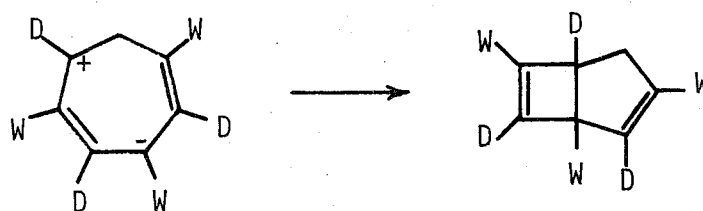


continued

Presume hypothetical intermediate zwitterion



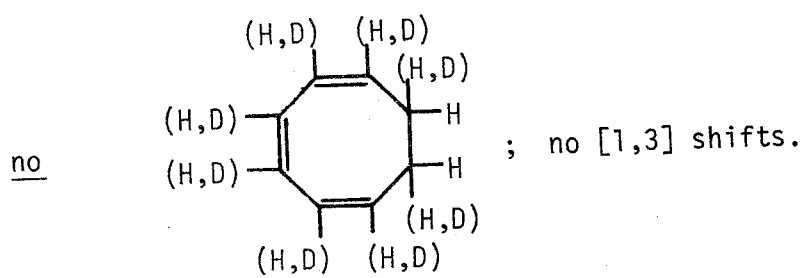
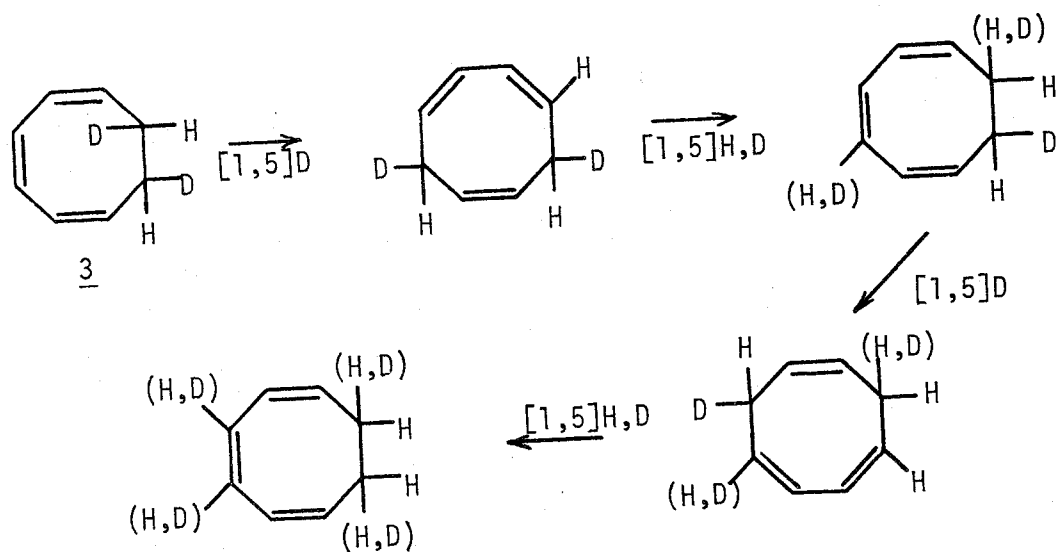
Substituents should stabilize one zwitterion, not the other. (D = electron-donating substituent, W = electron-withdrawing substituent.)



(6-3D)

Reference: A. R. Brember, A. A. Gorman, R. L. Leyland, and J. B. Sheridan, Tetrahedron Lett., 2511 (1970).

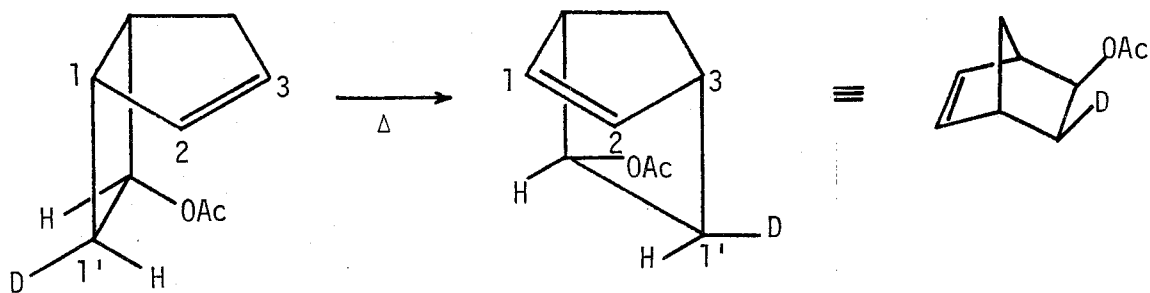
6-4



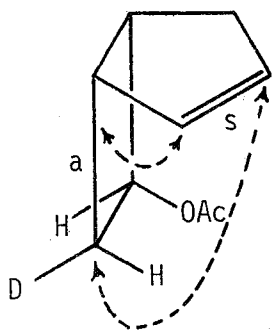
Reference: W. R. Roth, Ann. Chem., 671, 25 (1964).

6-5

The reaction is a [1,3] sigmatropic rearrangement; suprafacial, migrating group must invert.

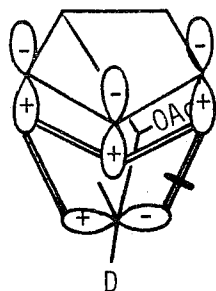


in S-A



$\pi^2_s + \sigma^2_a$
 Δ allowed

in H-M

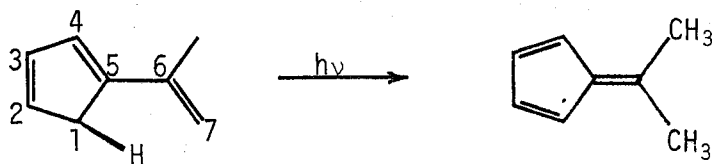


one inversion, 4 e
 Δ allowed

Review: J. A. Berson, Accounts Chem. Research, 1, 152 (1968).

6-6

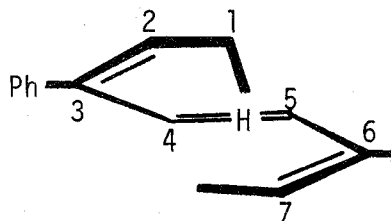
The [1,7] hydrogen shift is constrained to be suprafacial; photochemical.



Reference: L. J. M. van de Ven, J. L. M. Keulemans-Lebbink, J. W. de Haan, and H. Kloosterziel, Chem. Commun., 1509 (1970).

6-7

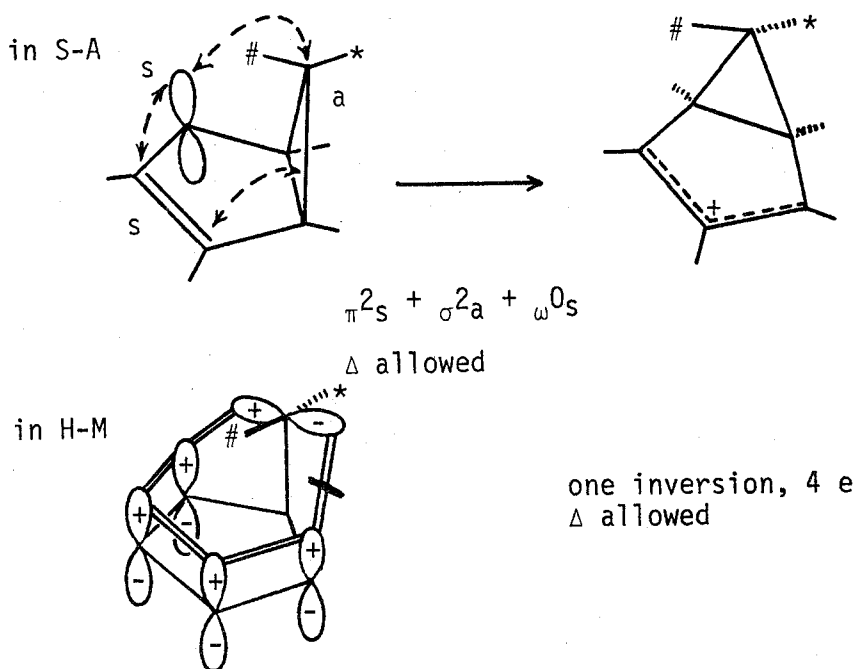
Due to coiling in the all-cis polyene chain, the [1,7] hydrogen shift must be antarafacial; thermal.



Reference: P. Courtot and R. Rumin, Tetrahedron Lett., 1849 (1970).

6-8

The suprafacial [1,4] rearrangement takes place with inversion at the migrating center (see Problem 6-1).

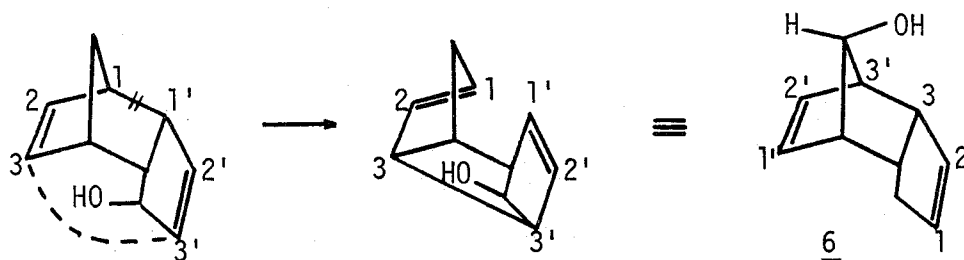


The * always remains exo, the # remains endo; the methyl groups are not interconverted.

Reference: R. F. Childs and S. Winstein, J. Amer. Chem. Soc., 90, 7146 (1968).

6-9

The reaction is a [3,3] sigmatropic (Cope) rearrangement, constrained to be supra-supra.

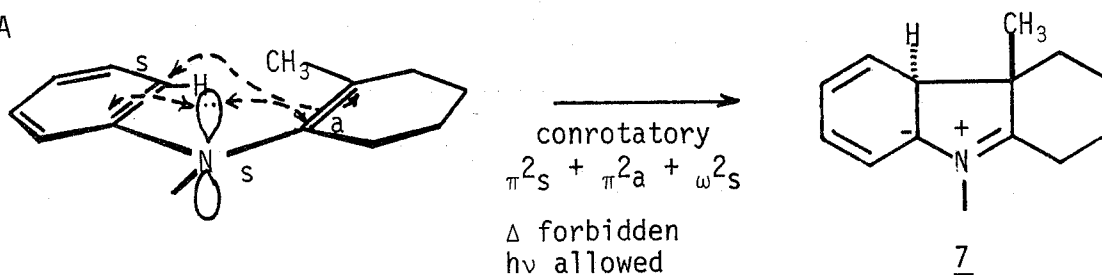


Reference: R. B. Woodward and T. J. Katz, Tetrahedron, 5, 70 (1959).

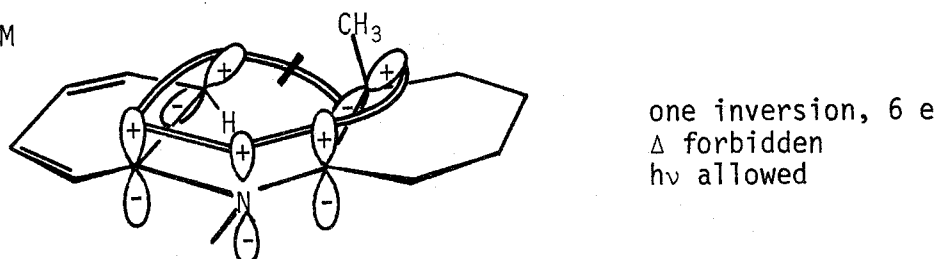
6-10

First step: 6-electron electrocyclic reaction, conrotatory in the excited state.

in S-A

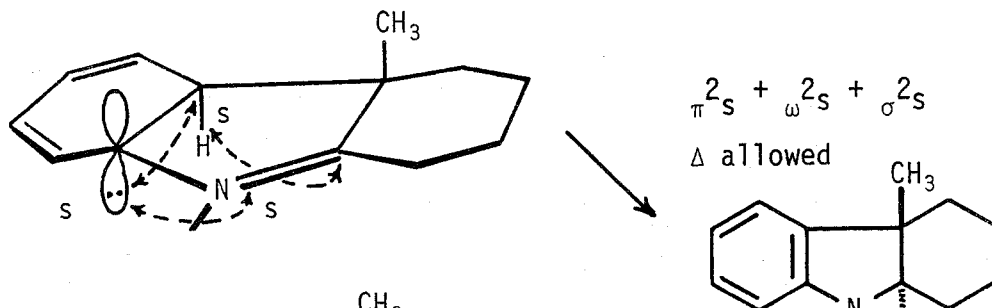


in H-M

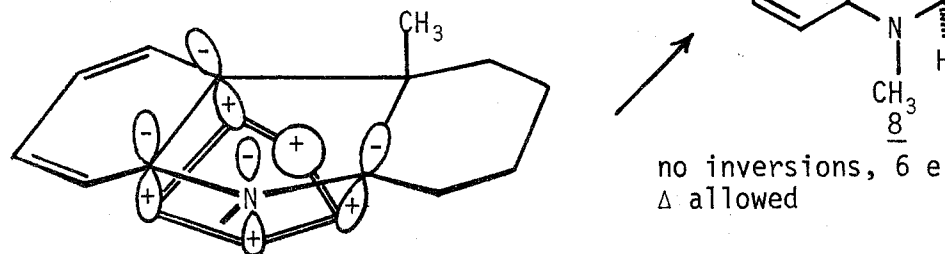


Second step: [1,4] sigmatropic rearrangement, isoelectronic with usual [1,5] hydrogen shift; suprafacial.

in S-A

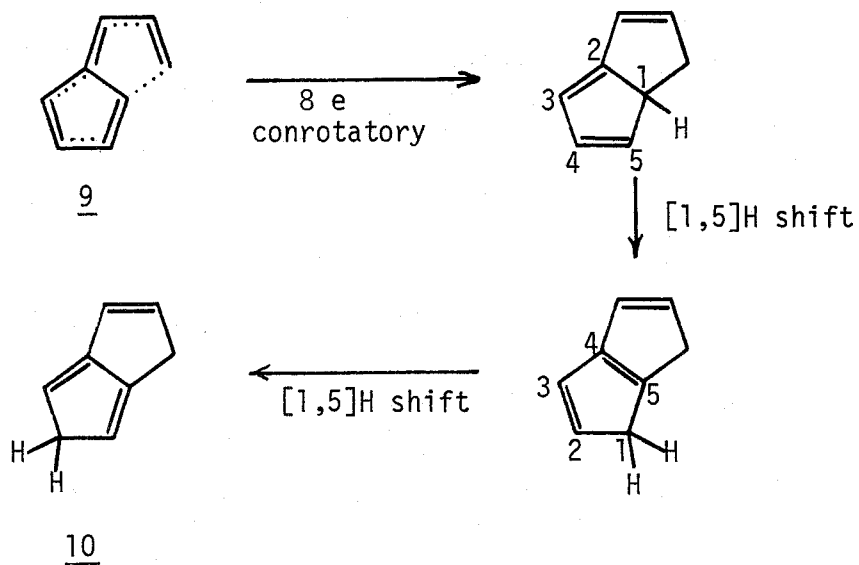


in H-M



Reference: O. L. Chapman, G. L. Eian, A. Bloom, and J. Clardy, J. Amer. Chem. Soc., 93, 2918 (1971).

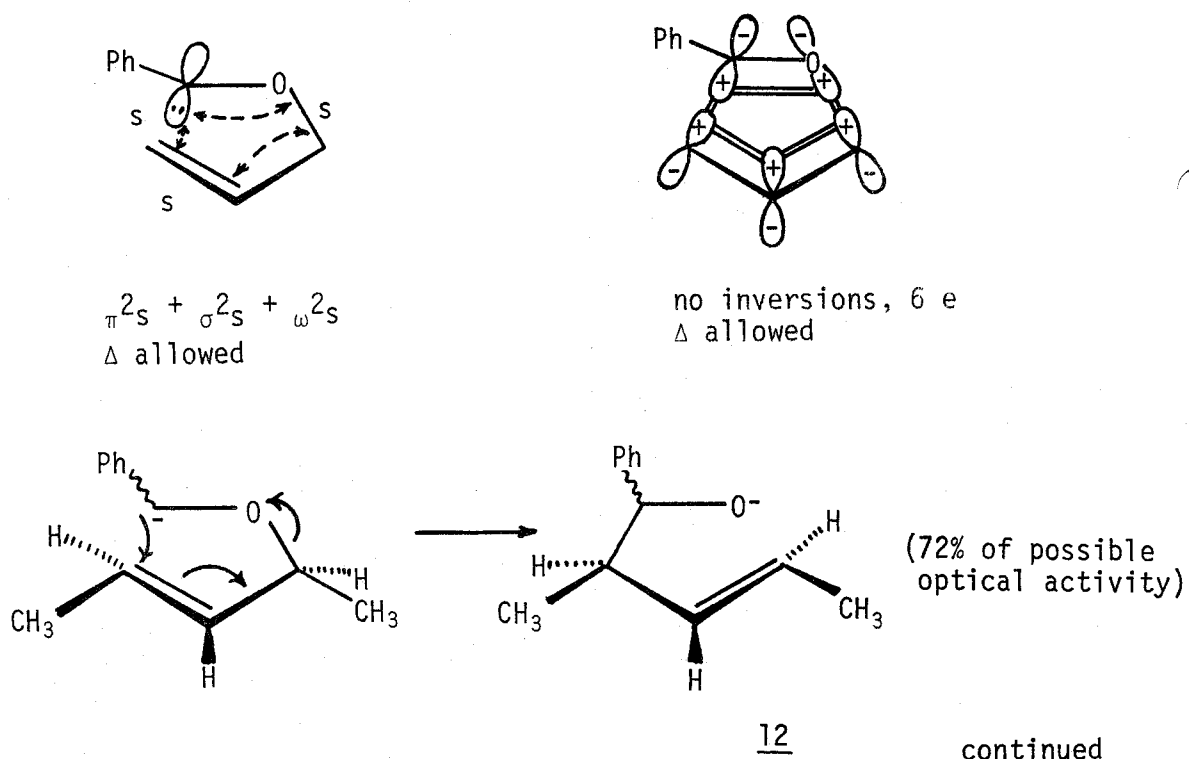
6-11



Reference: J. J. Gajewski and C. J. Cavender, Tetrahedron Lett., 1057, (1971).

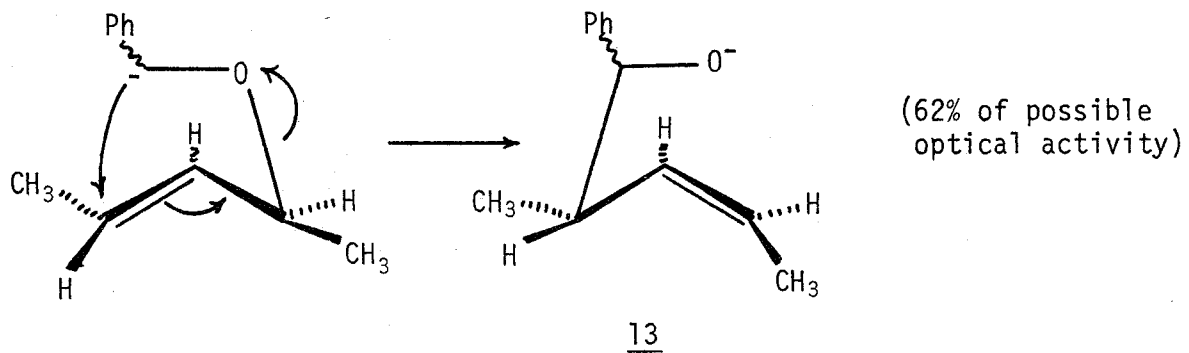
6-12

The products arise from $[2,3]$ sigmatropic rearrangements on different conformations of the conjugate base of the starting material.

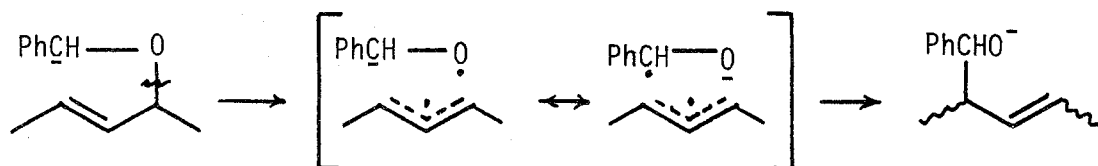


continued

Starting with another conformation

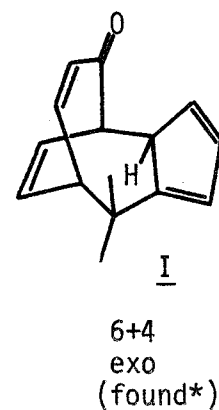
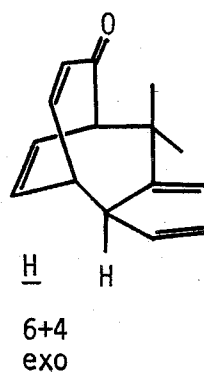
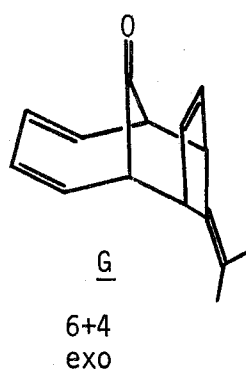
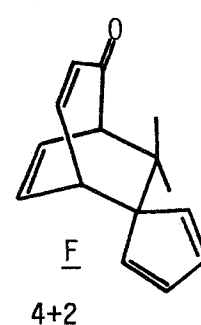
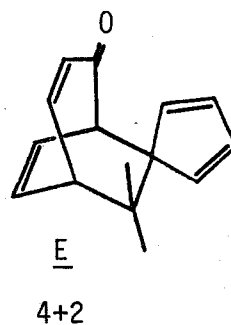
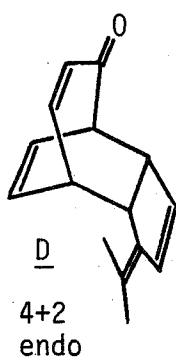
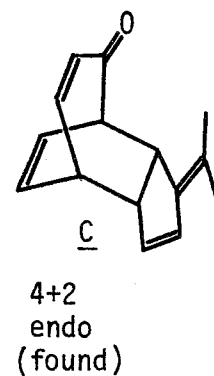
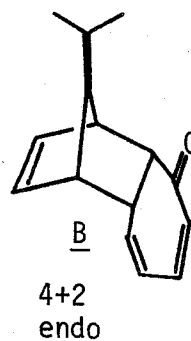
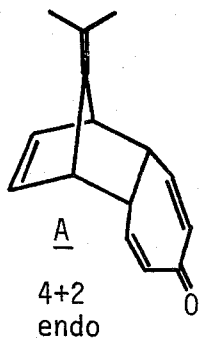


Loss in optical activity arises from competing non-concerted pathway:



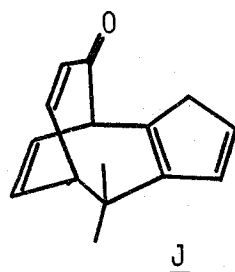
Reference: J. E. Baldwin and J. E. Patrick, J. Amer. Chem. Soc., 93, 3556 (1971).

7-1

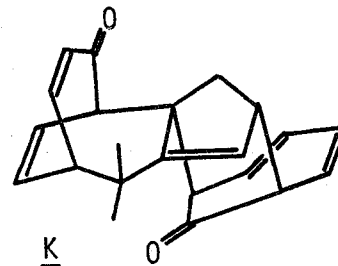


Other combinations are prohibited by Bredt's rule.

* after [1,5] hydrogen shift and further reaction with tropone to give



+



Reference: K. N. Houk, L. J. Luskus, and N. S. Bhacca, J. Amer. Chem. Soc., 92, 6392 (1970).

continued

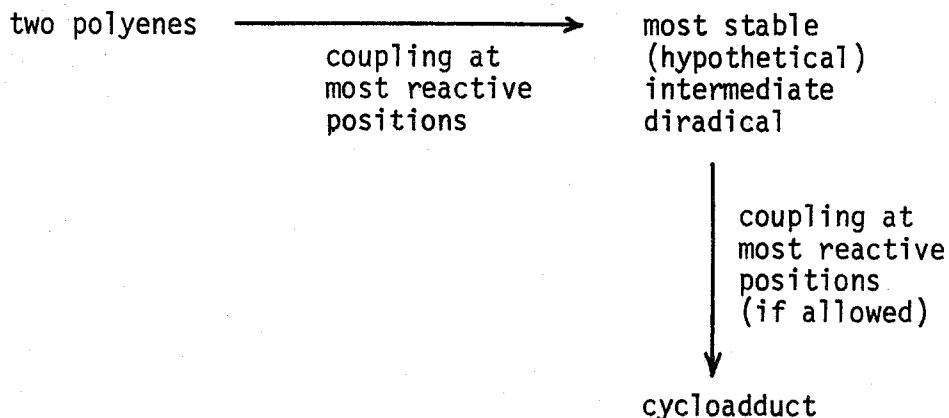
V. important

Predicting favored paths among allowed cycloadditions.

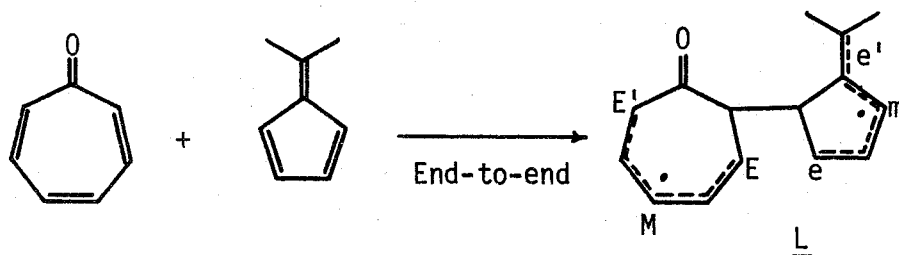
Theoretical methods: Review: W. C. Herndon, Chem. Rev., 72, 157 (1972).

Empirical method:

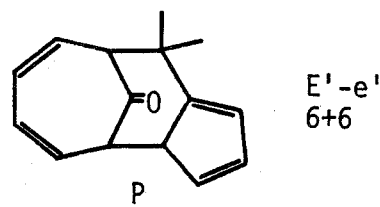
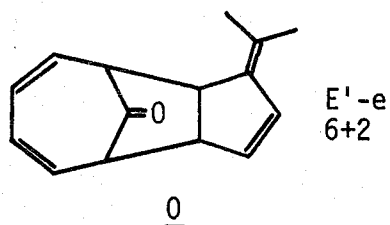
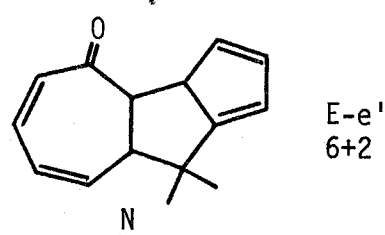
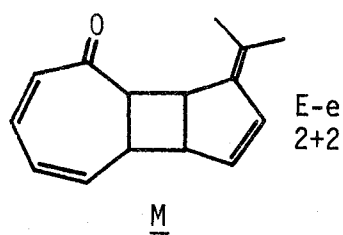
Regard cycloaddition as two-step reaction



For polyolefins, and for conjugated radicals, most reactive positions are at ends of chain; addition to terminus of conjugated polyene chain also gives most conjugated radical.



End-to-end coupling

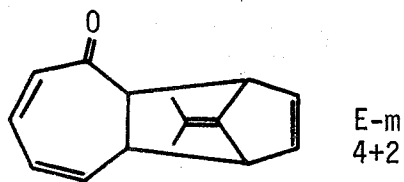


All are forbidden

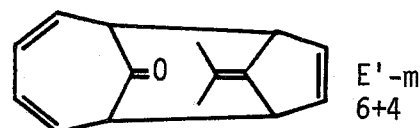
continued

End-to-middle coupling is next most favorable.

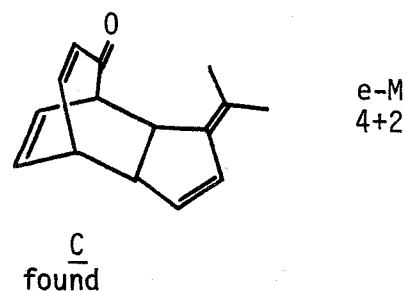
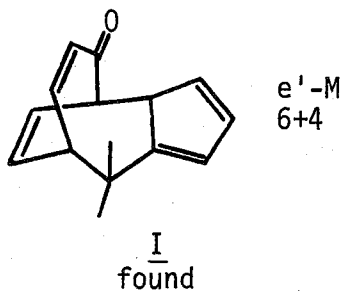
Predicted products:



Q



R



Reference: G. L. Goe, J. Org. Chem., 37, 2434 (1972).

Related treatment for Diels-Alder reaction: Yu. A. Titov, Russ. Chem. Rev., 31, 267 (1962).

Concerted reaction: No intermediates; no minima along reaction path except starting material and product.

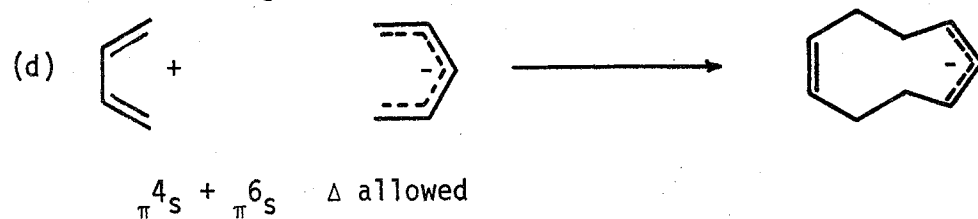
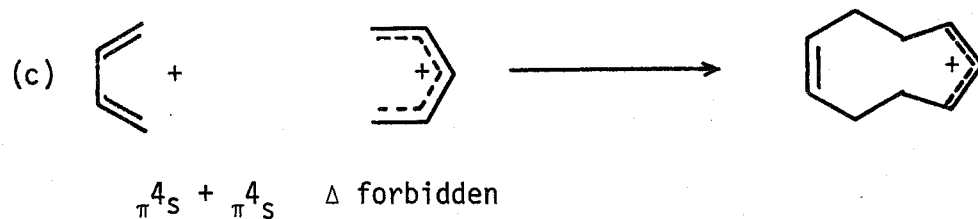
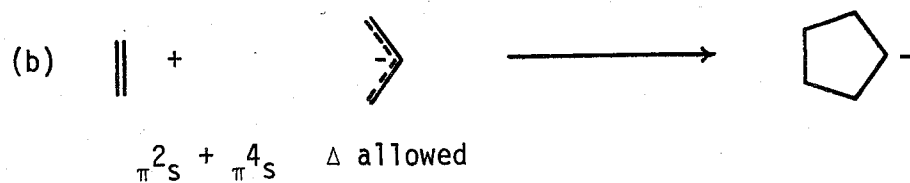
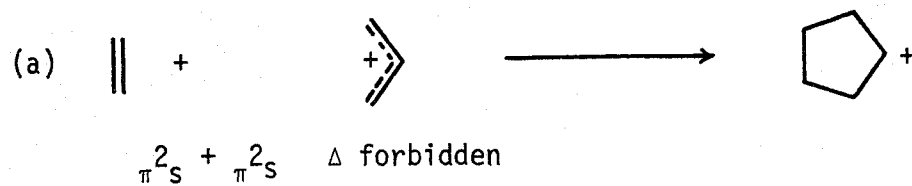
If two bonds are formed in a concerted reaction, they need not be formed at the same rate (synchronously). Success of diradical method may indicate lack of synchronism in cycloadditions.

Predicted that cycloadditions as large as, or larger than, Diels-Alder reaction should be non-synchronous.

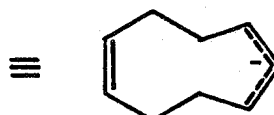
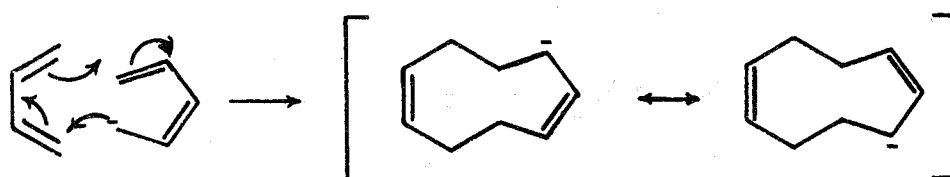
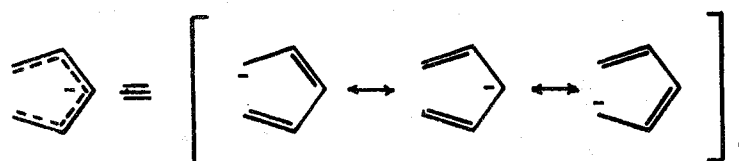
Reference: J. W. McIver, Jr., J. Amer. Chem. Soc., 94, 4782 (1972).

Discussion of synchronism in concerted reactions: J. E. Baldwin and R. H. Fleming, Fortschr. Chem. Forsch., 15 281 (1970).

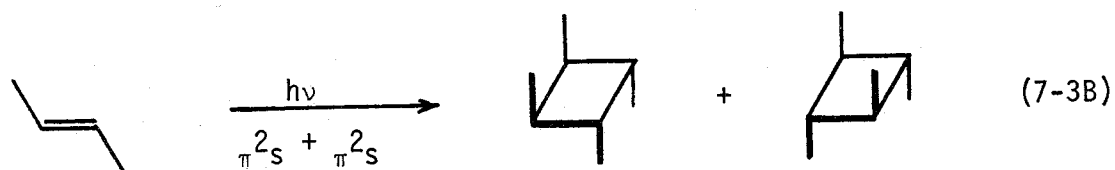
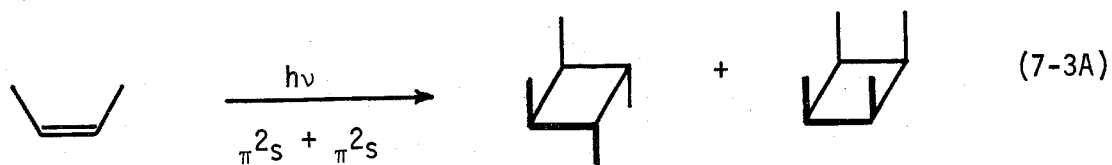
7-2



Use resonance structures and arrows if dotted lines confusing.

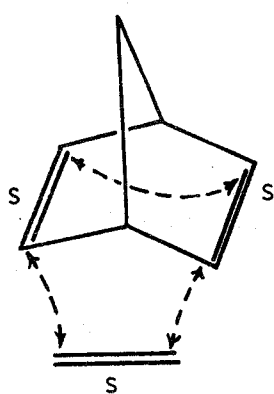


7-3

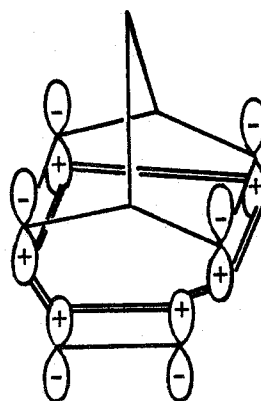


Reference: H. Yamazaki and R. J. Cvetanović, J. Amer. Chem. Soc., 91, 520 (1969).

7-4



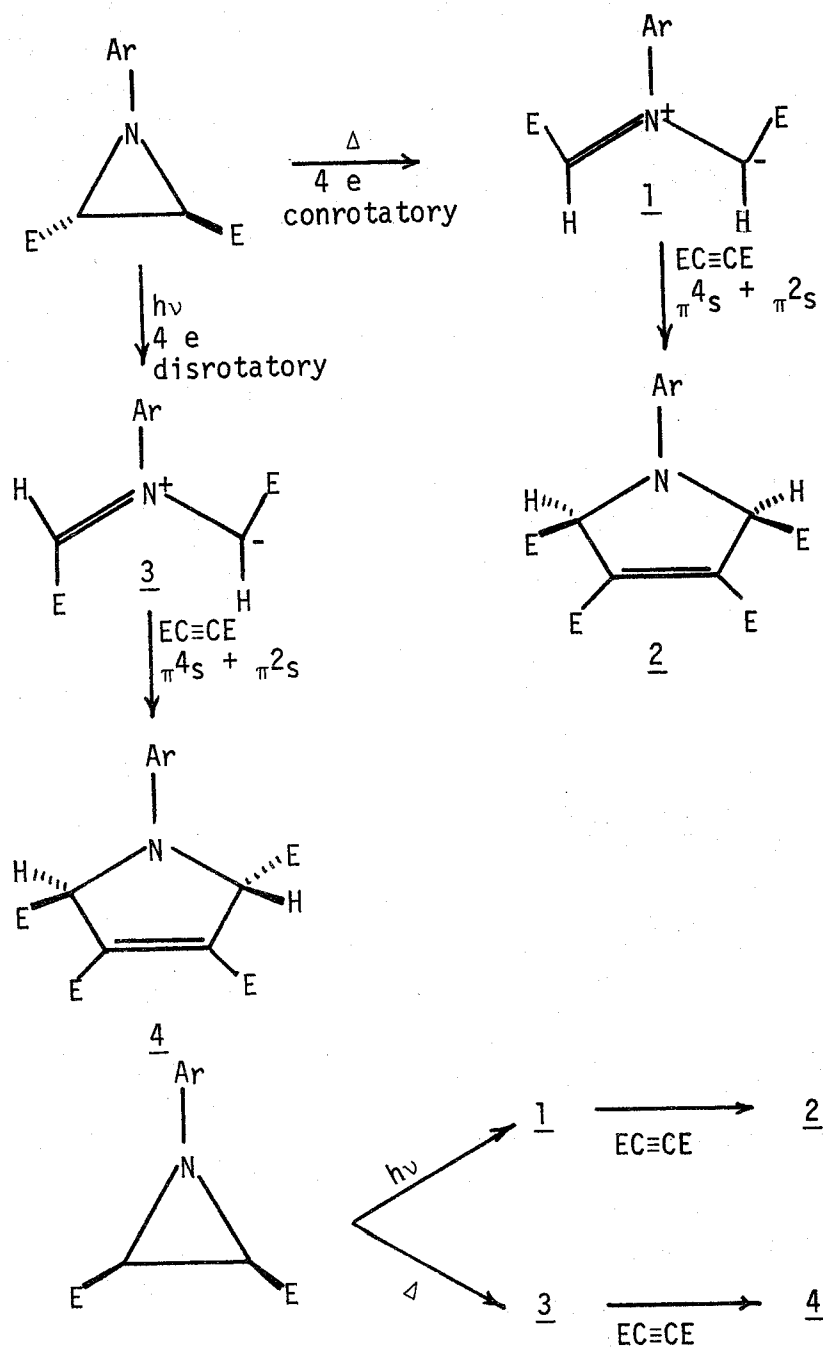
$\pi^2_S + \pi^2_S + \pi^2_S$ Δ allowed



no inversions, 6 e

Reference: R. Huisgen, R. Grashey, and J. Sauer, in "The Chemistry of Alkenes," Vol. 1, S. Patai, Ed., Interscience, New York, N. Y., 1964, p 739.

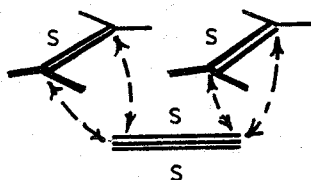
7-5



Reference: R. Huisgen, XXIIIrd Int. Congr. Pure Appl. Chem., 1, 175 (1971), and references cited therein; cf. T. DoMinh and A. M. Trozzolo, J. Amer. Chem. Soc., 94, 4046 (1972).

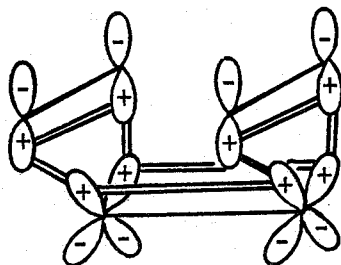
7-6

in S-A



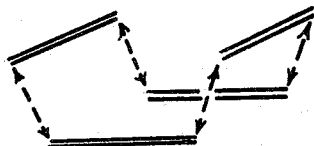
$\pi^2_s + \pi^2_s + \pi^2_s + \pi^2_s$
 Δ forbidden, $h\nu$ allowed

in H-M



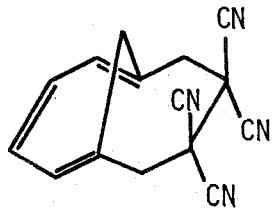
no inversions, 8 e
 Δ forbidden, $h\nu$ allowed

Acetylene π bonds act independently, so reaction could also be shown as

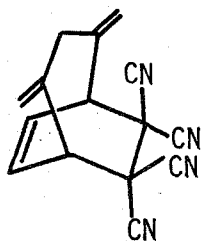


Reference: D. C. Owsley and J. J. Bloomfield, J. Amer. Chem. Soc., **93**, 782 (1971), and references cited therein.

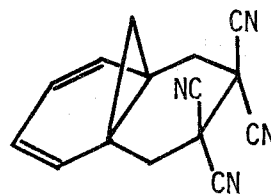
7-7



A
 8+2
 (found)



B
 4+2



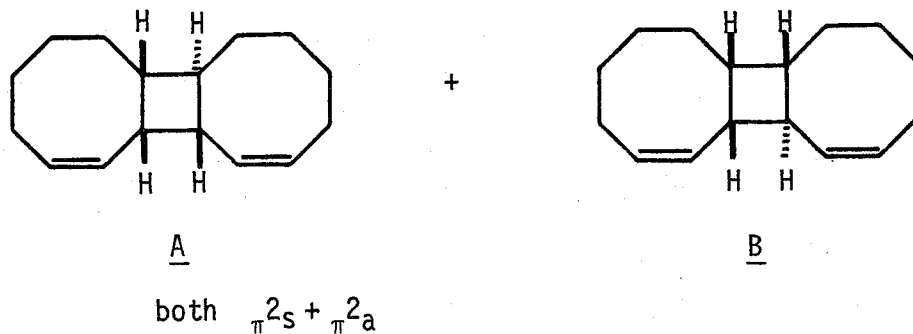
C
 $\pi^2_s + \pi^2_s + \pi^2_s$

A \nleftrightarrow C possible

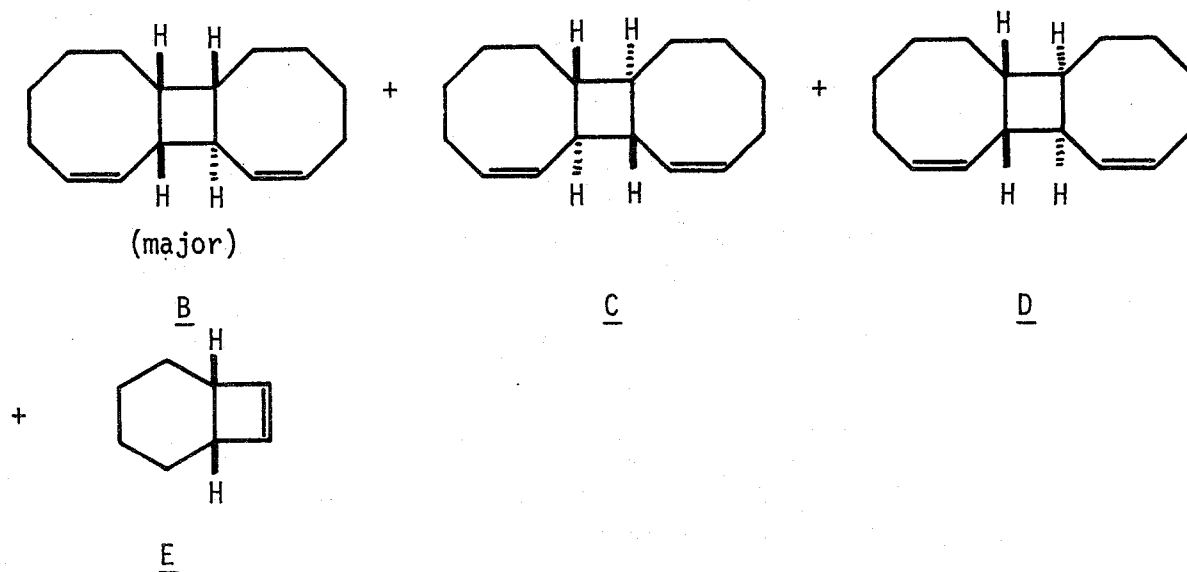
Reference: G. C. Farrant and R. Feldman, Tetrahedron Lett., 4979 (1970).

7-8

Predict:



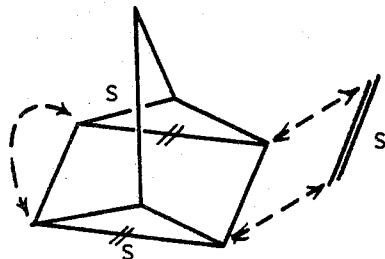
Found:



Reference: A. Padwa, W. Koehn, J. Masaracchia, C. L. Osborn, and D. J. Trecker, *J. Amer. Chem. Soc.*, **93**, 3633 (1971).
 cf. G. L. Lange and E. Neidert, *Tetrahedron Lett.*, 4215 (1971); 1349 (1972).
 J. Leitich, *Angew. Chem., Int. Ed. Engl.*, **8**, 909 (1969).
 P. G. Gassman, H. P. Benecke, and T. J. Murphy, *Tetrahedron Lett.*, 1649 (1969).
 J. J. Bloomfield and J. S. McConaghy, Jr., *ibid.*, 3723 (1969).

7-9

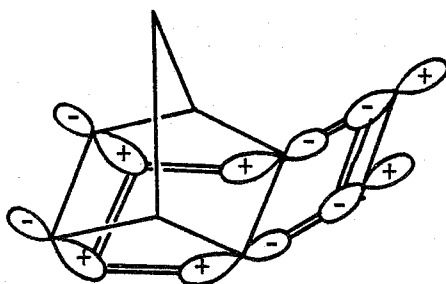
in S-A



$$\pi^2_s + \sigma^2_s + \sigma^2_s$$

Δ allowed

in H-M



no inversions, 6 e
 Δ allowed

Reference: T. Tabushi, K. Yamamura, and Z. Yoshida, J. Amer. Chem. Soc., 94, 787 (1972), and references cited therein.

8-1

Figure 8-1A.

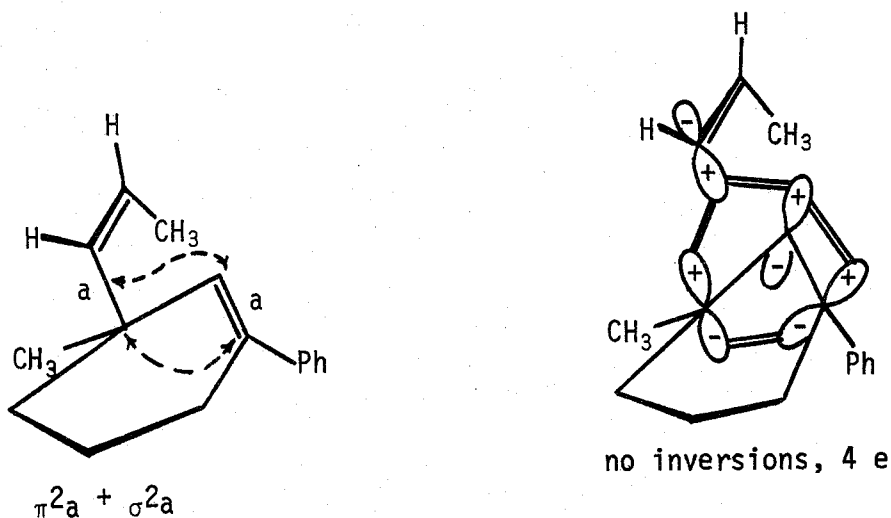
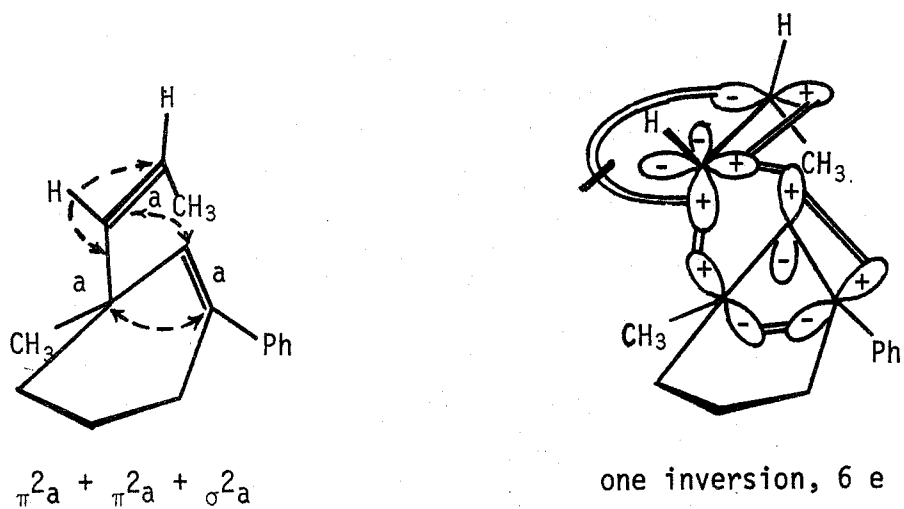


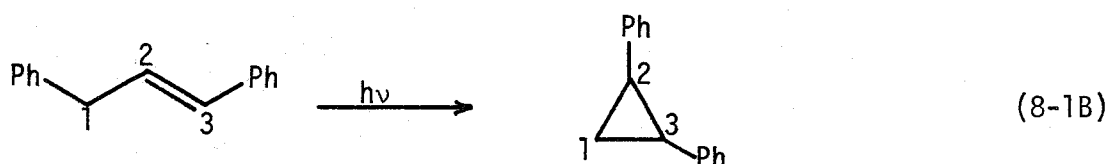
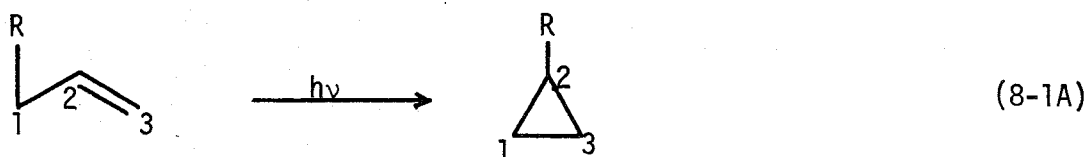
Figure 8-1B.



Reference: P. S. Mariano and J. Ko, *J. Amer. Chem. Soc.*, **94**, 1766 (1972), and references cited therein; cf. H. E. Zimmerman and R. D. Little, *ibid.*, **94**, 8256 (1972).

continued

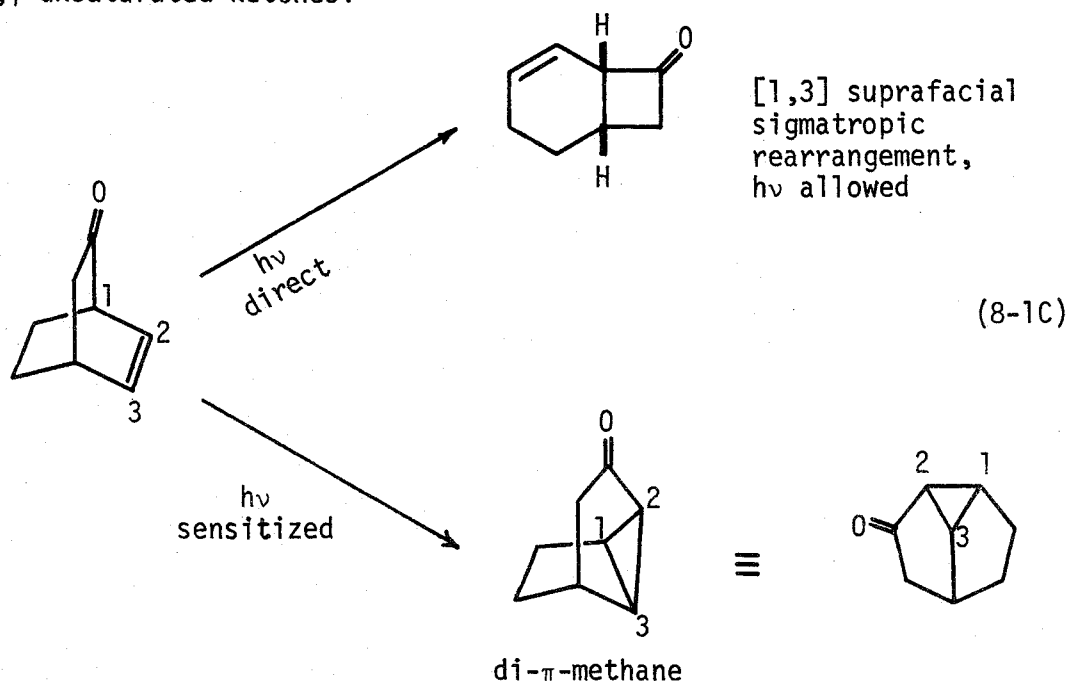
"Di- π -methane rearrangement"



Related to many common photochemical rearrangements:

1,4-dienes (see above)

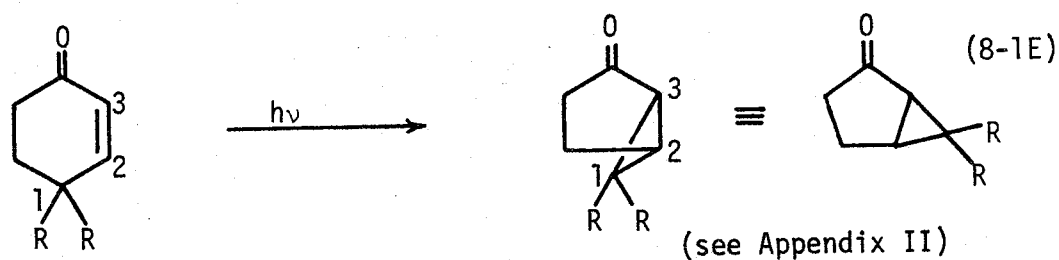
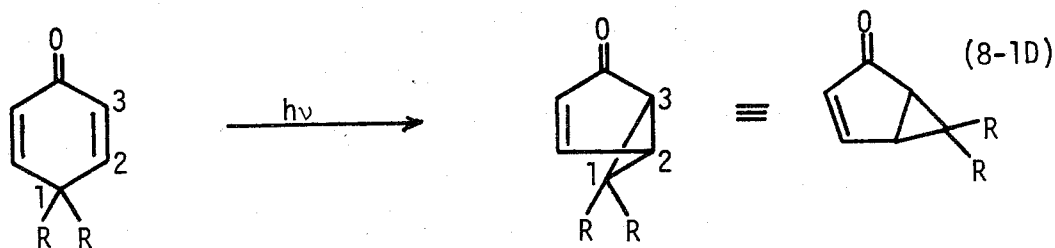
β,γ -unsaturated ketones:



References: R. S. Givens, W. F. Oettle, R. L. Coffin, and R. G. Carlson, *J. Amer. Chem. Soc.*, **93**, 3957 (1971), and references cited therein; cf. D. I. Schuster, G. R. Underwood, and T. P. Knudsen, *ibid.*, **93**, 4304 (1971).

continued

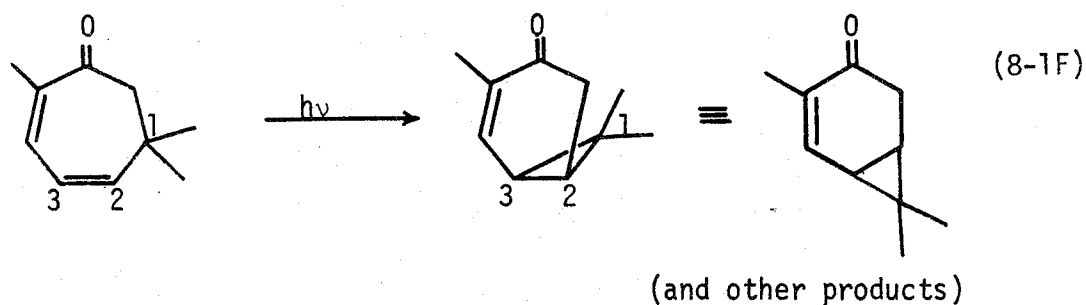
Cyclohexenones, and cyclohexadienones:



Reviews: P. J. Kropp in "Organic Photochemistry," Vol. 1, O. L. Chapman, Ed., Marcel Dekker, New York, N. Y., 1967, pp 1-90, and references cited therein.

H. E. Zimmerman, Angew. Chem., Int. Ed. Engl., 8, 1 (1969).

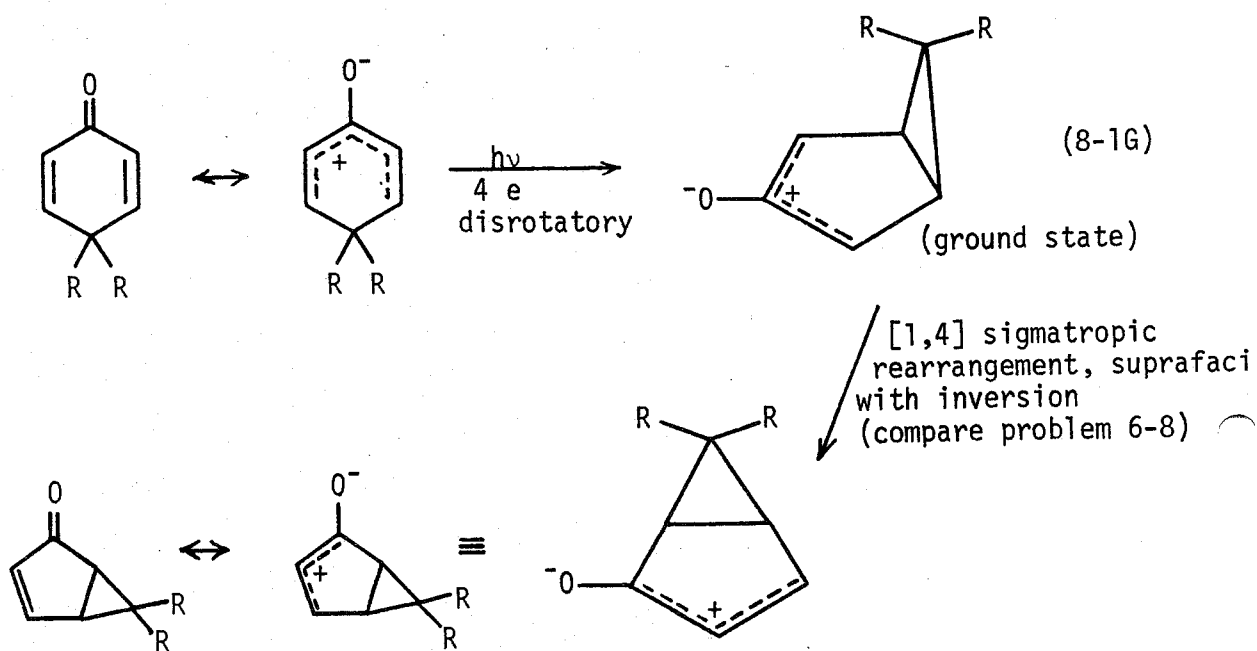
Other compounds:



Reference: H. Hart and T. Takino, J. Amer. Chem. Soc., 93, 720 (1971).

continued

Reaction mechanisms may be more complicated, not the same in all cases.



Moral:

The principles of orbital symmetry apply only to one-step (i.e., concerted) reactions; but any multi-step reaction should be factorable into many one-step reactions. Orbital symmetry can be applied to many of these steps (if they are pericyclic).

8-2

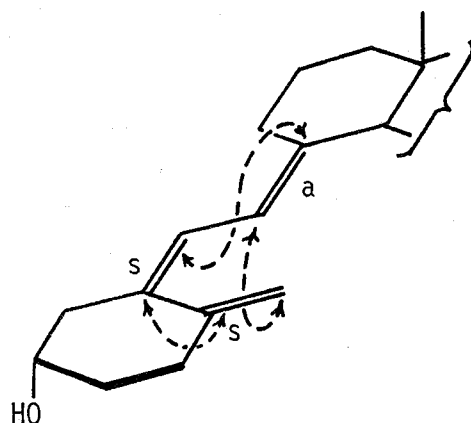
- A 6 e, conrotatory; $h\nu$
- B [1,7] antarafacial H shift (see models); Δ
- C $\pi^4_s + \pi^2_a$ (see below); $h\nu$
- D,E 6 e, disrotatory; Δ
- F,G 4 e, disrotatory; $h\nu$

Review: G. M. Sanders, J. Pot, and E. Havinga in "Fortschritte der Chemie Organischer Naturstoffe," Vol. 27, L. Zechmeister, Ed., Springer-Verlag, Vienna, 1969, p 131.

continued

Reaction C:

Figure 8-2A.

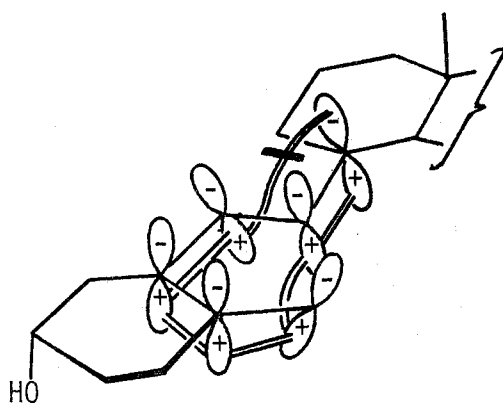


$$\pi^2_s + \pi^2_s + \pi^2_a$$

$$(\text{or } \pi^4_s + \pi^2_a)$$

Δ forbidden, $h\nu$ allowed

Figure 8-2B.



one inversion, 6 e

Δ forbidden,
 $h\nu$ allowed

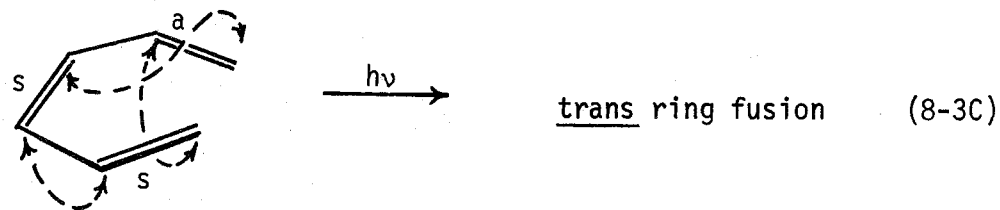
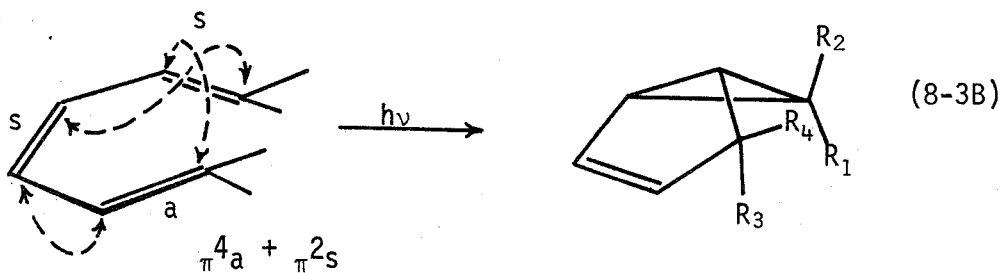
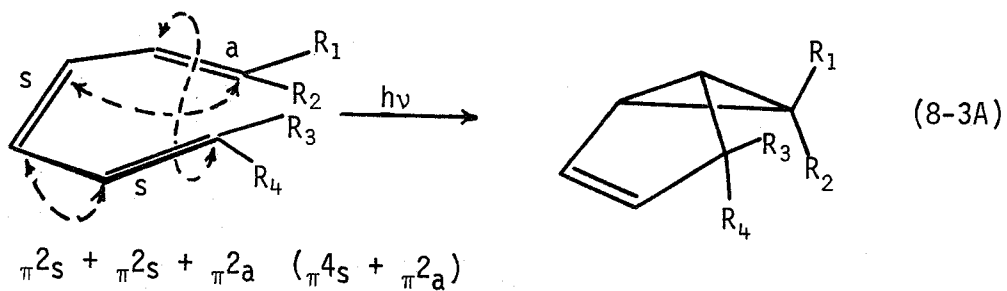
Not enough information about CH_2 stereochemistry.

Common reaction of conjugated trienes.

8-3

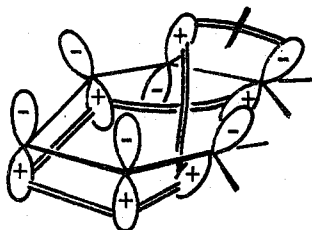
Can be solved in s-cis,s-cis or s-cis,s-trans conformations.

in S-A



in H-M

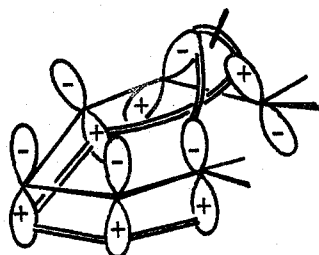
Figure 8-3A.



one inversion, 6 e
same as $\pi^4_s + \pi^2_a$

continued

Figure 8-3B.



one inversion, 6 e

same as $\pi^4_a + \pi^2_s$

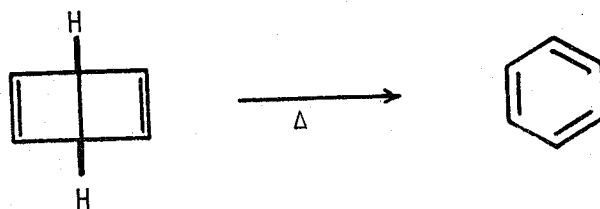
Experimental findings: $\pi^4_s + \pi^2_a$ is preferred.

Reference: A. Padwa, L. Brodsky, and S. Clough, J. Amer. Chem. Soc., 94, 6767 (1972).

But: In many cases forbidden products predominate.

Reference: D. A. Seeley, ibid., 94, 4378, 8647 (1972); cf. W. G. Dauben, J. Rabinowitz, N. D. Vietmeyer, and P. H. Wendschuh, ibid., 94, 4285 (1972).

8-4



4 e, disrotatory; Δ forbidden

Review: E. E. van Tamelen, Accounts Chem. Research, 5, 186 (1972), and references cited therein.

8-5

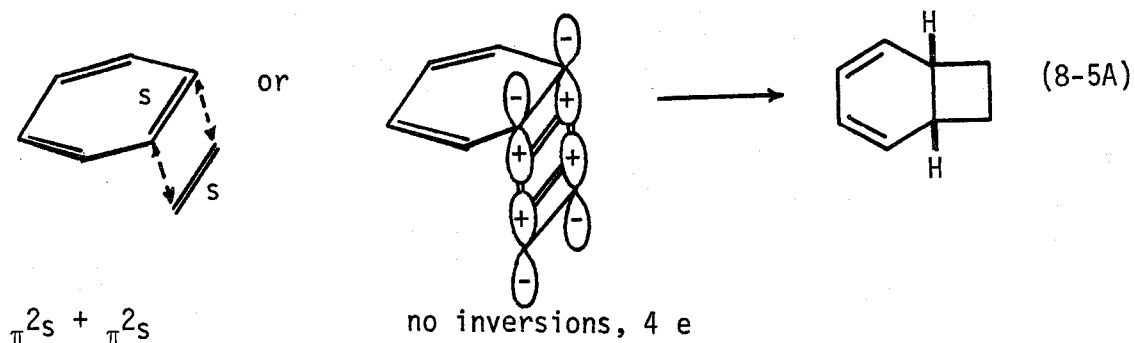
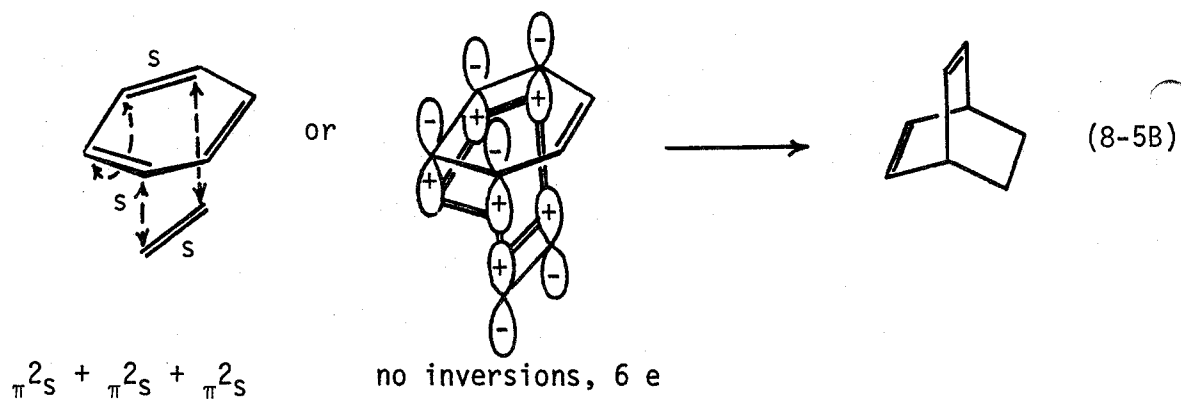
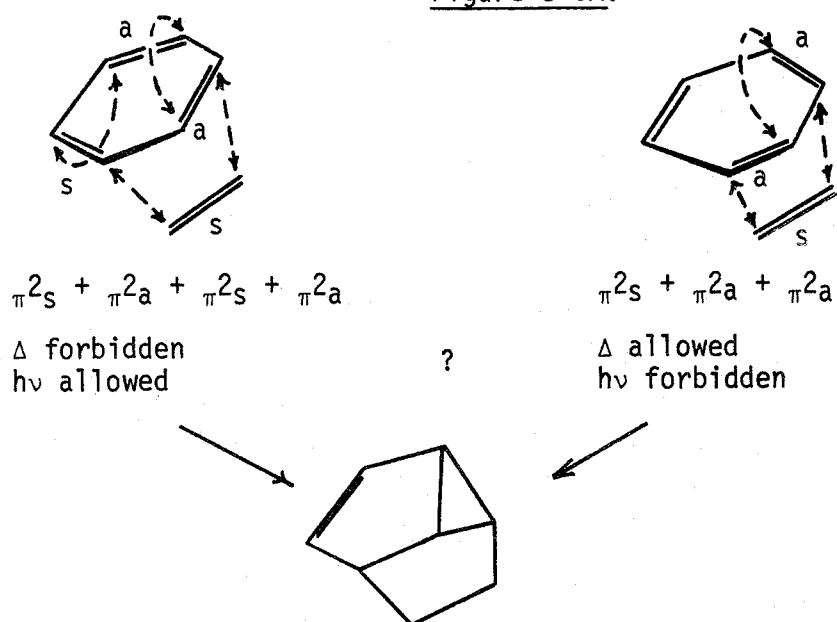
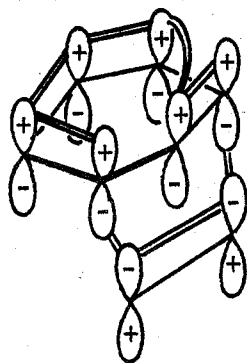
 Δ forbidden, $h\nu$ allowed Δ allowed, $h\nu$ forbidden

Figure 8-5A.

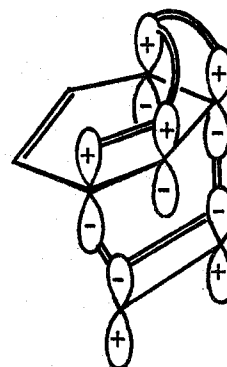


continued

Figure 8-5B.



no inversions, 8 e
 Δ forbidden
 $h\nu$ allowed



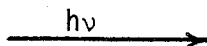
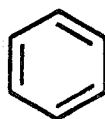
no inversions, 6 e
 Δ allowed
 $h\nu$ forbidden

All these cycloadditions occur photochemically.

Reference: K. E. Wilzbach and L. Kaplan, *J. Amer. Chem. Soc.*, **93**, 2073 (1971), and references cited therein.

Problem should not be attempted without complete, proper MO's for benzene.

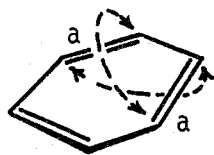
Reference: D. Bryce-Smith and H. C. Longuet-Higgins, *Chem. Commun.*, 593 (1966).



Benzvalene

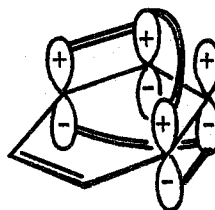
(8-5C)

Figure 8-5C.



$\pi^2_a + \pi^2_a$

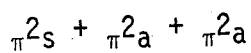
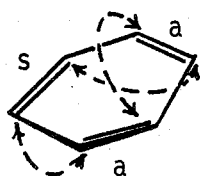
Δ forbidden, $h\nu$ allowed



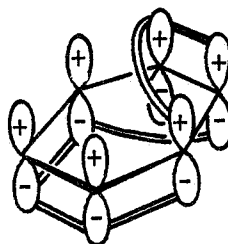
no inversions, 4 e

continued

Figure 8-5D.



Δ allowed, $h\nu$ forbidden



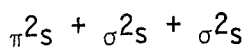
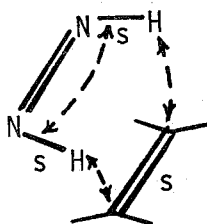
no inversions, 6 e

References above

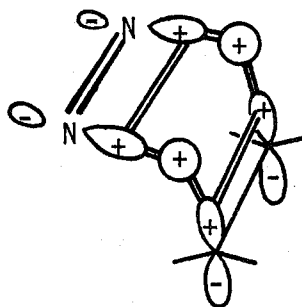
8-6

(1) and (3) are thermally allowed.

(1)



Δ allowed

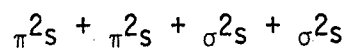
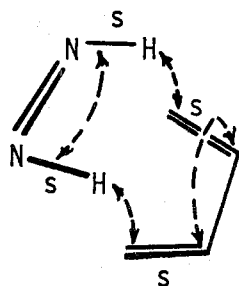


no inversions, 6 e

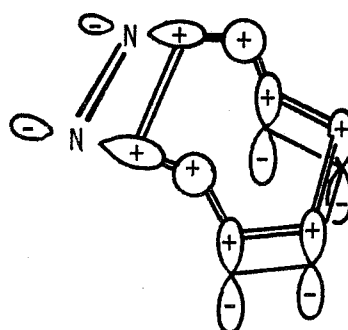
Review: L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," Wiley, New York, N. Y., Vol. 1, 1967, p 257; Vol. 2, 1969, p 139.

continued

(2)

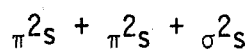
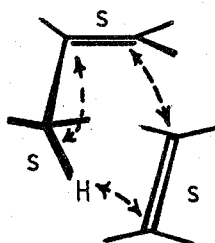


Δ forbidden



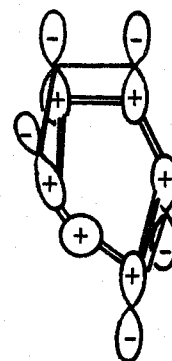
no inversions, 8 e

(3)



Δ allowed

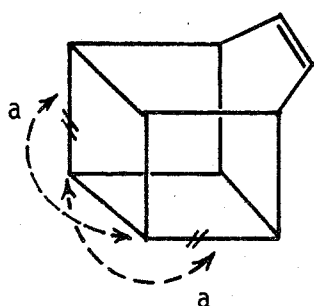
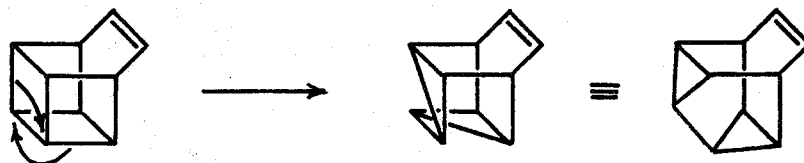
Alder "ene" synthesis



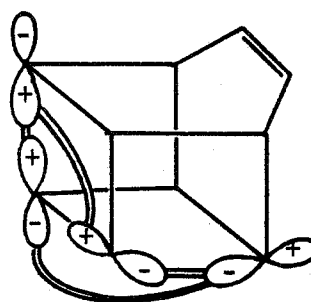
no inversions, 6 e

Review: H. M. R. Hoffmann, Angew. Chem., Int Ed. Engl., 8, 556 (1969).

8-7



$\sigma^2_a + \sigma^2_a$



no inversions, 4 e

Δ forbidden

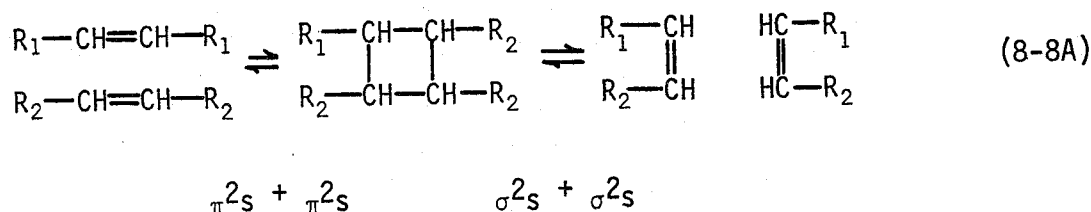
Reaction occurs at room temperature, in the presence of Ag^+ .
Reaction not concerted.

References: L. A. Paquette, Accounts Chem. Research, 4, 280 (1971),
and references cited therein.

8-8

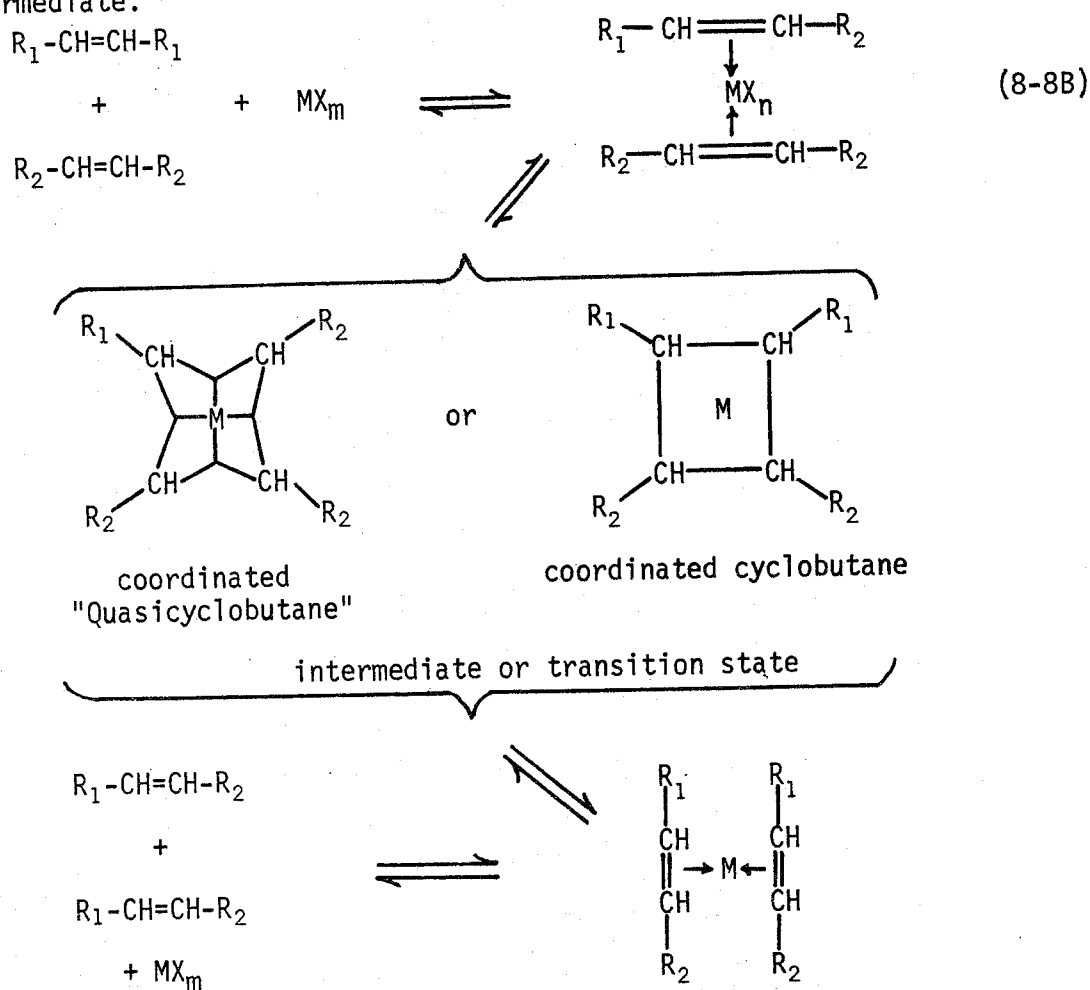
"Olefin metathesis reaction"

in two steps



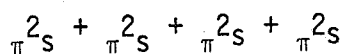
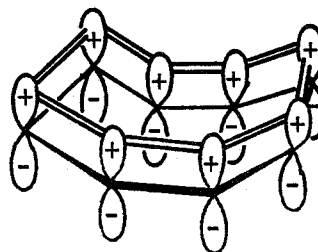
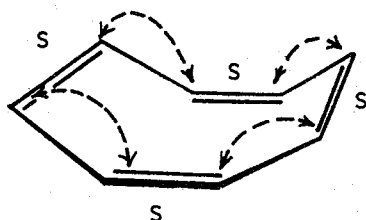
both Δ forbidden

Reaction occurs easily in the presence of transition metal catalysts - via coordinated cyclobutane or "quasicyclobutane" intermediate.



Review: N. Calderon, Accounts Chem. Research, 5, 127 (1972), and references cited therein; cf. F. D. Mango and J. H. Schachtschneider, J. Amer. Chem. Soc., 93, 1123 (1971).

8-9



no inversions, 8 e

Δ forbidden, $h\nu$ allowed

"No-reaction reaction"; observable in substituted compounds or by nmr.

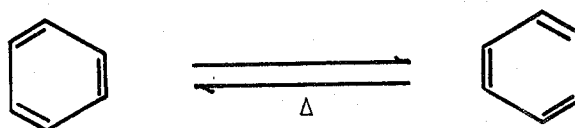
Photochemical reaction observed at low temperature.

Thermal reaction observed; $\Delta G^\ddagger = 17-19$ kcal/mole.

Ring inversion (tub-tub); $\Delta G^\ddagger \sim 15$ kcal/mole.

(If transition state for bond shift is planar, then planar equal-bond COT is only 2-4 kcal/mole higher in energy than planar alternant-bonded COT!)

Compare allowed reaction of same type:



"Transition state:"



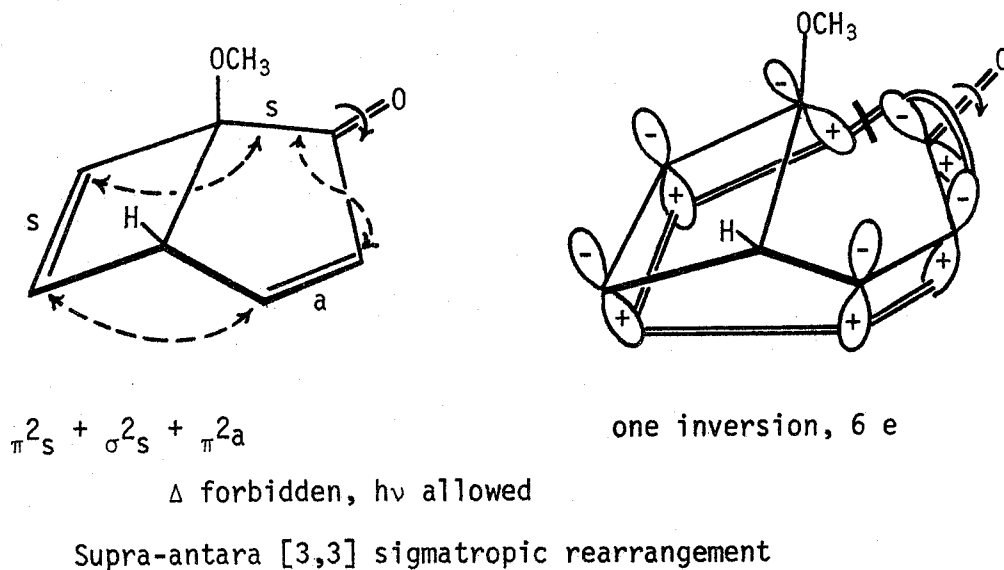
" ΔH^\ddagger " = $-E_{res}$ = -36 kcal/mole

$\Delta \Delta G^\ddagger > 50$ kcal/mole

Reference: F. A. L. Anet and L. A. Bock, J. Amer. Chem. Soc., **90**, 7130 (1968), and references cited therein; cf. M. J. S. Dewar, Fortschr. Chem. Forsch., **23**, 1 (1972).

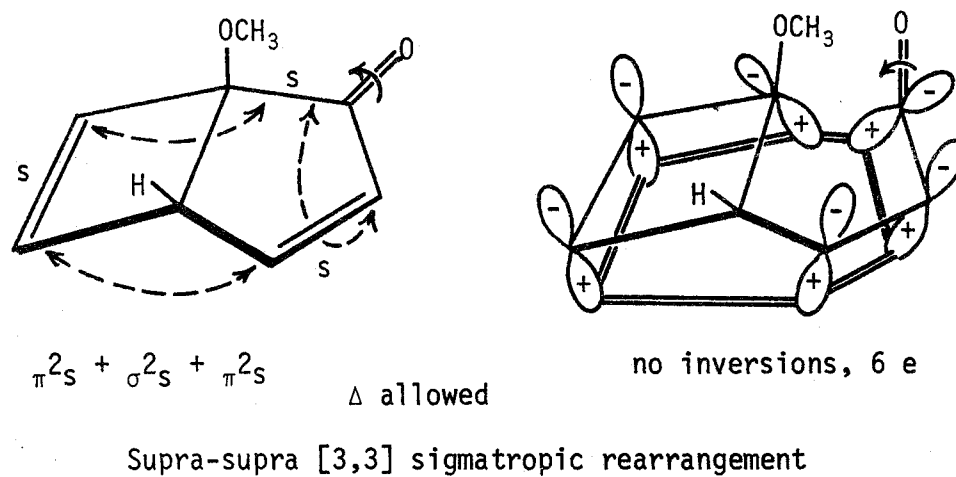
8-10
 $h\nu$ reaction (forward)

Figure 8-10A.

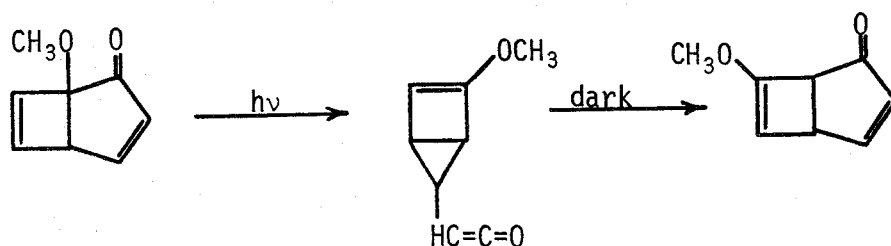


Δ back reaction; look at Δ forward reaction for clarity

Figure 8-10B.



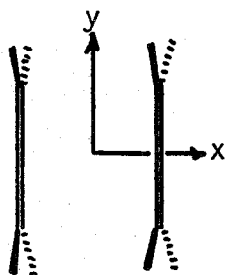
continued



Reference: O. L. Chapman and J. D. Lassila, J. Amer. Chem. Soc., **90**, 2449 (1968).
Cycloadditions of ketenes and allenes: R. B. Woodward and R. Hoffmann, op. cit., pp 163-168; J. E. Baldwin and R. H. Fleming, Fortschr. Chem. Forsch., **15**, 281 (1970); R. Sustmann, A. Ansmann, and F. Vahrenholt, J. Amer. Chem. Soc., **94**, 8099 (1972), and references cited therein.

Appendix I

The $\pi^2_s + \pi^2_s$ Cycloaddition in D_{2h} Symmetry



Linear combinations to give symmetry-correct combinations (see Figure 2-36).

$$\Pi_{\alpha} = \pi_1 + \pi_2$$

$$\Pi_{\beta} = \pi_1 - \pi_2$$

$$\Pi_{\alpha}^* = \pi_1^* + \pi_2^*$$

$$\Pi_{\beta}^* = \pi_1^* - \pi_2^*$$

$$\Sigma_{\alpha} = \sigma_1 + \sigma_2$$

$$\Sigma_{\beta} = \sigma_1 - \sigma_2$$

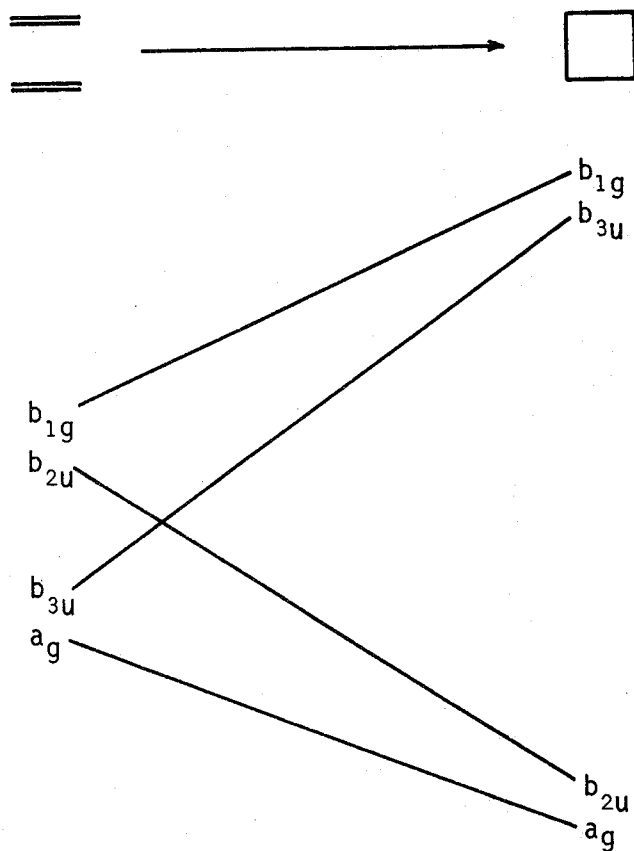
$$\Sigma_{\alpha}^* = \sigma_1^* + \sigma_2^*$$

$$\Sigma_{\beta}^* = \sigma_1^* - \sigma_2^*$$

Classification of symmetry-correct orbitals in D_{2h}

	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$	
Π_α	1	1	1	1	1	1	1	1	a_g
Π_β	1	-1	-1	1	-1	1	1	-1	b_{3u}
Π_α^*	1	-1	1	-1	-1	1	-1	1	b_{2u}
Π_β^*	1	1	-1	-1	1	1	-1	-1	b_{1g}
Σ_α	1	1	1	1	1	1	1	1	a_g
Σ_β	1	-1	1	-1	-1	1	-1	1	b_{2u}
Σ_α^*	1	-1	-1	1	-1	1	1	-1	b_{3u}
Σ_β^*	1	1	-1	-1	1	1	-1	-1	b_{1g}

Orbital correlation diagram



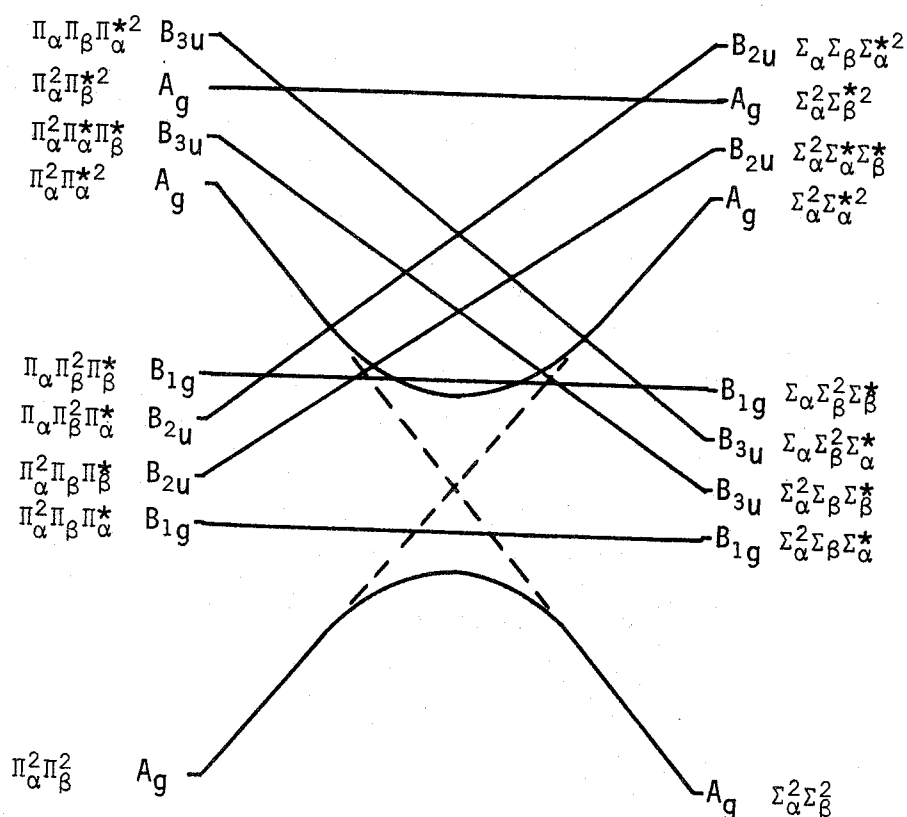
The orbital correlation diagram looks the same as that made using only two planes even though less symmetry was used.

State symmetry is direct product of occupied orbital symmetries.

$$\pi_{\alpha}^2 \pi_{\beta}^2 = a_g \times a_g \times b_{3u} \times b_{3u} = A_g$$

$$\pi_{\alpha}^2 \pi_{\beta} \pi_{\alpha}^* = a_g \times a_g \times b_{3u} \times b_{2u} = B_{1g}$$

State correlation diagram including all singly-excited states and the states they correlate with.



The two ground states do not correlate directly because of the lack of orbital correlation. The problem may also be solved using a lower symmetry subgroup of D_{2h} .

Appendix II

Use of Molecular Models in the S-A Method

Properly used, molecular models are a valuable assistance in working orbital symmetry problems. All problems can be worked out on paper, but some only with very good draftsmanship.

The most helpful available models are the kind using plastic tubing joined by metal connectors with fixed geometry - tetrahedral, trigonal bipyramidal, or octahedral (Prentice-Hall Framework Models); the greatest use comes from using the models in the manner described below.

(1) Use full-length tubing for all bonds; precise bond lengths are not important for orbital symmetry problems.

(2) Cut some full-length tubing in half and join using the linear connectors (acetylene bonds); these bonds may be easily broken in the course of a reaction. The half-length tubing may also be used to represent half of a p orbital, and joined later to another half-length tubing to form a new σ bond.

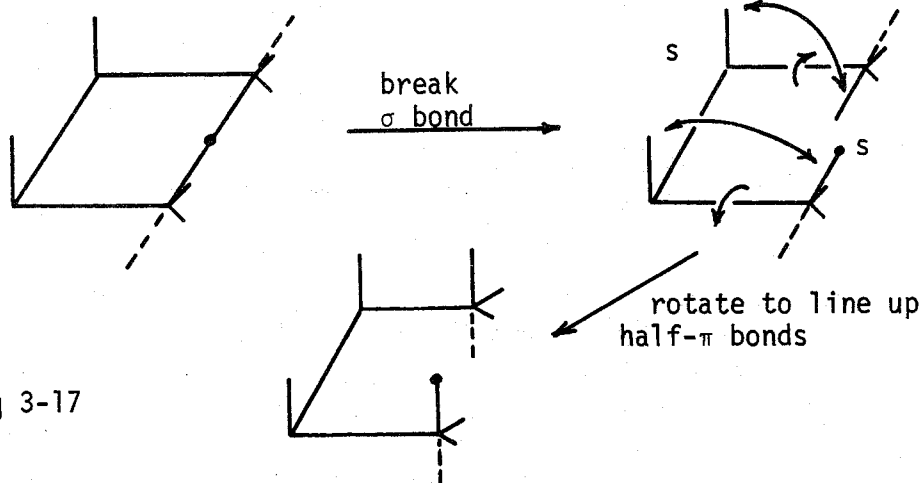
(3) Use the trigonal bipyramid connector for an sp^3 carbon if one of the σ bonds to it is to be broken to form part of a π bond, or if inversion at that carbon is desired. The tubing representing the bond to be broken should be attached to one of the apical points of the connector. To accomplish inversion at that carbon, use a piece of half-length tubing of a different color at the other apex to form a new σ or half- π bond.

Examples.

(1) Cyclobutene - butadiene, $\pi 2_s + \sigma 2_s$ (disrotatory)

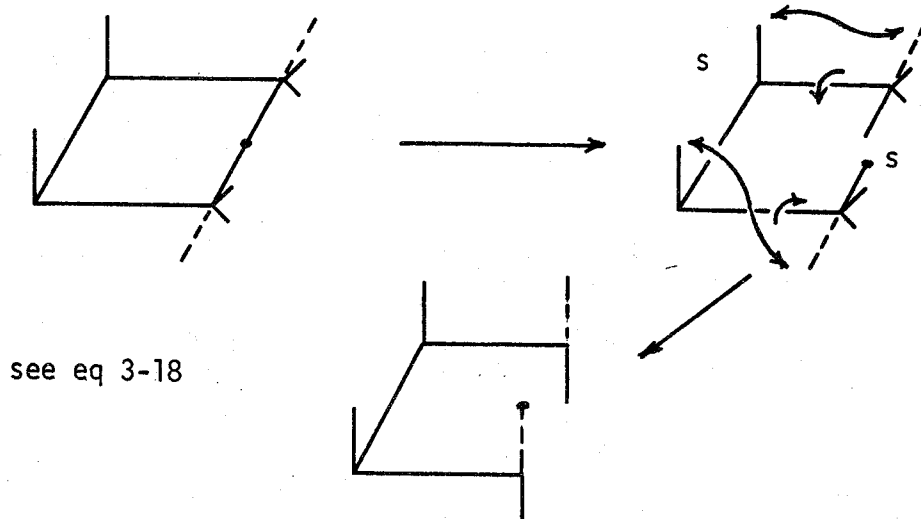
All carbons are trigonal bipyramids.

• = connector; --- = half-length tubing, odd color retention-retention on $\sigma 2_s$

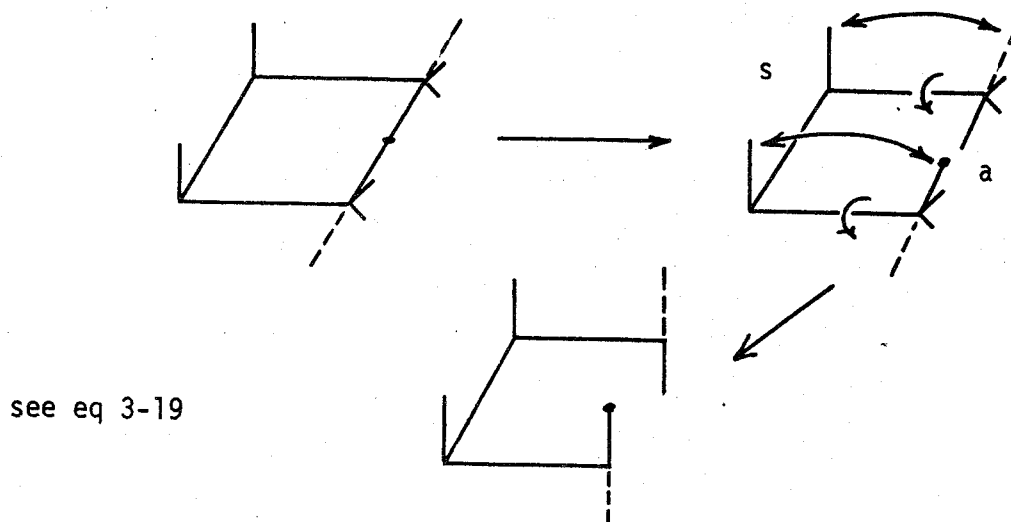


see eq 3-17

inversion-inversion on σ^2_s

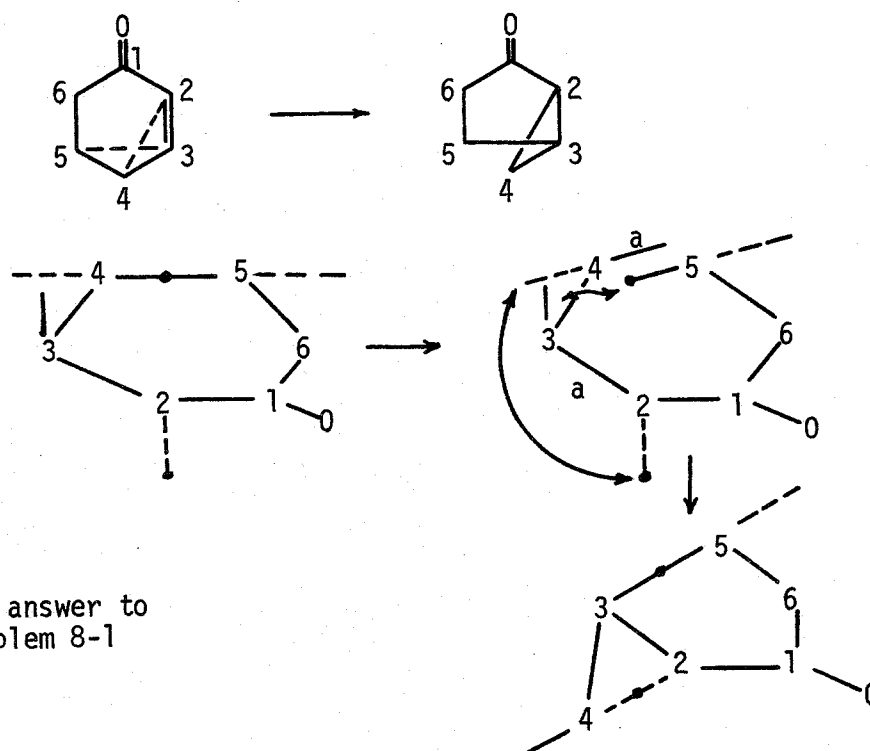


(2) conrotatory - $\pi^2_s + \sigma^2_a$



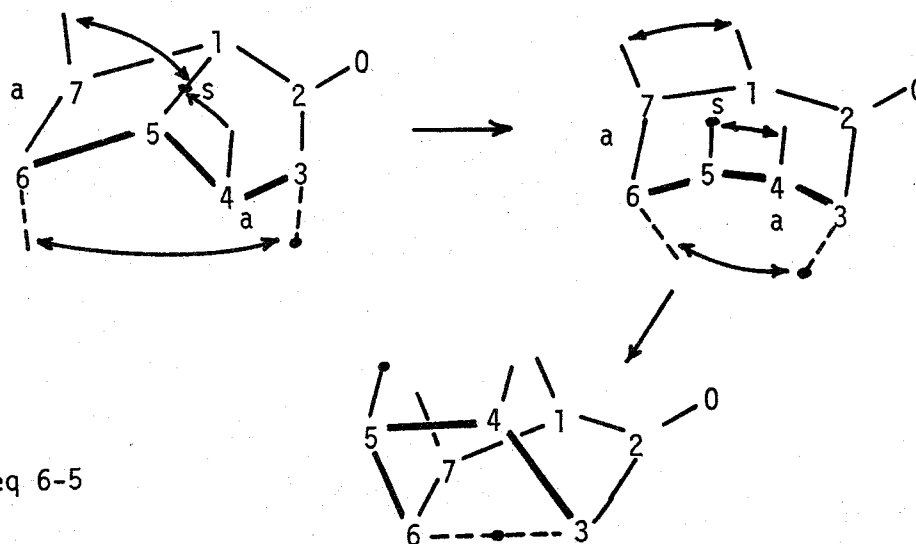
Notice that the metal connectors cannot rehybridize during the reaction, so starting material or product, or both, are likely to have unrealistic geometries. Models used in this fashion are not useful for assessing conformations.

(3) Enone photorearrangement - $\pi^2_a + \sigma^2_a$



see answer to
problem 8-1

(4) [3,3] antara-antara sigmatropic (Cope) rearrangement; $\pi^2_a + \sigma^2_s + \pi^2_a$



see eq 6-5

Try these examples with models.