

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 π -systems. The concerted nature of the reactions leads to good stereochemical control of the product. Pericyclic reactions are usually rearrangement reactions.

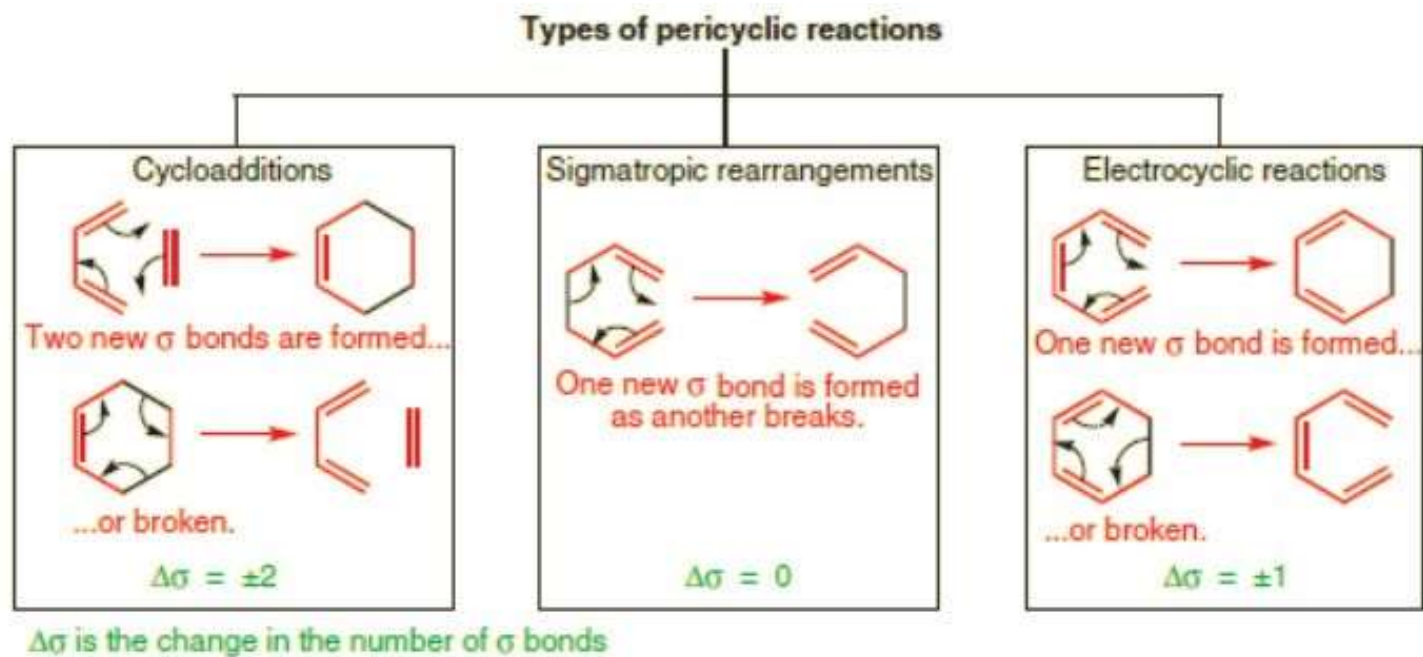
The salient features of these reactions are:

- Pericyclic reactions have a cyclic transition state.*
- While in this transition state, a concerted rearrangement of the electrons takes place that causes σ and π -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.*

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 σ bonds formed or broken.



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Course Instructor: **Dr Bhar Saha**
Dept. of Science & Mathematics
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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.

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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

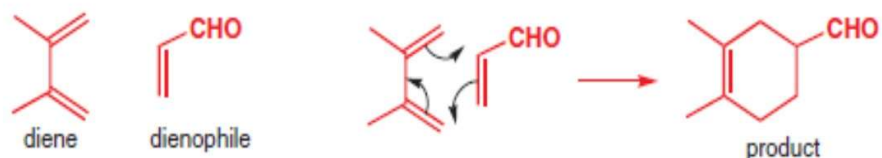
HOMO + HOMO -> antibonding MO

LUMO + LUMO -> null interaction (no electrons)

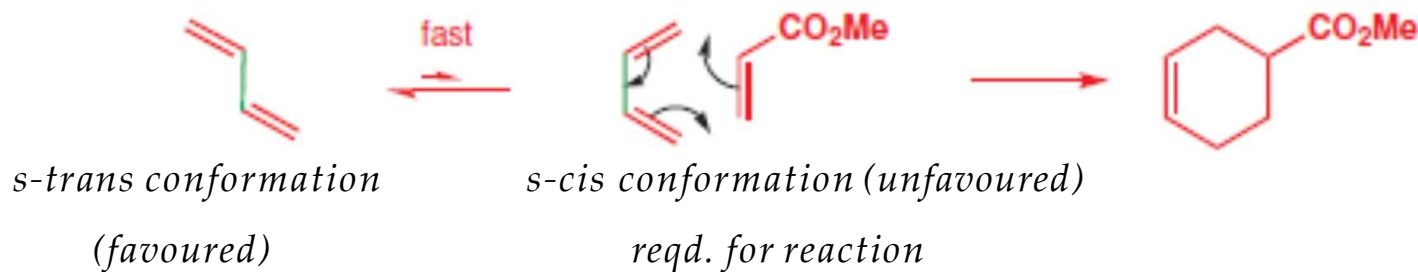
SOMO + SOMO -> bonding MO

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 π -systems, including Diels-Alder cycloaddition.

Cycloaddition reactions: A concerted combination of two π -electron systems to form a ring of atoms having two new σ bonds and two fewer π bonds is called a cycloaddition reaction. e.g. Diels–Alder reaction, between a conjugated diene and an alkene, usually called the 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 σ bond). The energy barrier to rotation about the central σ bond is small (about 30 kJ mol⁻¹ at room temperature) and rotation to the less favourable but reactive *s-cis* conformation is rapid.

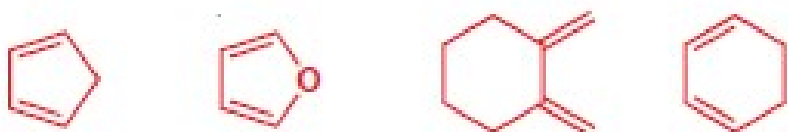


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Cyclic dienes permanently in the s-cis conformation are ideal for Diels–Alder reactions but cyclic dienes that are permanently in the s-trans conformation and cannot change to the s-cis conformation will not undergo Diels–Alder reaction at all.



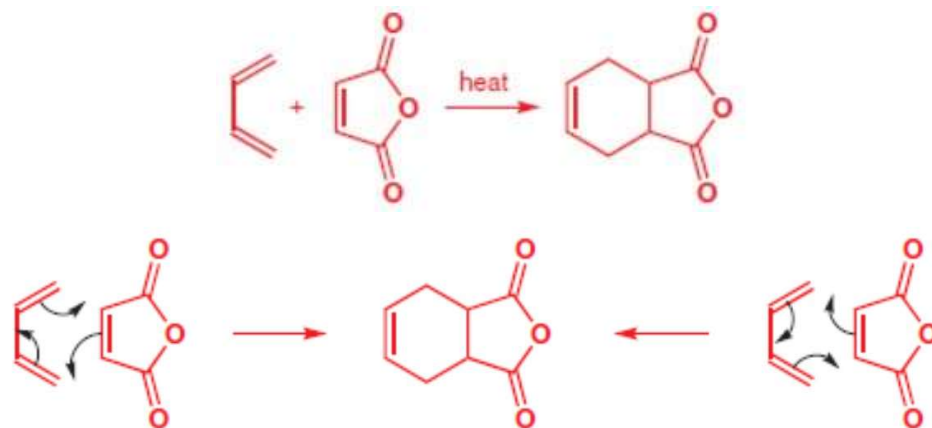
s-cis conformation



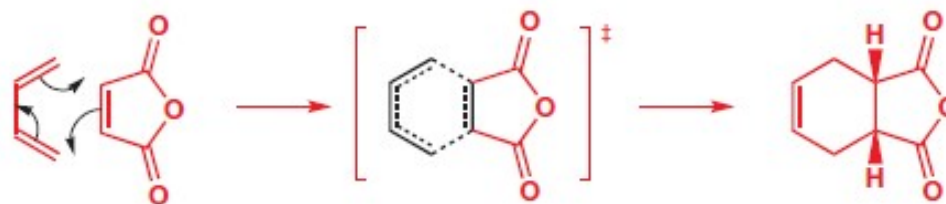
s-trans conformation

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 π bonds disappear and two σ bonds take their place by the electrons moving smoothly out of the π orbitals into the σ orbitals. The cyclic transition state has six delocalized π electrons.

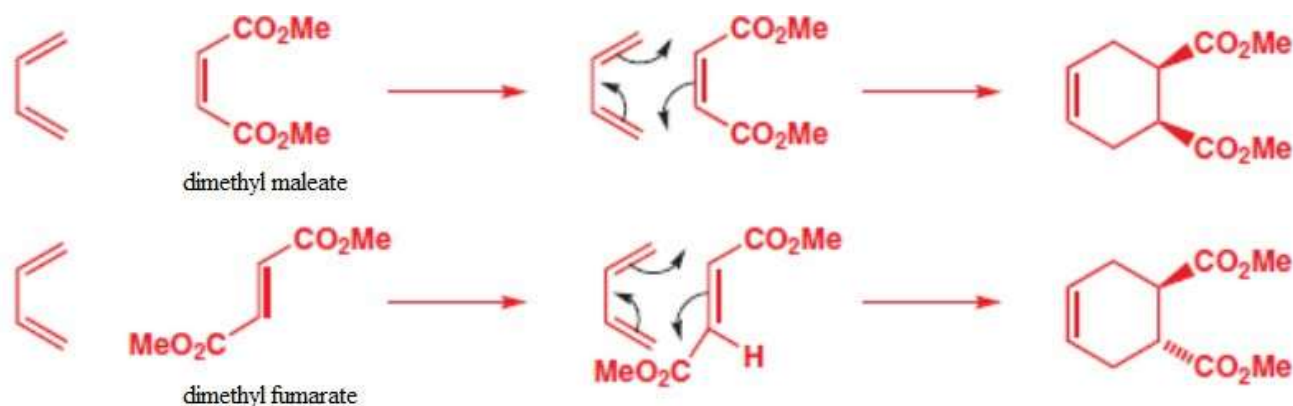


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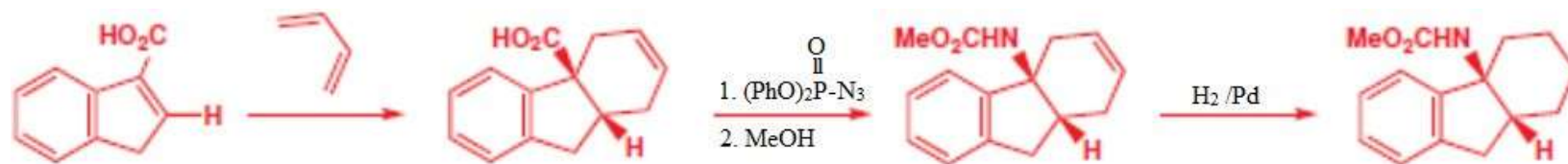
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Stereochemistry of product: The Diels–Alder reaction is stereospecific. i.e. the stereochemistry in the dienophile is correctly reproduced in the product. Thus *cis* and *trans* dienophiles give different diastereoisomers of the product. Esters of 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.



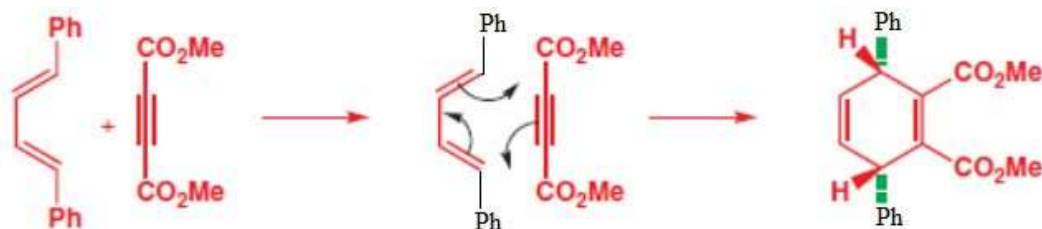
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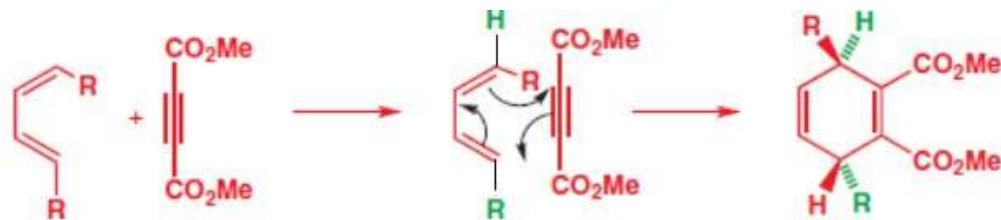
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Stereochemistry of the diene:

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).



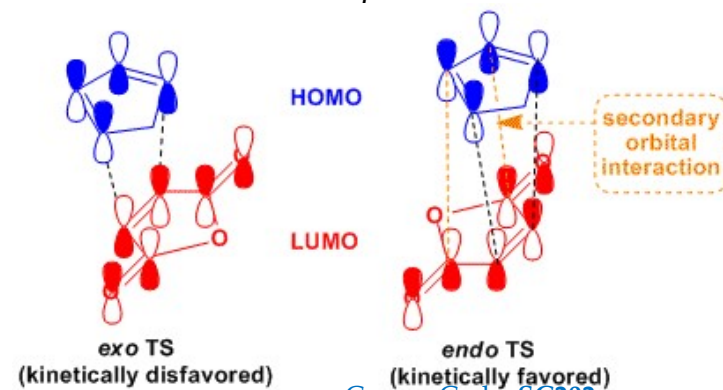
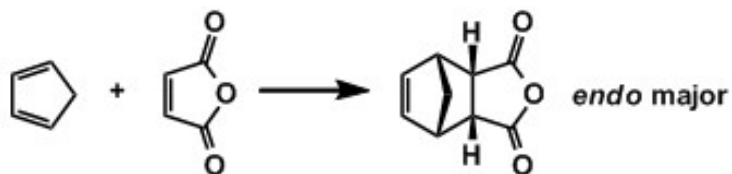
[4 + 4] cycloaddition

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 π 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.

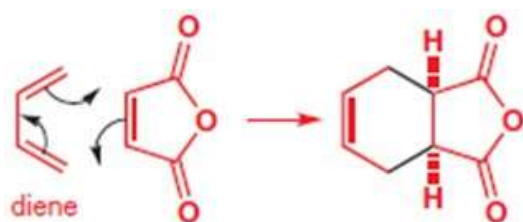


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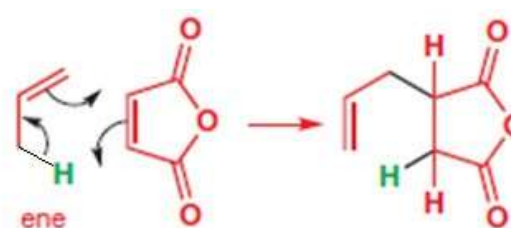
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It is also pertinent to note that the Diels–Alder reaction is a cycloaddition reaction with an aromatic transition state that is ortho and para directing. Other thermal cycloadditions include the Alder-ene reaction.



Diels-Alder reaction



Alder-ene reaction

*The cycloadditions are all suprafacial — they occur on one face only of each π 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.*

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.

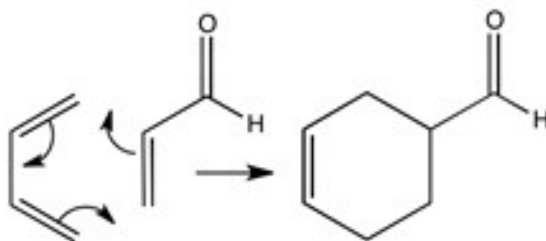
That is,

For a thermal pericyclic reaction to be allowed/possible,

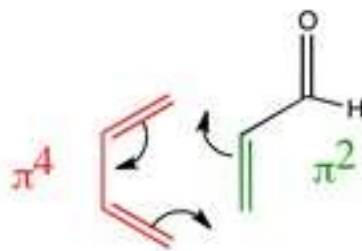
the sum: number of suprafacial components with 2, 6, or 10 electrons + number of antarafacial components with 0, 4, or 8 electrons = an odd number

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,

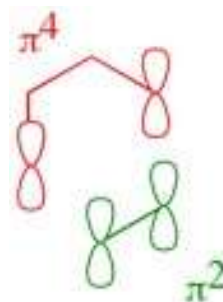
1. Draw the reaction mechanism.



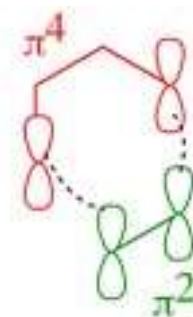
2. Choose the components. All the bonds taking part in the mechanism must be included and no others.



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.

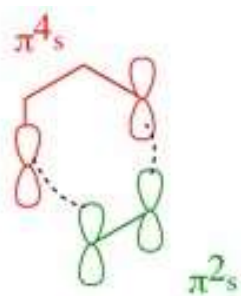


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5. Label each component 's' or 'a' depending on whether new bonds are formed on the same or on opposite sides. [Suprafacial: If a component undergoes addition (forms bond) on the same face, it is called a suprafacial component; Antarafacial: If a component 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.

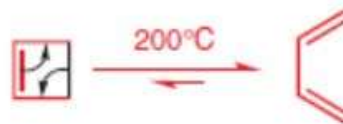
Therefore, total = 1, so it is an allowed reaction.

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

Electrocyclic reactions: An electrocyclic reaction is the concerted cyclization of a conjugated π -electron system by converting one π -bond to a ring forming σ -bond. In an electrocyclic reaction, a ring is always broken or formed. E.g. hexatriene heated upto 500°C.

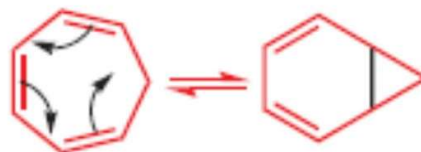


The reverse reaction may be called electrocyclic ring opening. E.g. electrocyclic ring opening of cyclobutene due to ring strain in the four-membered ring; ring-opening is preferred to ring closure.



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

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



A double bond is a π_2 component. The number 2 is the most important part of this designation and simply refers to the number of electrons. The prefix π tells us the type of electrons.

A component may have any number of electrons (a diene is a π_4 component) but may not have mixtures of π and σ 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 π_2 component and so it is of the $(4q + 2)$ kind while a diene is a π_4 component and so is of the $(4r)$ kind.

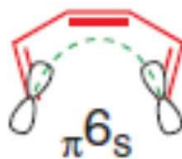
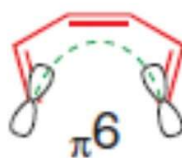
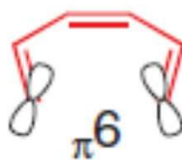
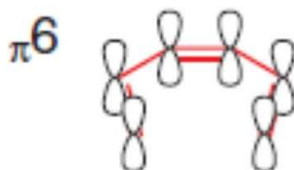
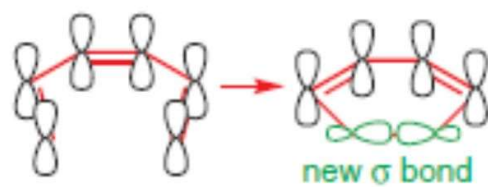
Woodward–Hoffmann Rules:

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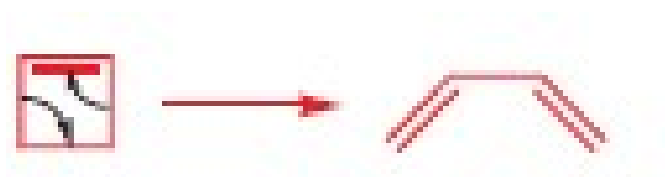
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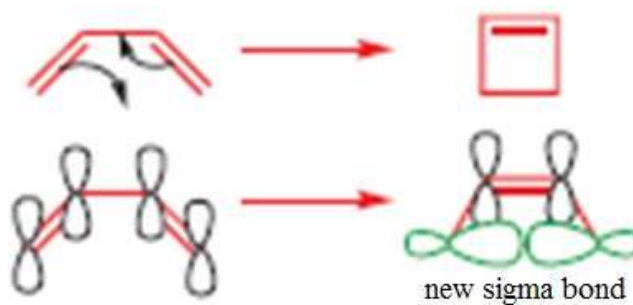
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The Woodward–Hoffmann rules does not predict the mechanism of the reaction, it only conveys if the reaction is allowed/disallowed.

Consider the reaction



Conversely, for the reverse reaction



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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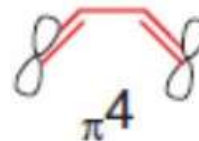
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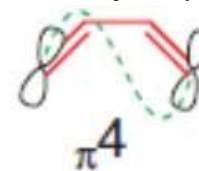
Apply Woodward–Hoffmann Rules again:

Repeat steps 1 & 2.

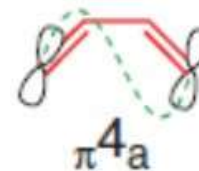
3. Make a three-dimensional drawing of the way in which the components come together for the reaction, putting in orbitals at the ends of the components.



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 ring closure : both clockwise or both anticlockwise.

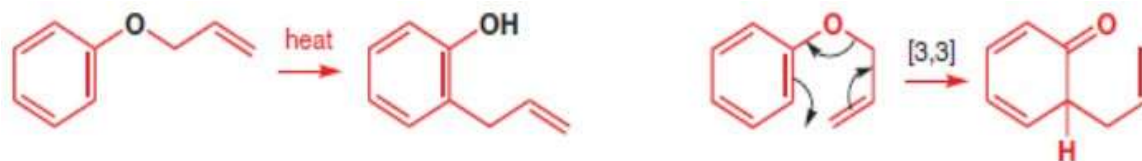
In disrotatory reactions, one group rotates clockwise and one anticlockwise.

Rules for electrocyclic reactions:

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

Sigmatropic Reactions:

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



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

Rules for thermal sigmatropic migrations of hydrogen

	[1,3]H shift	[1,5]H shift	[1,7]H shift
stereochemistry	antarafacial	suprafacial	antarafacial
feasibility	impossible	easy	possible

Photochemical [1,n] H sigmatropic shifts follow the opposite rules. i.e. [1,7]H photochemical sigmatropic shift is suprafacially possible.

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.

