

## Pericyclic reactions

*Generally organic reactions are ionic where electrons flow in one direction in each step—towards the positive charge. However, in some reactions, electrons move round a circle and there are no positive or negative charges on any intermediates. A pericyclic reaction is a type of organic reaction in which the transition state of the molecule has a cyclic geometry, and the reaction progresses in a concerted (single-step) manner. They represent an important class of concerted processes involving  $\pi$ -systems. The concerted nature of the reactions leads to good stereochemical control of the product. Pericyclic reactions are usually rearrangement reactions.*

*The salient features of these reactions are:*

- Pericyclic reactions have a cyclic transition state.*
- While in this transition state, a concerted rearrangement of the electrons takes place that causes  $\sigma$  and  $\pi$ -bonds to simultaneously break and form.*
- Pericyclic reactivity can be understood in terms of frontier molecular orbital (FMO) theory and the outcome of reactions can be predicted using the Woodward-Hoffmann rules.*

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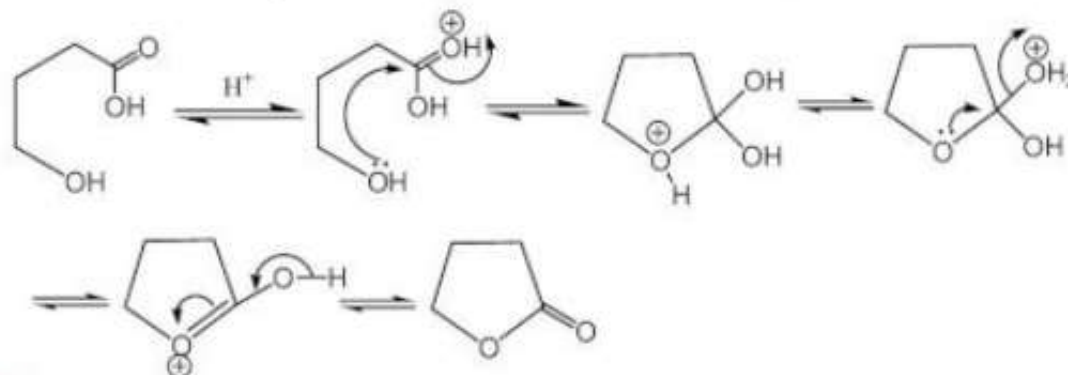
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## Three Classes of Organic Reactions

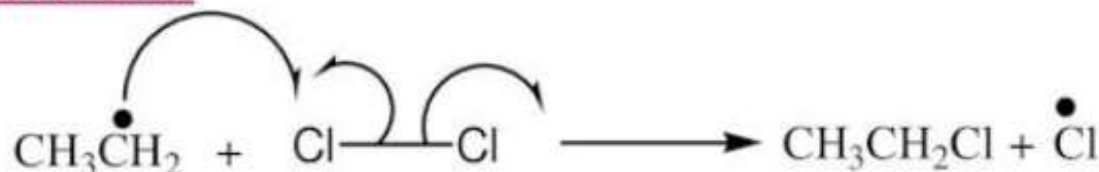
### Polar reactions



R = aliphatic as well as aromatic

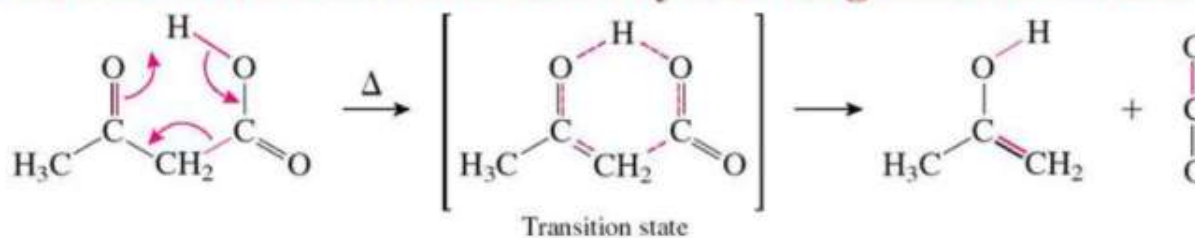


### Radical reactions



### Pericyclic reactions

This reaction occurs as a result of a cyclic reorganization of electrons

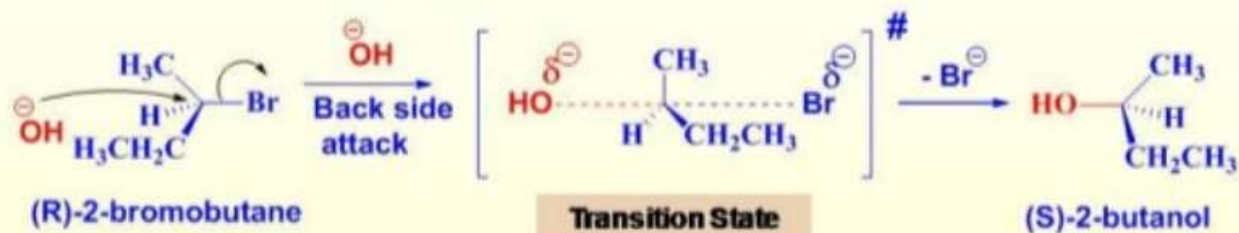


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### Concerted ionic Reaction



Pericyclic reactions are characterized by a **concerted bonding changes** taking place through the reorganization of  $\pi$  and  $\sigma$  bonding electron in a cyclic T.S. which is associated with cyclic array of interacting orbitals.

### Concerted Pericyclic Reaction



The combination of steps is called a **concerted process** where intermediates are skipped

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## Salient Features of Pericyclic Reactions

1. Bonding changes must be concerted i.e.; all bonds breaking and bond forming steps are **simultaneous but not necessarily synchronous**. That means that all bond breaking and making may not occur to the same extent at all stages during the formation of transition state.
2. Pericyclic reactions are **reversible** in nature and follow the **microscopic reversibility** path.
3. The reaction involves **no distinct polar intermediates** during the course of the reaction.
4. Reaction proceeds in **a single step** through the formation of **non polar transition state**.
5. There is little solvent effect on the rate of pericyclic reactions (unless the reactants themselves happen to be charged species) and normally occur in the gas phase with no solvent.
6. There is **no nucleophilic or electrophilic component**.
7. Normally **no catalyst** is needed to promote the reactions. However, many transition metal complexes can catalyze pericyclic reactions by virtue of their d-orbital participation. Lewis acids also catalyze many pericyclic reactions, either directly, or by changing the mechanism of the reaction so that it becomes a stepwise process.
8. Pericyclic reactions normally show very **high stereo specificity and regioselectivity**.
9. **No. of  $\sigma$  and or  $\pi$  electrons** are important in predicting the stereochemistry of the products.
10. Pericyclic reactions can be **promoted by light as well as heat**. The stereochemistry of products under two sets of conditions is different and it is just opposite.

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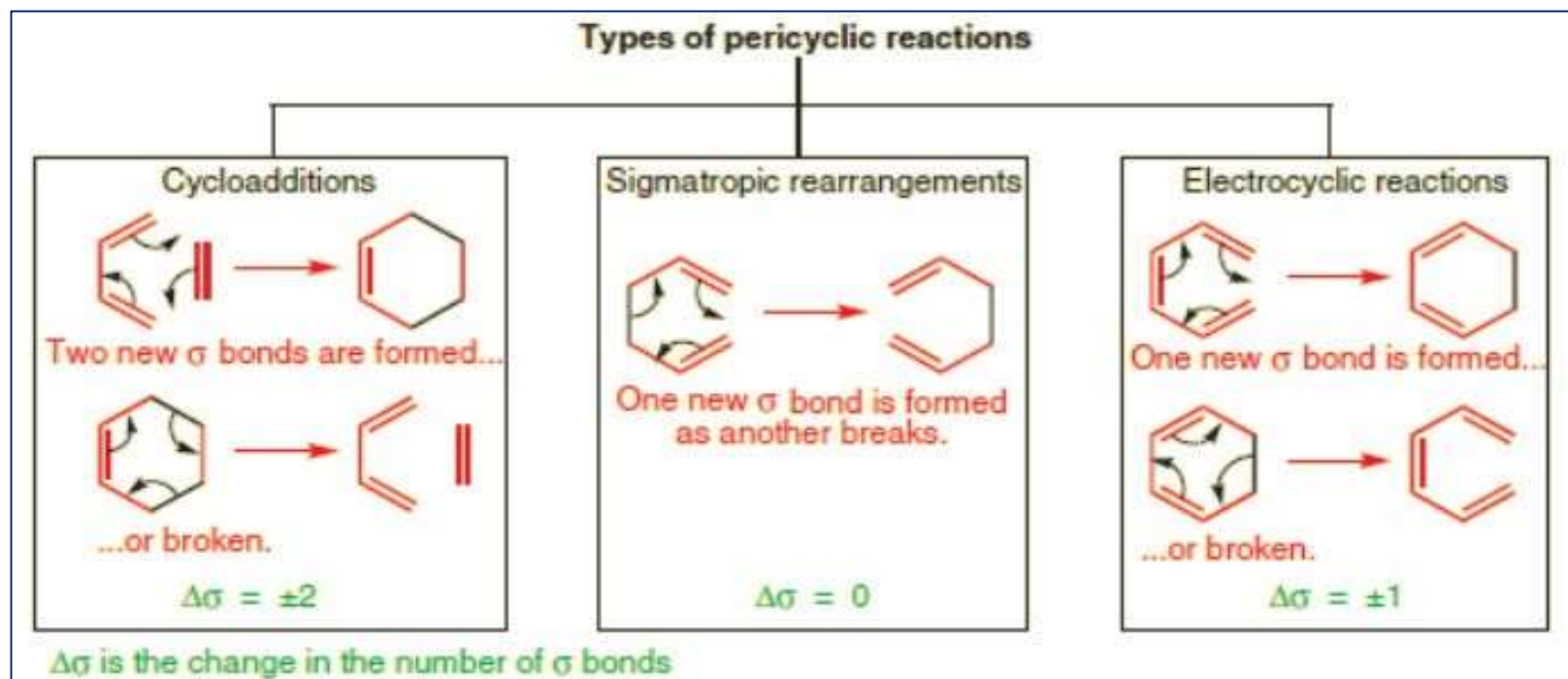
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*The four principal classes of pericyclic reactions are termed:*

- *Cycloaddition,*
- *Electrocyclic,*
- *Sigmatropic, and*
- *Ene Reactions.*

*Pericyclic reactions can be distinguished/characterized by the no. of  $\sigma$  bonds formed or broken.*

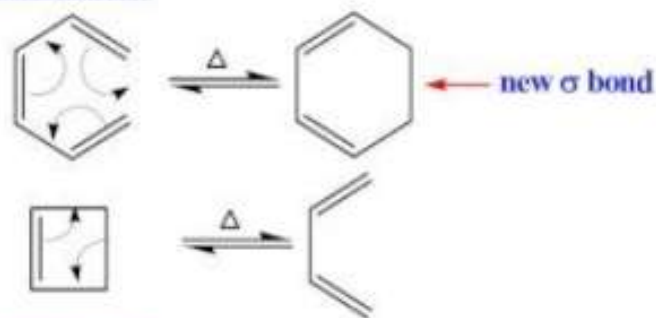


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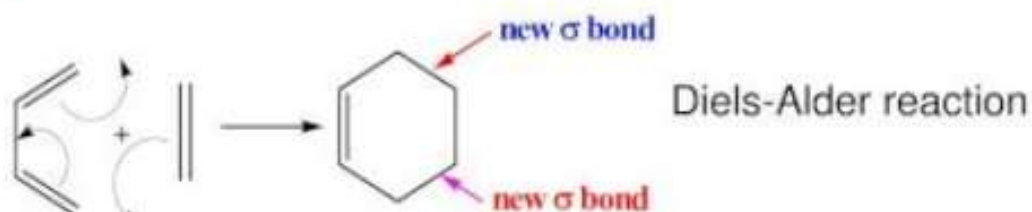
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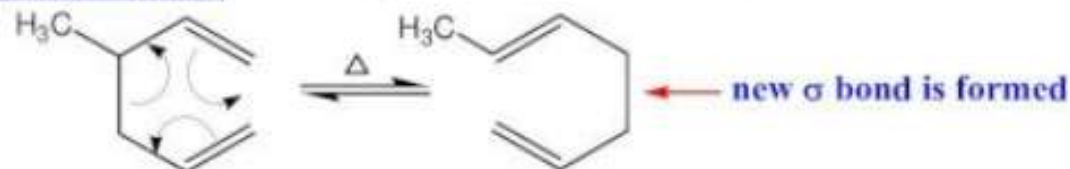
### Electrocyclic reactions



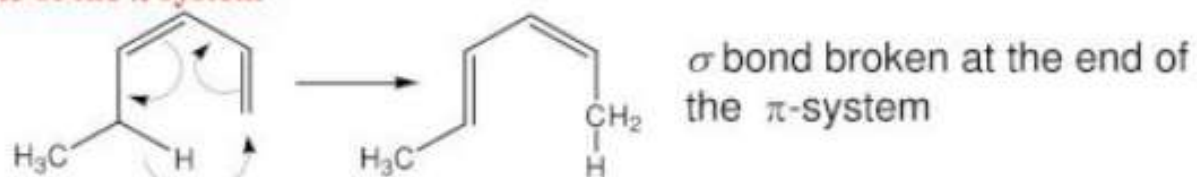
### Cycloaddition reactions



### Sigmatropic reactions



$\sigma$  bond is broken in the middle of the  $\pi$  system



- As the reactions are concerted, they are highly stereoselective
- The reactions are generally not effected by catalysts or by a change in solvent

#### Product configuration depends on

- Configuration of the reactant
- The number of double bonds in the reactant
- Whether the reaction is photochemical or thermal

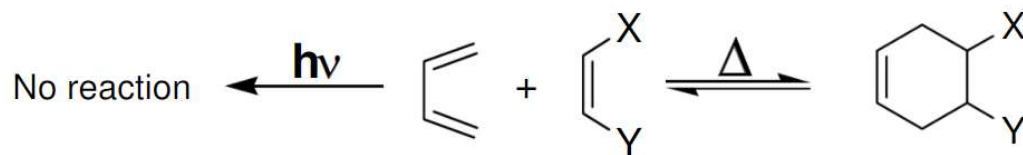
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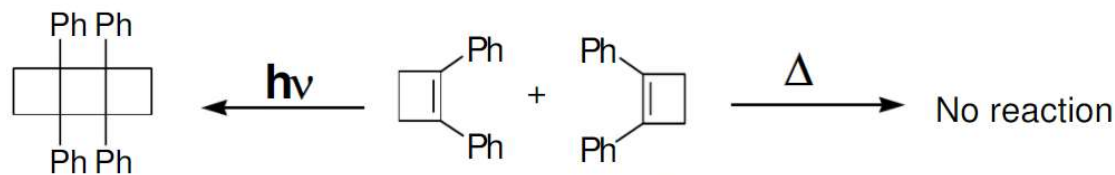
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pericyclic reactions are induced **thermally** or **photochemically**

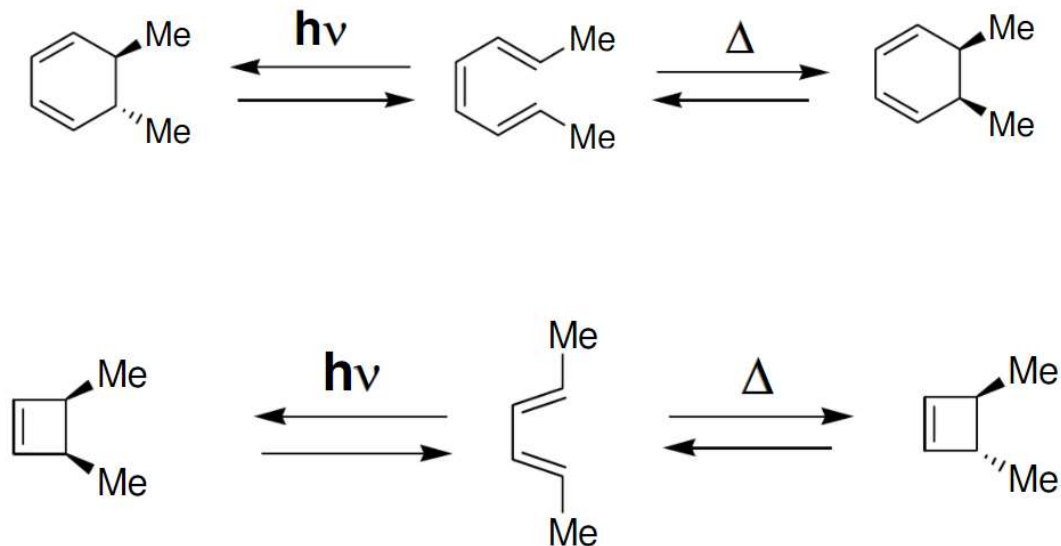
[4+2]-cycloaddition (Diels-Alder reaction)



[2+2]-cycloaddition



**Electrocyclic reaction**



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*The configuration of the product formed in a pericyclic reaction depends on*

*1. the configuration of the reactant*

*2. the number of conjugated double bonds or pairs of electrons in the reacting system*

*3. whether the reaction is a thermal reaction or a photochemical reaction*

*A photochemical reaction is a reaction that occurs when a reactant absorbs light. A thermal reaction takes place without the absorption of light.*

*Pericyclic reactions can be explained on the basis of the Conservation of Orbital Symmetry theory which states that in-phase orbitals overlap during the course of a pericyclic reaction. The conservation of orbital symmetry theory was based on the Frontier Molecular Orbital theory put forth by Kenichi Fukui.*

- If the symmetries of both reactant and product orbitals match the reaction is said to be **symmetry allowed** under the **Woodward-Hoffmann Rules** (these relate the electronic configuration of reactants to the type of pericyclic reaction and its stereochemical imperatives)
- If the symmetries of reactant and product orbitals do not correlate, the reaction is **symmetry-disallowed** and there are no low energy concerted paths
- Fukui's approach: we need to consider only the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), called the frontier orbitals

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## Frontier Molecular Orbital [FMO] theory:

*Cycloaddition can be explained using frontier molecular orbital (FMO) theory.*

*Chemical reactivity can often be explained in terms of interacting Highest Occupied MOs (HOMOs), Lowest Unoccupied MOs (LUMOs) and Singly Occupied MOs (SOMOs).*

*HOMO + LUMO -> bonding MO*

*HOMO + HOMO -> antibonding MO*

*LUMO + LUMO -> null interaction (no electrons) SOMO + SOMO -> bonding MO*

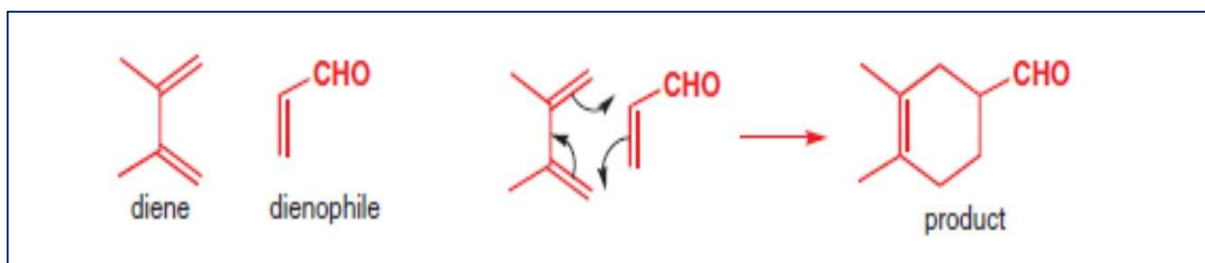
*The FMO approach was developed by Woodward & Hoffmann in the late nineteen sixties who used it to explain an apparently diverse set of reactions involving  $\pi$ -systems, including Diels-Alder cycloaddition.*

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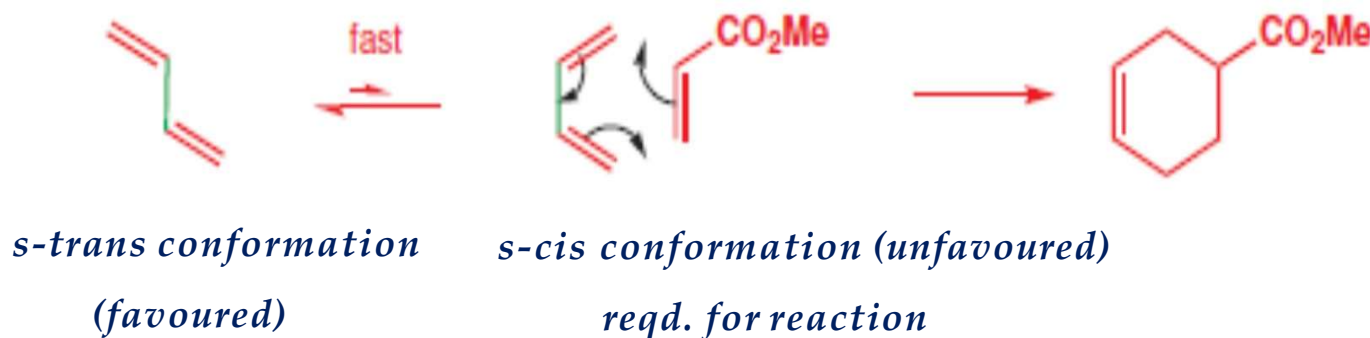
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*Cycloaddition reactions: A concerted combination of two  $\pi$ -electron systems to form a ring of atoms having two new  $\sigma$  bonds and two fewer  $\pi$  bonds is called a cycloaddition reaction: Diels–Alder reaction, between a conjugated diene and an alkene, usually called dienophile, in presence of heat.*



*The diene component in the Diels–Alder reaction can be open-chain or cyclic and it can have many different kinds of substituents. However, there is only one limitation: it must be able to take up the conformation shown in the mechanism. Butadiene normally prefers the *s-trans* conformation with the two double bonds as far away from each other as possible for steric reasons (s refers to  $\sigma$  bond). The energy barrier to rotation about the central  $\sigma$  bond is small (about 30 kJ mol<sup>-1</sup> at room temperature) and rotation to the less favourable but reactive *s-cis* conformation is rapid.*

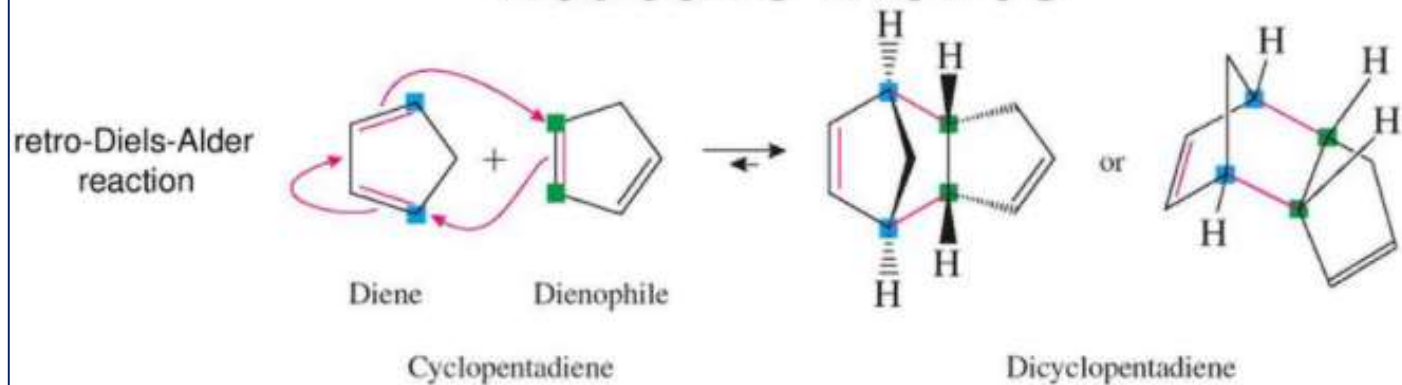


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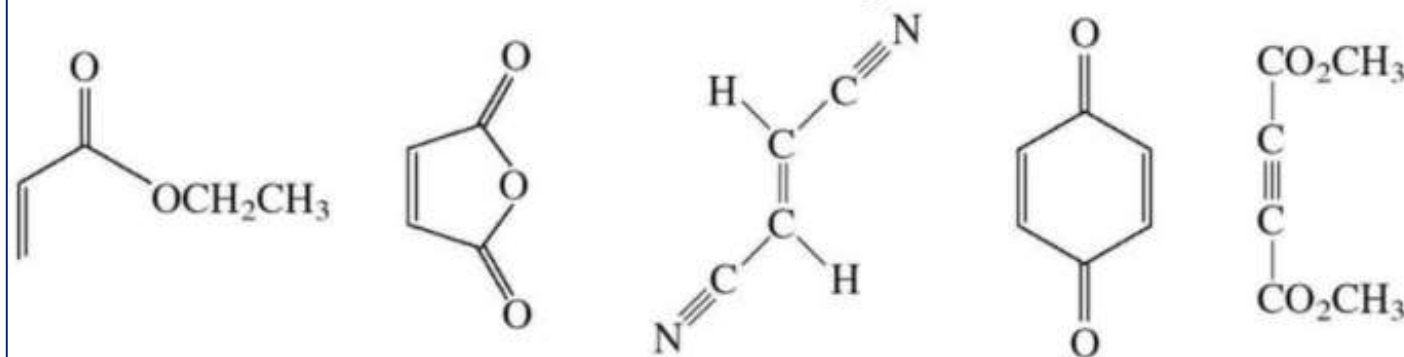
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## Reactive Dienes



## Reactive Dienophiles

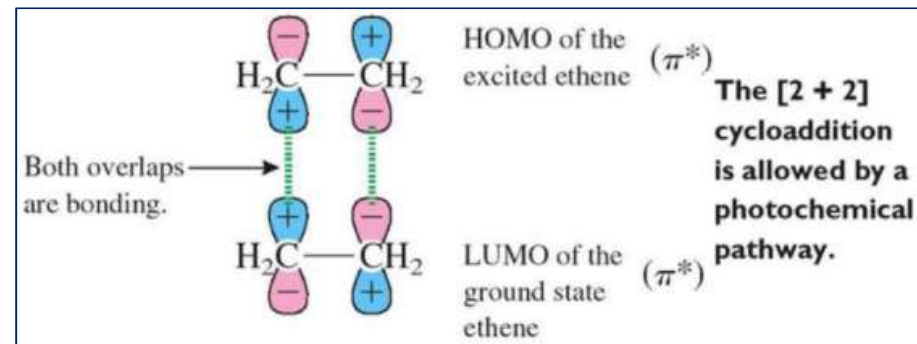
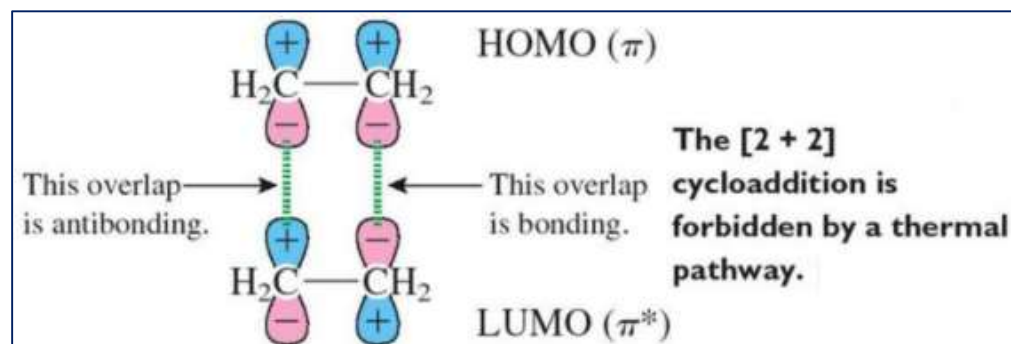
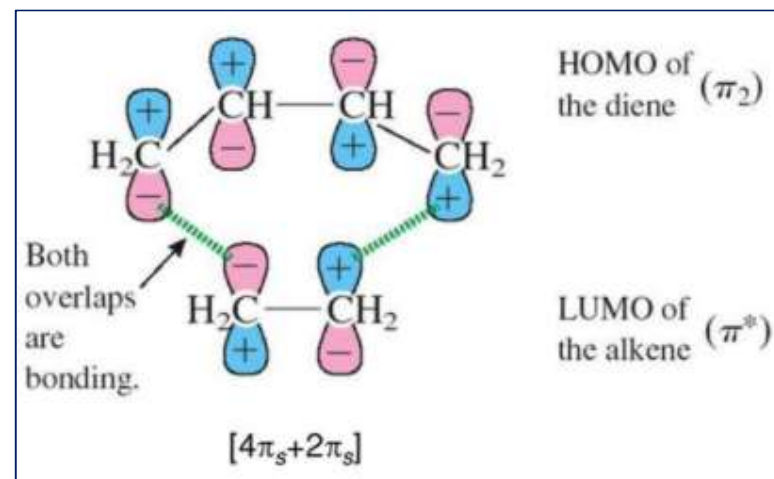
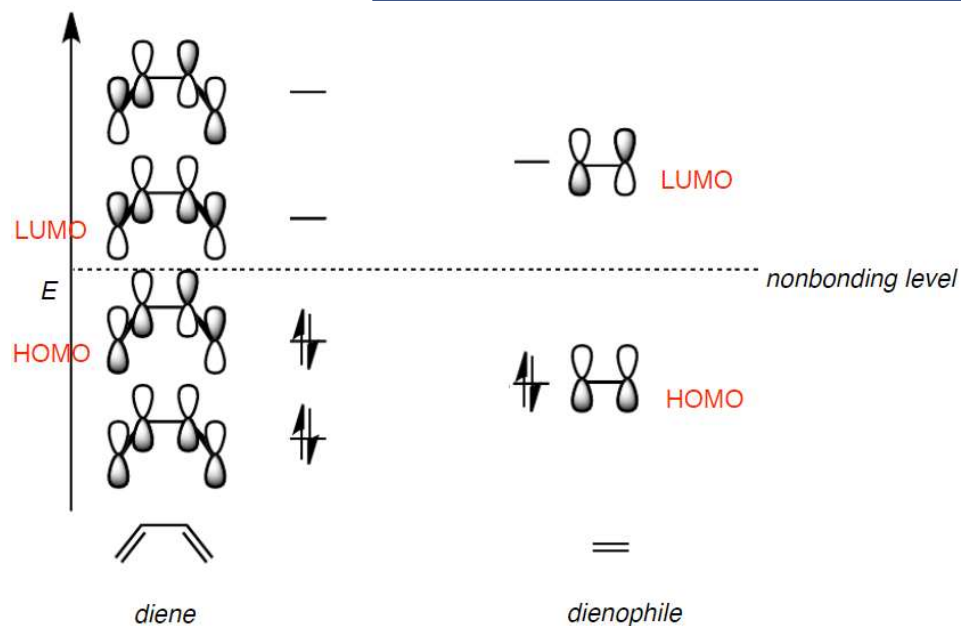


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# Fukui: Frontier Molecular Orbital (FMO) Theory



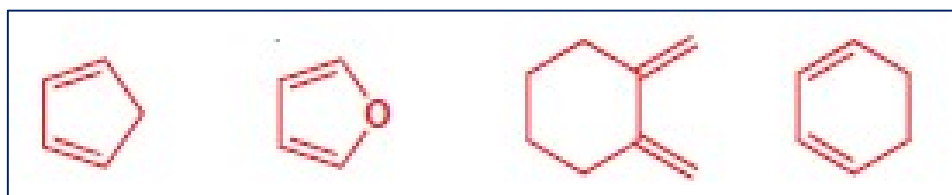
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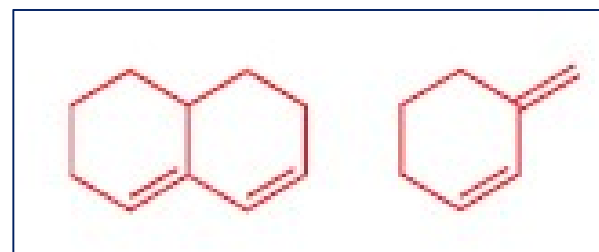
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*Cyclic dienes permanently in the s-cis conformation are ideal for Diels–Alder reactions but cyclic dienes that are permanently in the s-trans conformation and cannot change to the s-cis conformation will not undergo Diels–Alder reaction at all.*



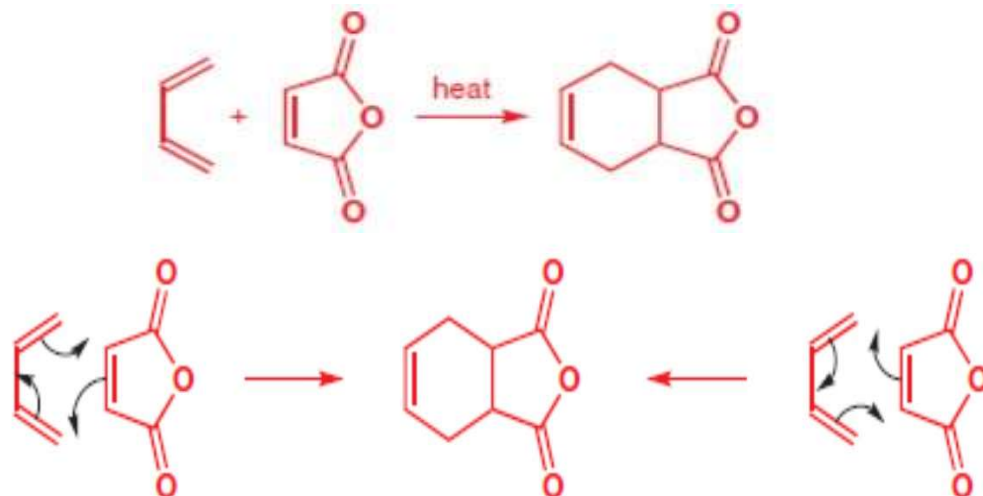
*s-cis conformation*



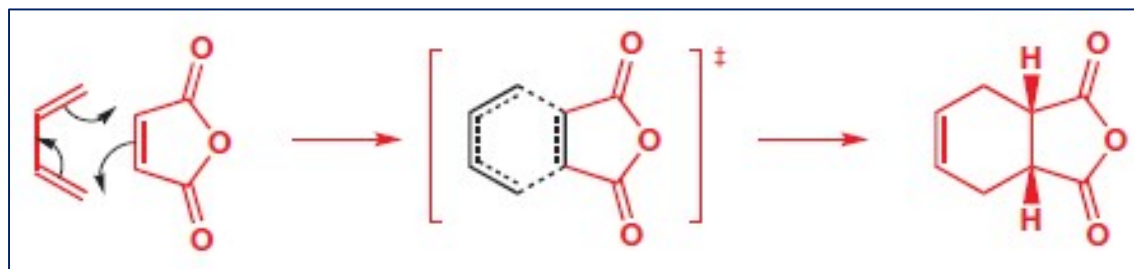
*s-trans conformation*

*In dienophiles, there must be some extra conjugation—at least a phenyl group or a chlorine atom— or the cycloaddition does not occur.*

*Consider the reaction between 1,3-butadiene and maleic anhydride:*



*Electrons are shown as rotating clockwise and anticlockwise respectively. Both mechanisms are equally correct as the electrons do not really rotate at all. The two  $\pi$  bonds disappear and two  $\sigma$  bonds take their place by the electrons moving smoothly out of the  $\pi$  orbitals into the  $\sigma$  orbitals. The cyclic transition state has six delocalized  $\pi$  electrons.*

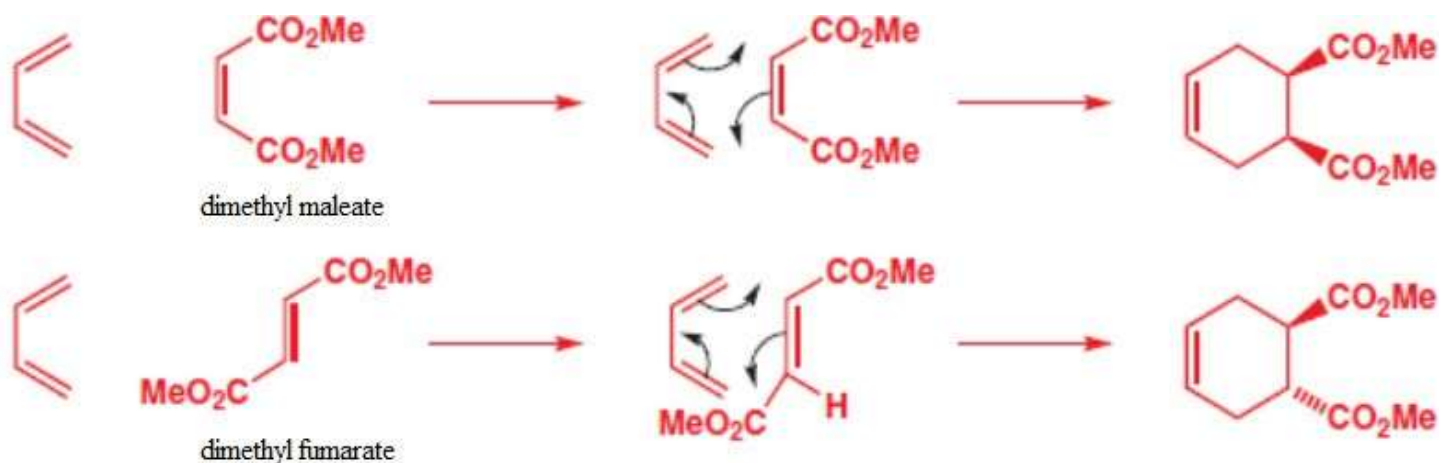


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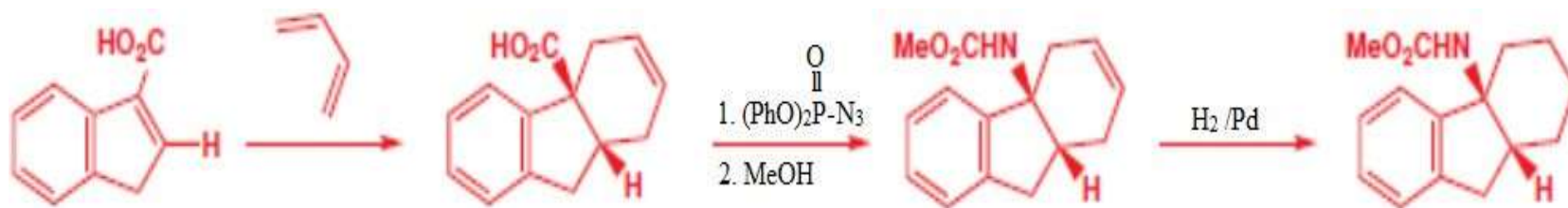
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Stereochemistry of product: The Diels–Alder reaction is stereospecific. i.e. the stereochemistry in the dienophile is correctly reproduced in the product. Thus *cis* and *trans* dienophiles give different diastereoisomers of the product. Esters of maleic and fumaric acids on reaction with 1,3-butadiene provide a simple example.



The stereochemistry at the ring junction must be *cis* because the cyclic dienophile can have only a *cis* double bond.



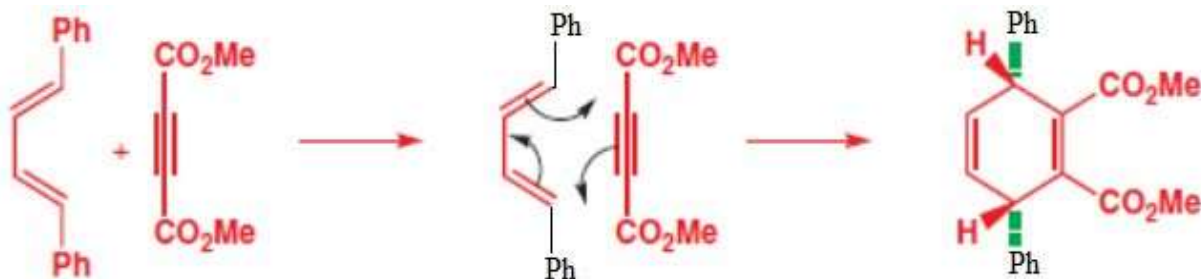
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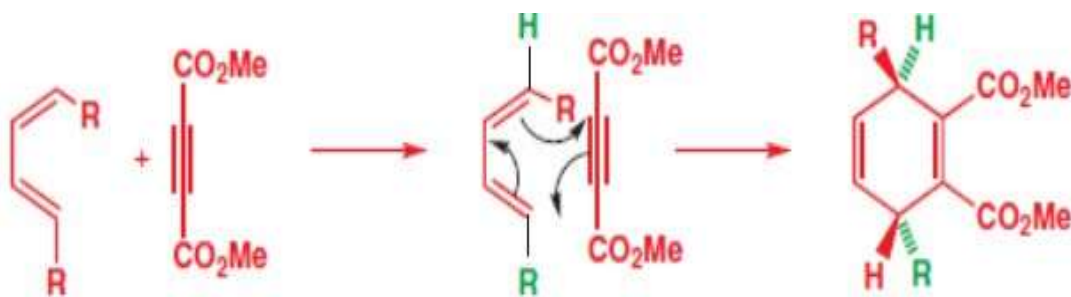
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### Stereochemistry of the diene:

*This is slightly more complicated as the diene can be cis,cis, or cis,trans (there are two of these if the diene is unsymmetrical), or trans,trans. A trans, trans-diene gives a product with the two substituents cis.*



*In case of the cis, trans unsymmetrical diene, the two substituents end up on opposite sides of the new six-membered ring.*





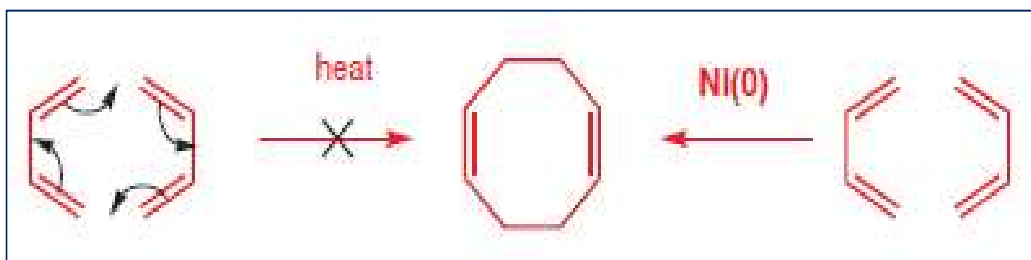
### *Cycloaddition reactions: Dimerizations of dienes*

*Dimerizations of dienes are reactions in which one molecule of the diene plays the role of the dienophile. This symmetry is called [4 + 2] cycloaddition (no. of atoms taking part).*



### *[4 + 2] cycloaddition*

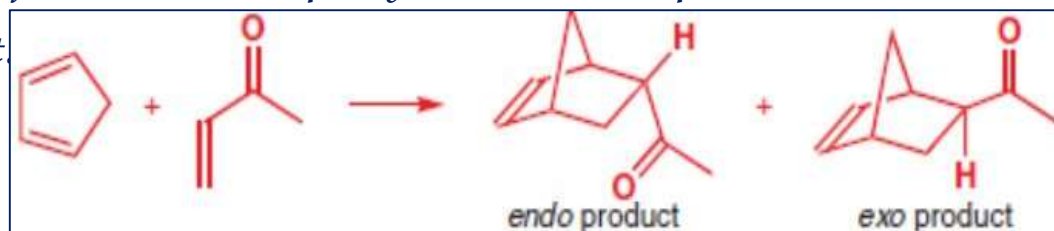
*However, dienes cannot undergo a [4 + 4] cycloaddition to form an eight-membered ring in one step (possible with transition metal catalysts).*



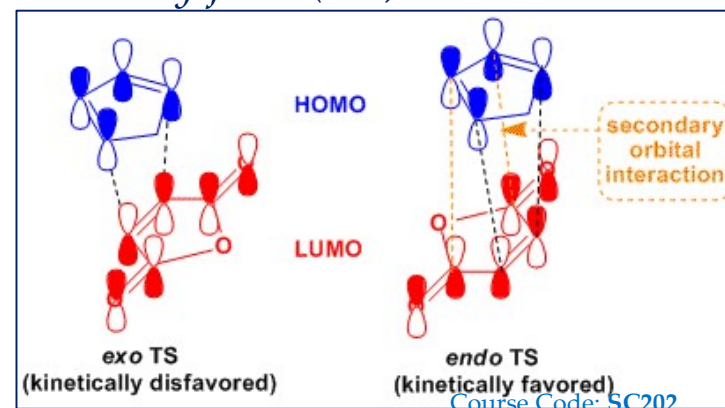
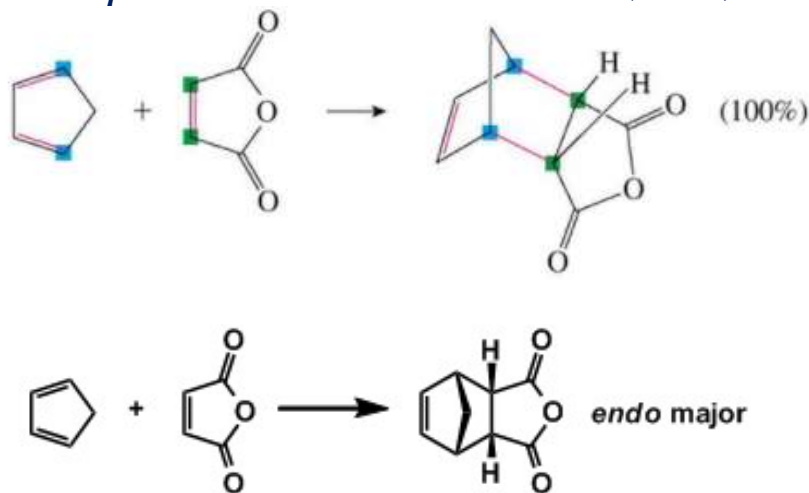
### *[4 + 4] cycloaddition*

*Solvents in Diels–Alder reaction: The reaction does not need a solvent and often the two reagents are mixed together and heated. However, water, an unsuitable solvent for organic reactions, has a hugely accelerating effect on this Diels–Alder reaction. Little water added to an organic solvent accelerates the reaction and the endo product selectivity of these reactions is far better than in other hydrocarbon solvents.*

The endo rule for Diels-Alder reaction: In case the Diels-Alder reaction is reversible and therefore under thermodynamic control, the *exo* product is formed instead of the preferred *endo* product. The *endo* product is less stable than the *exo* product however, it is preferred in irreversible Diels-Alder reactions. Therefore, it must be the kinetic product of the reaction. When a reaction produces more than one product, the product formed most rapidly is the *kinetic* product; the most stable product is the *thermodynamic* product.



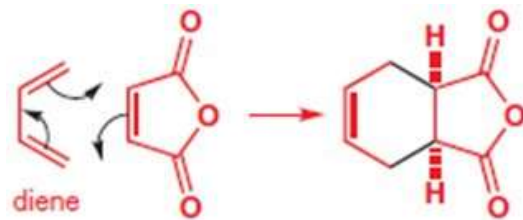
The *endo* product is formed faster when the dienophile has a substituent with  $\pi$  electrons. It has been suggested that this is due to stabilization of the transition state by the interaction of the  $p$  orbitals of the dienophile's substituent with the  $p$  orbitals of the new double bonds being formed in what was the diene. This interaction, called secondary orbital overlap, can occur only if the substituent with the  $p$  orbitals lies underneath (*endo*) rather than away from (*exo*) the six-membered ring.



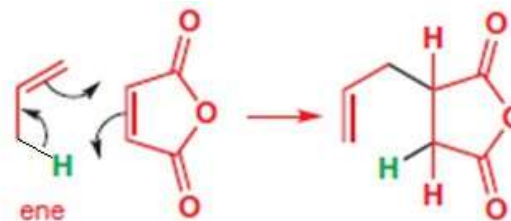
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*It is also pertinent to note that the Diels–Alder reaction is a cycloaddition reaction with an aromatic transition state that is ortho and para directing. Other thermal cycloadditions include the Alder-ene reaction.*



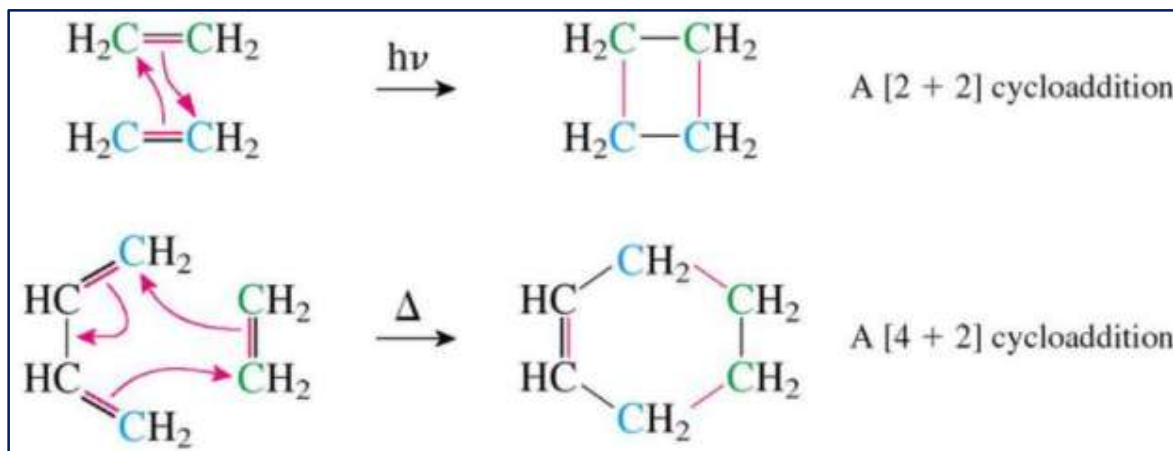
*Diels-Alder reaction*



*Alder-ene reaction*

*The cycloadditions are all suprafacial—they occur on one face only of each  $\pi$  system— For a thermally allowed reaction there should be  $4n + 2$  electrons in the mechanism, For a photochemically allowed reaction there should be  $4n$  electrons in the mechanism. These rules are dictated by orbital symmetry.*

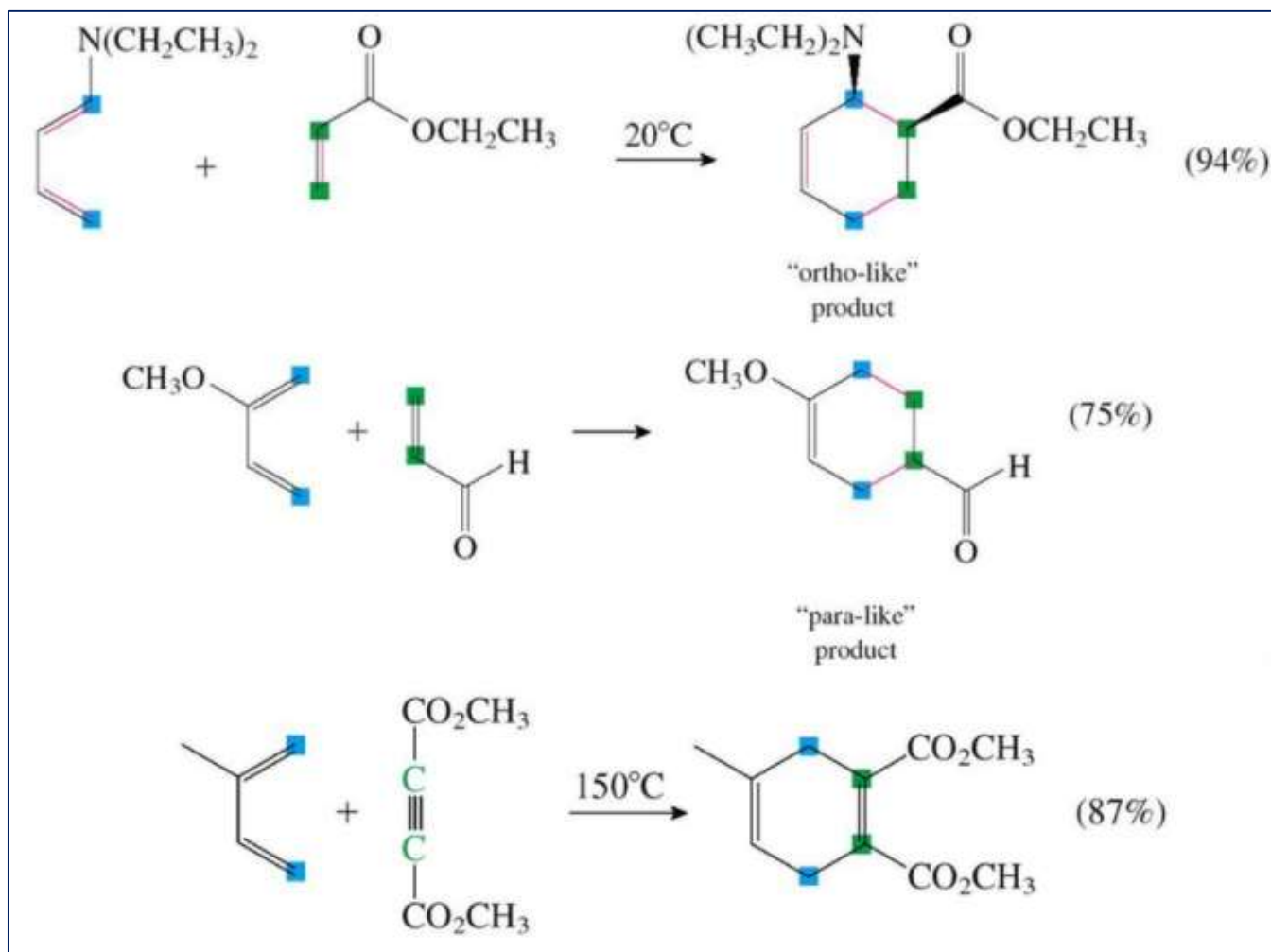
- HOMO of one reactant combines with LUMO of other
- Possible in thermal  $[4 + 2]$  cycloaddition
- Photochemical  $[2 + 2]$  cycloaddition reaction occurs smoothly



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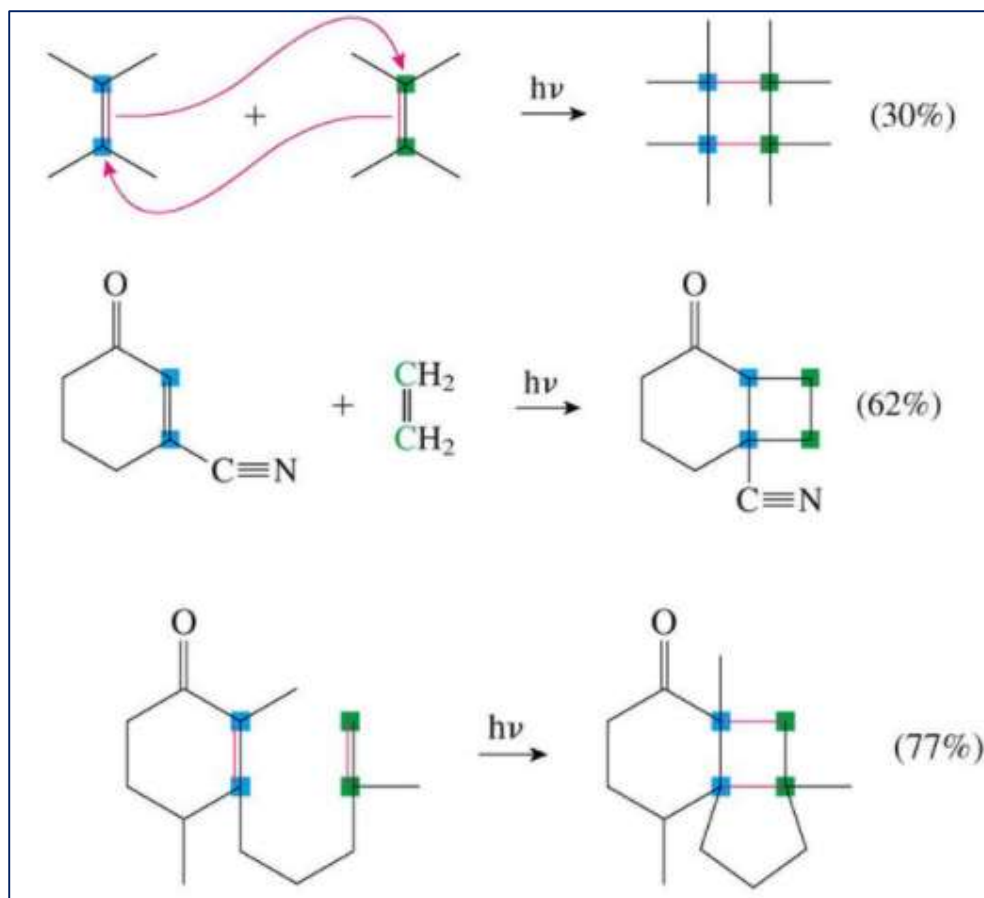
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## [2+2] cycloaddition-photo irradiation



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*Woodward–Hoffmann rules as applicable to Diels–Alder reaction:*

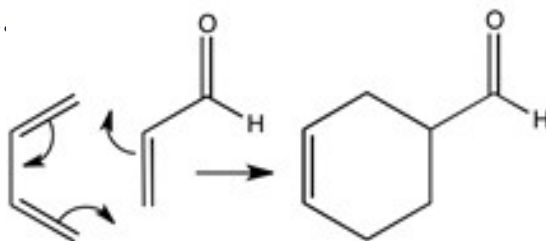
*In a thermal pericyclic reaction, the total number of  $(4q + 2)s$  and  $(4r)a$  components must be odd. That is,*

*For a thermal pericyclic reaction to be allowed/possible,  
the sum: number of suprafacial components with 2, 6, or 10 electrons + number of  
antarafacial components with 0, 4, or 8 electrons = an odd number*

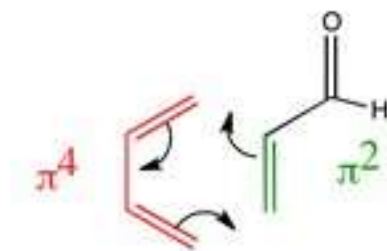
*Only the number of relevant components that must be odd, not the number of electrons,  
are to be accounted. Ignore any components like suprafacial components with four  
electrons as they do not*

*count. When applied to Diels–Alder reaction mentioned above,*

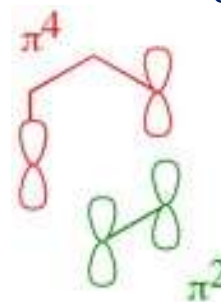
*1. Draw the reaction mechanism.*



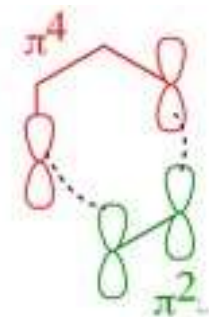
2. Choose the components. All the bonds taking part in the mechanism must be included and no others.



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. Link the components by dotted lines at sites of new bond formation.

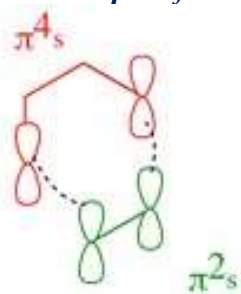


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5. Label each component 's' or 'a' depending on whether new bonds are formed on the same or on opposite sides. [Suprafacial: If a component undergoes addition (forms bond) on the same face, it is called a suprafacial component; Antarafacial: If a component undergoes addition on opposite faces, it is called an antarafacial component]. In most of cycloadditions both components react suprafacially.



6. 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  $(4r)_a$  (antarafacial) components.

Therefore, total = 1, so it is an allowed reaction.

Components of the other symmetry, that is  $(4q + 2)_a$  and  $(4r)_s$  components, do not count.

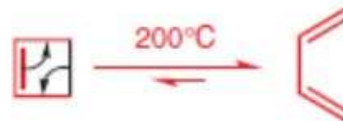


Electrocyclic reactions **These reactions are defined as involving the cyclization of an  $n$   $\pi$ -electron system to an  $(n-2)\pi + 2\sigma$ -electron system or the reverse process.**

An electrocyclic reaction is the concerted cyclization of a conjugated  $\pi$ -electron system by converting one  $\pi$ -bond to a ring forming  $\sigma$ -bond. In an electrocyclic reaction, a ring is always broken or formed. E.g. hexatriene heated upto  $500^\circ\text{C}$ .

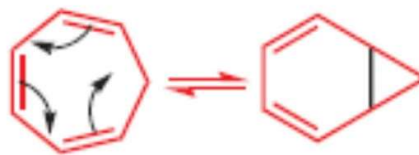


The reverse reaction may be called electrocyclic ring opening. E.g. electrocyclic ring opening of cyclobutene due to ring strain in the four-membered ring; ring-opening is preferred to ring closure.



In case of cycloheptatriene, it exists in equilibrium with its bicyclic isomer norcaradiene. The decrease in ring strain is counterbalanced by formation of a  $\sigma$  bond by breaking a  $\pi$  bond.

In cycloaddition reaction, two new  $\sigma$  bonds are formed/broken. whereas in a sigmatropic rearrangement one  $\sigma$  bond forms while one breaks

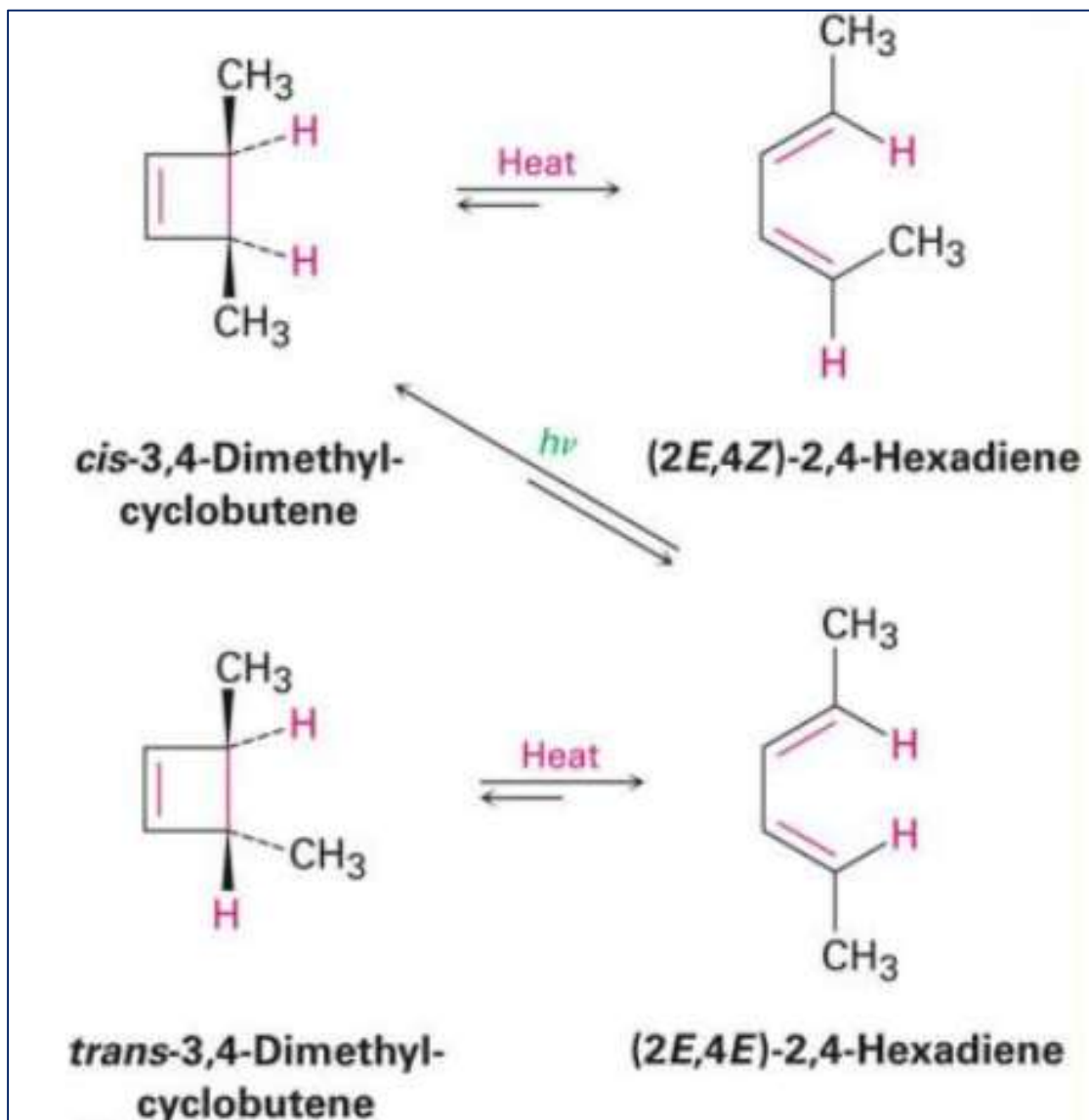
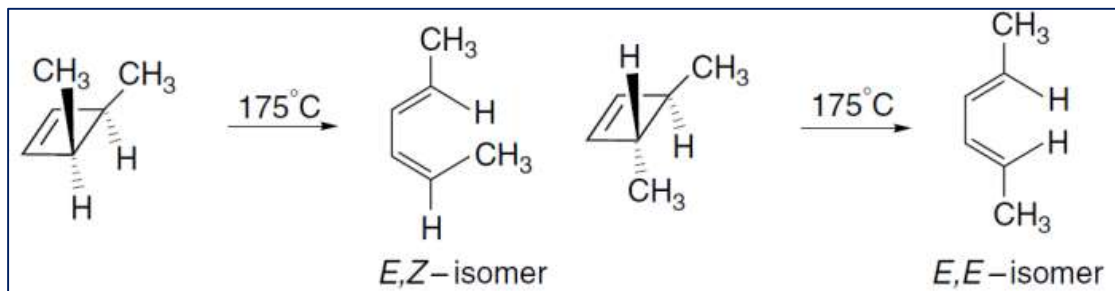


Stereochemical Rules for Electrocyclic Reactions		
Electron pairs (double bonds)	Thermal reaction	Photochemical reaction
Even number	Conrotatory	Disrotatory
Odd number	Disrotatory	Conrotatory

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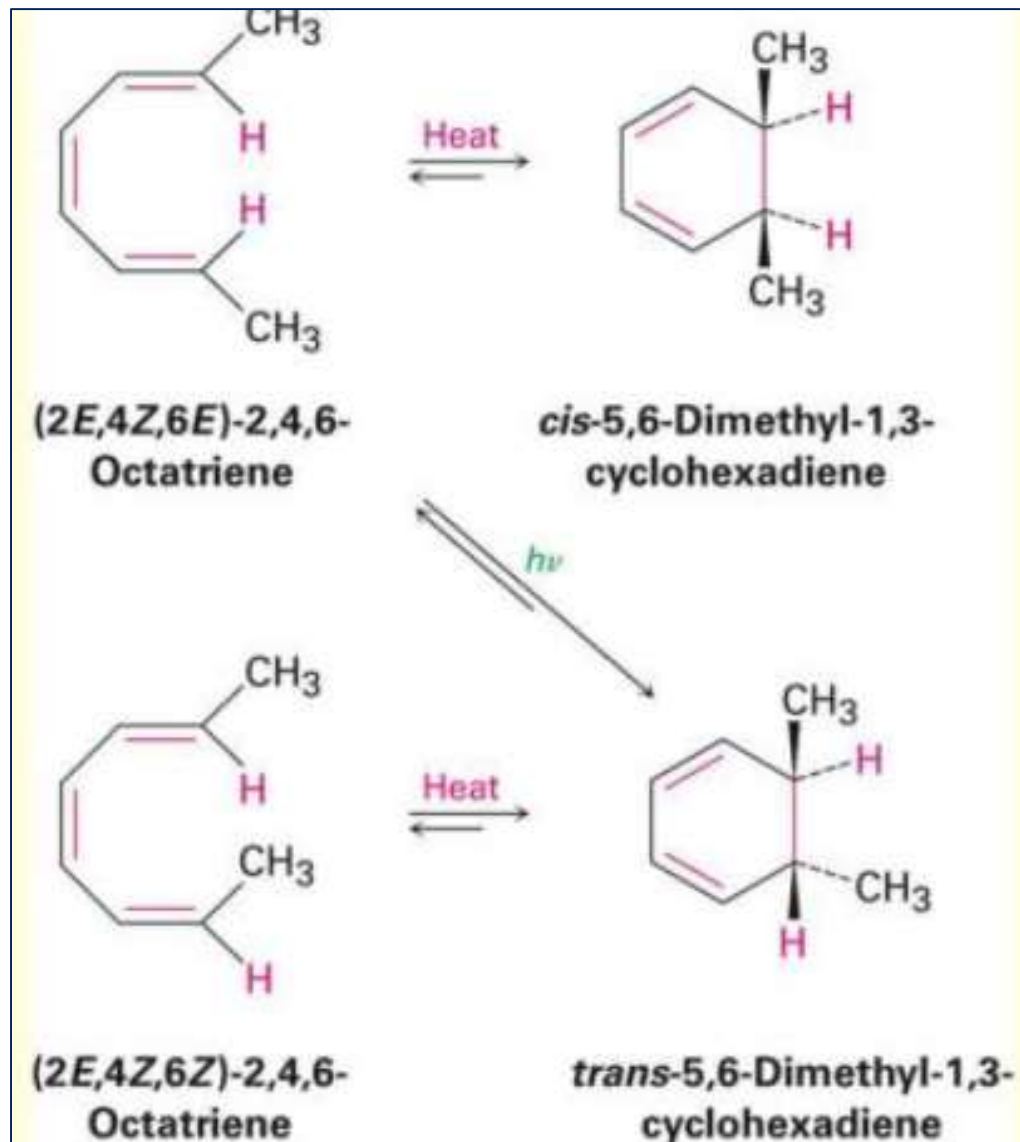
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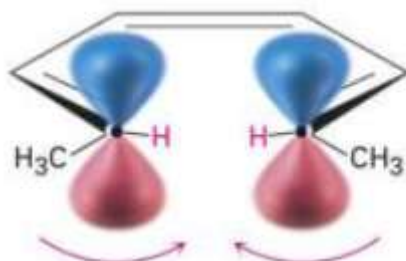
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# Two distinct modes are possible

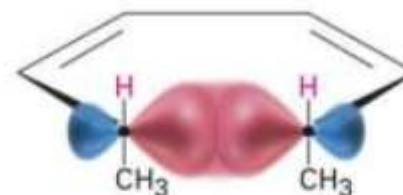
disrotatory  
ring closure



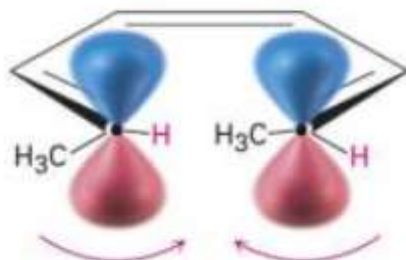
conrotatory  
ring closure



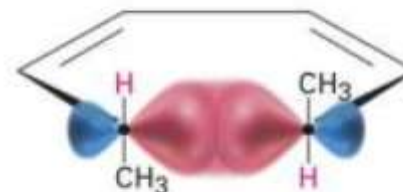
(2E,4Z,6E)-2,4,6-Octatriene



cis-5,6-Dimethyl-1,3-cyclohexadiene



(2E,4Z,6Z)-2,4,6-Octatriene



trans-5,6-Dimethyl-1,3-cyclohexadiene

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*A double bond is a  $\pi_2$  component. The number 2 is the most important part of this designation and 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) but may not have mixtures of  $\pi$  and  $\sigma$  electrons.*

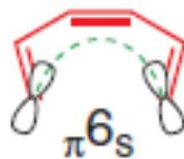
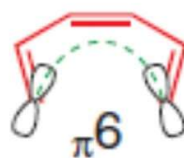
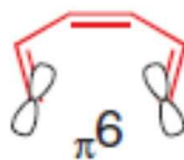
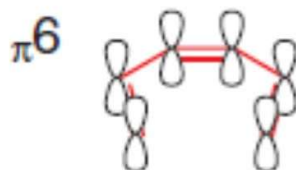
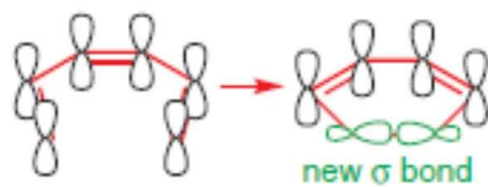
*The notations  $(4q + 2)$  and  $(4r)$  simply refer to the number of electrons in the component where  $q$  and  $r$  are integers.*

*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.*



### *Woodward–Hoffmann Rules:*

- 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 (only!).*
- 4. Join up the components where new bonds are to be formed. Make sure you join orbitals that are going to form new bonds.*
- 5. Label each component s or a depending on whether new bonds are formed on the same or on opposite sides. We called this reaction 's' because the top halves of the two  $\pi$  orbitals join together.*
- 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.*



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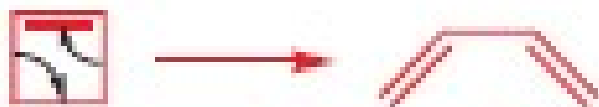
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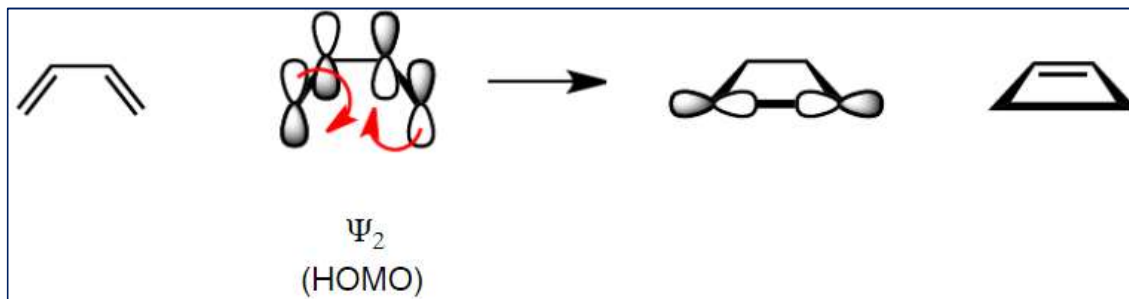
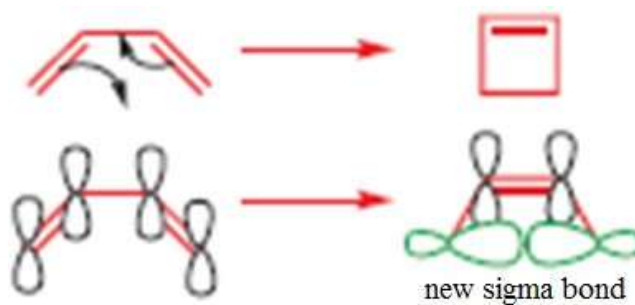
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*The Woodward–Hoffmann rules does not predict the mechanism of the reaction, it only conveys if the reaction is allowed/disallowed.*

*Consider the reaction*



*Conversely, for the reverse reaction*



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*Apply Woodward–Hoffmann Rules:*

- 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. Make sure you join orbitals that are going to form new bonds.*
- 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. However, the reaction does take place.*

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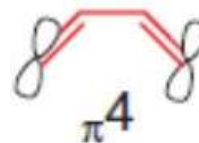
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*Apply Woodward–Hoffmann Rules again:*

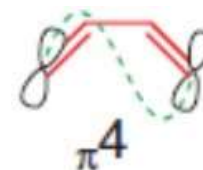
*Repeat steps 1 & 2.*

*3. Make a three-dimensional drawing of the way in which the components come together for the*

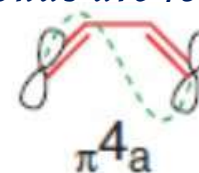
*reaction, putting in orbitals at the ends of the components.*



*4. Join up the components where new bonds are to be formed. Make sure you join orbitals that are going to form new bonds.*



*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 one  $(4r)a$  component. Total = 1 so this is an allowed reaction.*

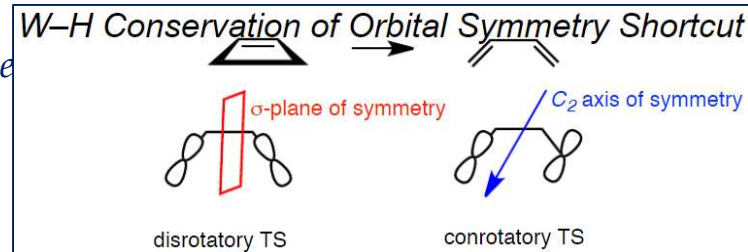
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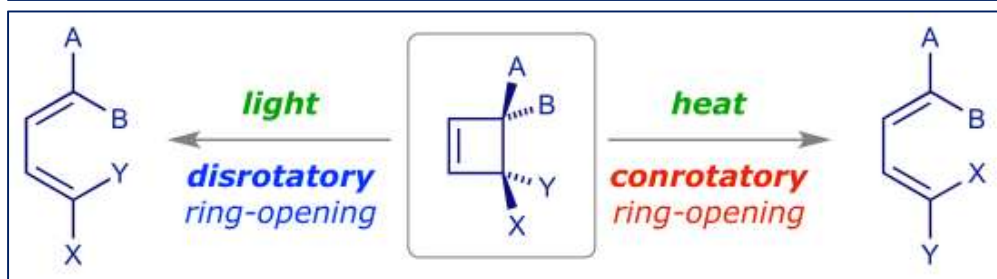
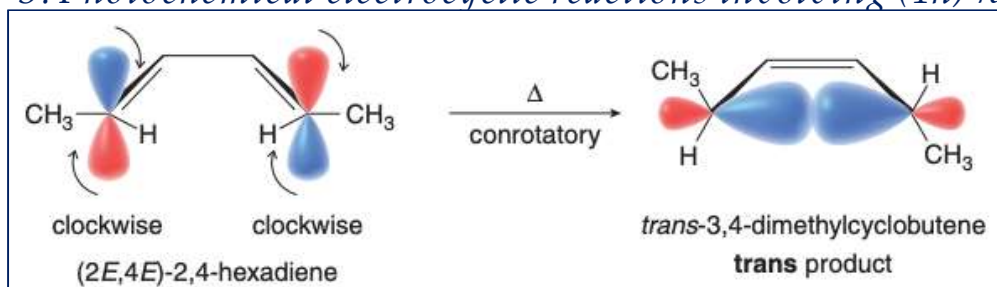
Conrotatory reactions are those in which the two substituents located at the termini of a conjugated double bond system rotate in the same direction during ring opening or closure: both clockwise or both anticlockwise.

In disrotatory reactions, one group rotates clockwise, one anticlockwise



Rules for electrocyclic reactions:

1. All electrocyclic reactions are allowed, both thermal and photochemical provided the rotation is right.
2. Thermal electrocyclic reactions involving  $(4n + 2) \pi$  electrons are disrotatory.
3. Thermal electrocyclic reactions involving  $(4n) \pi$  electrons are conrotatory.
4. Photochemical electrocyclic reactions involving  $(4n + 2) \pi$  electrons are conrotatory.
5. Photochemical electrocyclic reactions involving  $(4n) \pi$  electrons are disrotatory.



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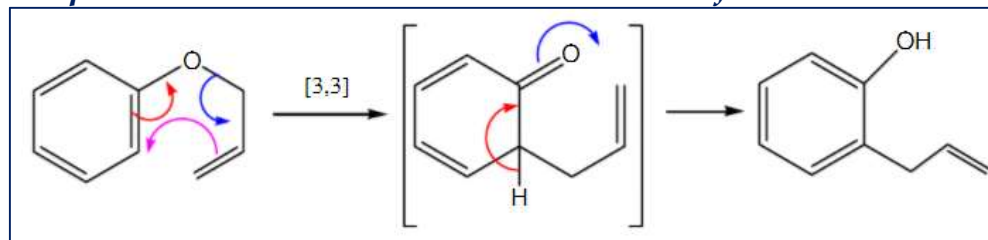
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Sigmatropic Reactions: These reactions are defined as involving migration of a  $\sigma$  bond that is flanked by one or more conjugated systems to a new position within the system

Molecular rearrangements in which a  $\sigma$ -bonded atom or group, flanked by one or more  $\pi$ -electron systems, shifts to a new location with a corresponding reorganization of the  $\pi$ -bonds are called sigmatropic reactions. The total number of  $\sigma$ -bonds and  $\pi$ -bonds remain unchanged.



The difference between this and a cycloaddition is that one of the arrows starts on a  $\sigma$  bond instead of on a  $\pi$  bond. The second step in the reaction is a simple ionic proton transfer to regenerate aromaticity.

Stereochemical Rules for Sigmatropic Rearrangements		
Electron pairs (double bonds)	Thermal reaction	Photochemical reaction
Even number	Antarafacial	Suprafacial
Odd number	Suprafacial	Antarafacial

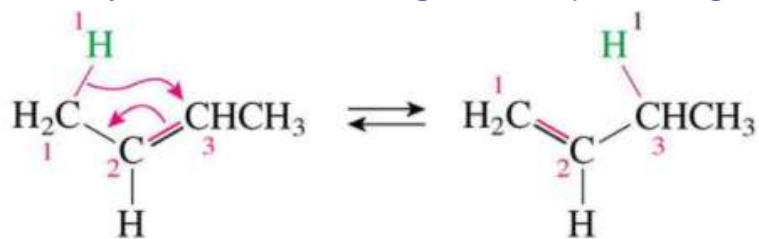
hydrogen is forced to migrate suprafacially in cases where there is an odd number of electron pairs involved in the migration (symmetric HOMO) and antarafacially in cases where there is an even number of pairs of electrons involved in the migration (antisymmetric HOMO).

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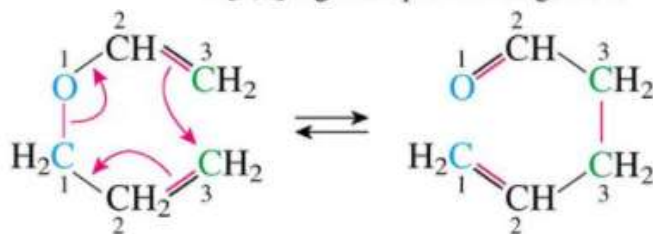
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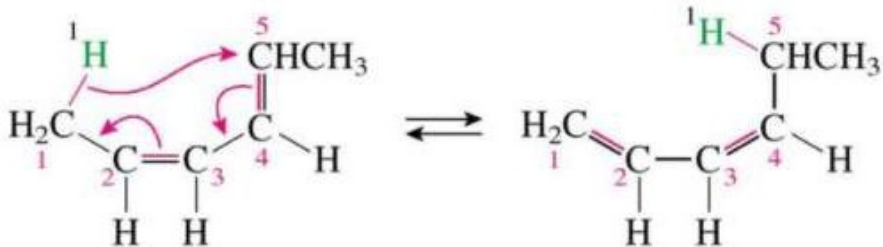
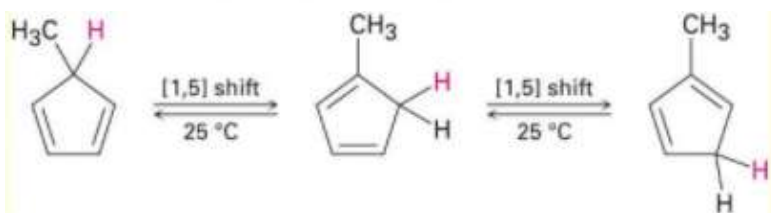
# Rules for thermal sigmatropic migrations of hydrogen



A [1,3] sigmatropic rearrangement



A [3,3] sigmatropic rearrangement



A [1,5] sigmatropic rearrangement

[1,3]H shift

stereochemistry  
feasibility

antarafacial  
impossible

[1,5]H shift

suprafacial  
easy

[1,7]H shift

antarafacial  
possible

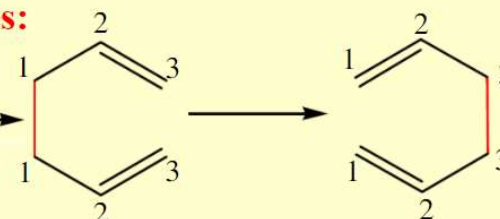
Photochemical [1,n] H sigmatropic shifts follow the opposite rules. i.e.

[1,7]H photochemical sigmatropic shift is suprafacially possible.

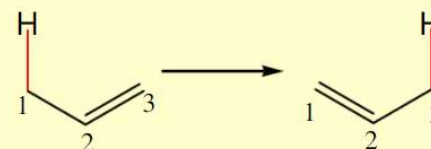
The reaction is termed [i, j] sigmatropic shift when the bond migrates from position [1,1] to position [i,j].

Examples:

migrating  $\sigma$  bond



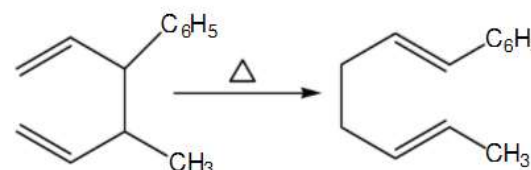
[3,3] sigmatropic shift



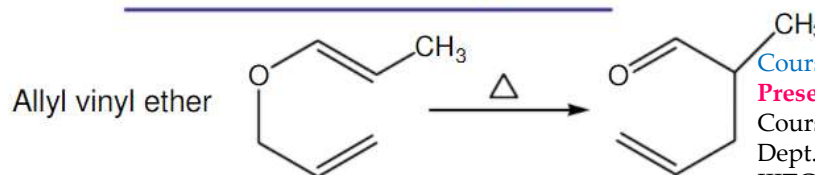
[1,3] sigmatropic shift

Suprafacial [3,3] Cope and Claisen Rearrangements

**A Cope rearrangement**



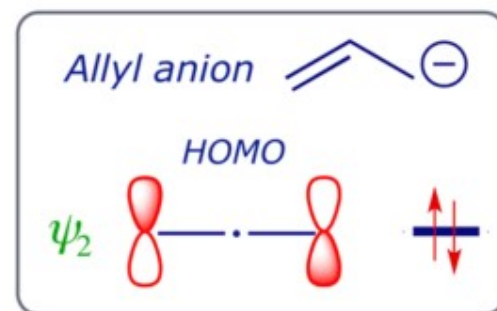
**A Claisen rearrangement**



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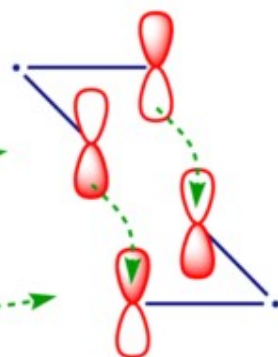
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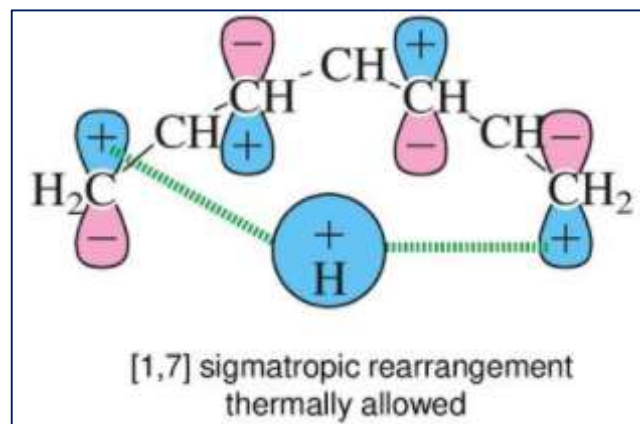
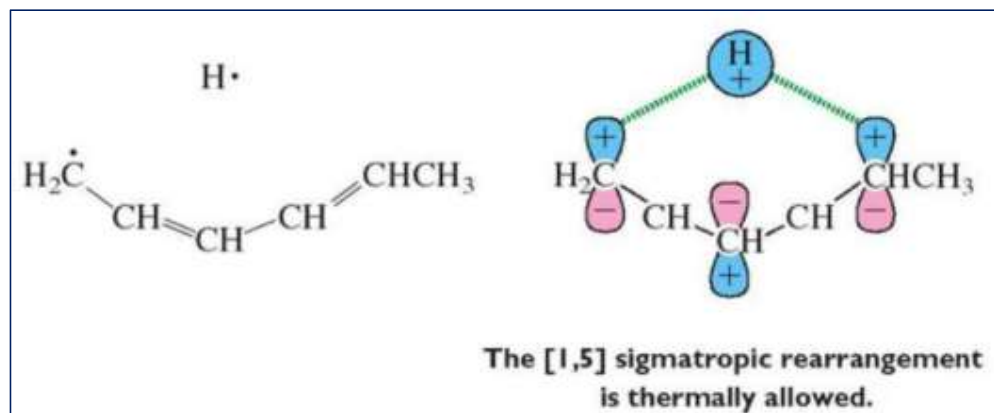
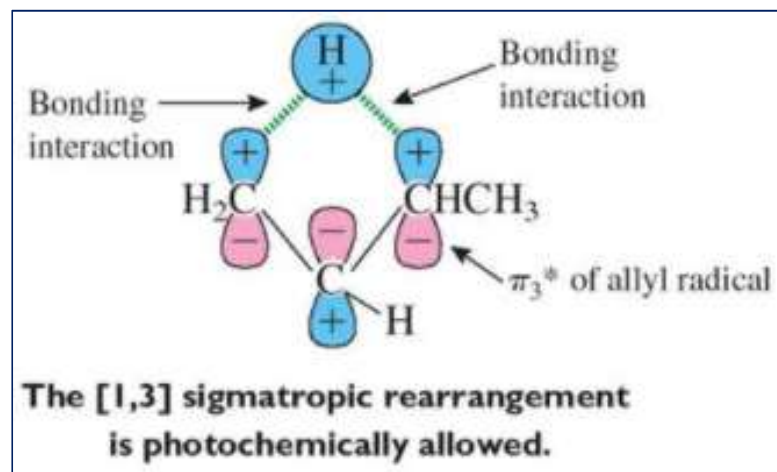
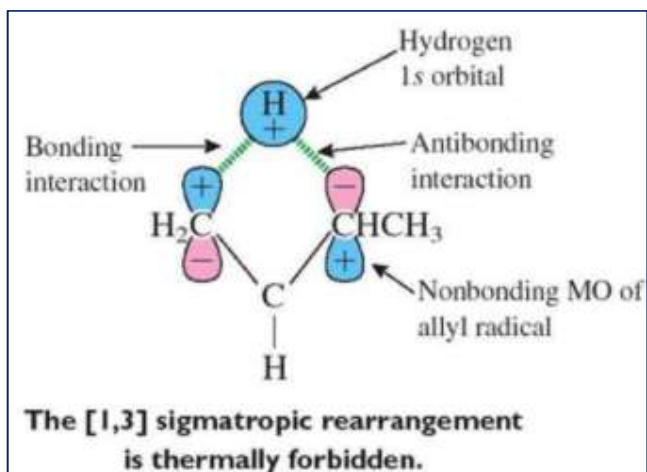


LUMO ( $2e^-$ )  
allyl cation  $\psi_2$

HOMO ( $4e^-$ )  
allyl anion  $\psi_2$



*[3,3] Sigmatropic rearrangement viewed as the  **$[\pi 4s + \pi 2s]$  cycloaddition** of allyl anion to allyl cation. Both components can react **suprafacially** through a chair-like transition structure.*



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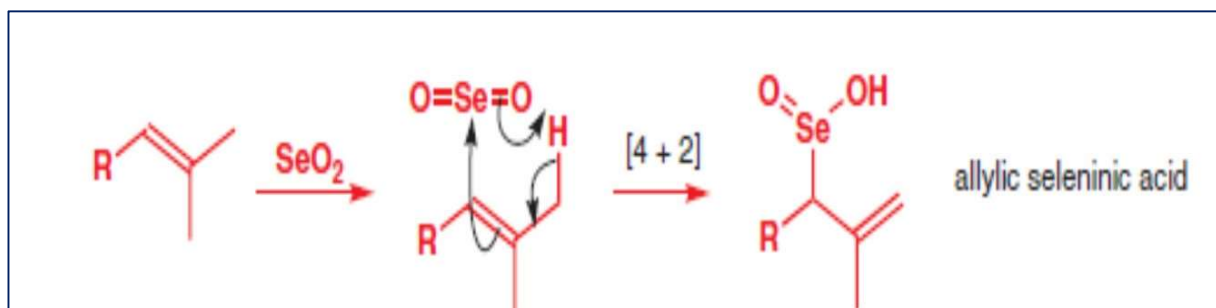
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### Ene Reactions:

The joining of a double or triple bond to an alkene reactant having a transferable allylic hydrogen is called an ene reaction. The reverse process is called a retro ene reaction. E.g.

Selenium dioxide will react with alkenes in a  $[4 + 2]$  cycloaddition reminiscent of the ene reaction.





Stereochemical Rules for Pericyclic Reactions				
Electronic state		Electron pairs		Stereochemistry
Ground state (thermal)		Even number		Antara-con
		Odd number		Supra-dis
Excited state (photochemical)		Even number		Supra-dis
		Odd number		Antara-con
Electrocyclic $\Delta$	$4n+2$	disrot	$4n$	conrot
Electrocyclic $h\nu$	$4n+2$	conrot	$4n$	disrot
Sigmatropic $\Delta$	$4n+2$	supra	$4n$	antara
Sigmatropic $h\nu$	$4n+2$	antara	$4n$	Supra
cycloaddition $\Delta$	$4n+2$	Supra-supra	$4n$	Supra-antara
cycloaddition $h\nu$	$4n+2$	Supra-antara	$4n$	Supra-supra

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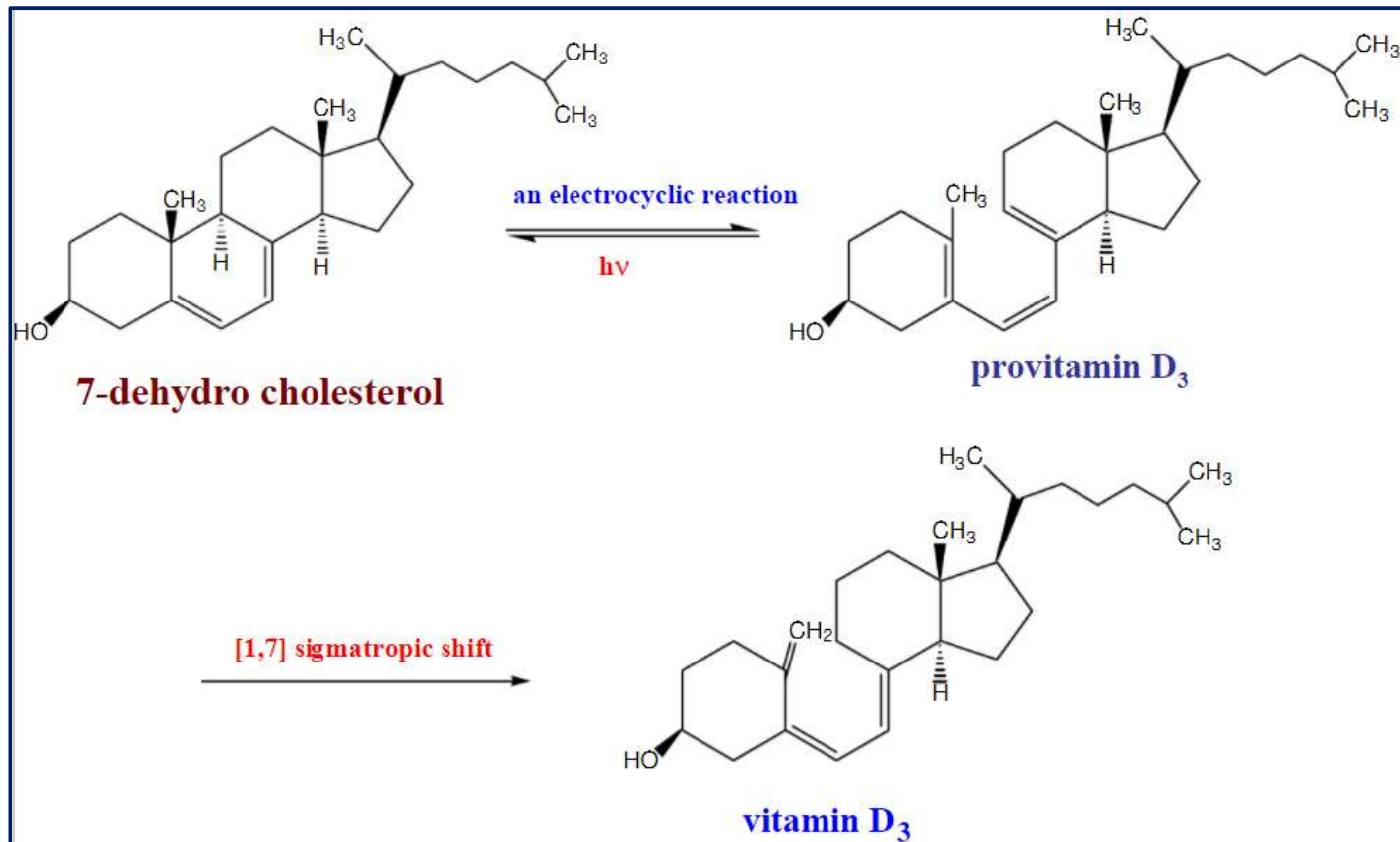
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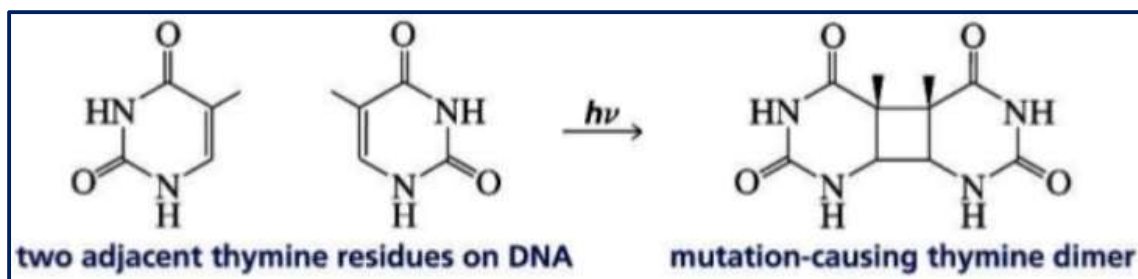
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**A biological reaction involving an electrocyclic reaction and a sigmatropic reaction**



**7-dehydrocholesterol, a steroid formed in skin, is converted into Vitamin D<sub>3</sub> by two pericyclic reactions**



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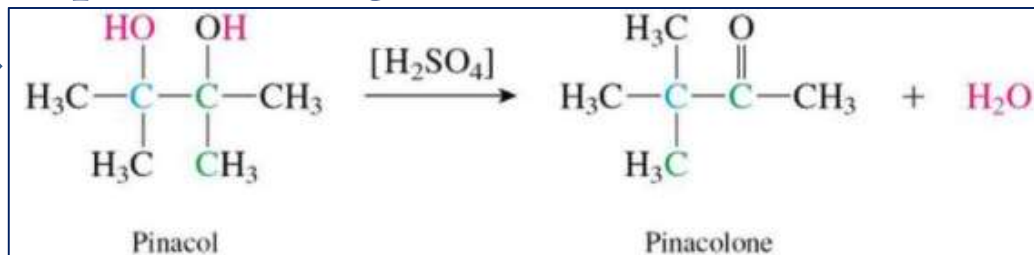
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## Important Sigmatropic Rearrangements

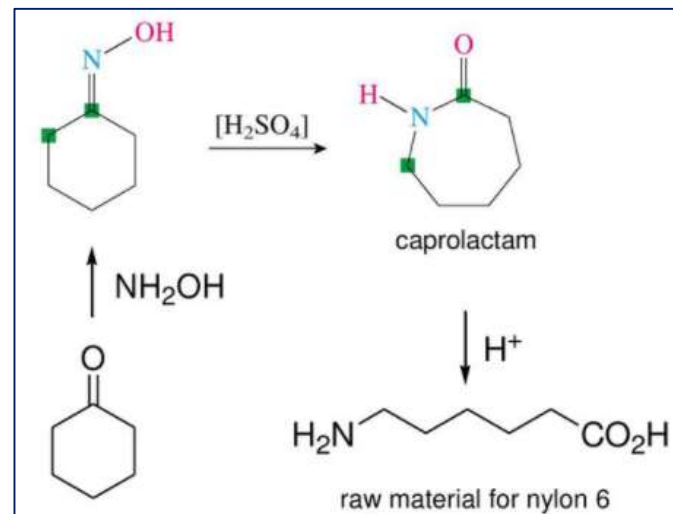
□ Pinacol rearrangement: 1,2-alkyl shift

◆ [1,2] sigmatropic shift to a carbocation



□ Beckmann rearrangement: 1,2-shift

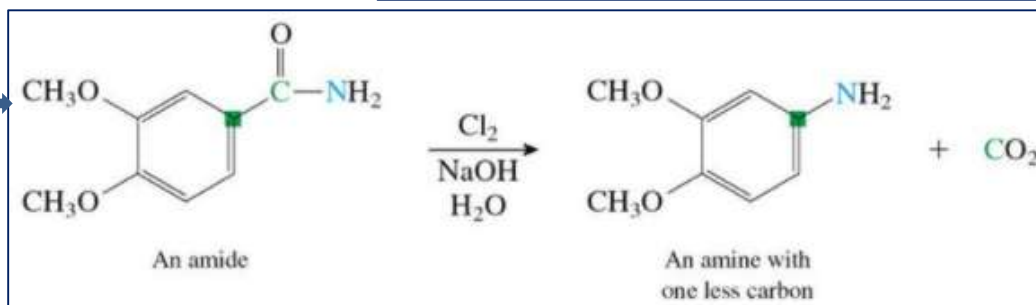
◆ R anti to OH of an oxime: caprolactam



□ Hofmann rearrangement: amide with  $\text{X}_2$

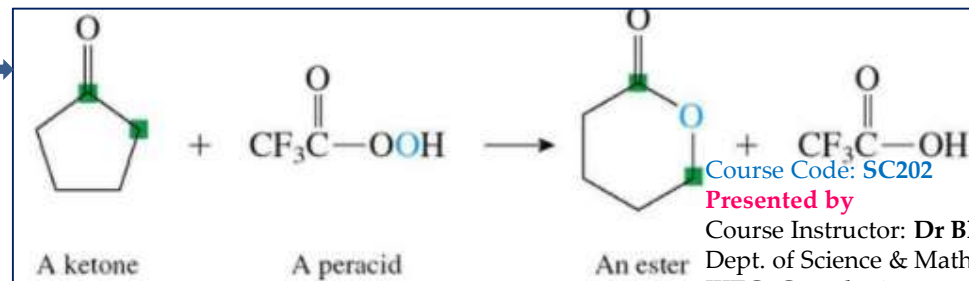
◆ one less carbon homologation:  $\text{RCO}_2\text{H} \rightarrow \text{RNH}_2$

◆ Curtius rearrangement:  $\text{RCON}_3$



□ Baeyer-Villiger rearrangement

◆ ketones to esters / cyclic ketones to  $\omega$ -hydroxyesters



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