

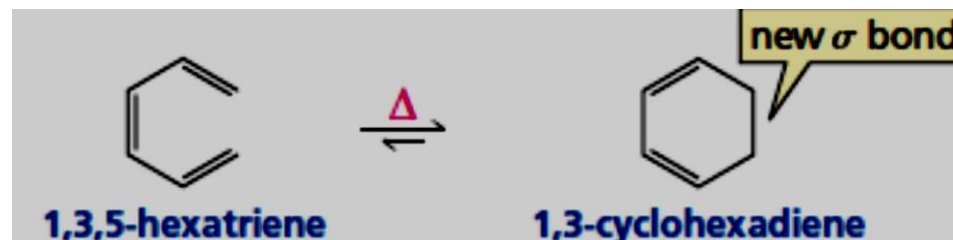
**COURSE CODE:** SC202(CHEMISTRY)  
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DEPT. OF SCIENCE AND MATHEMATICS  
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LECTURE-PERICYCLIC REACTIONS  
DATE: 22.03.2023

# Pericyclic Reactions

A pericyclic reaction is one in which the bonds are made or broken in a **concerted cyclic transition state**. A concerted reaction is one which involves no intermediates during the course of the reaction. A **pericyclic reaction** occurs as a result of reorganizing the electrons in the reactant(s).

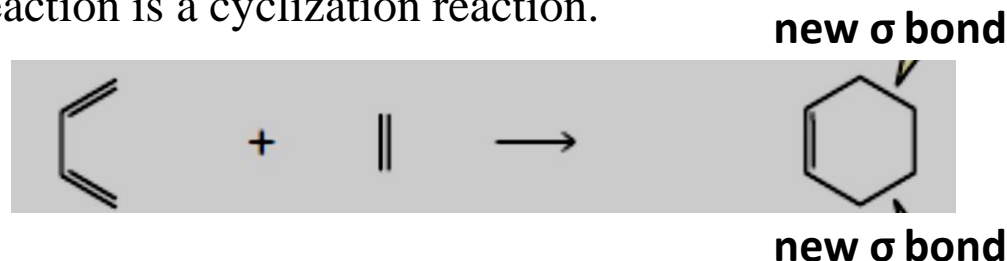
## Three Kinds of Pericyclic Reactions

An **electrocyclic reaction** is an intramolecular reaction in which a new (sigma) bond is formed between the ends of a conjugated (pi) system. This reaction is easy to recognize—the product is a *cyclic* compound that has one new ring and one pi bond *less* than the reactant.

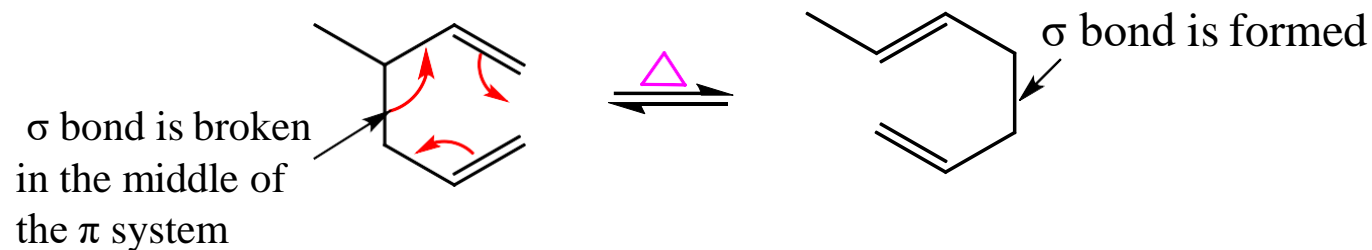


Electrocyclic reactions are **reversible**. In the reverse direction, an electrocyclic reaction is one in which a  $\sigma$  bond in a cyclic reactant breaks, forming a conjugated  $\pi$  system that has one *more*  $\pi$  bond than the cyclic reactant.

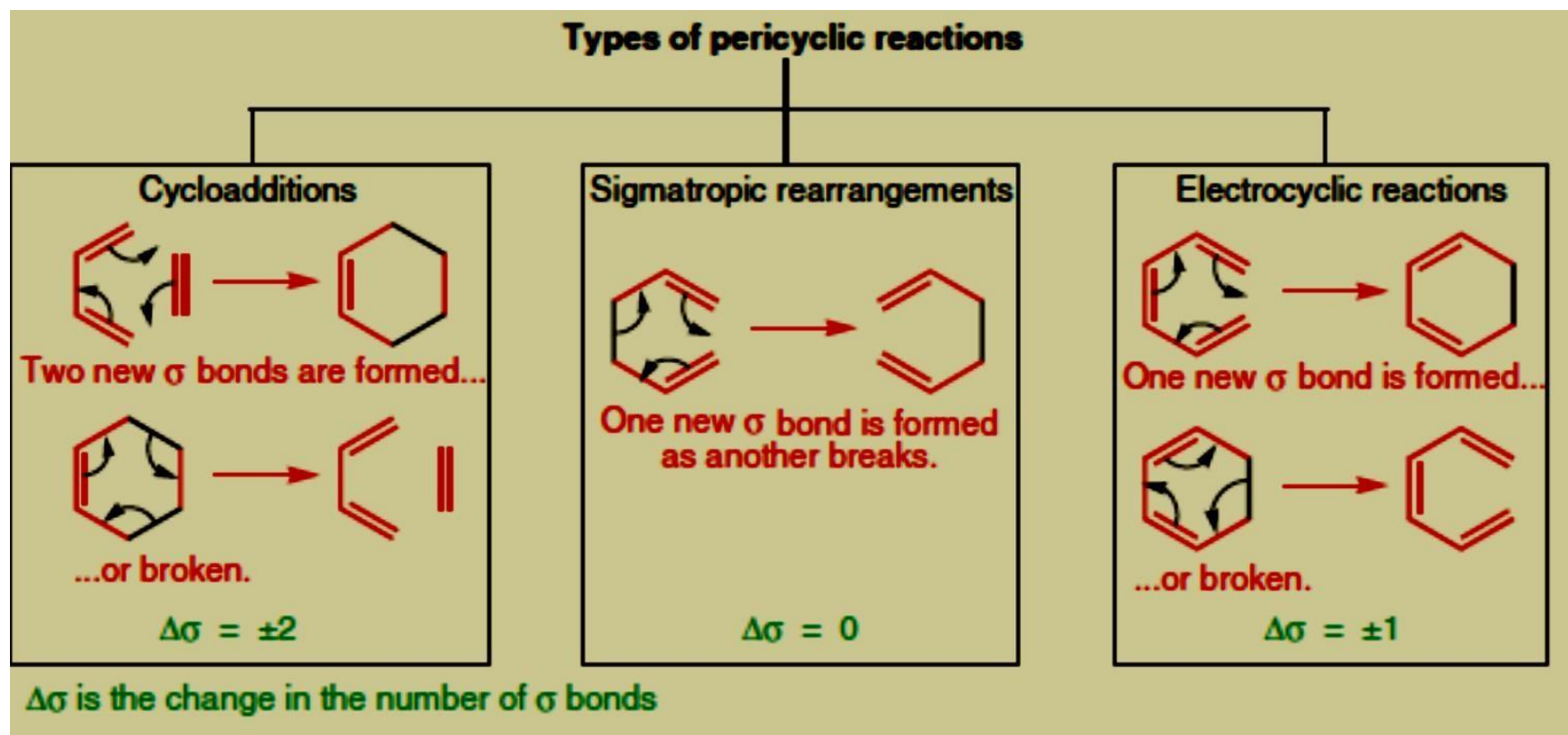
A **cycloaddition** is a pericyclic reaction in which "two or more unsaturated molecules (or parts of the same molecule) combine with the formation of a cyclic adduct in which there is a net reduction of the bond multiplicity." The resulting reaction is a cyclization reaction.

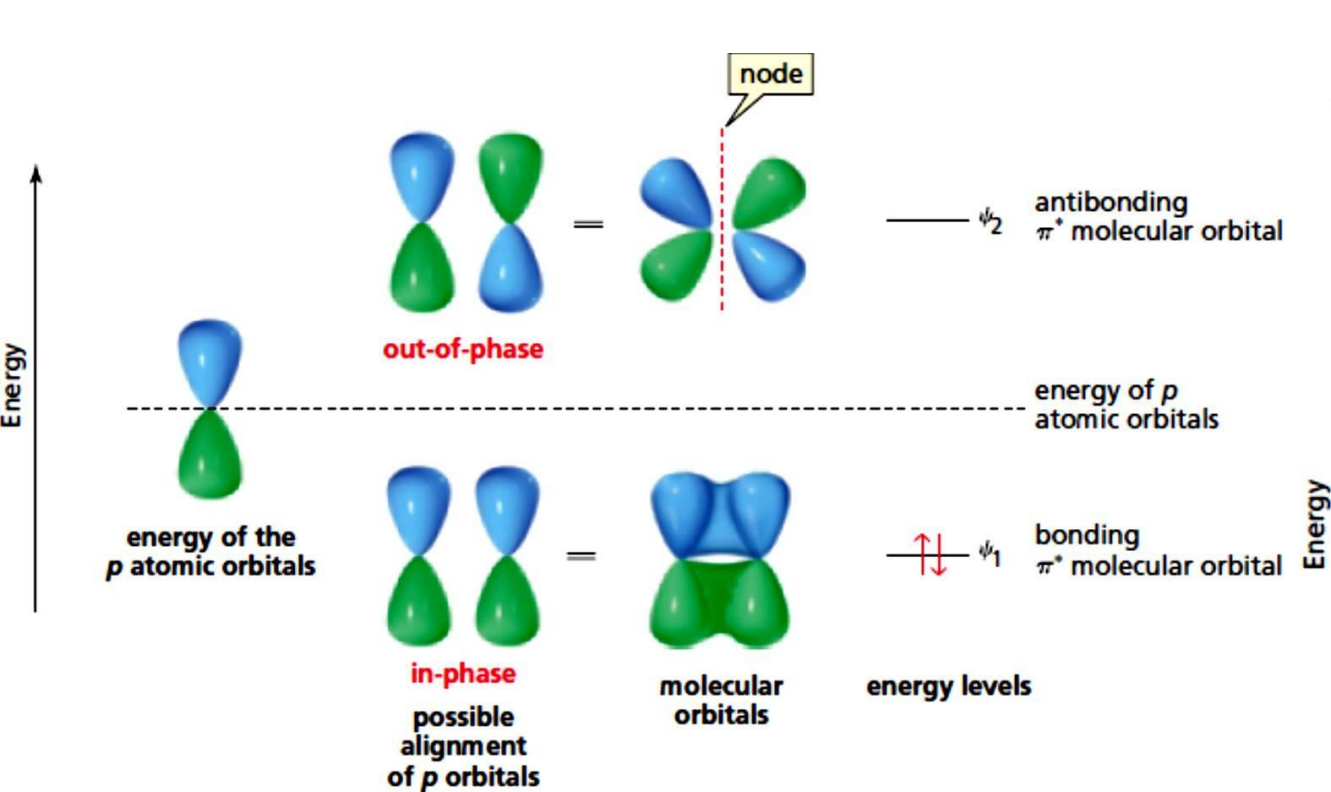


In a **sigmatropic rearrangement**, a  $\sigma$  bond is broken in the reactant, a new  $\sigma$  bond is formed in the product, and the  $\pi$  bonds rearrange.



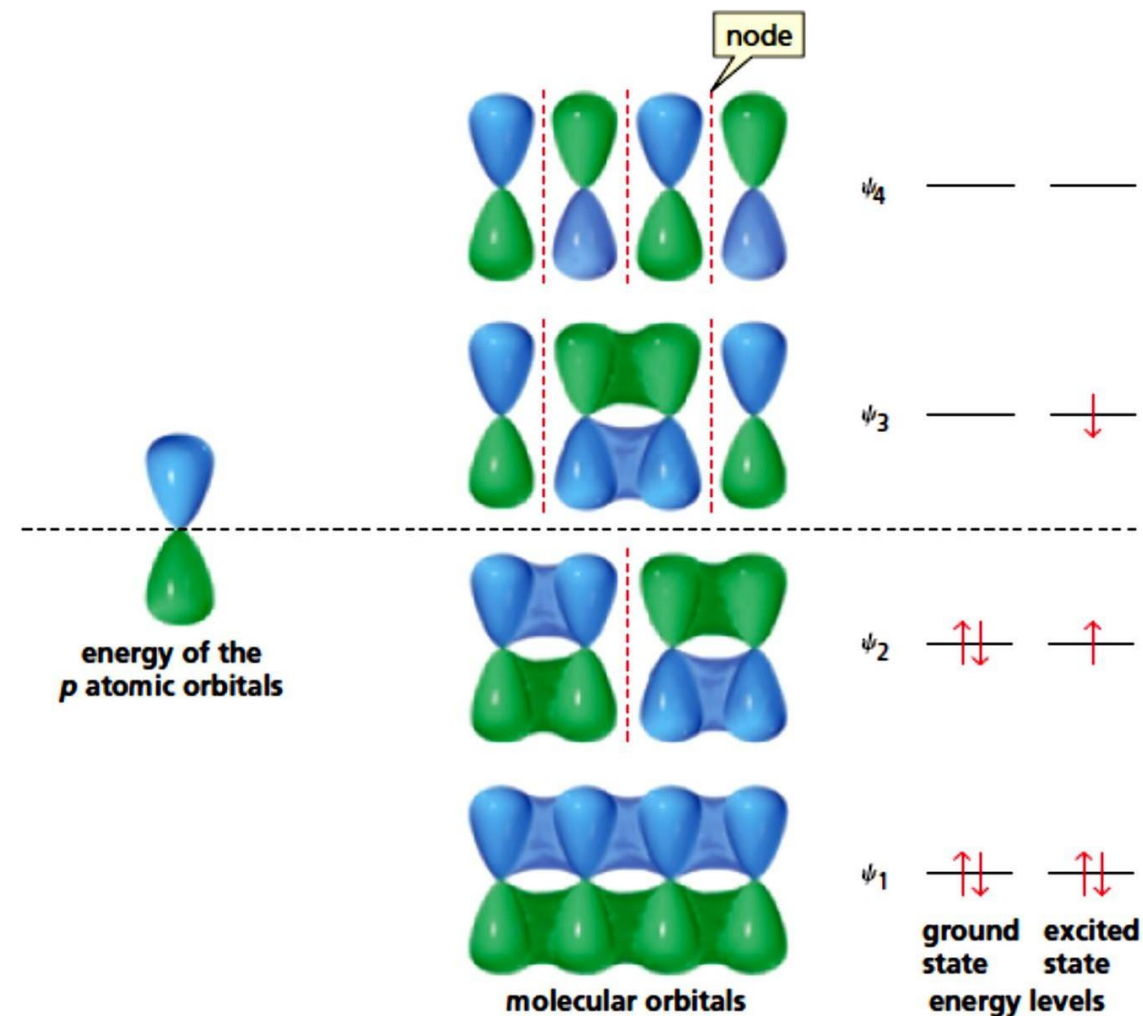
The types of pericyclic reactions are distinguished by the number of  $\sigma$  bonds made or broken.





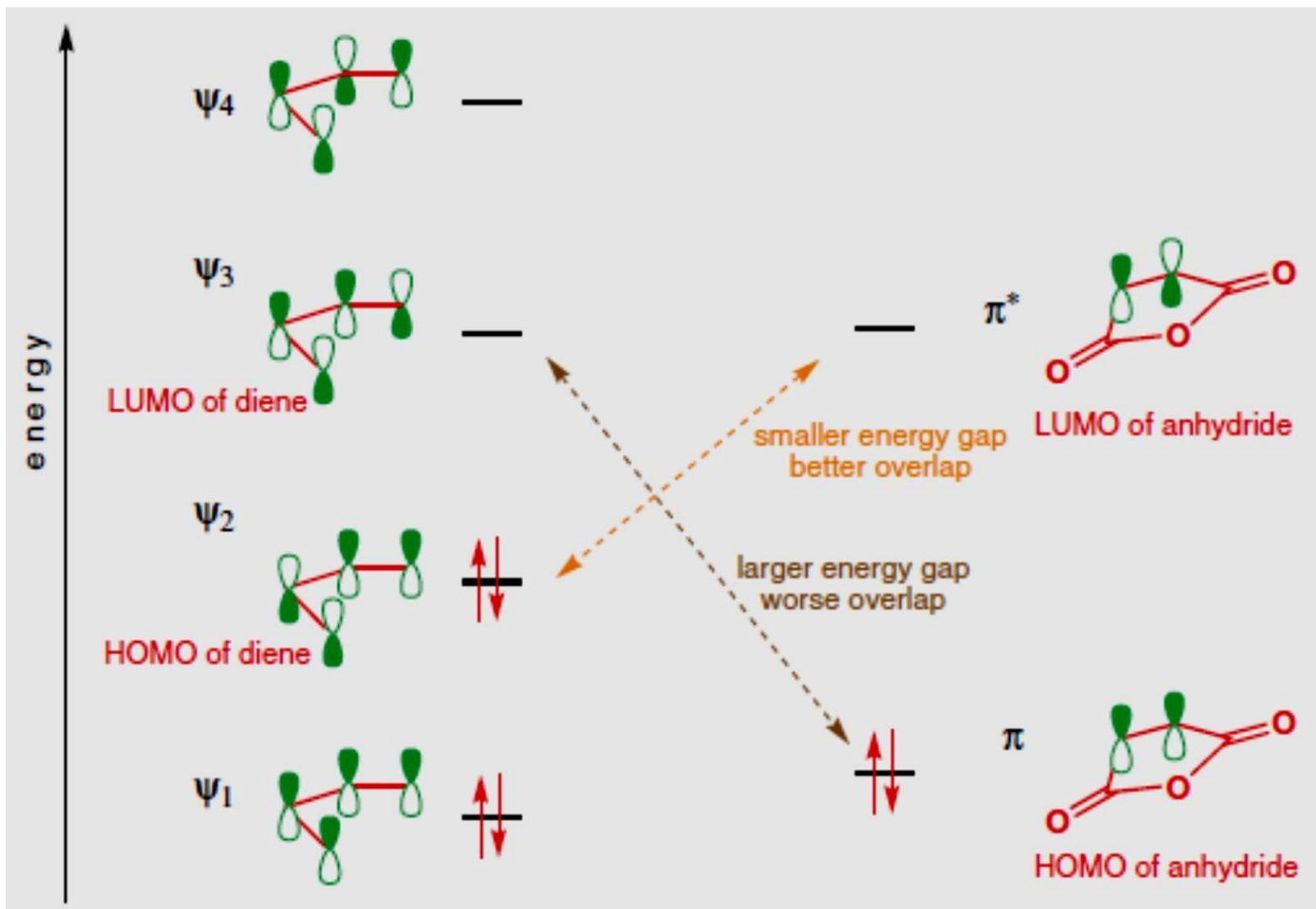
Interaction of in-phase  $p$  atomic orbitals gives a bonding  $\pi$  molecular orbital that is lower in energy than the  $p$  atomic orbitals. Interaction of out-of-phase atomic orbitals gives an antibonding  $\pi^*$  molecular orbital that is higher in energy than the  $p$  atomic orbitals.

Two  $p$  atomic orbitals interact to give the two  $\pi$ -molecular orbitals ethylene.

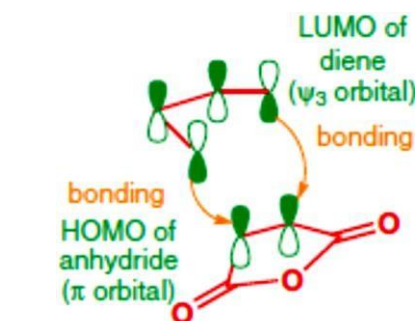
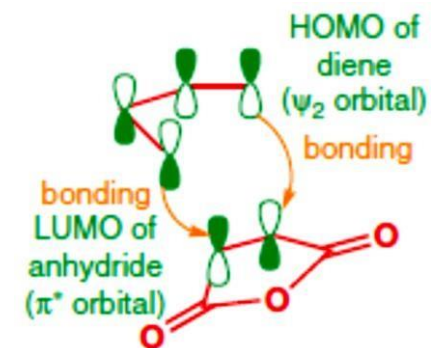
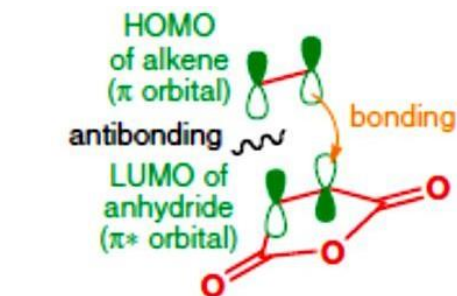
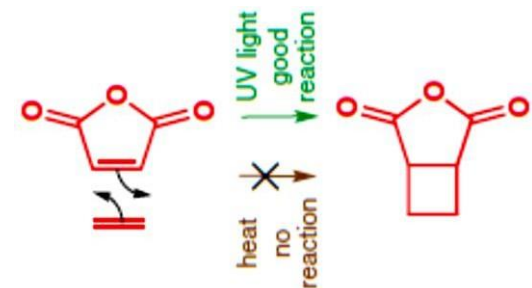


Four  $p$  atomic orbitals interact to give the four  $\pi$ -molecular orbitals of 1,3-butadiene.

# The frontier orbital description of cycloadditions



The two molecular orbitals—the **highest occupied molecular orbital (HOMO)** of one partner and the **lowest unoccupied molecular orbital (LUMO)** of the other or vice versa—are known as the **frontier orbitals**.



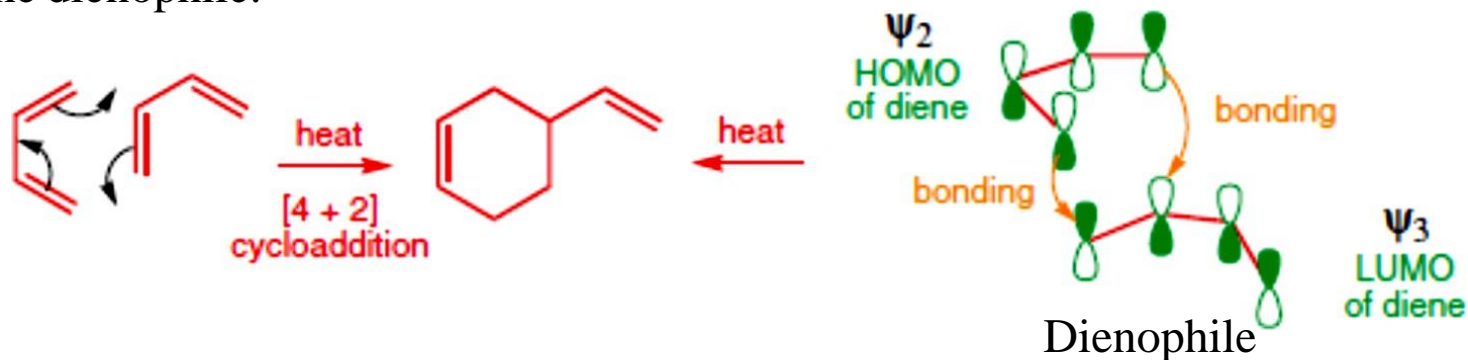
Ref: Organic Chemistry, Clayden



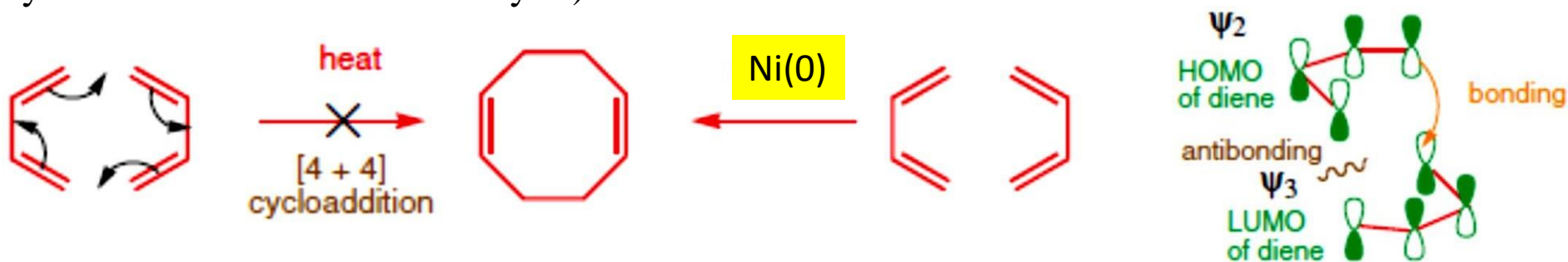
# Cycloaddition Reactions

## Dimerizations of dienes by cycloaddition reactions

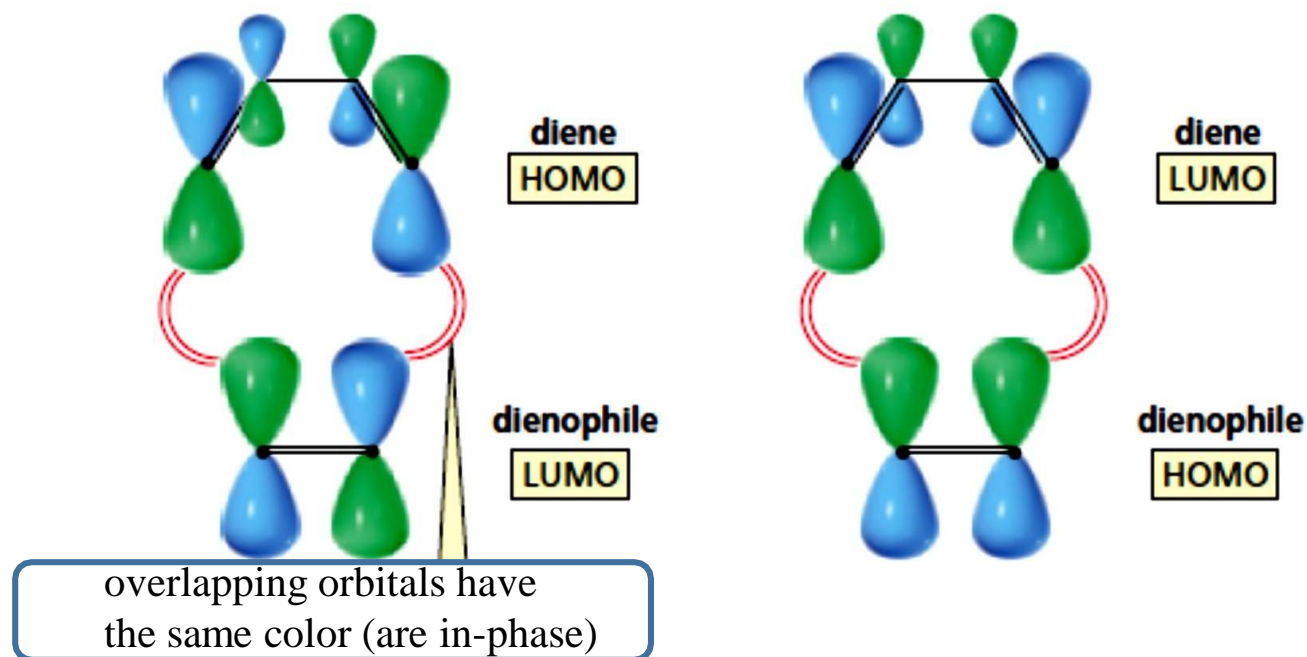
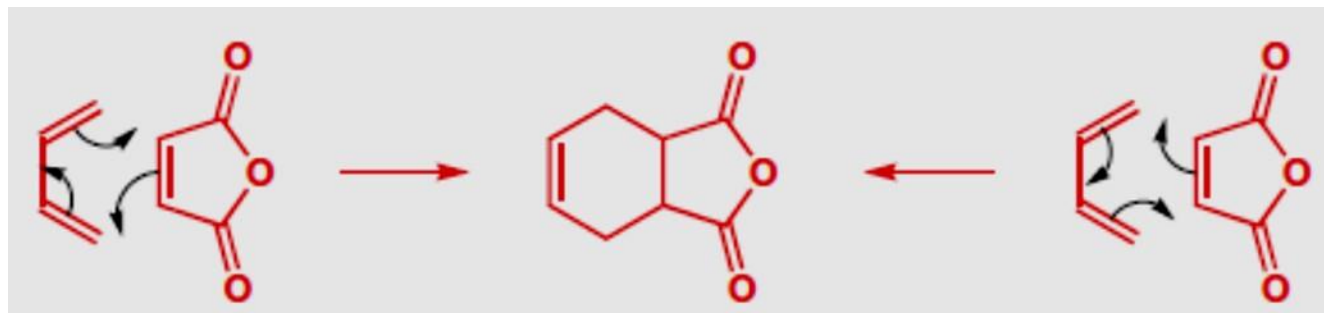
Dienes can dimerize by a Diels–Alder reaction [4+2] cycloaddition. One molecule of the diene plays the role of the dienophile.



Dienes cannot form an eight-membered ring in one step, in a [4 + 4] cycloaddition (although this is possible photochemically or with transition metal catalysis).

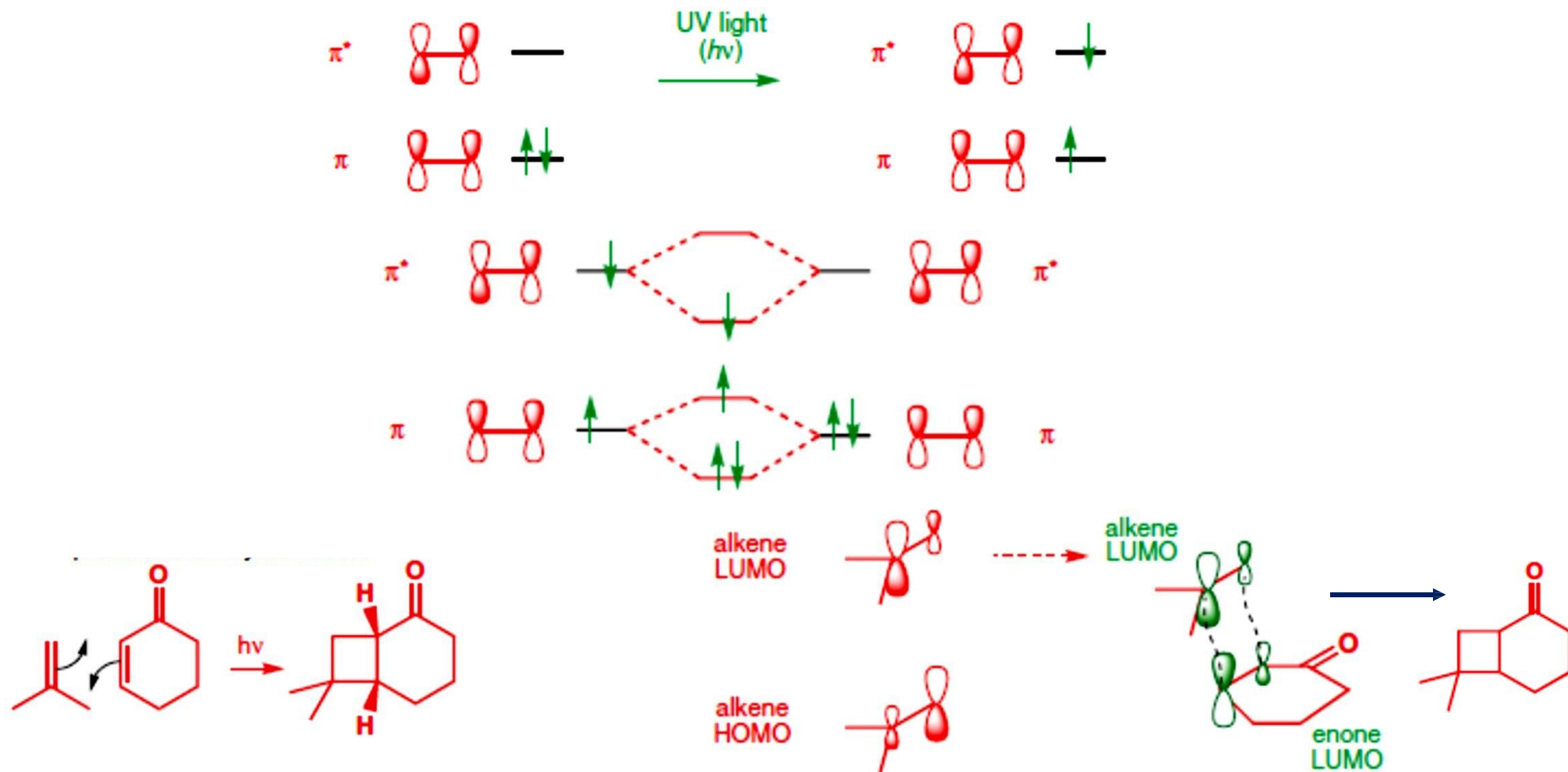


## Diels–Alder reaction



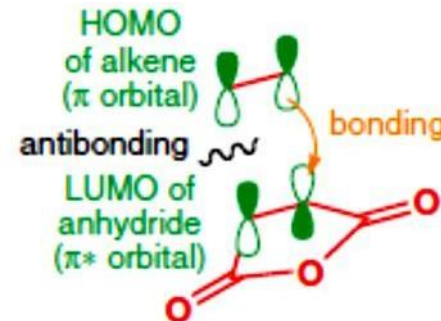
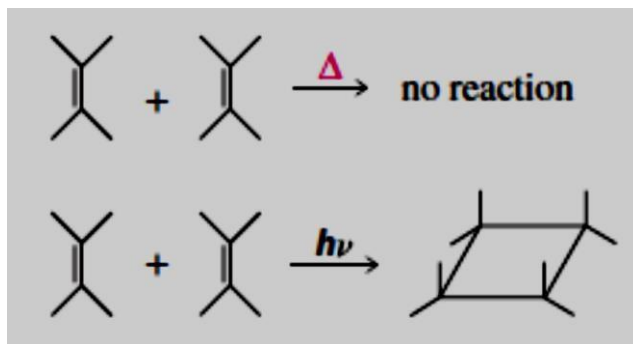
**Frontier orbital analysis** of a cycloaddition reaction shows that overlap of in-phase orbitals to form the two new  $\sigma$  bonds requires **suprafacial** orbital overlap. This is true whether we use the LUMO of the dienophile and the HOMO of the diene (a system with two conjugated bonds) or the HOMO of the dienophile and the LUMO of the diene.

Under photochemical conditions, the rules switch such that, all the cycloadditions which are not allowed thermally are allowed photochemically. This works because the problem of the incompatible symmetry, in trying to add two alkenes together, is avoided by converting one of them into the excited state photochemically. First, one electron is excited by the light energy, from the  $\pi$  to the  $\pi^*$  orbital.

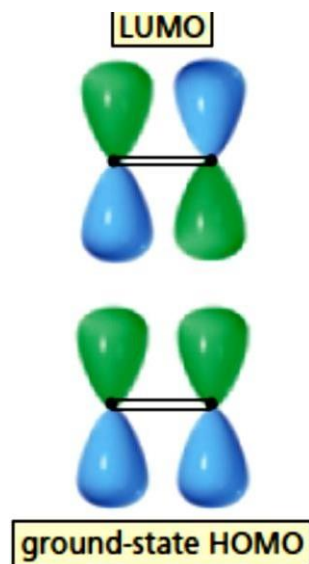




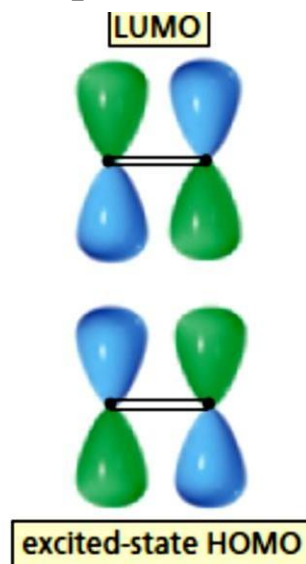
## [2+2] cycloaddition



thermal conditions

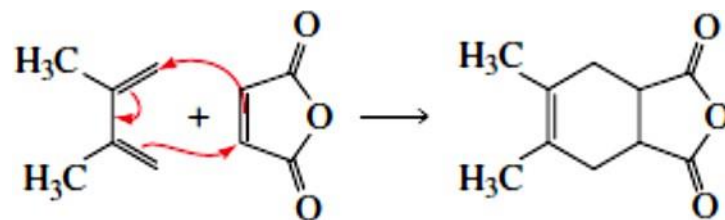


photochemical conditions

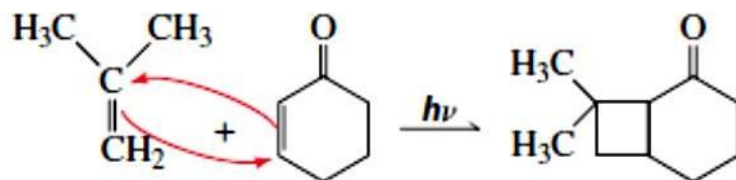


A **[2+2] cycloaddition** reaction does not occur under thermal conditions, but does take place under photochemical conditions

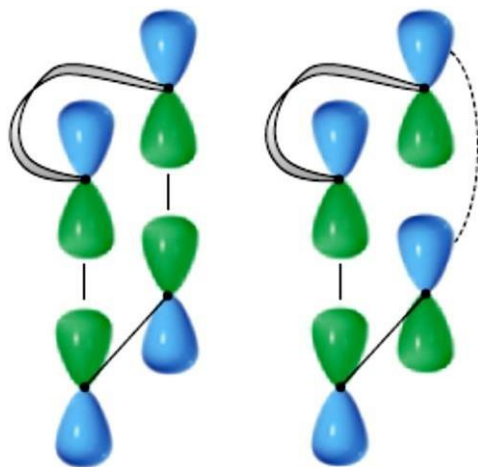
[4 + 2] cycloaddition (a Diels–Alder reaction)



[2 + 2] cycloaddition



There are two modes of orbital overlap, for the simultaneous formation of two  $\sigma$  bonds—*suprafacial* and *antarafacial*. Bond formation is **suprafacial** if both  $\sigma$  bonds form on the same side of the  $\pi$  system. Bond formation is **antarafacial** if the two  $\sigma$  bonds form on opposite sides of the  $\pi$  system. Suprafacial bond formation is similar to syn addition, whereas antarafacial bond formation resembles anti addition.



suprafacial  
bond formation

antarafacial  
bond formation

## The Woodward–Hoffmann description of the Diels–Alder reaction

### Woodward–Hoffmann rules

In a **thermal** pericyclic reaction, the total number of  $(4q + 2)_s$  and  $(4r)_a$  components must be **odd**.

A component is a bond or orbital taking part in a pericyclic reaction as a single unit. A double bond is a  $\pi_2$  component. The number 2 simply refers to the number of electrons. The prefix  $\pi$  tells us the type of electrons. A component may have any number of electrons (a diene is a  $\pi_4$  component).

The designations  $(4q + 2)$  and  $(4r)$  simply refer to the number of electrons in the component where  $q$  and  $r$  are integers.

An alkene is a  $\pi_2$  component and so it is of the  $(4q + 2)$  kind while a diene is a  $\pi_4$  component and so is of the  $(4r)$  kind. The suffix 's' stands for **suprafacial** and 'a' for **antarafacial**.

A **suprafacial** component forms new bonds on the **same** face at both ends while an **antarafacial** component forms new bonds on **opposite** faces at both ends.

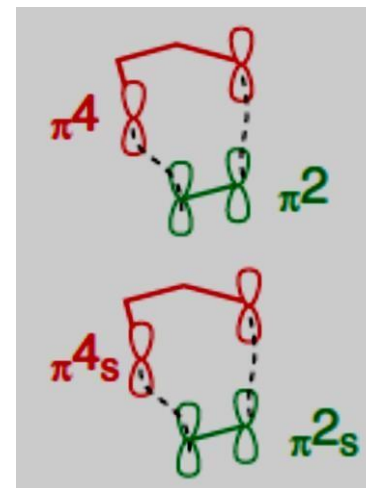
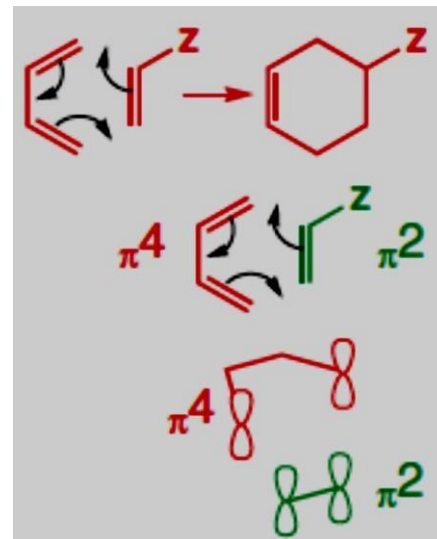
### Woodward–Hoffmann rules: alternative version

In an allowed thermal pericyclic reaction the sum (*number of suprafacial components with 2, 6, or 10 electrons + number of antarafacial components with 0, 4, or 8 electrons*) will be an odd number.

## The Diels–Alder reaction

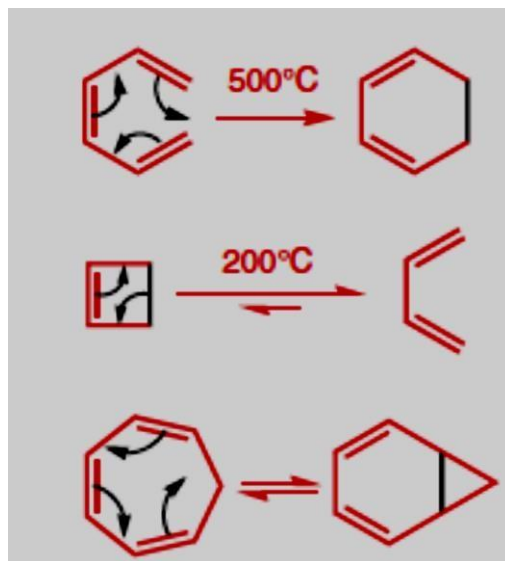
1. Draw the mechanism for the reaction.
2. Choose the components. All the bonds taking part in the mechanism must be included and no others.
3. Make a three-dimensional drawing of the way the components come together for the reaction, putting in orbitals at the ends of the components. The orbitals are just unshaded p orbitals, and do not make up HOMOs or LUMOs nor any particular molecular orbital. Join up the components where new bonds are to be formed.
4. Label each component as 's' or 'a' depending on whether new bonds are formed on the same or on opposite sides. In all of the cycloadditions, you have seen so far both components react suprafacially.
5. Count the number of  $(4q + 2)s$  and  $(4r)a$  components. If the total count is odd, the reaction is allowed.

In this case, **there is one  $(4q + 2)s$  component (the alkene) and no  $(4r)a$  components. Total = 1 so it is an allowed reaction.** Components of the other symmetry, that is  $(4q + 2)a$  and  $(4r)s$  components, is not of consideration.



# Electrocyclic reaction

In an electrocyclic reaction a ring is broken or formed. Rings may, of course, be formed by cycloadditions as well, but the **difference** with electrocyclic reactions is that just **one new  $\sigma$  bond** is formed (or broken) across the ends of a single conjugated  $\pi$  system. In a cycloaddition, **two new  $\sigma$  bonds** are always formed (or broken), and in a sigmatropic rearrangement one  $\sigma$  bond forms while one breaks.

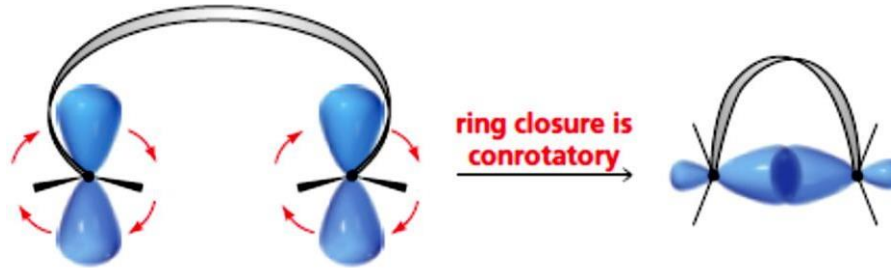


**An electrocyclic reaction is the formation of a new  $\sigma$  bond across the ends of a conjugated polyene or the reverse.**

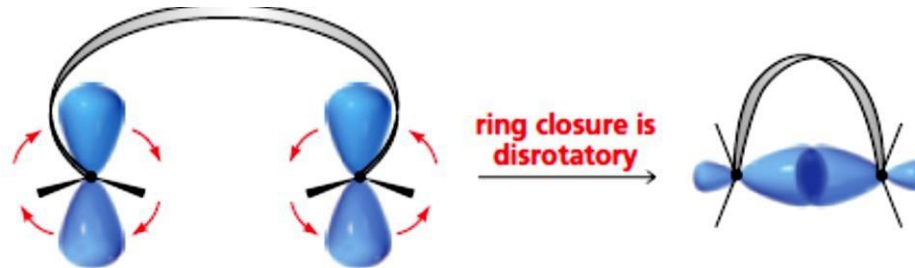


## Electrocyclic reaction

- The product of an electrocyclic reaction results from the formation of a new bond. For this bond to form, the  $p$  orbitals at the ends of the conjugated system must rotate so they overlap head-to-head. Rotation can occur in two ways. If both orbitals rotate in the **same direction** (both clockwise or both counterclockwise), ring closure is **conrotatory**.



- If the orbitals rotate in the **opposite directions** (one clockwise, the other counterclockwise), ring closure is **disrotatory**.

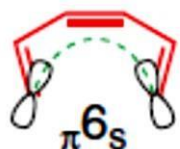
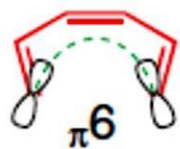
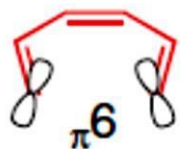
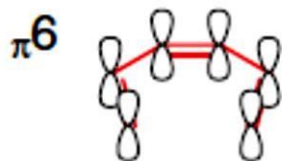
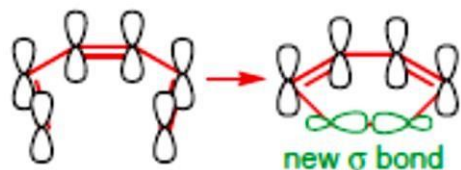


- The mode of ring closure depends on the **symmetry of the HOMO** of the compound undergoing ring closure. If the HOMO is **symmetric** (the end orbitals are identical), rotation will have to be **disrotatory** to achieve in-phase overlap. In other words, **disrotatory** ring closure is **symmetry-allowed**, whereas **conrotatory** ring closure is **symmetry-forbidden**.
- If the **HOMO is asymmetric**, rotation has to be **conrotatory** in order to achieve inphase overlap. In other words, **conrotatory** ring closure is **symmetry-allowed**, whereas **disrotatory** ring closure is **symmetry-forbidden**.

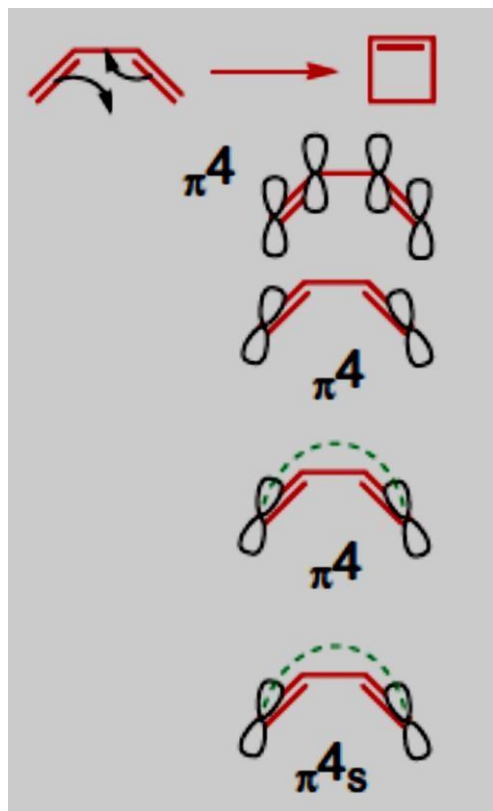
Hexatriene is a  $6\pi$  conjugated system and, on forming cyclohexadiene, the end two orbitals must rotate through  $90^\circ$  to form a  $\sigma$  bond.

So, now for the Woodward–Hoffmann treatment:

1. Draw the mechanism for the reaction.
2. Choose the components. All the bonds taking part in the mechanism must be included and no others.
3. Make a three-dimensional drawing of the way the components come together for the reaction, putting in orbitals at the ends of the components.
4. Join up the components where new bonds are to be formed.
5. Label each component “s or a” depending depending on whether new bonds are formed on the same or on opposite sides.
6. Add up the number of  $(4q + 2)s$  and  $(4r)a$  components. If the sum is odd, the reaction is allowed.



**Here, there is one  $(4q + 2)s$  component and no  $(4r)a$  components. Total = 1 so this is an **allowed** reaction.**

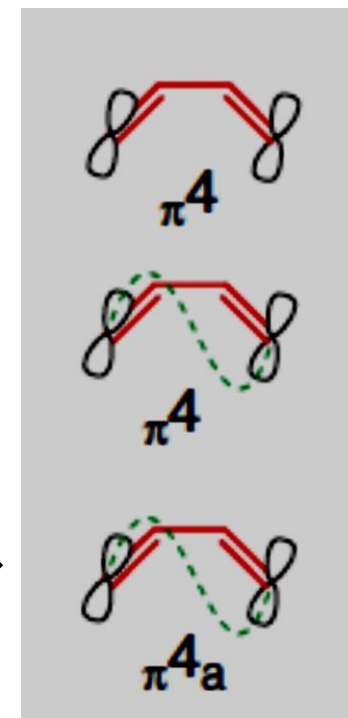


And the Woodward–Hoffmann treatment again.

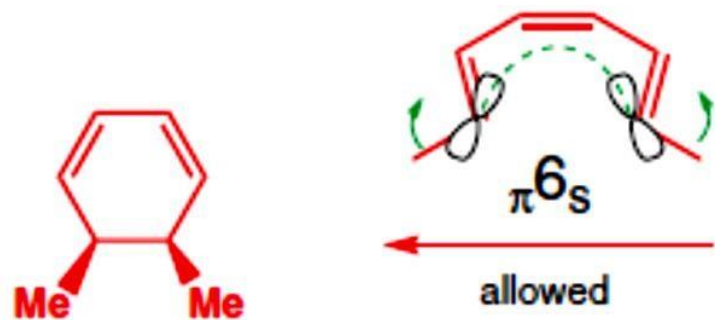
1. Draw the mechanism for the reaction.
2. Choose the components. All the bonds taking part in the mechanism must be included and no others.
3. Make a three-dimensional drawing of the way the components come together for the reaction, putting in orbitals at the ends of the components.
4. Join up the components where new bonds are to be formed.
5. Label each component “s or a” depending on whether new bonds are formed on the same or on opposite sides.
6. Add up the number of  $(4q + 2)s$  and  $(4r)a$  components. If the sum is odd, the reaction is allowed.

There are no  $(4q + 2)s$  components and no  $(4r)a$  components. Total = 0 so this is a **disallowed** reaction.

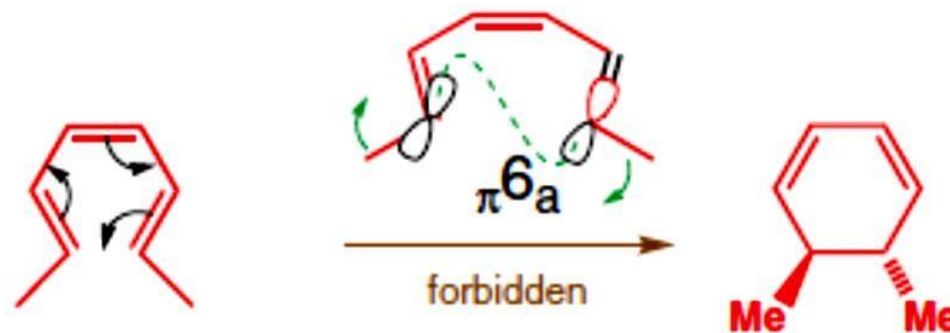
**Add up the number of  $(4q + 2)s$  and  $(4r)a$  components. If the sum is odd, the reaction is allowed. There are no  $(4q + 2)s$  components and one  $(4r)a$  component. Total = 1 so this is an **allowed** reaction.**



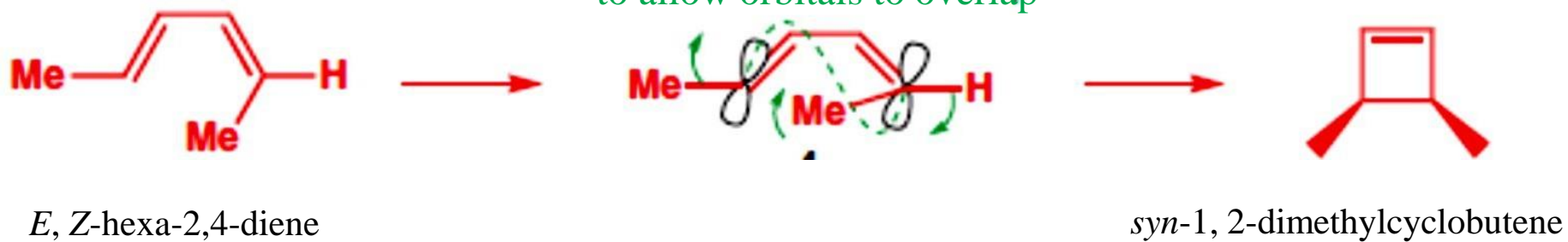
Both methyl groups rotate upwards to allow orbitals to overlap



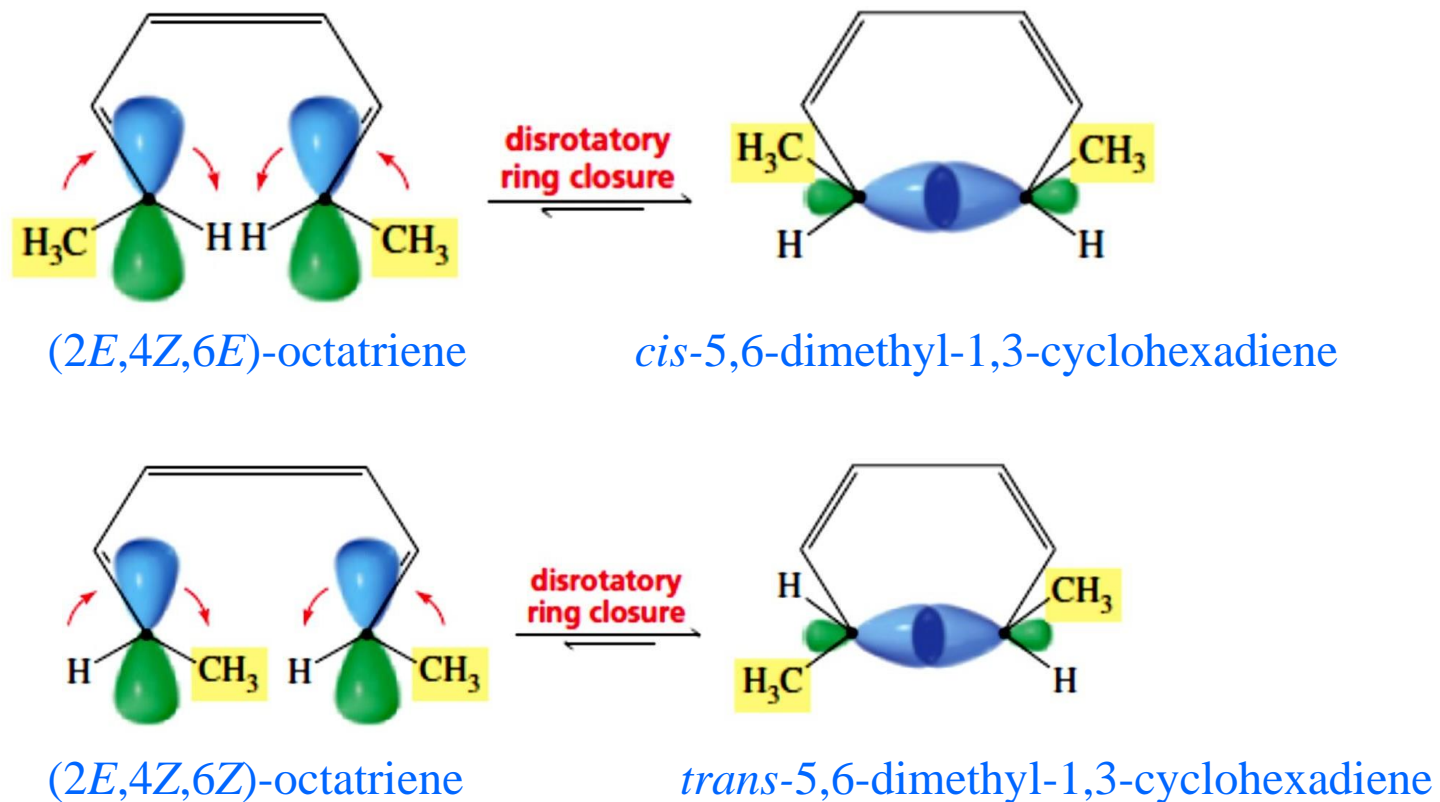
One methyl group rotates upwards and one downwards to allow orbitals to overlap



Both methyl groups rotate upwards to allow orbitals to overlap

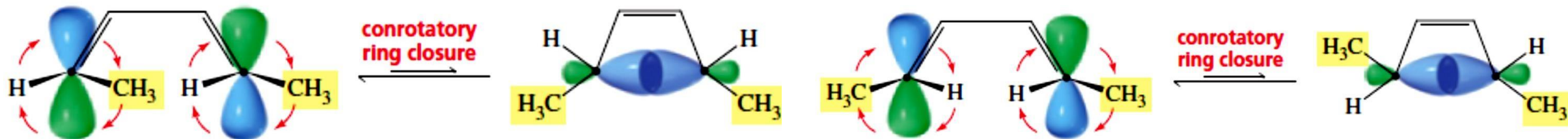
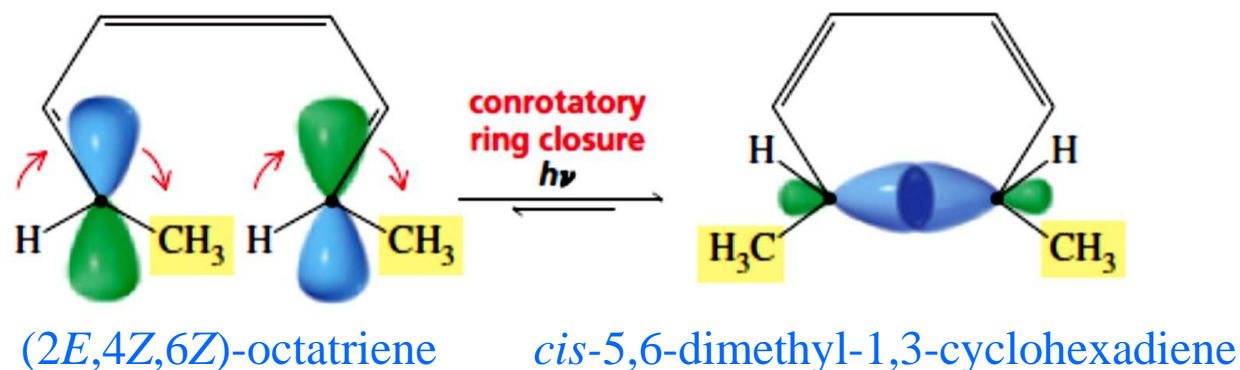


The ground-state HOMO of a compound with three conjugated  $\pi$  bonds, such as (2*E*,4*Z*,6*E*)-octatriene, is **symmetric**. This means that ring closure under *thermal conditions is disrotatory*. In disrotatory ring closure of (2*E*,4*Z*,6*E*)-octatriene, the methyl groups are both pushed up (or down), which results in formation of the *cis* product.





If the reaction takes place under *photochemical conditions*, we must consider the excited-state HOMO rather than the ground-state HOMO. The **excited-state HOMO** of a compound with three bonds is **asymmetric**. Therefore, under photochemical conditions, (2*E*,4*Z*,6*Z*)-octatriene undergoes conrotatory ring closure, so both methyl groups are pushed down (or up) and the *cis* product is formed.



If we examine molecular orbital diagrams for compounds with four, five, six, and more conjugated double bonds; we can conclude that *the ground-state HOMO of a compound with an even number of conjugated double bonds is asymmetric, whereas the ground-state HOMO of a compound with an odd number of conjugated double bonds is symmetric.*

## Rules for electrocyclic reactions

- All electrocyclic reactions are allowed.
- Thermal electrocyclic reactions involving  $(4n + 2)$   $\pi$  electrons are disrotatory.
- Thermal electrocyclic reactions involving  $(4n)$   $\pi$  electrons are conrotatory.
- In conrotatory reactions, the two groups rotate in the same turning sense: both clockwise or both anticlockwise.
- In disrotatory reactions, one group rotates clockwise and one anticlockwise.

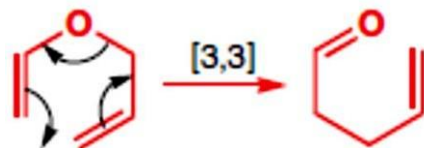
Woodward–Hoffmann Rules for Electrocyclic Reactions		
Number of conjugated $\pi$ bonds	Reaction conditions	Allowed mode of ring closure
Even number	Thermal	Conrotatory
	Photochemical	Disrotatory
Odd number	Thermal	Disrotatory
	Photochemical	Conrotatory

## Sigmatropic Rearrangements

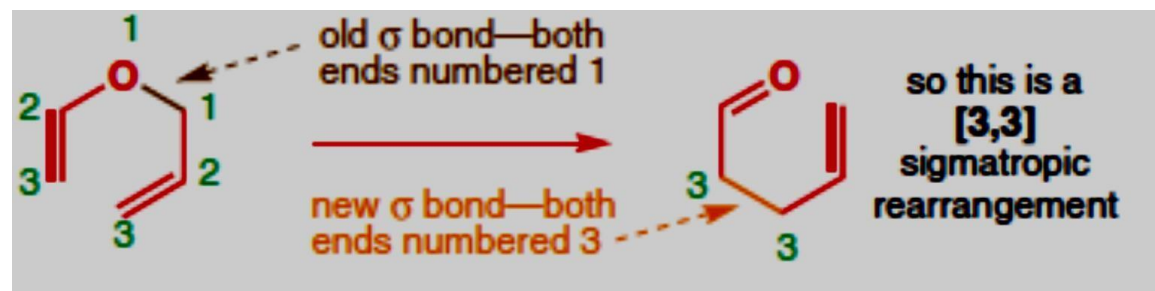
When an aryl allyl ether was heated without solvent, an *ortho*-allyl phenol resulted. This reaction is known as **Claisen rearrangement**.



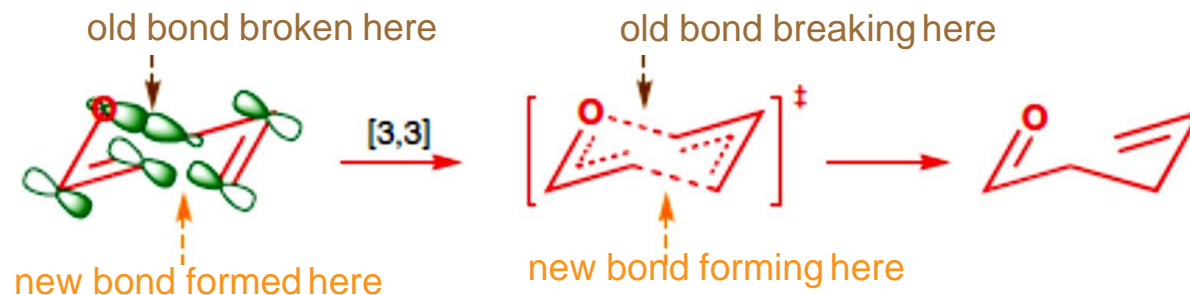
It was later found that the same sort of reaction occurs without the aromatic ring. This is called either the aliphatic Claisen rearrangement or the Claisen–Cope rearrangement.



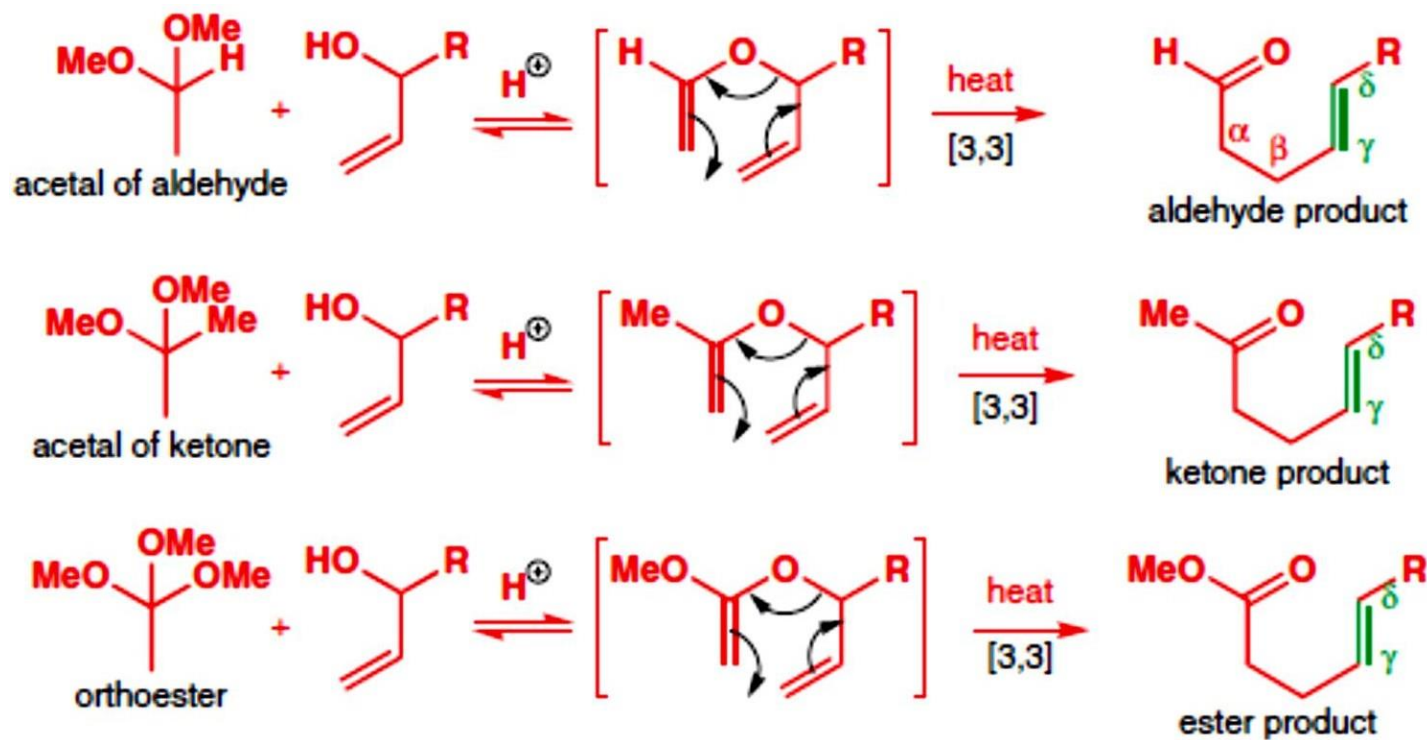
All these reactions are called sigmatropic because a  $\sigma$  bond appears to move from one place to another during the reaction. This particular reaction is called a [3,3]-sigmatropic rearrangement because the new  $\sigma$  bond has a 3,3-relationship to the old  $\sigma$  bond.



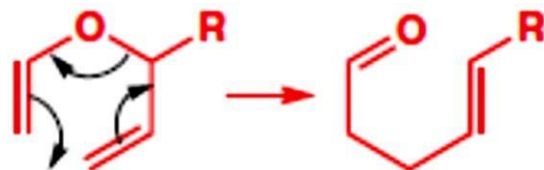
These [3,3]-sigmatropic rearrangements happen through a chair-like transition state, which allows us both to get the orbitals right and to predict the stereochemistry of the new double bond.



**The Claisen rearrangement is a general synthesis of  $\gamma,\delta$ -unsaturated carbonyl compounds**



## Orbital descriptions of [3,3]-sigmatropic rearrangements

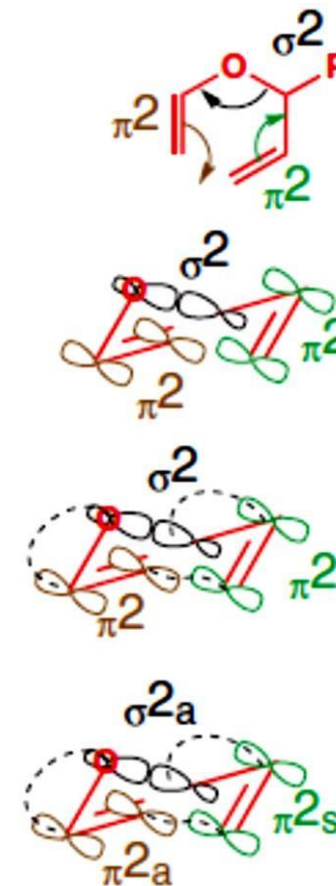


### The Woodward–Hoffman rules

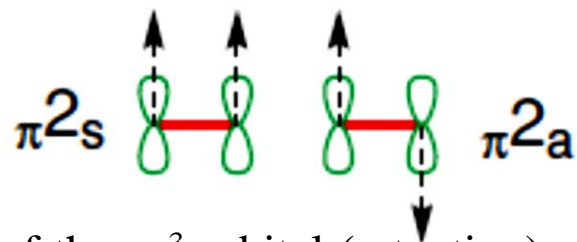
In a thermal pericyclic reaction, the total number of  $(4q + 2)s$  and  $(4r)a$  components must be odd.

1. Draw the mechanism for the reaction.
2. Choose the components. All the bonds taking part in the mechanism must be included and no others.
3. Make a three-dimensional drawing of the way the components come together for the reaction, putting in orbitals at the ends of the components.
4. Join up the components where new bonds are to be formed.
5. Label each component "s or a" depending whether new bonds are formed on the same or on opposite sides.
6. Add up the number of  $(4q + 2)s$  and  $(4r)a$  components. If the sum is odd, the reaction is allowed. Here there is: *one*  $(4q + 2)s$  component (one alkene) and *no*  $(4r)a$  components.

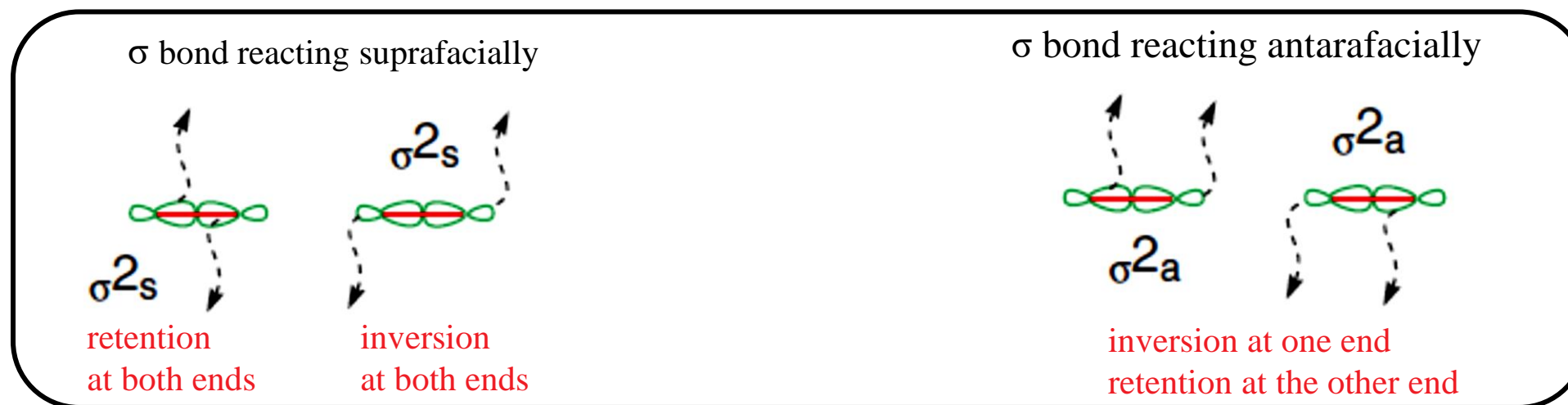
**Total=1, so this is an allowed reaction.**



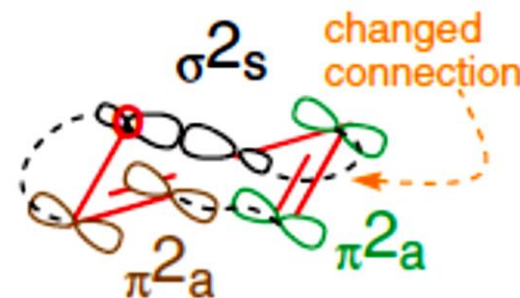
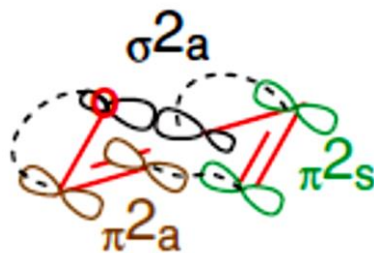




The  $\sigma$  bond reacts using the large lobe of the  $sp^3$  orbital (retention) or the small lobe (inversion). If it reacts with retention at both ends or inversion at both ends, it reacts suprafacially, while if it reacts with retention at one end and inversion at the other, it reacts antarafacially. There are four possibilities.



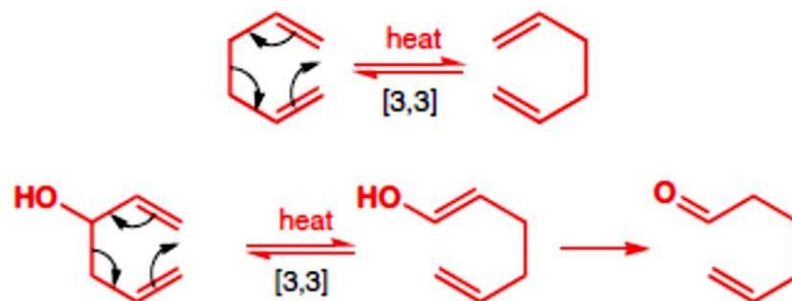
no. of  $(4q + 2)s$  components: 1  
 no. of  $(4r)a$  components: 0  
 sum = 1  
 —reaction is allowed thermally



no. of  $(4q + 2)s$  components: 1  
 no. of  $(4r)a$  components: 0  
 sum = 1  
 —reaction is allowed thermally

## Cope rearrangement

The Cope rearrangement is a [3,3]-sigmatropic rearrangement with only carbon atoms in the ring.



The reaction is accelerated if the starting alcohol is treated with base (KH is the best) to make the alkoxide. The product is then the potassium enolate, which is more stable than the simple potassium alkoxide starting material. As the reaction proceeds, conjugation is growing between O<sup>-</sup> and the new  $\pi$ -bond.

