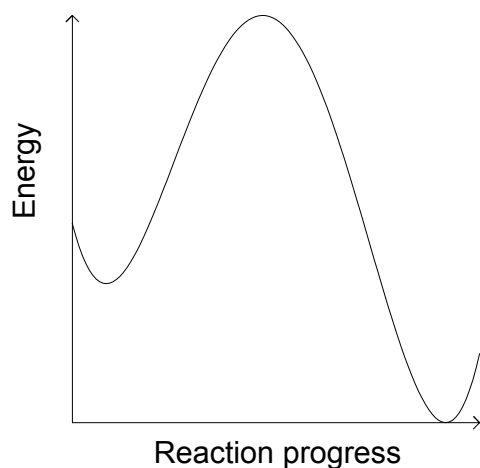


## Concerted Reactions.

Introduction: scope and some definitions

Much of the discussion in this course focuses on reactive intermediates. To the extent that transition states (the key species between the various energy minima) are considered it is largely to point to the extent that these resemble the reactive intermediates, and hence that reactivity patterns may be predicted with considerable confidence by consideration of the factors that affect the stability of the various intermediates. In the discussion which follows in this section we shall examine an important feature of single step reactions. The discussion applies to each step of any multistep process, but is perhaps seen most clearly in transformations involving only stable species (without formation of an intermediate). Such processes have been given a number of names but that which we will use is "concerted reactions". Concerted reactions are those in which the breaking of one bond is accompanied by formation of another (i.e. the breakage and formation processes are "in concert"). The energy diagram for such a process has a single maximum.



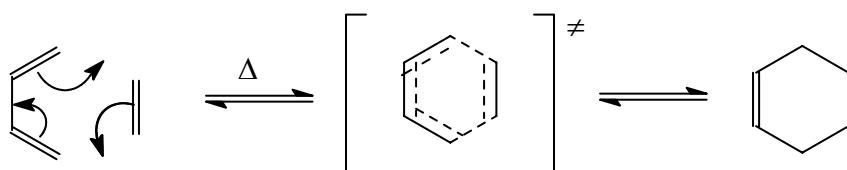
The particular category of concerted reactions that we are most concerned with here are pericyclic reactions, concerted reactions with a cyclic transition state. Of the categories of pericyclic reactions, we shall discuss in particular,

- (a) cycloaddition reactions
- (b) electrocyclic reactions
- (c) sigmatropic rearrangements

#### a) Cycloaddition

two components come together to form a ring or at least react via a cyclic TS

e.g. Diels-Alder

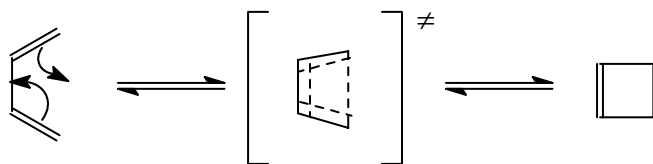


the reverse reaction may be called retro-Diels-Alder, cycloreversion, cycloelimination or retrocycloaddition

The Diels-Alder reaction involves 4 electrons on one component and 2 electrons on the other and may be referred to as a  $[4+2]$  cycloaddition or even as a  $[4\pi+2\pi]$  cycloaddition .

#### (b) Electrocyclic reaction

The formation of a single bond between the ends of a linear system of  $n$   $\pi$ -electrons, and the reverse process.



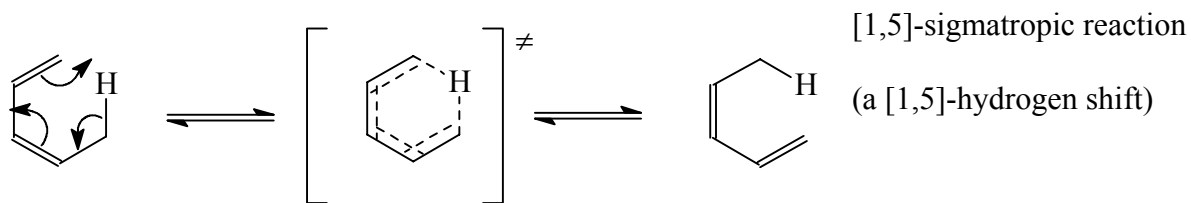
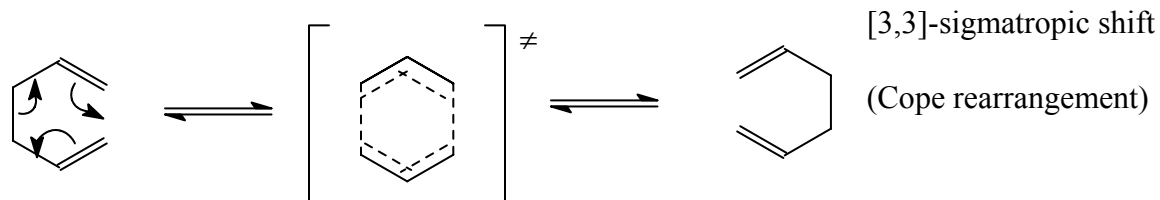


The direction of the arrows (clockwise or counterclockwise) is immaterial.

(c) Sigmatropic reaction

A cyclic migration of a  $\sigma$ -bond, more exactly and formally "a sigmatropic change of the order [i,j]" is the migration of a  $\sigma$ -bond, flanked by one or more  $\pi$ -electron systems, to a new position whose termini are  $i-1$  and  $j-1$  atoms removed from the original bonded loci, in an uncatalyzed intramolecular process."

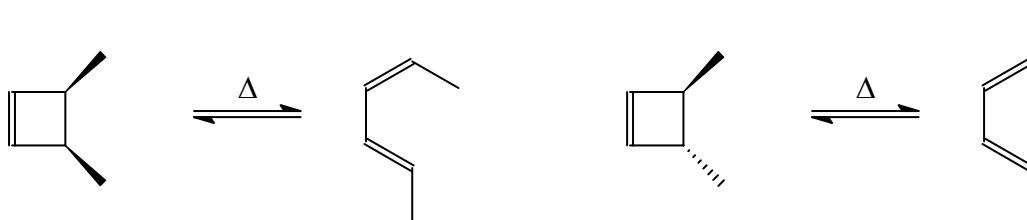
Examples.



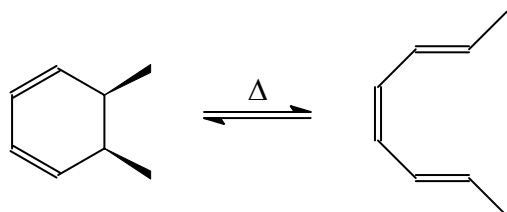
Some observations and questions arising

(a) Pericyclic reactions are commonly stereospecific

e.g.

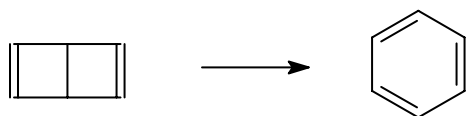


also

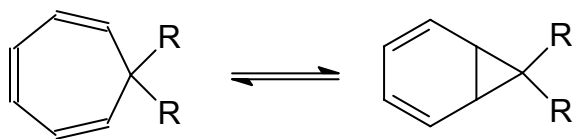


(I) Some reactions represented by cyclic arrow shifts go easily and some do not. (for reasons not immediately apparent)

"Dewar benzene"  $\Delta H \approx -60 \text{ kcal mol}^{-1}$  ( $-250 \text{ kJ mol}^{-1}$ ) but reaction is not fast at room temperature ( $t_{1/2} \approx 2 \text{ days at } 25^\circ\text{C}$ ,  $\Delta H^\ddagger = 23 \text{ kcal mol}^{-1}$  ( $96 \text{ kJ mol}^{-1}$ ))

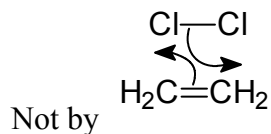
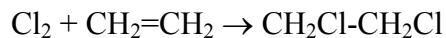


by contrast



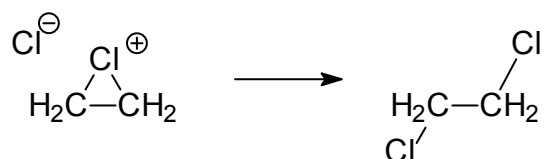
rapid at room temperature (e.g.  $\Delta H^\ddagger \approx 7 \text{ kcal mol}^{-1}$  ( $29 \text{ kJ mol}^{-1}$ ) when  $R = \text{COOCH}_3$ ); an example of "valence tautomerism".

(ii) Many reactions for which a cycloaddition is readily imagined do not take place by a concerted mechanism.

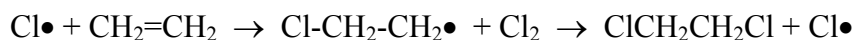


Chlorination of alkenes does not take place by a cycloaddition

Instead it occurs by either an ionic pathway:

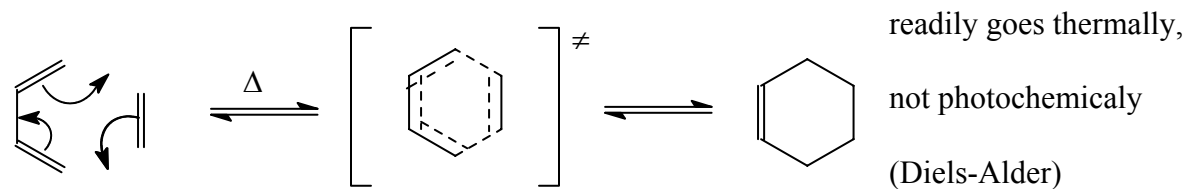
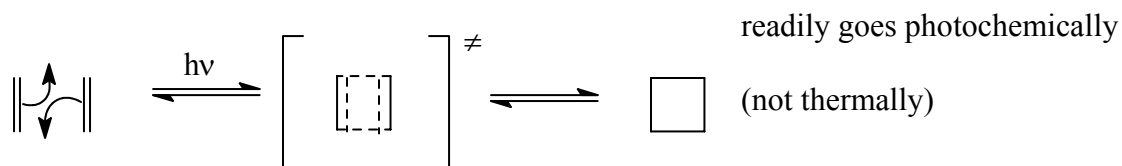


or perhaps by a radical pathway:



but not by a concerted cycloaddition

(iii) Thermal and photochemical reactions differ



- Questions:
- (i) Why the stereospecificity?
  - (ii) Why the differences in ease of reaction?
  - (iii) Why the differences between photochemical and thermal processes?

Since about 1965 a number of ways of looking at concerted reactions have been proposed. In somewhat different ways, these look at the symmetries of the reacting molecular

orbitals. Those reactions which are perceived to have 'correct' symmetries are "symmetry allowed", those which do not are "symmetry forbidden". We shall discuss three approaches to determining if a reaction is symmetry allowed or forbidden.

- (i) Frontier molecular orbital (FMO) theory (K. Fukui.)
- (ii) Woodward and Hoffmann correlation of molecular orbital symmetries (R.B. Woodward and R. Hoffmann),
- (iii) Hückel-Möbius aromatic transition state picture (M.J.S. Dewar, H.E. Zimmerman).

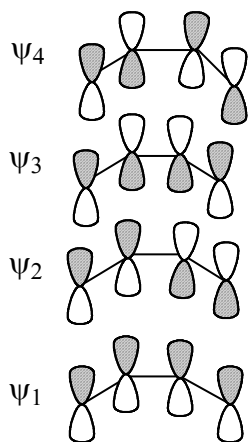
(Note that these approaches are only used for concerted processes)

Before we get started it will be helpful to review the nature of the  $\pi$ -molecular orbitals for conjugated systems.

FOR CONJUGATED POLYENES:

Combine n A.O.'s to get n M.O.'s

we draw M.O.'s as individual p lobes for convenience.



filling orbitals

lowest MO has 1 nodal plane

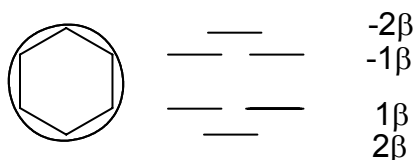
each higher energy has 1 extra nodal plane

try  $n = 3, 5, 6, 7, 8$  (nodes & orbitals)

ODD ones have nodes where orbitals should be (occasionally!)

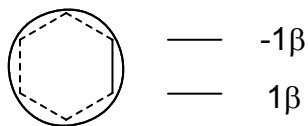
For cyclic polyenes there is a convenient mnemonic for the pattern of MO energies.

A convenient mnemonic for the orbitals (not really a practical calculation) is the circle method. Draw a circle with radius  $2\beta$ . ( $\beta$  is the “bond integral” from a quantum mechanical treatment of  $\pi$  systems; it is a negative quantity.) For monocyclic hydrocarbons, inscribe in the circle the polygon corresponding to the hydrocarbon, with one corner touching the lowest point in the circle. The molecular orbital energy levels correspond to the heights of the corners of the polygon.



To construct a drawing accurately enough to read off the energies is generally more work than to solve the determinant, but it is a good way to remember the qualitative order.

The same method can be used for linear polyenes: for a polyene of  $m$  carbons, inscribe a polygon with  $2m+2$  corners, and take the end of the polyene as one up from the bottom. Thus for ethene we use the same diagram as for benzene, but reinterpret it.

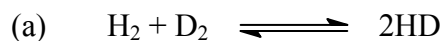


Cycloaddition reactions, for which the most natural seeming approach is that of:

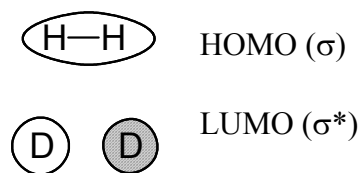
*FMO Theory*

Basic assumption: in a concerted bimolecular process there is a flow of electrons from the highest-energy occupied MO (HOMO) of one molecule to the lowest-energy unoccupied MO (LUMO) of the other. Rule: If the HOMO-LUMO interaction involves overlap of orbitals of the same symmetry (i.e. net bonding overlap) the reaction is symmetry- allowed and may proceed by a concerted. pathway. If the orbitals are of different symmetry the reaction is symmetry-forbidden, i.e. there is a high activation barrier, making the concerted pathway unfavorable.

Some simple cycloadditions provide illustration.

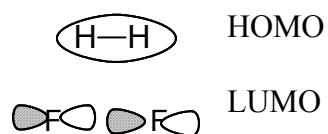
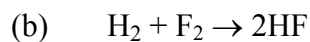
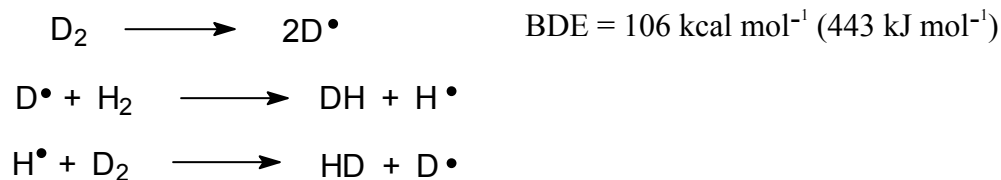


In FMO terms



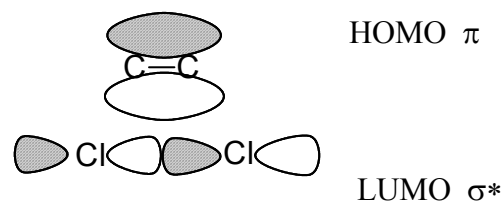
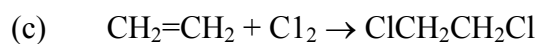
(There is a similar picture if one considers the HOMO of  $\text{D}_2$  and the LUMO of  $\text{H}_2$ .) The HOMO and LUMO have different symmetries (symmetric and anti-symmetric) and the net overlap is zero. Reaction is forbidden. According to ab initio calculations the activation energy for the "forbidden" reaction is  $123 \text{ kcal mol}^{-1}$  ( $514 \text{ kJ mol}^{-1}$ ). other mechanisms have lower energies, e.g.



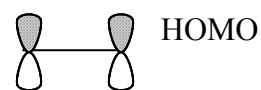
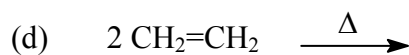


Total overlap = 0  $\therefore$  forbidden

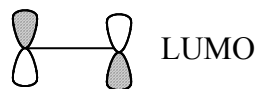
Note: HOMO of  $\text{H}_2$  and LUMO of  $\text{F}_2$  were chosen because the electrons would be expected to migrate toward the more electronegative species ( $\text{F}_2$ ) (For many years the reaction  $\text{H}_2 + \text{I}_2 \rightarrow 2\text{HI}$  was regarded as a four-center bimolecular process; this was shown to be incorrect in 1967).



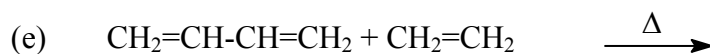
zero overlap,  $\therefore$  forbidden



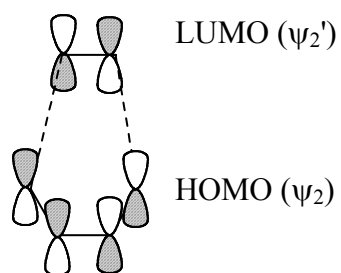
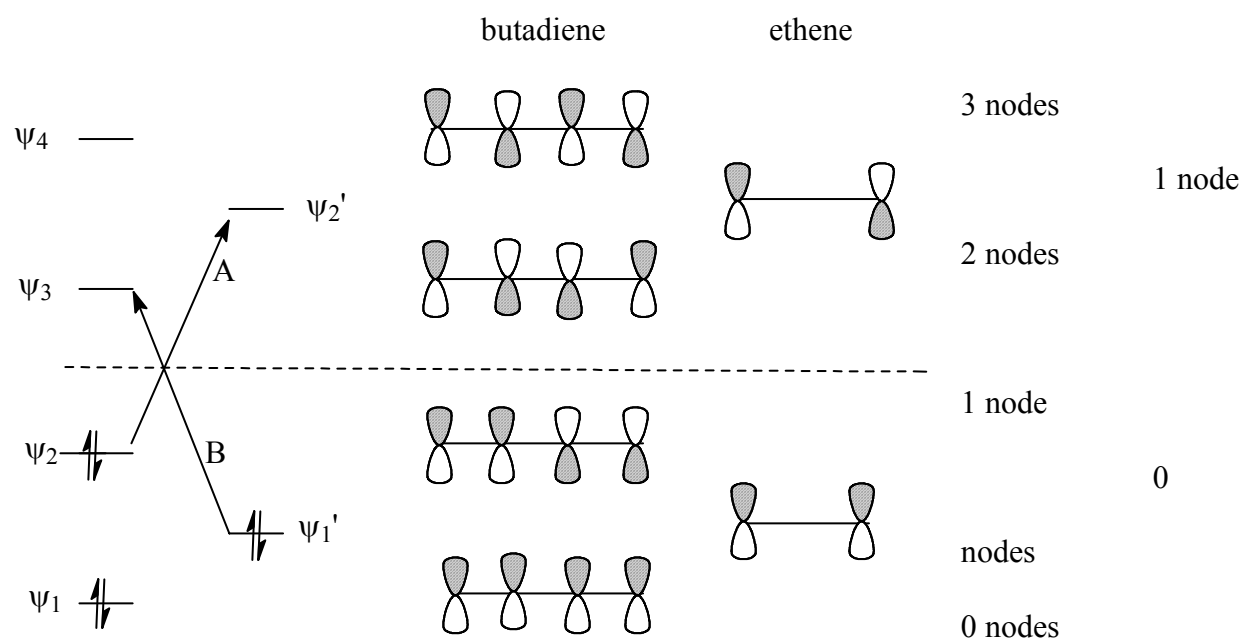
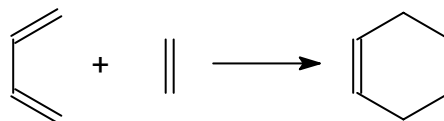
zero overlap,  $\therefore$  forbidden



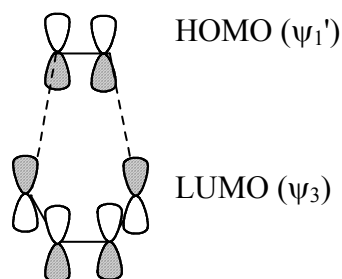
But contrast the next example



(Diels-Alder)

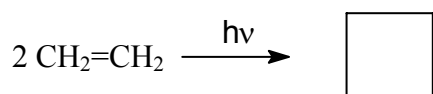
Bonding overlap  $\therefore$  allowed.

or alternatively



also bonding overlap  $\therefore$  allowed

contrast this with the photochemical reaction of two ethylenes:

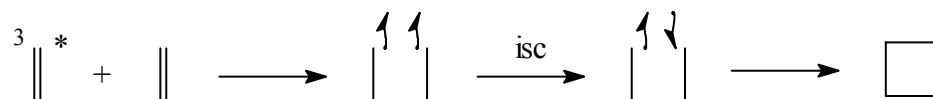


Positive overlap



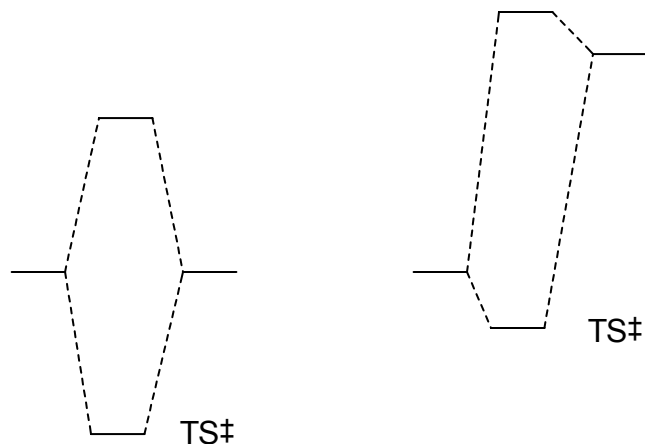
LUMO (for ground state ethylene, as before)

(this analysis applies to a singlet excited state: the triplet excited state can not react by a concerted mechanism: it must react by another stepwise mechanism:



FMO theory: for a reaction to be allowed requires:

- 1) The above examples emphasize the need for HOMO and LUMO to have the appropriate symmetry for positive overlap. This a necessary but not sufficient condition for a reaction to be allowed by FMO theory.
- 2) A further point: the energies of the interacting MO's must be reasonably close.



Strong splitting of levels

low TS<sup>‡</sup> energy

Weak splitting of levels

relatively high TS<sup>‡</sup> energy

3) In addition, there is the usual requirement that the overlap of the MO's (HOMO and LUMO) must be good.

#### Suprafacial and antarafacial cycloaddition

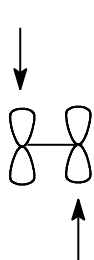
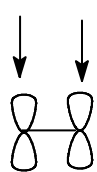
In example (d) it was shown that the cycloaddition of two ethylene molecules was forbidden if attempted in the way shown. Careful inspection, however, reveals the possibility of another mode of cycloaddition, in this case with positive overlap. Such a cycloaddition is therefore symmetry-allowed, though because of poor overlap (steric strain) would be expected to have high energy. In example (d) the proposed addition would have formation of the new bonds on the same side of the reference plane (i.e. the nodal plane) of each ethylene molecule. Such an addition is referred to as suprafacial (with respect to each ethylene), and may be called a [2s + 2s] cycloaddition (where the "s" stands for suprafacial), or, more fully, since the electrons are all  $\pi$ -electrons, [ $\pi 2s + \pi 2s$ ]. The other, symmetry-allowed, mode of addition involves formation of

the new bonds on opposite sides of one ethylene. Such a mode is called antarafacial. The reaction may therefore be described as a  $[\pi 2s + \pi 2a]$  cycloaddition.

Geometrical considerations: Suprafacial vs. Antarafacial addition

Suprafacial: for a  $\pi$ -system suprafacial bonding occurs if overlap of two lobes occurs on the same side of a nodal plane.

Antarafacial: overlap of two lobes on the opposite side of a nodal plane



these terms also apply to  $\sigma$ -bonds and single  $\pi$ -orbitals

Suprafacial

Antarafacial

Previously showed



LUMO

zero overlap, forbidden



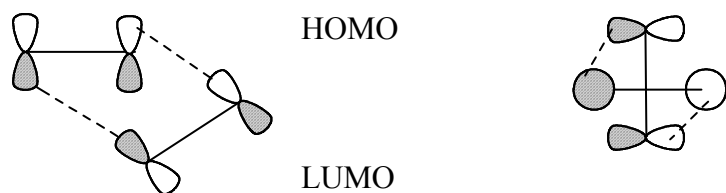
HOMO

Each ethylene has  $2\pi$  electrons. The suprafacial addition for each molecule can be symbolized:

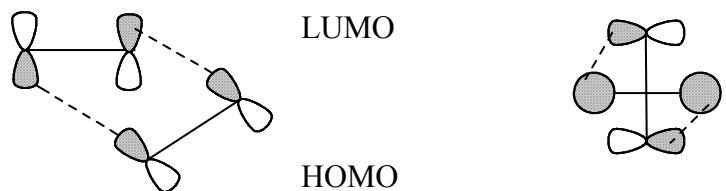
$2\pi s$

One way of describing the above situation is to say the  $[2\pi s 2\pi s]$  cycloaddition is forbidden.

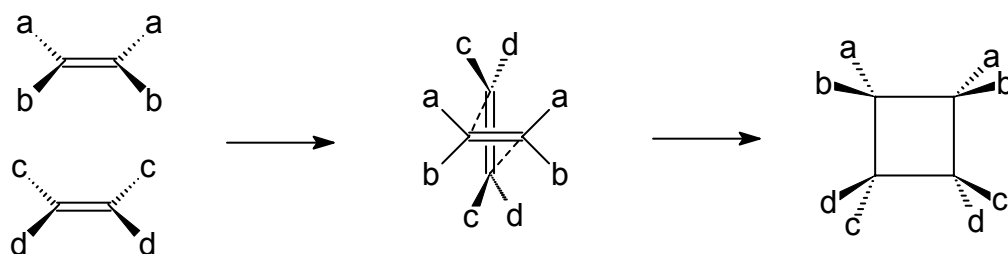
There is an alternative mode of addition: suprafacial for one ethylene and antarafacial for the other. This actually occurs for some systems and can be imagined for ethylene dimerization.



or



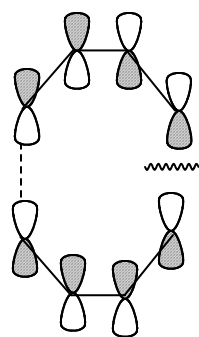
Note: addition is antarafacial to the LUMO ethylene, and the substituents initially cis in the LUMO become trans.



(along with the enantiomer)

This can happen if the crowding can be lessened.  $\text{CH}_2=\text{CH}_2$  plus  $\text{CH}_2=\text{CH}_2$  doesn't work, but  $\text{CH}_2=\text{CH}_2$  plus  $\text{CH}_2=\text{C}=\text{O}$  does.

## Examples

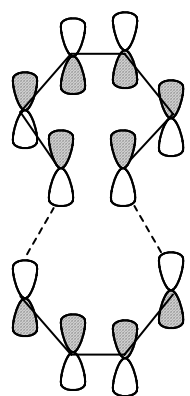
 $(\pi 4s + \pi 4s]$ 

HOMO

No net overlap  $\therefore$  forbidden

LUMO

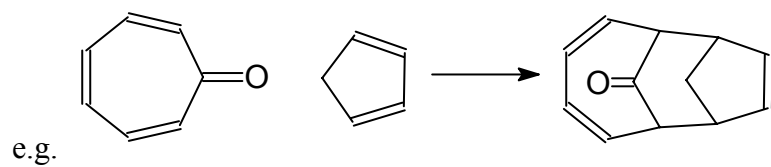
(no examples known)

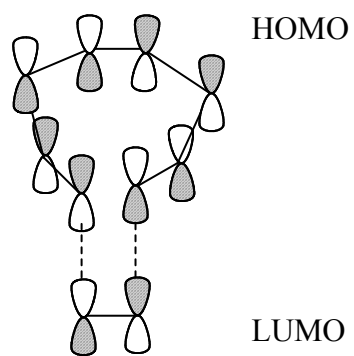
 $[\pi 6s + \pi 4s]$ 

HOMO

+ ve overlap  $\therefore$  allowed

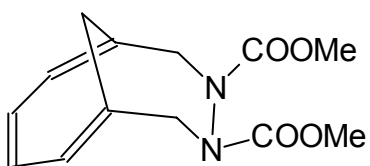
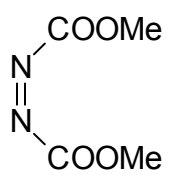
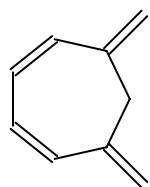
LUMO

 $(\pi 8s + \pi 2s]$

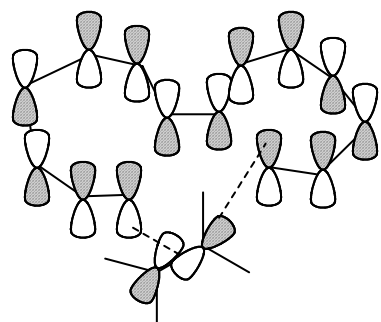


+ve overlap  $\therefore$  allowed

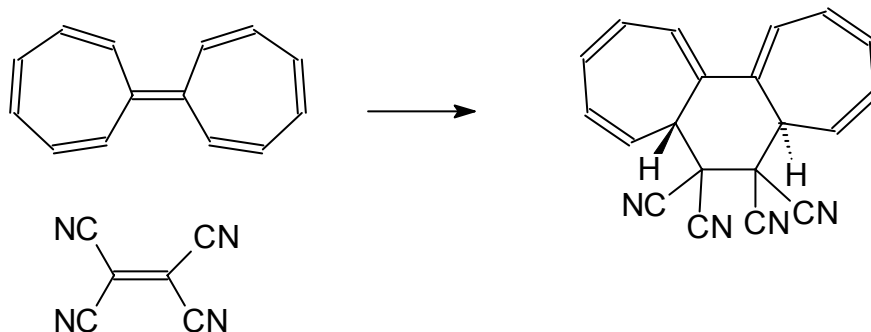
e.g.



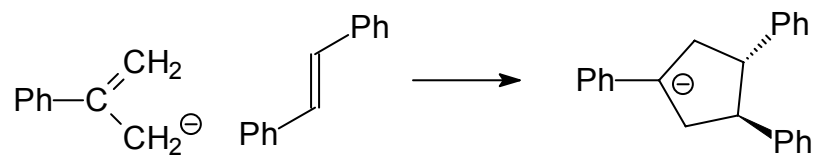
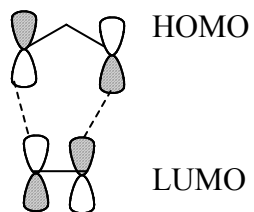


$[\pi 14a + \pi 2s]$ 


HOMO

+ve, overlap  $\therefore$  allowed

Orbital symmetry restrictions apply to ionic species as well.

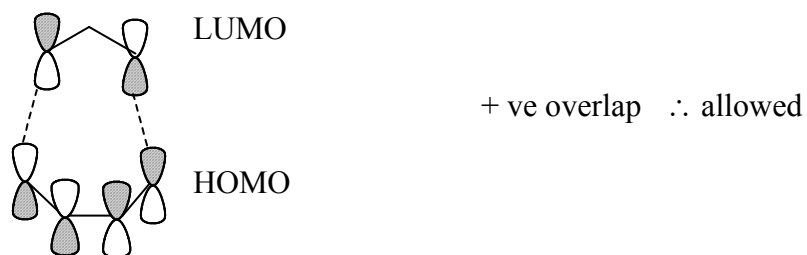
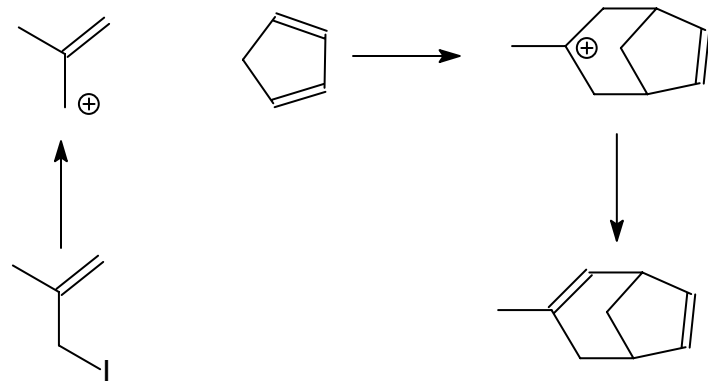

 $(\pi 4s + \pi 2s)$ 


HOMO

+ ve overlap  $\therefore$  allowed

LUMO

(Note: Use HOMO of the anion and LUMO of the alkene. Why?)



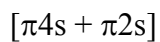
#### 4. Woodward-Hoffmann Pericyclic Rule

##### **General Woodward-Hoffmann rule for pericyclic reactions:**

A ground-state pericyclic change is symmetry allowed when the total number of  $(4q+2)s$  and  $(4r)a$  components is odd.

In this statement  $q$  and  $r$  refer to integers (0,1,2...etc.)

Illustration:



$\pi 2s$  is a  $(4q+2)s$  component in which  $q = 0$ ,

$\pi 4s$  is neither a  $(4q+2)s$  component nor a  $(4r)a$  component and is therefore ignored.

$$\Sigma[(4q+2)s + (4r)a] \text{ components} = 1 + 0 = 1 \text{ (odd)}$$

∴ the reaction is allowed.

Note: There is more than one applicable way of designating a reaction, but this does not affect the application of the rule. E.g. the Diels-Alder reaction can also be analyzed as

a  $(\pi 2s + \pi 2s + \pi 2s)$  or a  $[\pi 2s + \pi 2a + \pi 2a]$  cycloaddition

- or even a  $(\omega 0s + \omega 2s + \omega 0a + \omega 2a + \omega 0s + \omega 2s)$  process\* (where  $\omega$  refers to single orbitals)!

The rule predicts that each of these processes is allowed.

\* Woodward and Hoffmann cite this particular possibility "partly in a sportive spirit" (Angew. Chem. Int. Ed. Engl., 8, 781-853, esp. p. 850).

Pericyclic rule protocol:

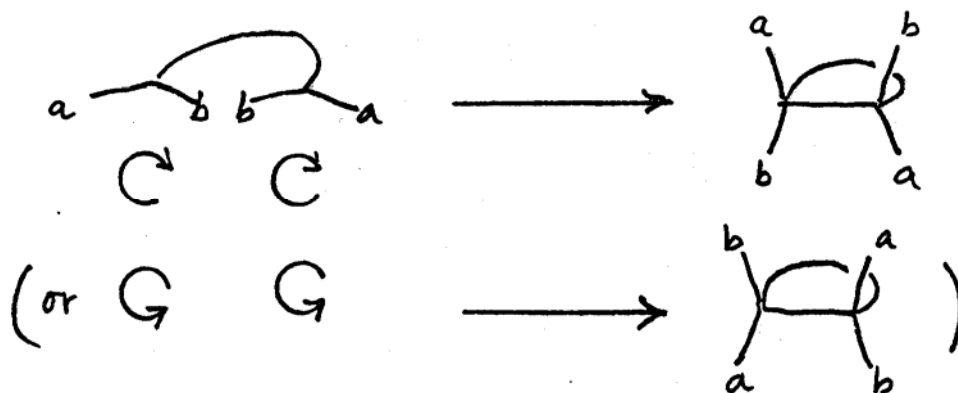
- (1) Draw the orbitals (without + or - signs).
- (2) Take each "largest unit" (for simplicity) and determine
  - (a) whether the attachment being made to this unit is a or s,
  - (b) if a then whether  $(4r)a$  or  $(4r+2)a$ , and if s whether  $(4r+2)s$  or  $(4r)s$ .
- (3) Sum the number of  $(4r)a$  and  $(4r+2)s$  sets (ignore the  $(4r)s$  and  $(4r+2)a$  sets).
- (4) If the sum is odd the reaction is allowed, if the sum is even the reaction is forbidden.

For cycloaddition reactions the FMO picture is particularly convenient; now we turn to electrocyclic reactions where another picture is more convenient.

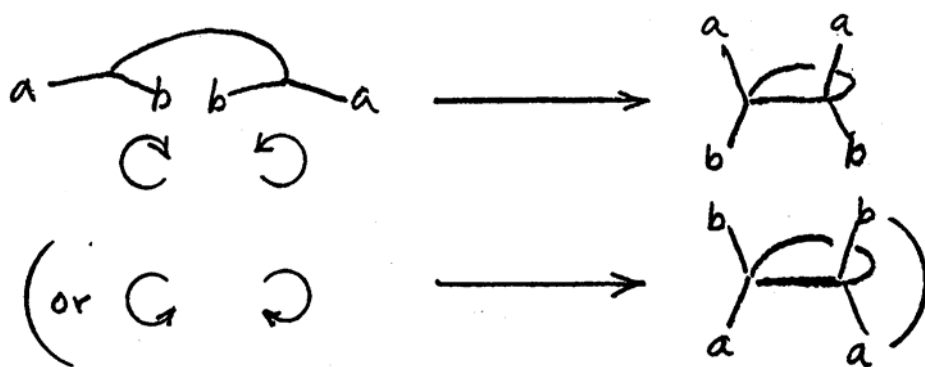
## 5. Orbital Correlation Diagrams and Electrocyclic Reactions

As noted in the examples of p. 96, electrocyclic reactions are stereospecific. In discussing this topic it is helpful to define two forms of ring-closure (or opening):

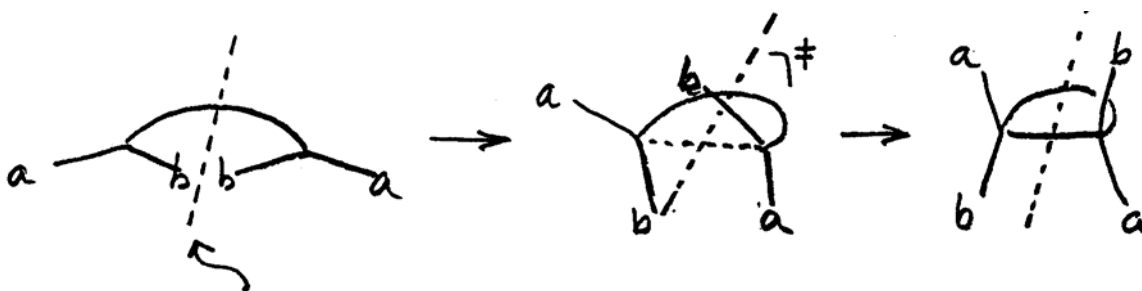
Conrotatory:



Disrotatory:

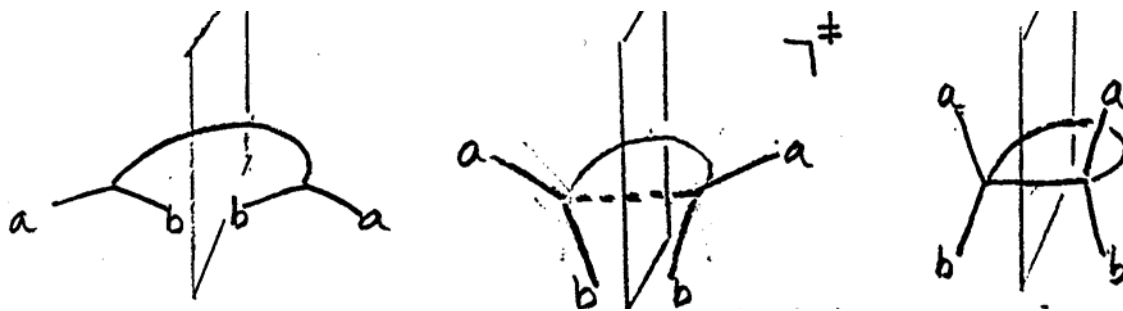


Note that in the conrotatory mode



a two-fold axis of symmetry ( $C_2$ -axis) is conserved.

In the disrotatory mode

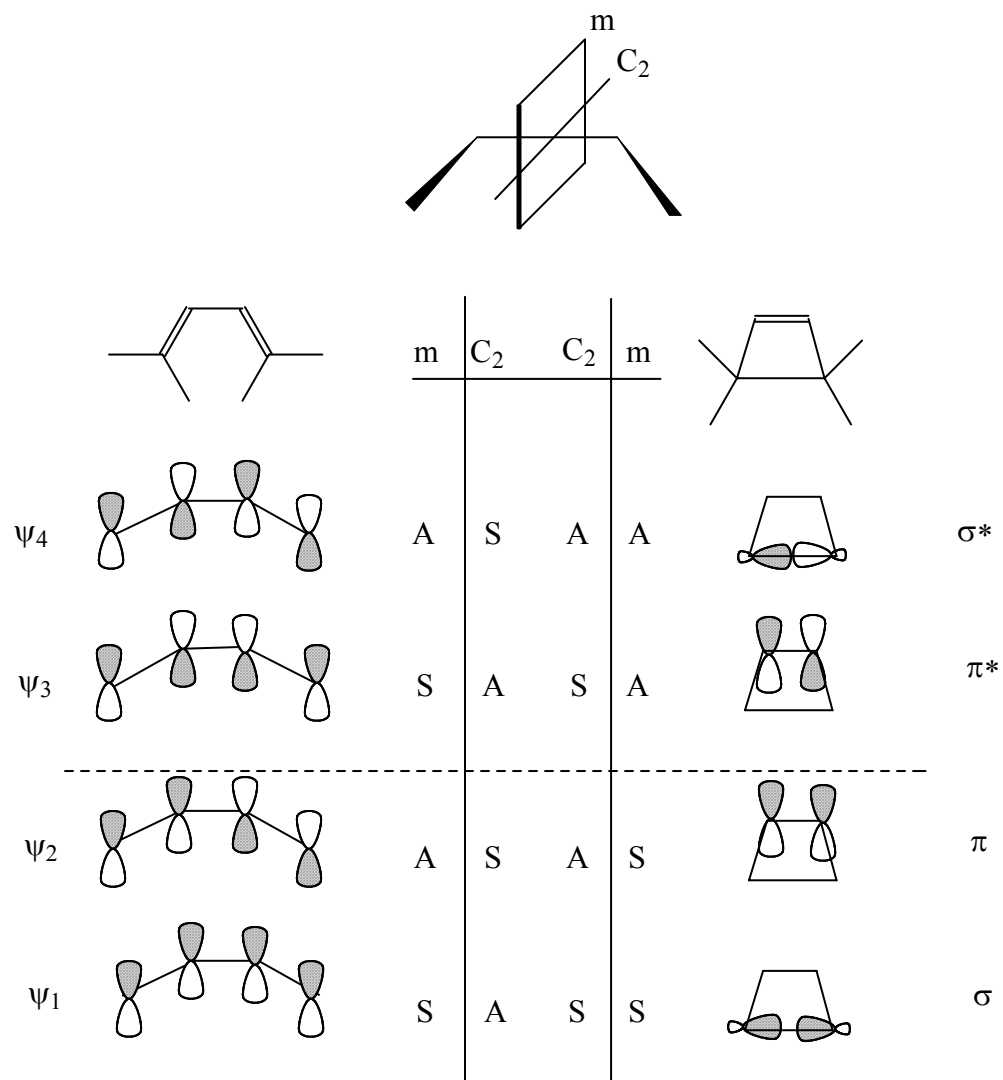


a plane of symmetry ( $\sigma$ -plane,  $C_s$ -symmetry) is conserved.

The key principle for using correlation diagrams is that orbital symmetry is conserved in concerted reactions. Hence an orbital in the starting material which is symmetric with respect to a particular symmetry operation (e.g. rotation around an axis of symmetry) must correlate with an orbital in the product which is symmetric with respect to the same axis, and an orbital which is anti-symmetric in the starting material must correlate with an orbital in the product which is also anti-symmetric with respect to that symmetry operation.

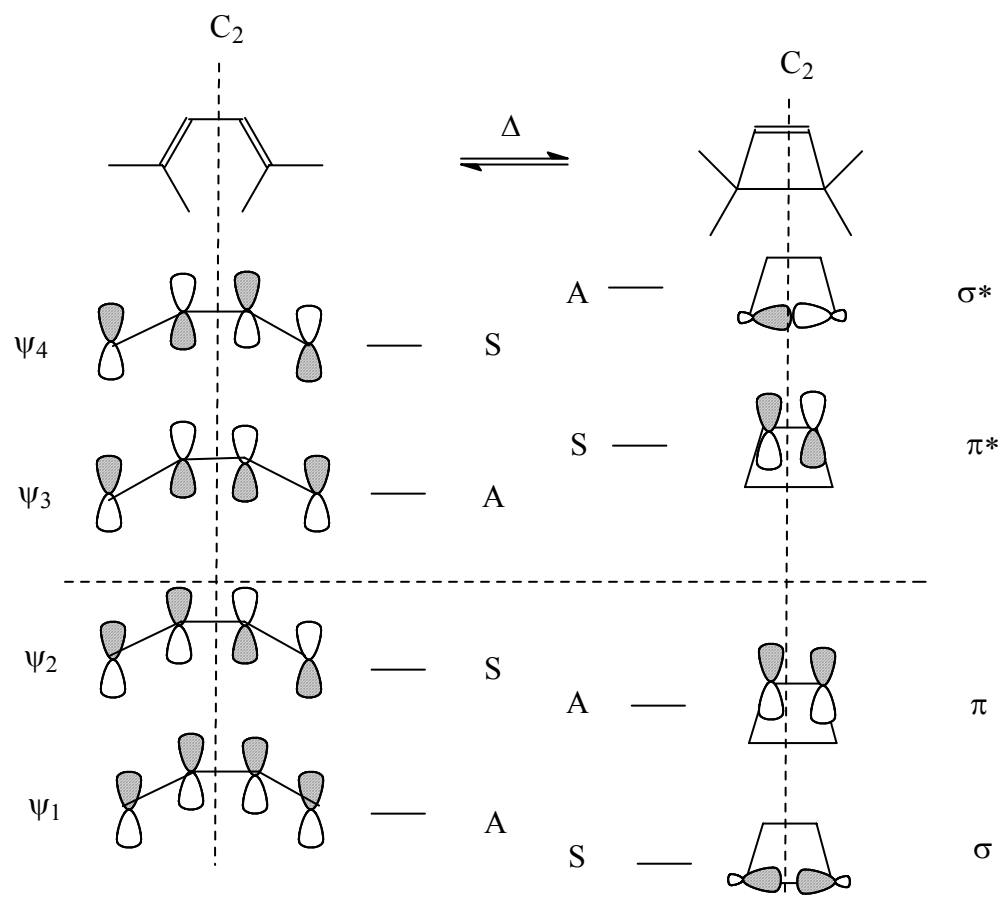
Consider the cyclobutene - butadiene transformation: On the next page we examine the symmetry properties of each reacting orbital to determine whether it is symmetric (S) or anti-symmetric (A) with respect to both the  $C_2$ -axis (conrotatory opening) and the plane of symmetry (disrotatory opening).

## Symmetry properties of the relevant orbitals

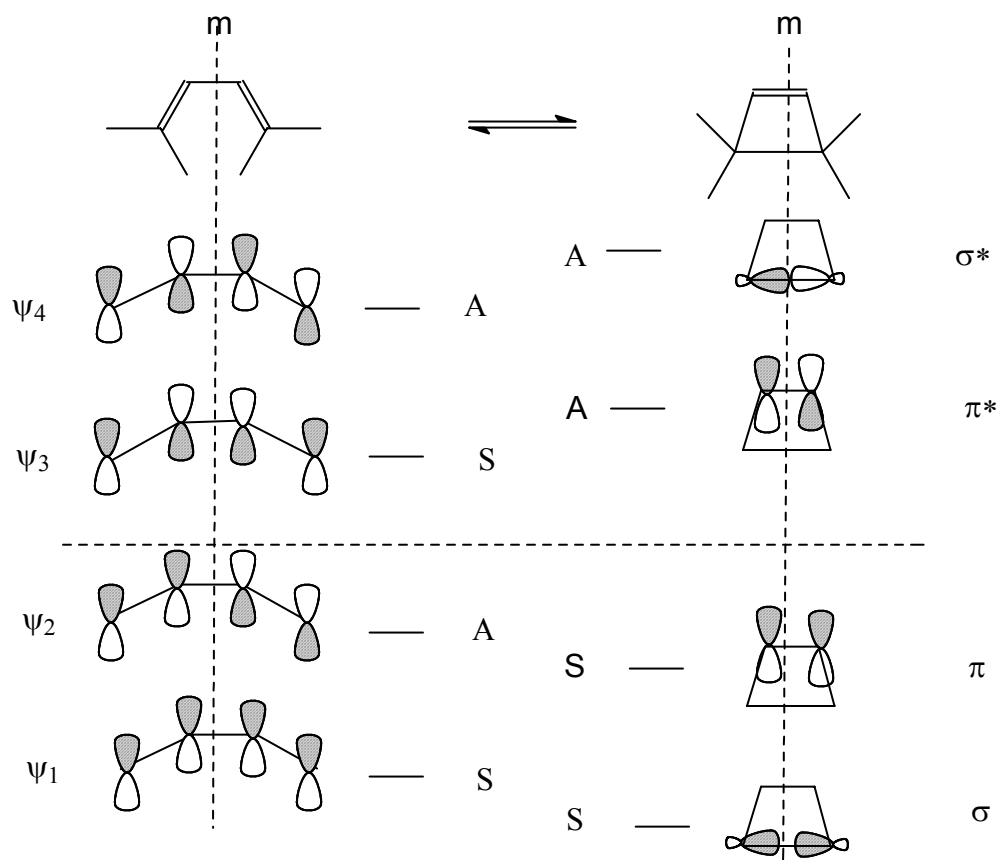


Arrange orbitals in increasing energy and correlate those of the same symmetry:

Conrotatory reaction -  $C_2$  symmetry (axis) conserved.



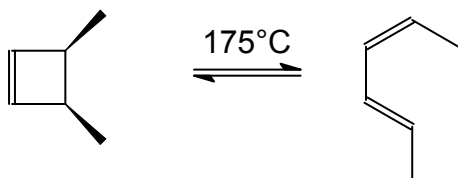
Disrotatory reaction - Cs symmetry (plane) conserved



Note that in the conrotatory reaction the two occupied orbitals of the starting material correlate with the two occupied orbitals of the product, but that this is not so for the disrotatory process.

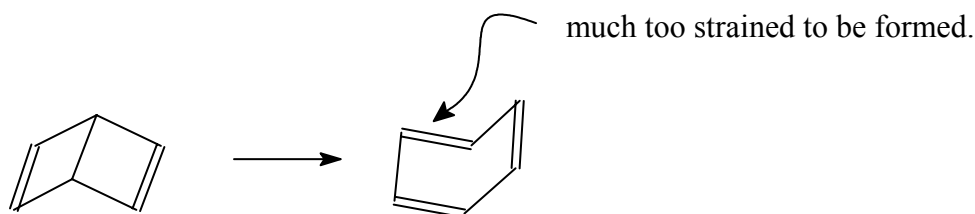
Predict: conrotatory allowed  
disrotatory forbidden.

This is in full accord with the examples of p.79.



and also with the stability of "Dewar benzene". Conrotatory opening would give the product with a trans double bond:





One may further readily predict that for the *photochemical* reaction the disrotatory process is the allowed pathway.

By extension one may readily show that the thermally-allowed process in the hexatriene-cyclohexadiene transformation is disrotatory (while the photochemical reaction is conrotatory).

We may summarize the Woodward-Hoffmann rules for electrocyclic reactions as follows.

Number of $\pi$ electrons	Reaction	Motion
$4n$	thermal	conrotatory
$4n$	photochemical	disrotatory
$4n + 2$	thermal	disrotatory
$4n + 2$	photochemical	conrotatory

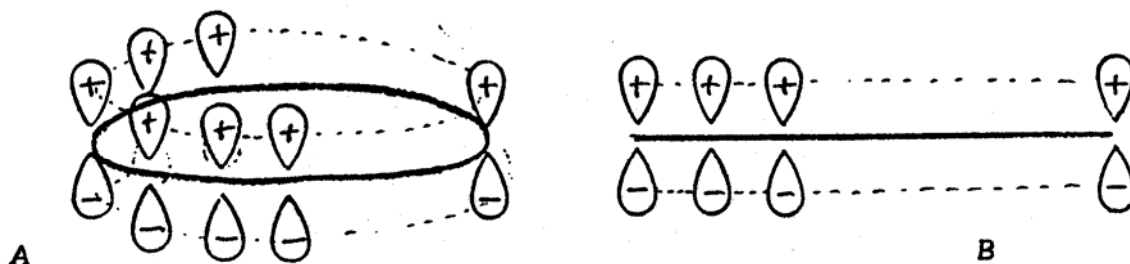
where  $n = 1, 2, 3$

Note: The generalized Woodward-Hoffmann rule for pericyclic reactions also covers electrocyclic reactions. When one recognizes that "conrotatory" is the electrocyclic equivalent of "antarafacial", the above summary and the rule for pericyclic reactions may be seen to concur.

A third way of thinking about concerted reactions is the Hückel-Möbius picture. This can be used for any concerted reaction but is particularly good for sigmatropic reactions.

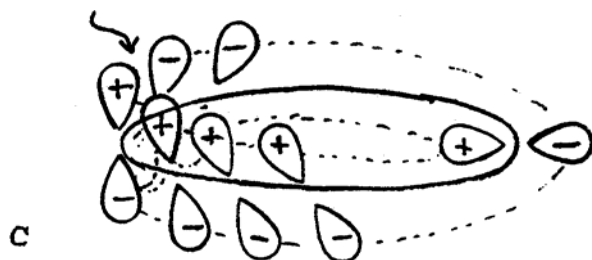
Hückel-Möbius Aromatic Transition State Picture.

It has already been noted that a cyclic array of  $\pi$ -electrons arranged as in A may be either more or less stable than the corresponding linear array (B). Specifically for the (above) Hückel MO picture:



$(4n+2)$ $\pi$ -electrons stabilized (aromatic) $4n$ $\pi$ -electrons destabilized (anti-aromatic)
---

It has been pointed out by Heilbronner (1964) that there could conceivably be another arrangement of a cyclic array of  $\pi$ -electrons and that this would lead to a different pattern of stability. The conversion of B to A may be thought of as arising by joining the ends in B so that a positive lobe on one end overlaps with the positive lobe of the other. If, however, the linear array in B is given a twist and then joined at the ends, one obtains a cyclic array with a phase reversal, i.e. a positive lobe next to a negative lobe, as in C.

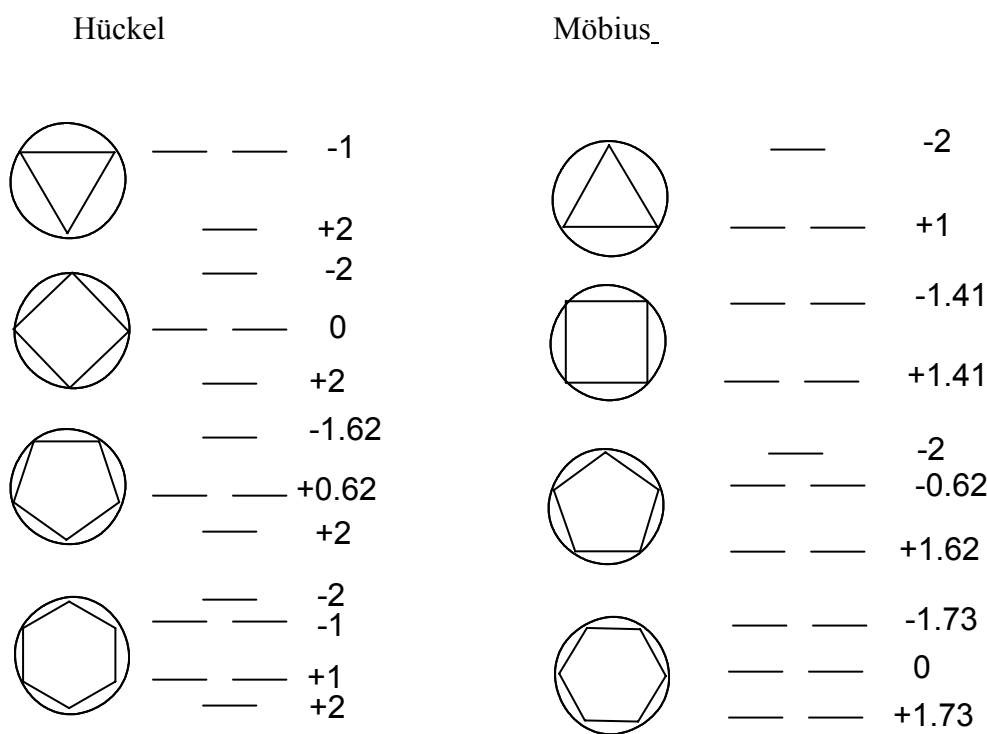


Such an array corresponds to the well-known Möbius strip (which is characterized by having only one continuous surface and one continuous edge, as opposed to the two surfaces and two

edges readily discerned in A). Heilbronner further noted that in the Möbius array (C) that the following pattern held:

$4n$   $\pi$ -electrons stabilized (aromatic)  
 $(4n+2)$   $\pi$ -electrons destabilized (anti-aromatic)

As Zimmerman observed, the Frost-Musulin mnemonic can be extended:

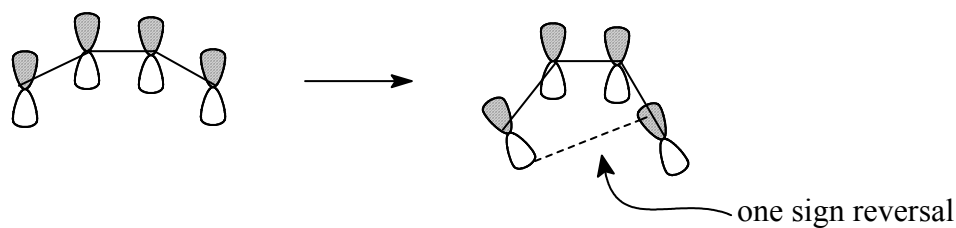


A "Hückel" array is defined as one with an even number (e.g. 0,2,4...) of sign reversals.

A Möbius (or anti-Hückel) array is defined as one with an *odd* number (1,3,5... ) of sign reversals. To obtain the Hückel orbital energies the polygon is inscribed point-down in the circle, whereas with the Möbius system the polygon is side-down (as above).

Although the application of the Möbius picture to ground-state molecules is, at most, limited, it would appear to be a useful concept for looking at transition states, as was pointed out

initially by M.G. Evans in 1939, and subsequently (and independently) by H.E. Zimmerman and M.J.S. Dewar in 1966 E.g.

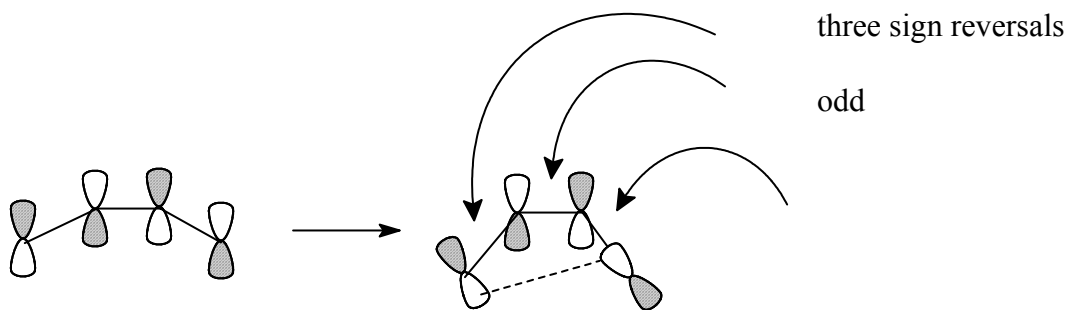
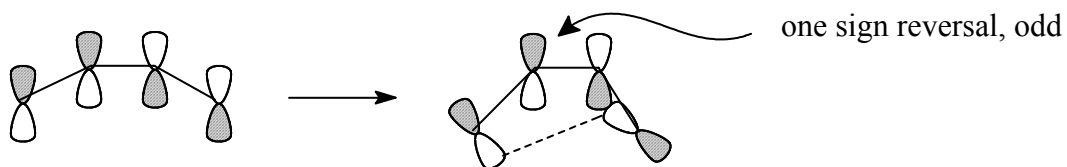


conrotatory closure as above shows one sign reversal and may therefore be described as a Möbius array. With  $4\pi$ -electrons such a system is therefore aromatic.

By including Möbius systems in the definition of aromatic compounds, the rule for thermal pericyclic reactions may be stated simply as follows:

Thermal pericyclic reactions take place  
via aromatic transition states.

Note that in the above example the original choice of orbital signs is immaterial



An odd number of sign reversals signifies a Möbius array - which, with 4 electrons, is aromatic.

## Protocol for using the Hückel-Möbius aromatic transition state

rule:

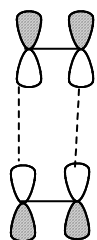
1. Draw the transition state as a series of: overlapping s and p orbitals.
2. Assign phases (+ve and -ve) to the orbitals such that the number of sign changes is minimal (for convenience, only).
3. Count the number of phase inversions between different orbitals.
4. Count the number of electrons involved.
5. Classify the transition state as being of the Hückel type (even number of sign inversions) or Möbius type (odd number of sign inversions). The reaction is aromatic and therefore *allowed* with  $(4n+2)$  electrons in a Hückel array or  $4n$  electrons in a Möbius system.

	Hückel	Möbius
$4n$	anti-aromatic	aromatic
	forbidden	allowed
$4n + 2$	aromatic	anti-aromatic
	allowed	forbidden

Note that this rule is concerned with sign inversions between different orbitals and therefore specifically excludes the sign inversion that necessarily occurs when both lobes of a p-orbital are involved (see the butadiene closures above).

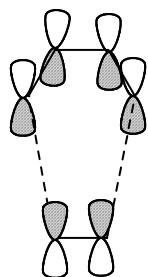
Examples:

[ $\pi 2s + \pi 2s$ ] cycloaddition



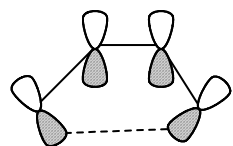
0 sign inversions  
 $\therefore$  Hückel  
 4 electrons  $\therefore$  anti-aromatic  
 $\therefore$  forbidden

$[\pi 4s + \pi 2s]$  cycloaddition



0 sign inversions  
 $\therefore$  Hückel  
 6 electrons  $\therefore$  aromatic  
 $\therefore$  allowed

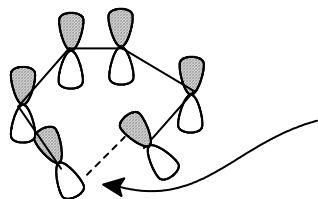
Disrotatory butadiene cyclization



0 sign inversions  
 $\therefore$  Hückel  
 4 electrons  $\therefore$  anti-aromatic  
 $\therefore$  forbidden

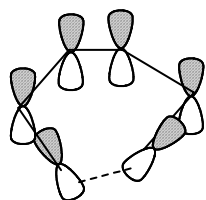
Hexatriene ring closure

(i) Conrotatory



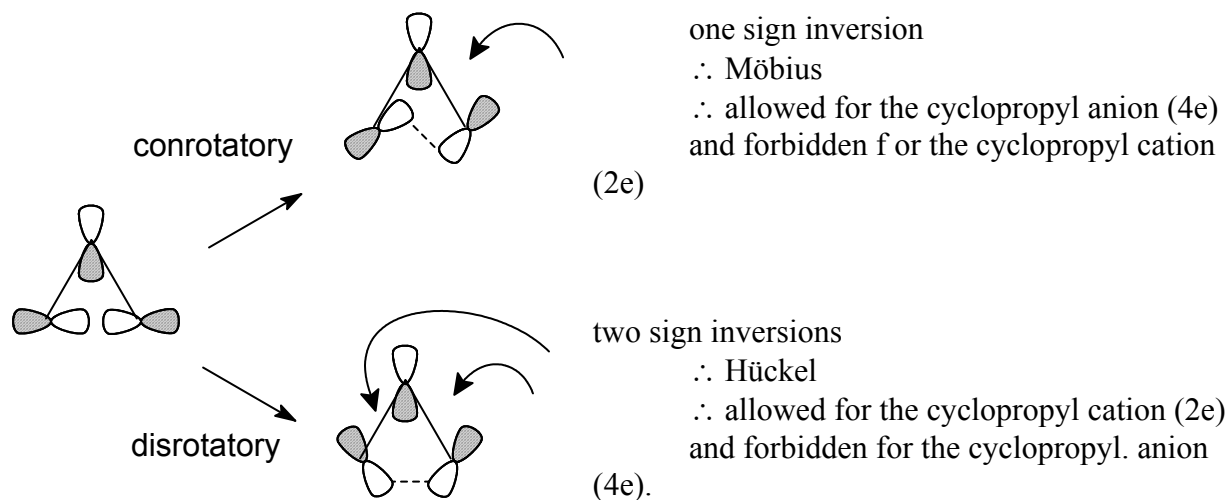
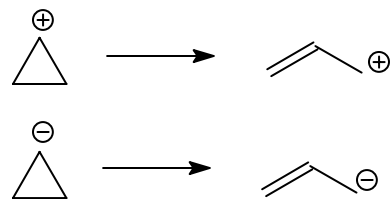
1 sign inversion  
 $\therefore$  Möbius  
 6 electrons  $\therefore$  anti-aromatic  
 $\therefore$  forbidden

(ii) Disrotatory



0 sign inversions  
 $\therefore$  Hückel  
 6 electrons  $\therefore$  aromatic  
 $\therefore$  allowed

Electrocyclic reactions of cyclopropyl ions

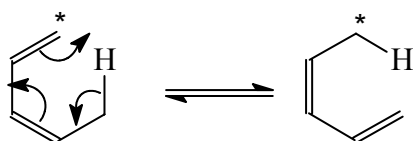


In practice reactions of cyclopropyl compounds that are expected to proceed via the cyclopropyl cation (e.g. halides, tosylates), give the products of disrotatory ring opening, but the reaction is also influenced by the stereochemistry of the leaving group, indicating the reaction to be more complex than a simple formation and electrocyclic opening of the cyclopropyl cation.

## 7. Sigmatropic Rearrangements

cyclic migrations of a  $\sigma$ -bond.

E.g. 1,5 H-shift

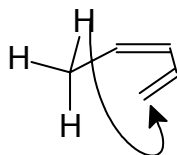
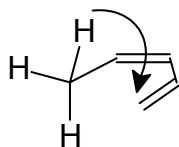


a [1,5] sigmatropic rearrangement

Can (in principle) be

*Suprafacial*

or

*antarafacial*

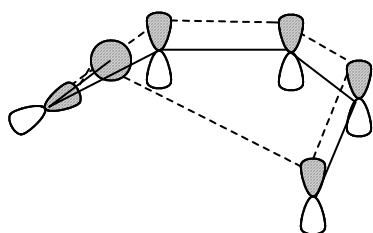
plane of symmetry

C<sub>2</sub>-axis

in transition state

in transition state

Applying the Hückel-Möbius aromaticity rule



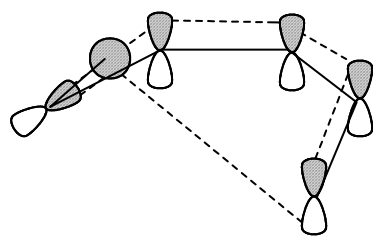
suprafacial mode.

no sign inversions

∴ Hückel

6 electrons ∴ aromatic

∴ allowed



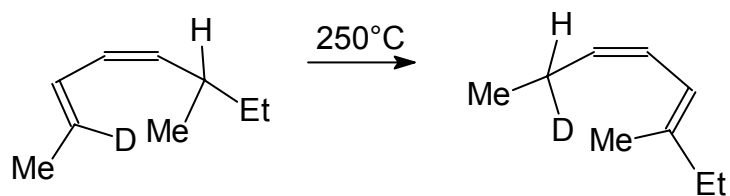
antarafacial mode

1 sign inversion

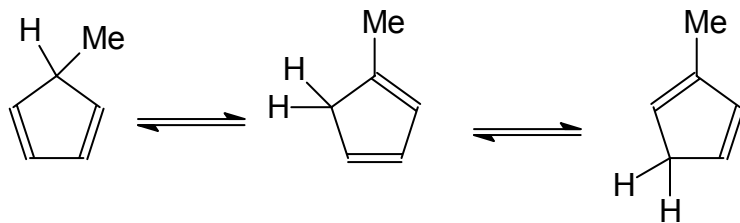
∴ Möbius

6 electrons ∴ anti-aromatic

∴ forbidden



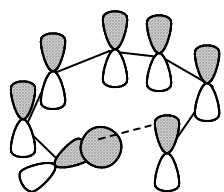




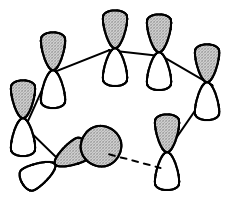
The second process occurs even at room temperature.

[1,7] Sigmatropic rearrangement

e.g. (1,7) H-shift

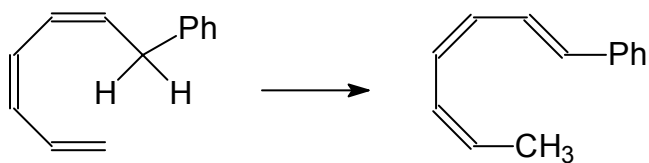


suprafacial  
no sign inversion  
∴ Hückel  
8 electrons ∴ anti-aromatic  
∴ forbidden

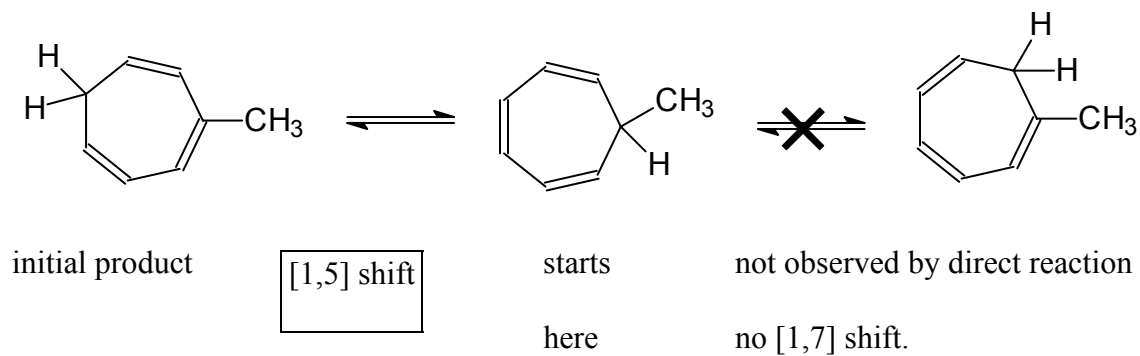


antarafacial  
one sign inversion  
∴ Möbius  
8 electrons ∴ aromatic  
∴ allowed

Experimentally:

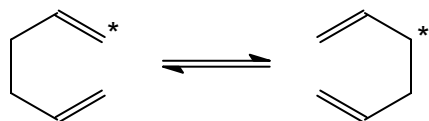


correct product for a [1,7] shift, but this does not prove the stereochemistry.

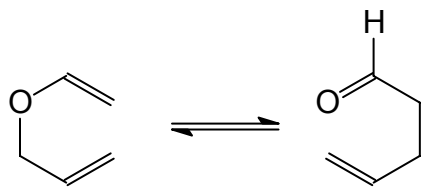


An antarafacial [1,7] shift would be excessively strained in such a cyclic system, whereas a suprafacial shift would be sterically easy - if allowed. Both observations are consistent with a 1,7 shift being obligatorily antarafacial.

[3,3] Sigmatropic rearrangement

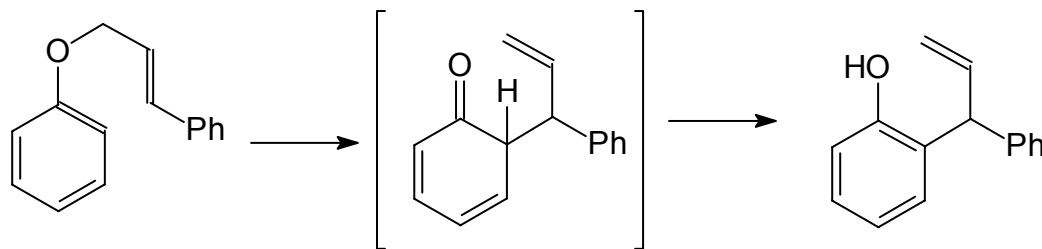


Cope rearrangement

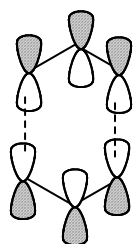


Claisen rearrangement

also



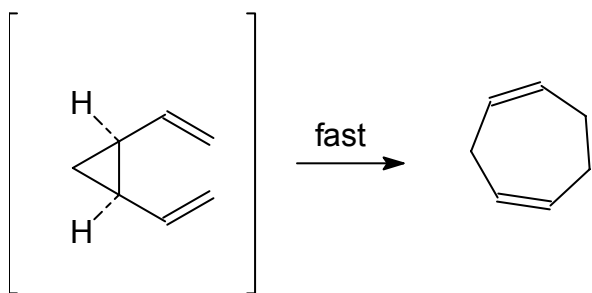
(Claisen)



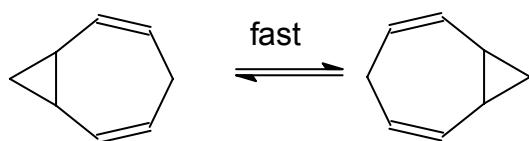
0 sign inversions  
 $\therefore$  Hückel  
 6 electrons  $\therefore$  aromatic  
 $\therefore$  allowed

supra-supra i.e. suprafacial with respect to both components.

Further examples:

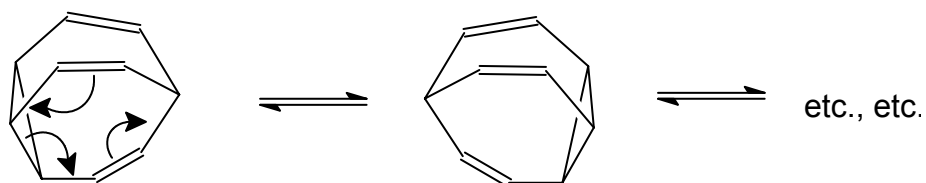


not isolated



( $k = 1 \text{ s}^{-1}$  at  $-50^\circ\text{C}$ , from nmr)

Bullvalene



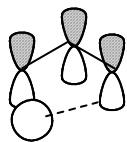
all carbons become equivalent!

(If the ten carbons were individually labeled there would be  $10!/3 = 1,209,600$  combinations!)

$^1\text{Hmr}$  shows one line at  $100^\circ\text{C}$ .

## [1,3] Sigmatropic rearrangements

e.g. [1,3] H-Shift

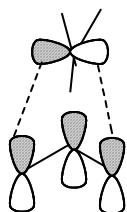


Suprafacial mode:  
 0 sign inversions  
 $\therefore$  Hückel  
 4 electrons  $\therefore$  anti-aromatic  
 $\therefore$  forbidden

In fact no [1,3] hydrogen shifts are known. The antarafacial mode would be allowed but it is difficult to see how its transition state could maintain overlap with (say) the top lobe of the C-1 p-orbital and the bottom lobe of the C-3 p-orbital. A [1,3] carbon shift presents an interesting added feature: the carbon can, in principle, undergo migration with retention (suprafacial) or inversion (antarafacial reaction). This leads to the following set of possibilities:

<u>carbon</u>	<u>double bond</u>	<u>orbital symmetry status</u>
supra (retention)	supra	forbidden
antara (inversion)	antara	forbidden (and sterically difficult)
supra (retention)	antara	allowed (but sterically very difficult)
antara(inversion)	supra	allowed - see below

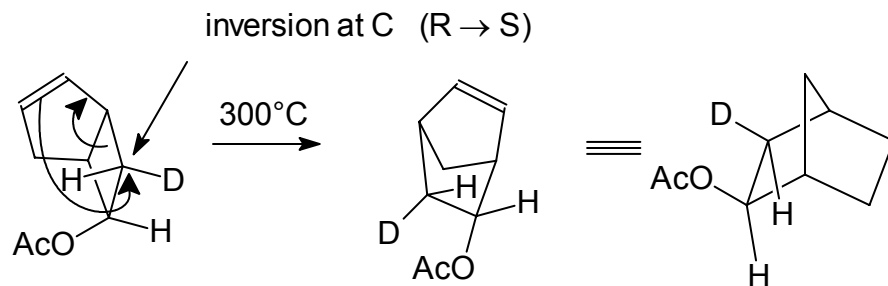
## [1,3] antara-supra shift



sign inversion  
 $\therefore$  Möbius  
 4 electrons  $\therefore$  aromatic  
 $\therefore$  allowed

Sterically it looks awkward,

but ...



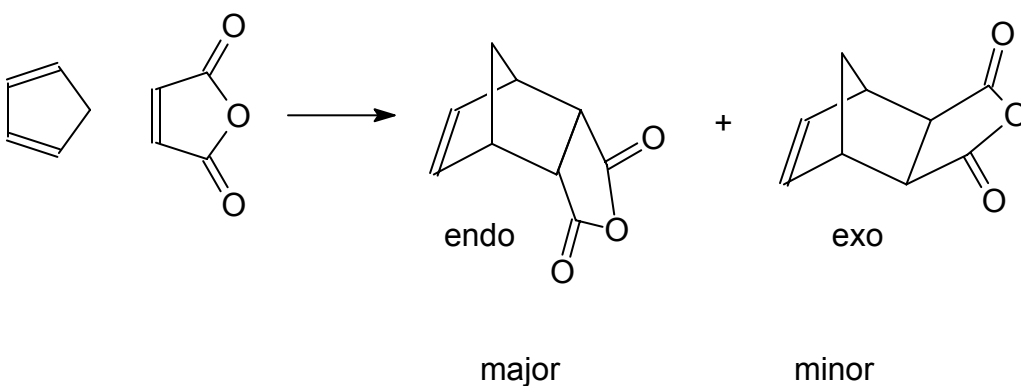
(Berson and Nelson, 1967).

## 8. Secondary Effects

The examples discussed thus far have dealt with the symmetry features of orbitals directly involved in the primary bond-making and bond-breaking processes. Other points also influence the course or rates of pericyclic reactions, though these effects are often smaller. An illustration:

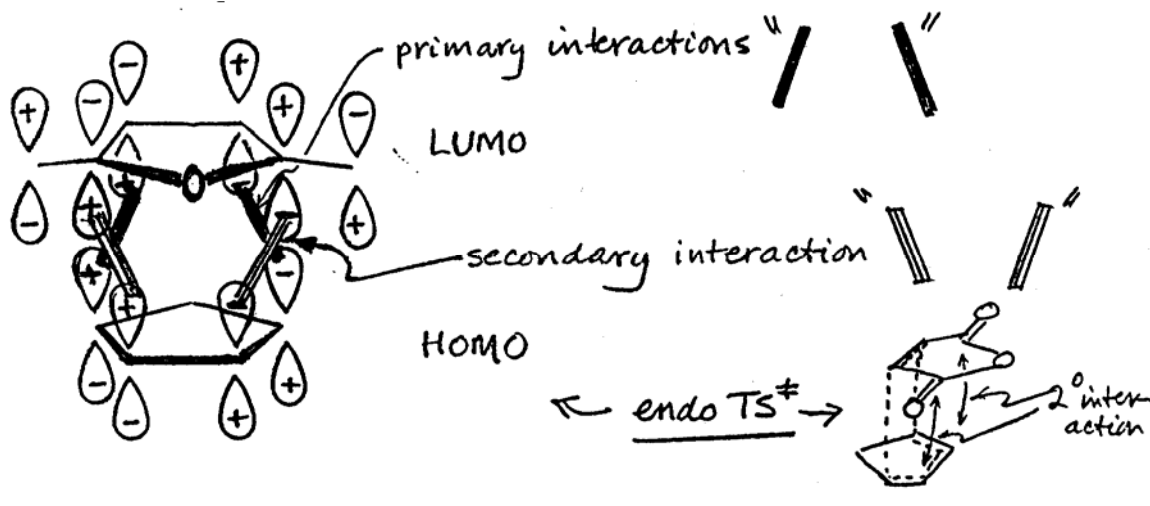
The Alder rule (the endo principle, the rule of maximum overlap):

In a Diels-Alder reaction the endo product is normally formed faster than the exo.

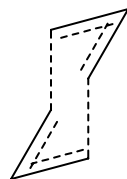


This is found even though the exo product usually has the lower free energy, and may become the major product if the products are allowed to equilibrate (e.g. by a longer reaction time).

The Alder Rule may be rationalized in FMO terms as arising from a favorable (bonding) overlap stabilizing the endo transition state: The primary (bond-making) interactions are shown by a double line; these are present equally in the endo and exo transition states and hence do not account for the endo preference. This is ascribed to the secondary interactions shown by the single lines, which are possible only in the endo transition state.



Note that the interaction of orbitals not directly involved in bonding is not always stabilizing. For example, experiments indicate that the preferred conformation for the transition state of the Cope rearrangement is chair-like, rather than boat-like.



chair-like



boat-like

The higher energy of the boat-like transition state is ascribed to anti-bonding destabilization of the boat-like form.