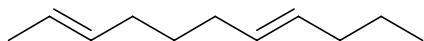


Conjugated Systems, Orbital Symmetry and UV Spectroscopy

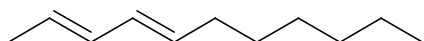
Introduction

There are several possible arrangements for a molecule which contains two double bonds (diene):

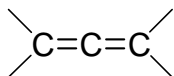
Isolated: (two or more single bonds between them)



Conjugated: (one single bond between them)



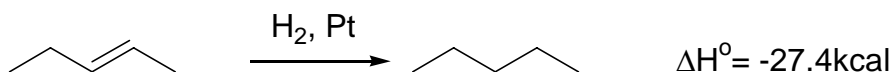
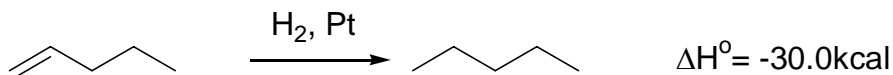
Cumulated: (zero single bonds between them: allenes)



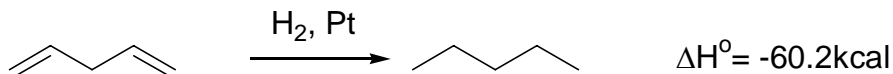
Conjugated double bonds are found to be the most stable.

Stabilities

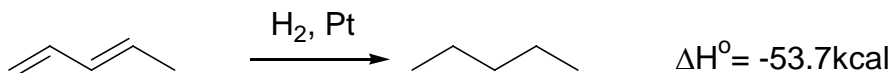
Recall that heat of hydrogenation data showed us that di-substituted double bonds are more stable than mono-substituted double bonds.



When a molecule has two **isolated** double bonds, the heat of hydrogenation is essentially equal to the sum of the values for the individual double bonds.

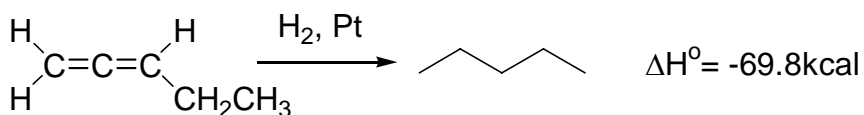


For **conjugated** dienes, the heat of hydrogenation is less than the sum of the individual double bonds.



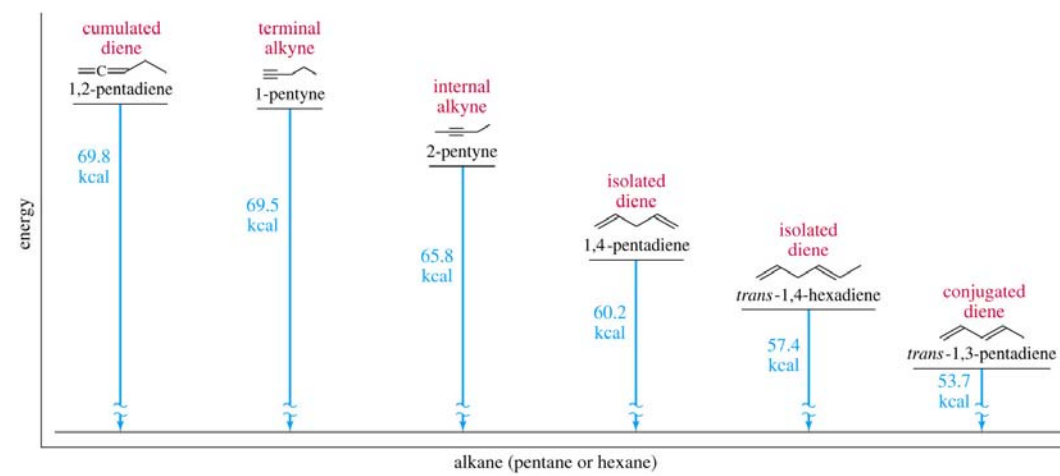
The **conjugated** diene is more stable by about 3.7kcal/mol.
(Predicted $-30 + (-27.4) = -57.4 \text{ kcal}$, observed -53.7 kcal)

Allenes, which have **cumulated** double bonds are less stable than isolated double bonds.



Increasing Stability Order (least to most stable)

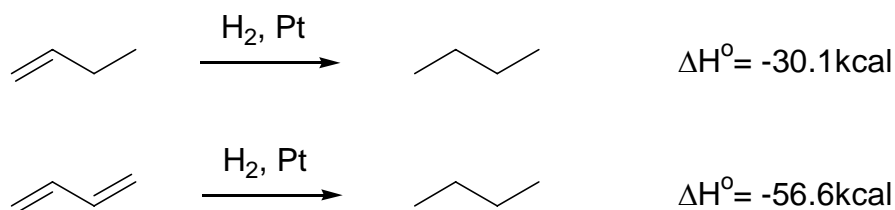
Cumulated diene	-69.8kcal
Terminal alkyne	-69.5kcal
Internal alkyne	-65.8kcal
Isolated diene	-57.4kcal
Conjugated Diene	-53.7kcal



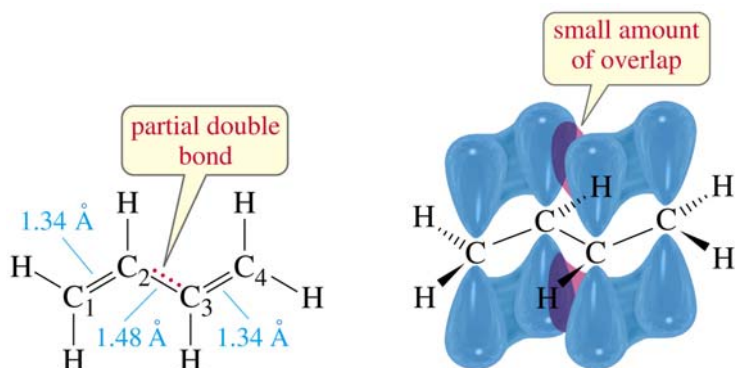
Molecular Orbital (M.O) Picture

The extra stability of conjugated double bonds versus the analogous isolated double bond compound is termed the **resonance energy**.

Consider 1,3-butadiene:



($2 \times -30.1 = -60.2 \text{ kcal}$). Resonance energy of 1,3-butadiene is 3.6 kcal.



The C2-C3 bond is much shorter than a normal alkane single bond (1.48 Å vs. 1.54 Å). This is mainly due to the π bonding overlap (resulting in some double bond character).

The planar arrangement, and the alignment of the p orbitals allows overlap between the two double bonds. The electrons are delocalized over the full length of the molecule.

This delocalization of electrons creates partial double bond character between C2 and C3.

Lewis structures cannot *accurately* depict delocalized structures, and we turn to molecular orbital theory.

M.O.'s of 1,3-butadiene

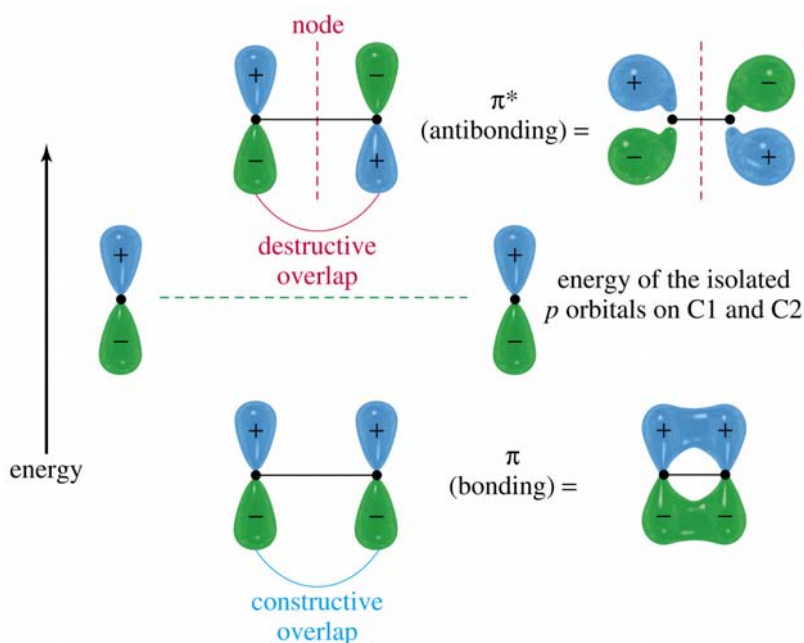
All four carbons are sp^2 hybridized, and in the planar conformation, all the p orbitals overlap.

But first, let us recap simple MO theory using ethene:

Each p orbital has two lobes, with differing wavefunction sign (+/-, black/white, shaded/unshaded – not electrical charges).

A π bonding orbital is formed by overlap of p lobes with the **same** wavefunction sign. (Constructive overlap).

A π anti-bonding orbital is formed by overlap of p lobes with **opposite** wavefunction sign. (Destructive overlap).



Electrons have a **lower** potential energy in the bonding MO than in the original p orbitals, and a **higher** potential energy in the anti-bonding orbitals.

In the ground state of ethene, two electrons fill the bonding MO, and the antibonding MO is empty.

MO Rules:

Constructive overlap = bonding

Destructive overlap = antibonding

Number of π MO's = Number of p orbitals

The MO energies are symmetrically distributed above and below the initial energies of the p orbitals.

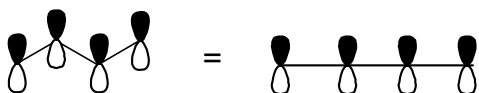
Half the MO's are bonding, the other half antibonding.)

So, now for 1,3-butadiene:

There are 4 p orbitals to consider.

The lowest energy MO will have the greatest number of favorable interactions (i.e. with all the p lobes interacting constructively).

This is called π_1 .



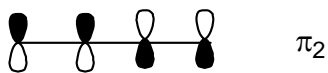
(Although 1,3-butadiene is **not** linear, it is easier and convenient to represent it as such).

This MO places electron density on all four carbon atoms.

There are 3 bonding interactions and this MO delocalizes the electrons over four nuclei.

This explains why there is **partial double bond** character between C2 and C3.

The next MO has a node in the center of the molecule.

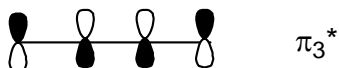


This is a classic diene MO, with bonding between C1-C2, and C3-C4.

There is an **antibonding** interaction between C2-C3.

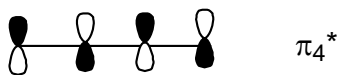
This MO has two bonding and one antibonding interactions – so we expect it to be overall **bonding**, but higher in energy than π_1 .

The third MO has two nodes.



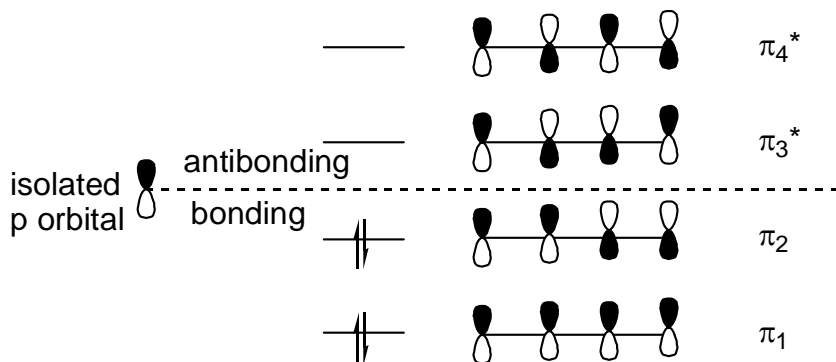
With two antibonding and one bonding interaction, overall this is an antibonding MO, and is denoted by an asterix (*).

The fourth MO has 3 nodes, and is completely antibonding.



This is the highest energy MO.

1,3-Butadiene has 4 π electrons to accommodate, and each MO can hold two electrons, with the lower energy MO's being filled first.

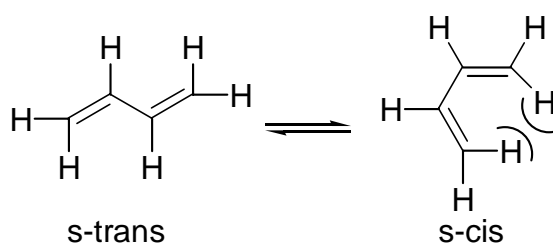


Both bonding MO's are filled, and the antibonding MO's are vacant.

Generally (and unsurprisingly!) stable molecules tend to have filled bonding MO's and vacant antibonding MO's.

The **planar** conformation of 1,3-butadiene is the most stable conformation since it allows the overlap of the 4 p orbitals.

There are two planar conformations that 1,3-butadiene can adopt. (s-trans and s-cis conformations).



They are **single** bond analogues of cis/trans isomers.

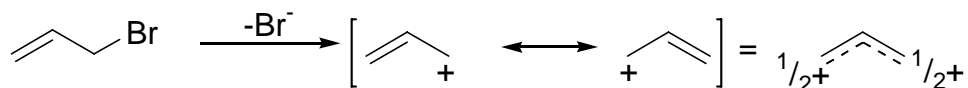
The s-trans (single-trans) conformation is about 2.3kcal **lower** in energy than the s-cis conformation, which arises from the steric repulsions of the hydrogens.

The barrier to rotation for these conformers is 4.9kcal.

This low energy difference means at room temperature these conformations are easily and rapidly interconverting.

Allylic Cations

Allylic cations are stabilized by resonance with the adjacent double bond, which delocalizes the positive charge over two carbon atoms.

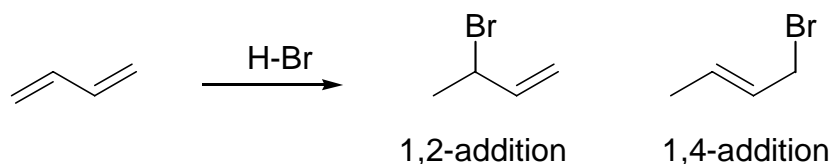


The delocalized cation can be represented by the two resonance structures or the combined structure.

1,2- and 1,4-Additions

Allylic cations are often intermediates when there is electrophilic addition to **conjugated** dienes.

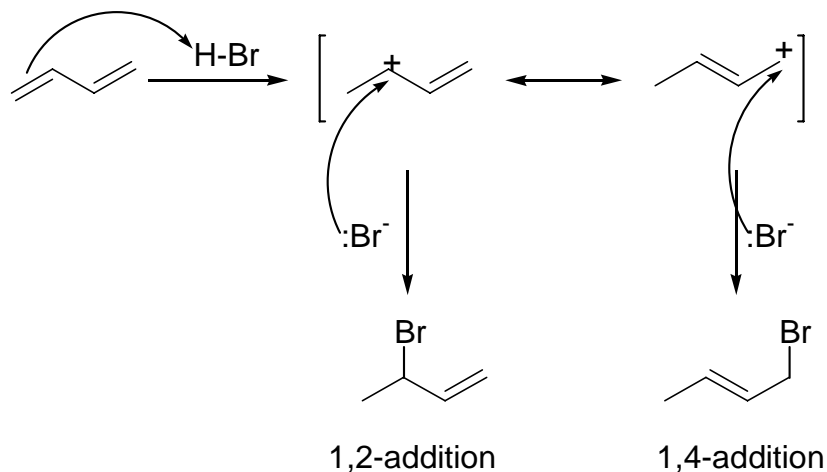
Consider the case of electrophilic H-Br addition to 1,3-butadiene:



1,2-Addition and 1,4-addition refer to the relationship of the carbon atoms to which the H and Br are added.

Mechanism for 1,2- and 1,4-Addition of HBr

The mechanism is the same as for any electrophilic addition (protonation gives a cation, nucleophile attacks the carbocation) except now the cation is allylic.

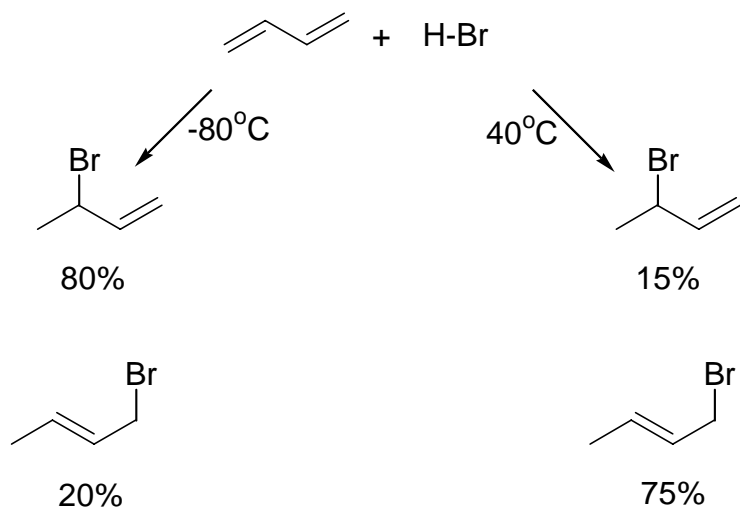


The allylic cation is resonance stabilized and the positive charge is spread over two carbon atoms.

The nucleophile (bromide ion) can now attack **either** of the positively charged carbons, generating the mixture of products.

Kinetic and Thermodynamic Control

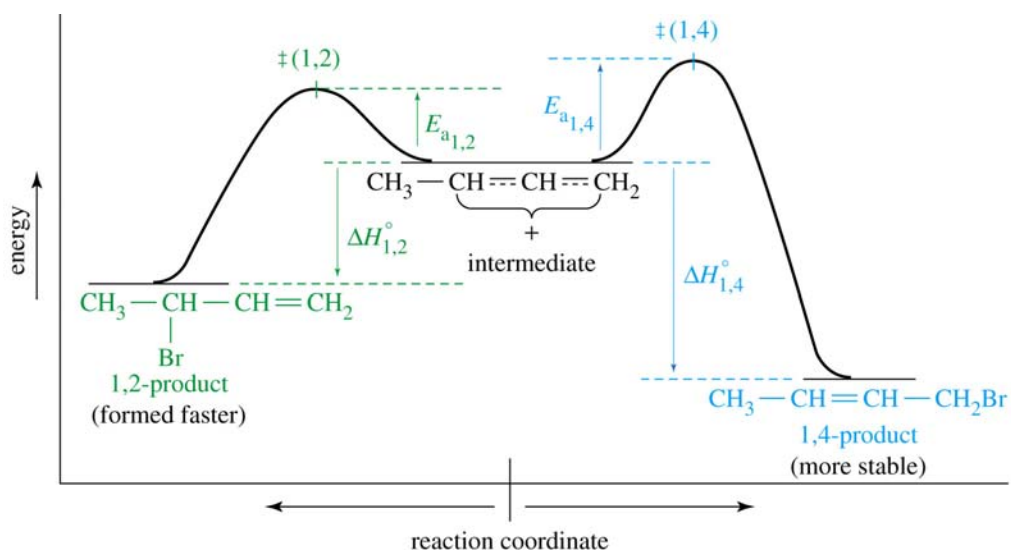
The addition of HBr to 1,3-butadiene is temperature dependant (i.e. the ratio of the products is greatly affected by variations in temperature).



At the lower temperature, the 1,2-addition product dominates, whereas at the higher temperature the 1,4-addition product is major.

The **more stable** product would be predicted to be the 1,4-addition product since it has an **internal** double bond.

Notice that at lower temperatures the more stable product is not the major product formed.



At -80°C

The T.S. for 1,2-addition has a **lower** activation energy because it generates a **more stable carbocation** (2° versus 1°).

The 1,2-addition will therefore always occur **faster** than the 1,4-addition.

The attack by bromide ion on the cation is highly **exothermic**, and therefore once the product has formed it is unlikely to undergo the reverse ionization reaction **at this temperature**.

Therefore at this temperature, the product that is formed more **quickly** is the product that dominates – this is called **Kinetic Control**.

(The 1,2-addition product is called the kinetic product).

At 40°C

At this higher temperature there is now sufficient energy for reverse reactions to proceed.

Notice that the activation energy required for the reverse reaction of the 1,2-product is **less** than for the 1,4-product.

This means it is **easier** for the 1,2-product to undergo the reverse reaction (i.e. regenerate the allylic cation).

Although the 1,2-product is still formed faster, it also returns to the allylic cation **faster** than the 1,4-product.

An equilibrium is set up, and now the relative **stabilities** of the two products determines their concentrations (product ratio).

The 1,4-product is the **more stable product**, and at this temperature it is the major product.

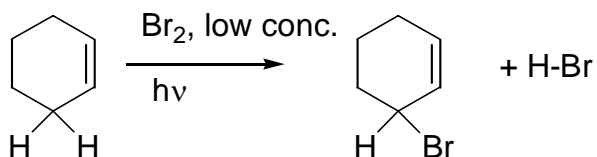
Since the thermodynamics now control the reaction, this reaction is said to be under **Thermodynamic Control**.

(And the product is the thermodynamic product).

In general, if a reaction is non-reversible, the kinetic product dominates. If the reaction is reversible, then the thermodynamic product dominates.

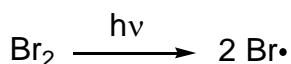
Allylic Radicals

In an analogous fashion, allylic radicals are also resonance stabilized.

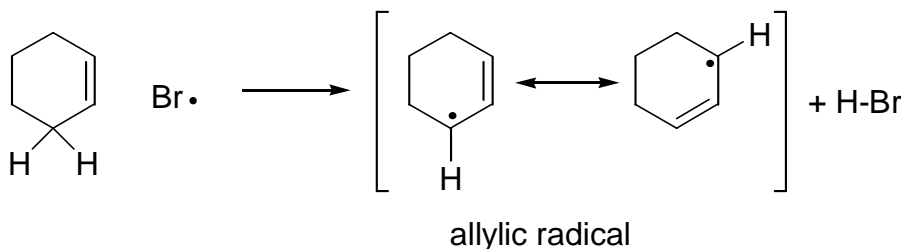


Recall that under free radical conditions, low concentrations of bromine will react with alkenes via **substitution** (as opposed to the classical **addition** processes).

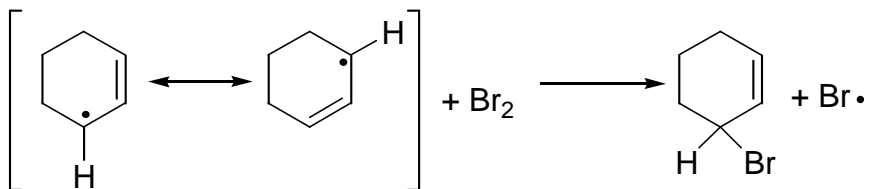
This is a free radical process. The light **initiates** the reaction by dissociating a bromine molecule into two Br radicals.



The $\text{Br}\cdot$ abstracts a hydrogen selectively from the allylic position, thus generating an allylic radical which is resonance stabilized.

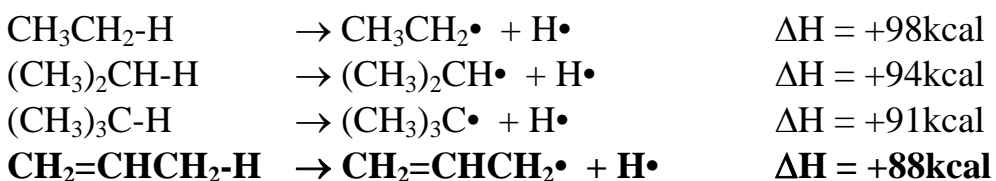


The allylic radical then abstracts a bromine **atom** from a bromine **molecule** to generate the allylic bromide product.



The Br• which is generated then continues the chain.

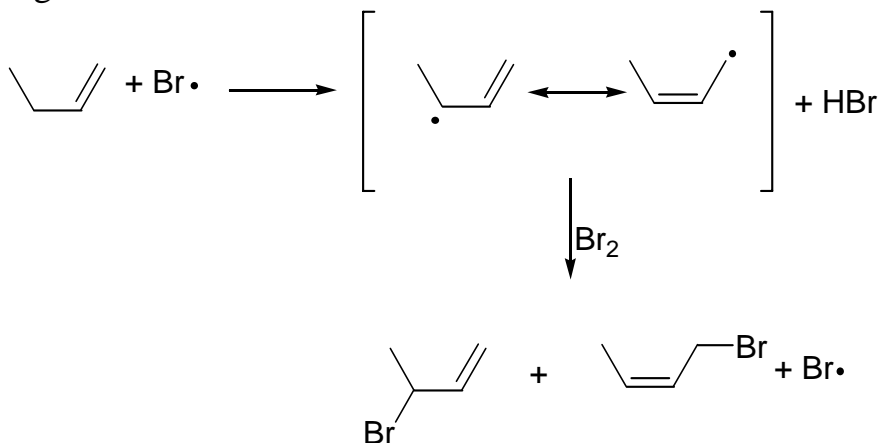
The allylic hydrogen is selectively removed since it has the **lower BDE**:



The allylic radical has the free electron delocalized over two carbons, and the bromine may become attached to **either** carbon.

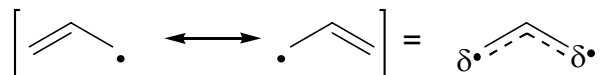
Unsymmetrical substrates can give rise to mixtures of products which result from allylic resonance structures.

E.g.



(In the laboratory, recall that NBS is often used for free radical brominations since it reacts with the generated HBr to produce small concentrations of Bromine).

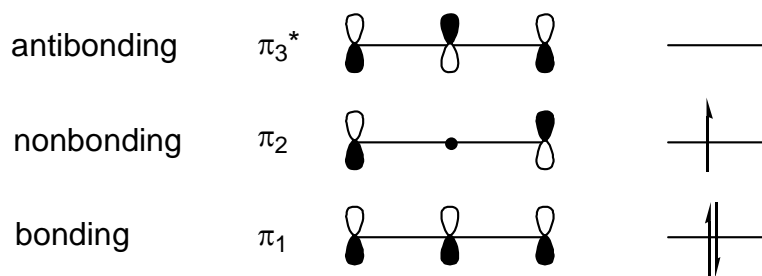
Molecular Orbitals of Allylic Systems



All three p orbitals must be aligned **parallel** so they can overlap.

There is partial π bonding between C1-C2 and C2-C3, and the radical is delocalized on the **end** two carbons.

The three overlapping p orbitals interact to form 3 MO's.



The **lowest** energy MO has all **bonding** interactions and the highest energy MO has all antibonding interactions.

Since MO's are symmetrically displaced about the energy of the isolated p orbital, for odd numbers of MO's, one MO must lie in the middle of the energy levels.

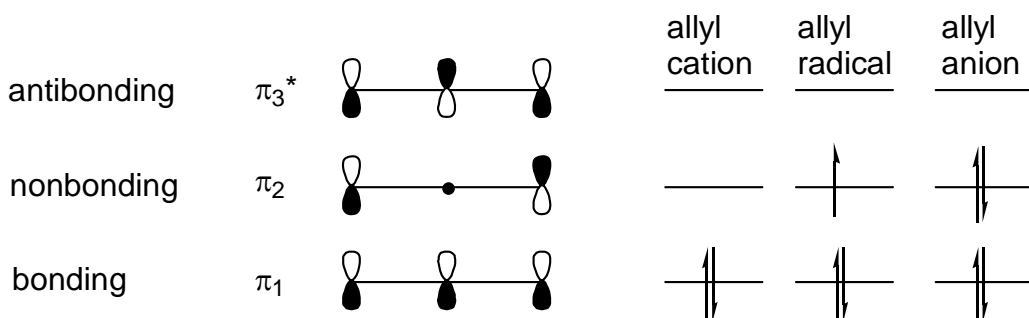
This is called the **Non-Bonding** MO, (π_2).

π_2 must contain one node, and so it has the (unusual) structure with a node at C2. This MO is non-bonding.

Note that the single electron (radical) is in π_2 which has density on C1 and C3 only.

Other Allyl Systems

The allyl cation, anion and radical all have the same MO structures, but differ in the **number of electrons** contained within them.



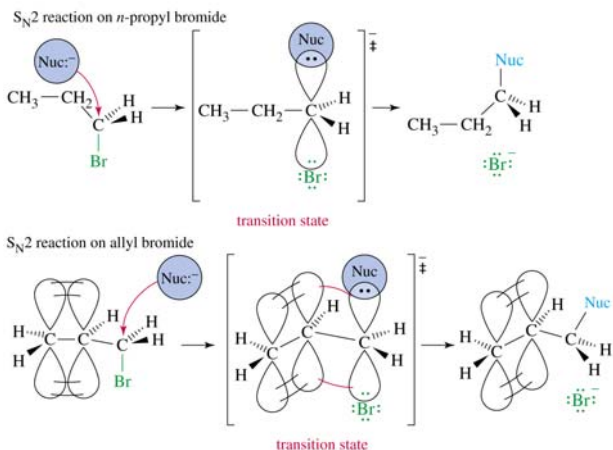
The allyl cation has no electrons in the π_2 MO, whereas the allyl anion has two electrons in the π_2 MO.

This MO description explains why the allylic anion and cation have partial charges on carbons C1 and C3.

S_N2 Displacements from Allylic Halides

Allylic halides and tosylates demonstrate enhanced reactivities in reactions with nucleophiles.

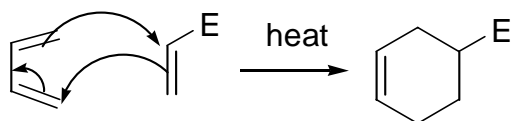
The rate is enhanced because the T.S. is lowered in energy through delocalization of electrons.



The T.S. for these S_N2 reactions resemble the allylic arrangement because of the perpendicular p orbital. This allows a delocalization of the electrons in the T.S. and so lowering the energy of the system, and therefore lowering the activation energy and thus enhancing the rate.

The Diels-Alder Reaction

This is one of the most powerful reactions in organic chemistry, and is especially useful for creating 6 membered rings.



diene dienophile

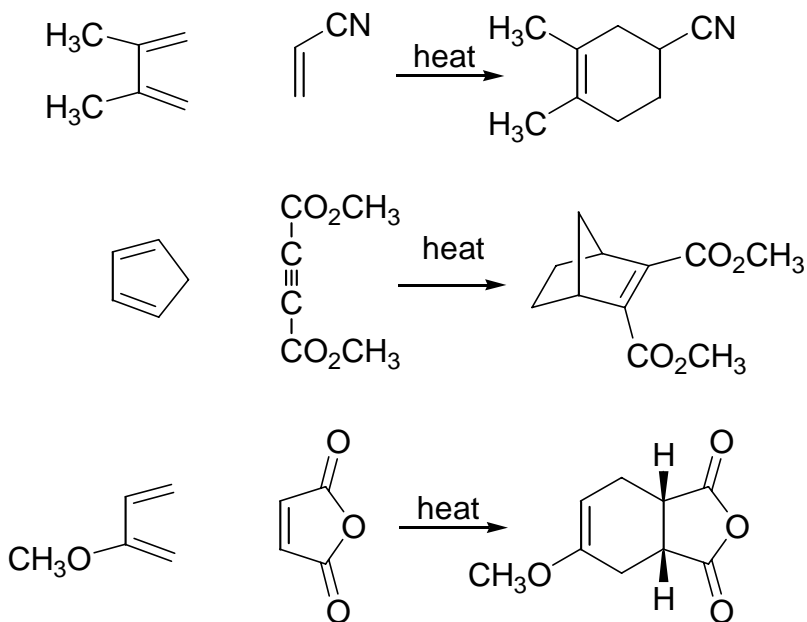
The Diels-Alder reaction is also called a [4+2] cycloaddition, because it involves 4π electrons from one molecule and 2π electrons from another.

The molecule that reacts with the **diene** component is called the **dienophile**, and is usually electron deficient (alkene or alkyne bearing electron withdrawing groups).

The **diene** molecule is usually electron rich, and electron donating groups enhance the reactivity of dienes in cycloadditions.

Two σ bonds are created at the cost of two π bonds (thus energetically favorable).

E.g.

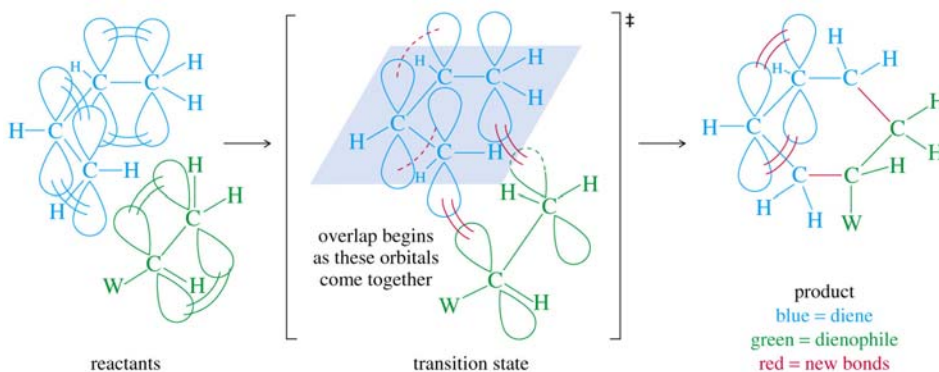


Mechanism

The mechanism of a Diels-Alder is a simultaneous cyclic movement of six electrons.

The reaction is concerted, with bonds breaking and forming at the same time.

The geometry required for the **concerted** process must allow the p orbitals at the ends of the diene to overlap with the p orbitals of the dienophile.



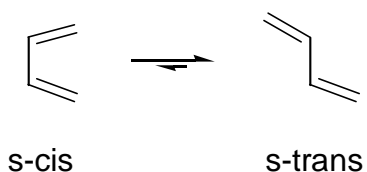
Stereochemistry of the T.S.

There are three main rules for Diels Alder reactions:

- (1) s-cis conformation of the diene
- (2) syn addition
- (3) Endo rule.

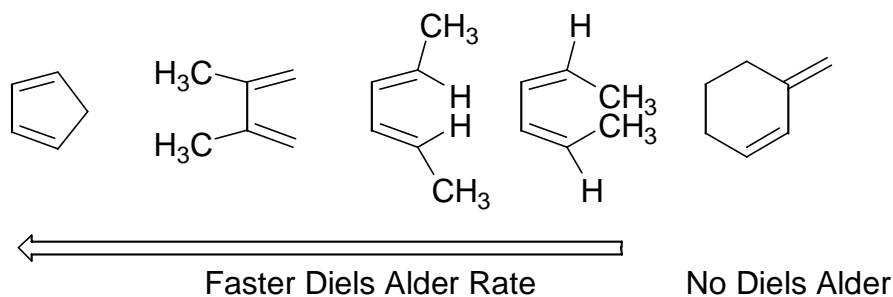
s-cis conformation

The diene must be in a s-cis conformation to react as a diene in a Diels Alder reaction.



This is so that the end p orbitals can still overlap with those on the dienophile.

Even though the s-trans is more stable than the s-cis conformation, the energy difference is low, and at reaction temperatures the equilibrium is fast enough for Diels Alder reactions to proceed.



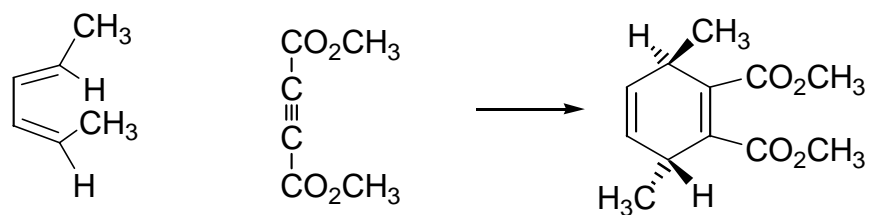
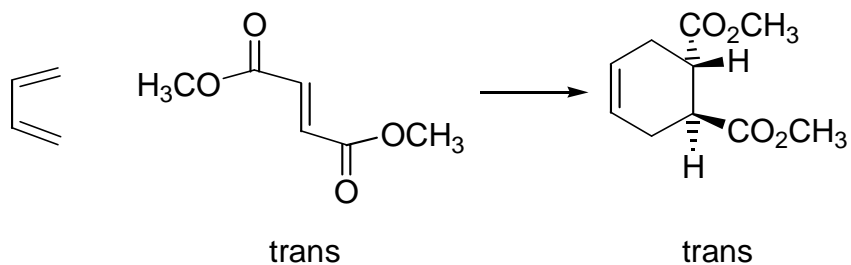
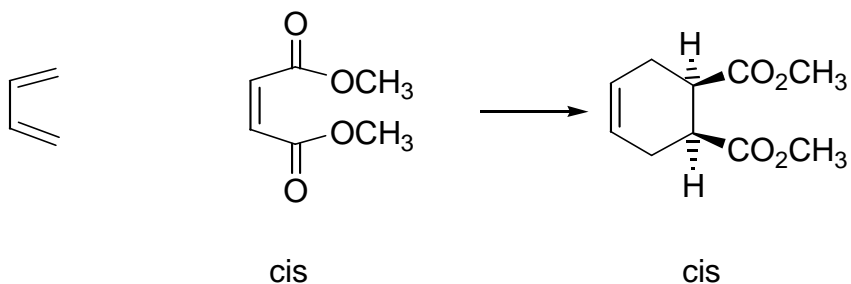
As expected, molecules with groups that disfavor the s-cis conformation will react slower, and dienes unable to attain the s-cis conformation will not undergo Diels Alder reactions.

Cyclopentadiene, which has the diene fixed in the s-cis formation, is a very **reactive** diene for DA reactions.

Syn Stereochemistry

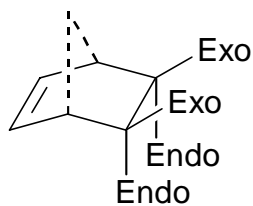
The dienophile adds to one face of the diene, and the concerted reaction mechanism does not allow for any substituents to change their stereochemistry.

E.g.

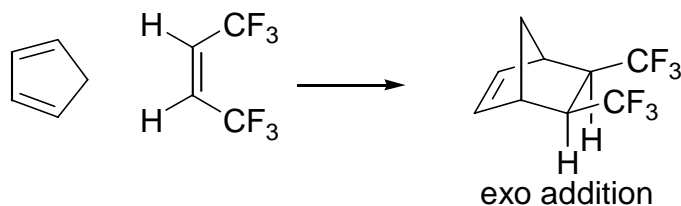


The Endo Rule

Substituents can end up either in the exo or endo positions.

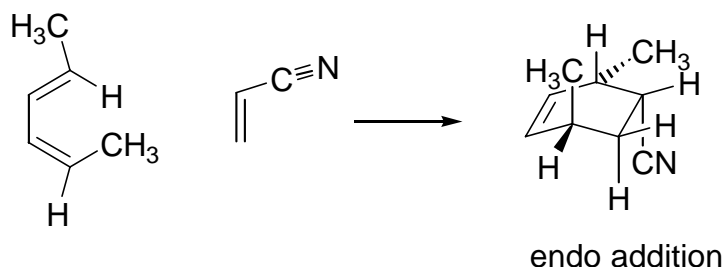
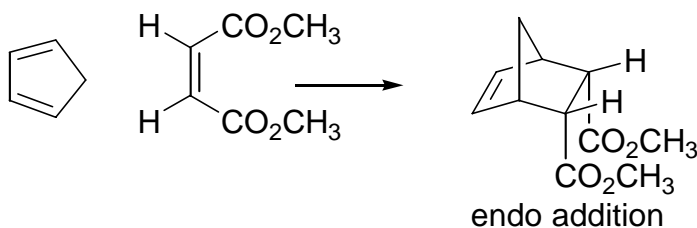


Normally the largest substituent goes into the exo position, because that is the sterically least demanding position.



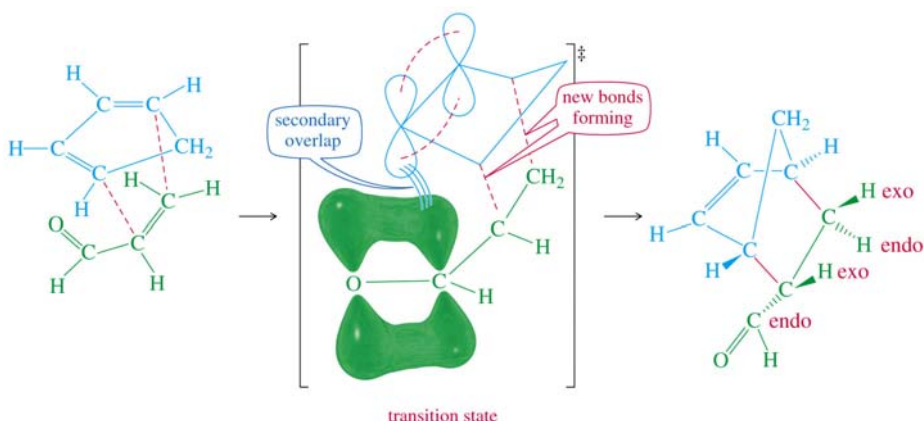
However, there is a more dominant effect: when a dienophile has a π bond as a substituent on the dienophilic multiple bond, there is secondary orbital overlap, which results in endo addition.

(Notice that almost all dienophiles have these type of substituents: E.g. $-\text{CN}$, $-\text{CO}_2\text{CH}_3$, etc.)



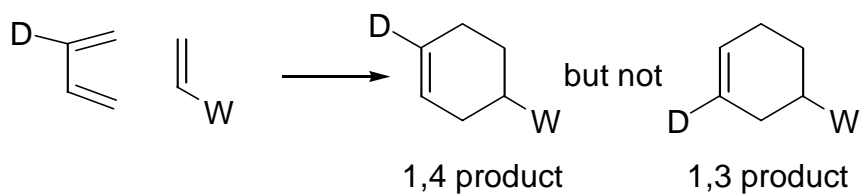
This is because the p orbitals in the electron withdrawing group interact with the p orbitals on the central C2 and C3 p orbitals of the diene.

This secondary overlap lowers the energy of the TS and so is favored.



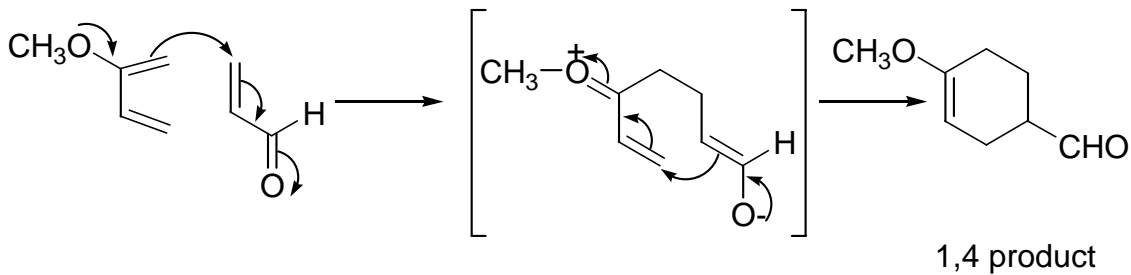
Diels Alder Reactions with Unsymmetrical Reagents

Often it is observed that single products result from DA reactions even with unsymmetrically substituted starting materials.



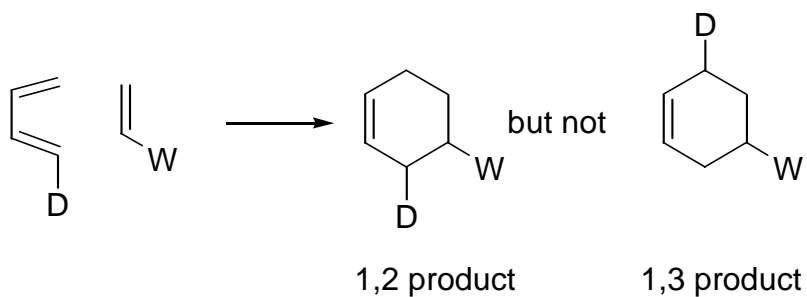
If group D is electron donating and W is electron withdrawing, only the 1,4 product is observed in DA reactions.

This can be explained by the hypothetical visualization of the reaction proceeding step wise as opposed to synchronously. (This not true – there are no charged intermediates).

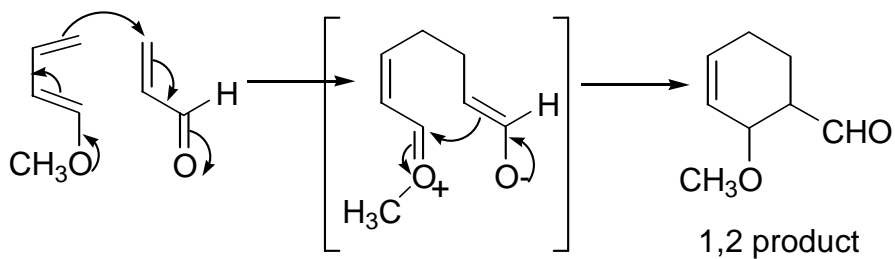


This is a **simplification** of the real explanation, but helps our understanding.

When the donor group is on the outside (C1) of the diene, then only 1,2 products are observed, for similar reasons.

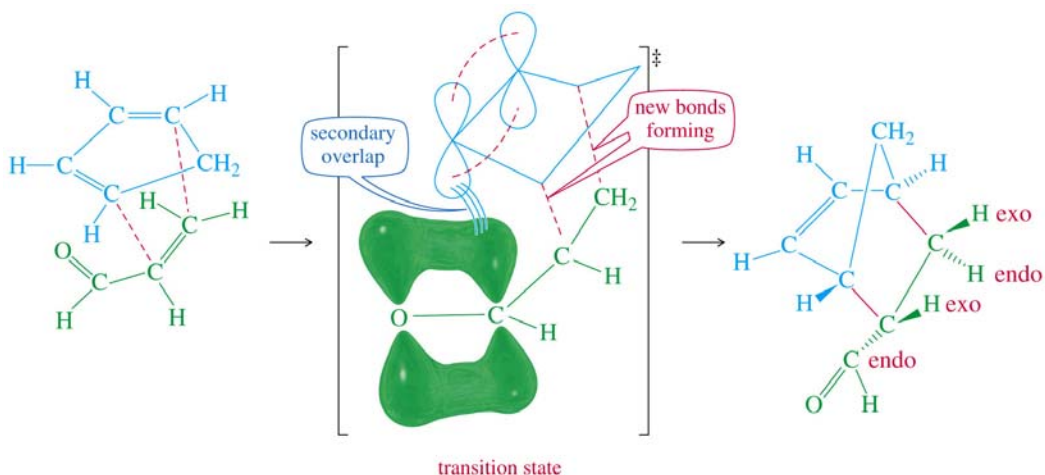


Again, this is just to help our understanding and the intermediate does not really involve charges.



Pericyclic Reactions

Pericyclic reactions involve concerted bond breaking and formation within a closed ring of interacting orbitals.



The Diels alder cycloaddition is a pericyclic reaction. The TS of the DA shows each carbon atom of the new ring contributing one orbital to the closed loop of orbitals.

A concerted pericyclic reaction has a single transition state, and the activation energy must be supplied either by heat (thermal initiation) or UV light (photochemical initiation).

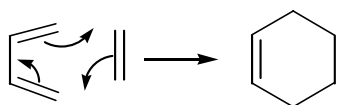
Many pericyclic reactions proceed only by one type of initiation.

Often if both types of initiation work, they give different products.

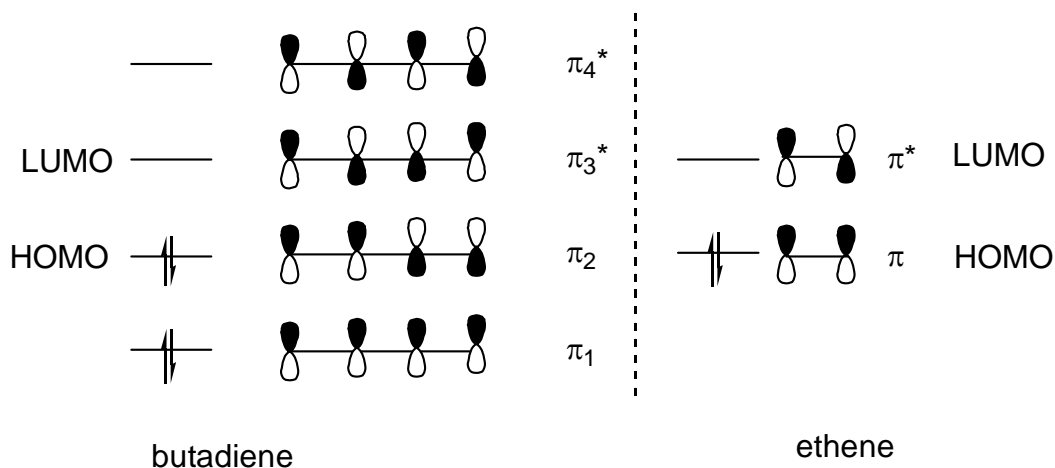
Woodward Hoffman Rules

Pericyclic reactions were not well understood until in 1965 the Woodward Hoffman rules of conservation of orbital symmetry were developed.

Consider the DA of butadiene and ethene:



Butadiene has 4 MO's, and ethene has two MO's.



The movement of electrons (i.e. reaction) involves the highest occupied molecular orbital (HOMO) of one molecule and the lowest unoccupied molecular orbital (LUMO) of another.

In a DA, the diene acts as the electron rich 'nucleophile' and the dienophile is the electrophilic counterpart.

The HOMO of the diene interacts with the LUMO of the dienophile.

The electrons that move are from the HOMO since they are the least tightly bound.

It is the arrangement of the orbitals in the HOMO (HOMO symmetry) that determines the course of the reaction.

The electrons are transferred into the LUMO of the electrophile – this is the π^* MO of ethene.

A concerted reaction may only take place if the electrons can flow smoothly from the HOMO to the LUMO.

This can only occur if the orbitals have the correct symmetry – this means the orbitals must interfere constructively (same wave sign with same wave sign).

Figure 15-19

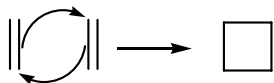
The bonding interactions **lower** the TS energy and promote the concerted reaction.

The matching of the orbital signs means this reaction is **Symmetry Allowed**.

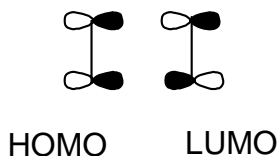
Forbidden Cycloadditions

If the interaction between orbitals had been **deconstructive**, the reaction would be said to be **symmetry forbidden**.

The cycloaddition between two molecules of ethene to generate cyclobutane is a symmetry forbidden reaction.



This [2+2] cycloaddition requires the HOMO of one ethene to interact with the LUMO of the other.

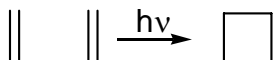


This causes antibonding interactions, orbital symmetry is not conserved – it is symmetry forbidden.

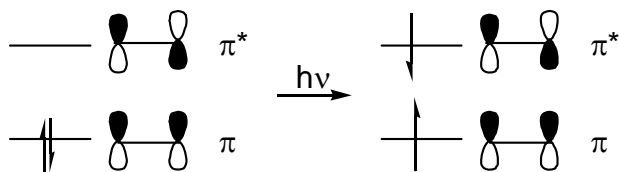
Thus, heating ethene **does not** generate cyclobutane.

Photochemical Cycloadditions

In general, thermally disallowed cycloadditions can be made to occur under photochemical initiation.

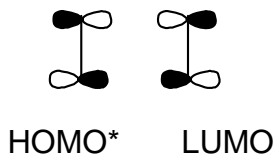


The photochemical [2+2] cycloaddition with two molecules of ethene does generate cyclobutane.



Photochemical initiation occurs when a photon of correct energy hits ethene, and a π electron is excited to the next highest energy level.

The DA reaction now involves the LUMO of one ethene and the HOMO (now π^* of the excited ethene, HOMO*) of the other.



This time the interaction is all **constructive**.

The [2+2] DA is **thermally** forbidden but photochemically allowed.

In general, thermally allowed reactions are photochemically forbidden, and vice versa.

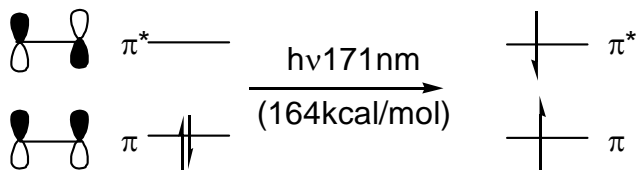
UV Absorption Spectroscopy

Ultraviolet (UV) spectroscopy measures electronic transitions, and gives useful information concerning double bonds and especially conjugation effects.

Sigma bonds in general do not become excited under irradiation, but π bonds have electrons that are easily excited into higher energy levels.

The difference in energy between the levels determines the wavelength of light absorbed.

Consider the excitation of ethene:



The $\pi \rightarrow \pi^*$ transition requires 164kcal, which corresponds to a wavelength of 171nm.

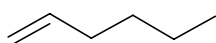
The wavelength of maximum absorbance is called λ_{\max} . (Recall that wavelength is inversely proportional to energy, so longer wavelength is lower energy).

Figure 15-27

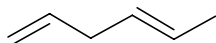
(At least) two factors can alter values of λ_{\max} .

Conjugation lowers the energy differences between energy levels, and so conjugated dienes absorb at longer wavelengths than isolated dienes, and trienes absorb at longer wavelengths than dienes, etc.

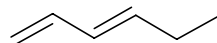
E.g.



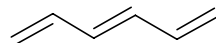
$$\lambda_{\max} = 176\text{nm}$$



$$\lambda_{\max} = 180\text{nm}$$



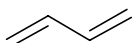
$$\lambda_{\max} = 223\text{nm}$$



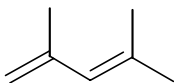
$$\lambda_{\max} = 258\text{nm}$$

Alkyl group substitution on double bonds also causes absorption to occur at longer wavelengths.

E.g.



$$\lambda_{\max} = 217\text{nm}$$



$$\lambda_{\max} = 232\text{nm}$$