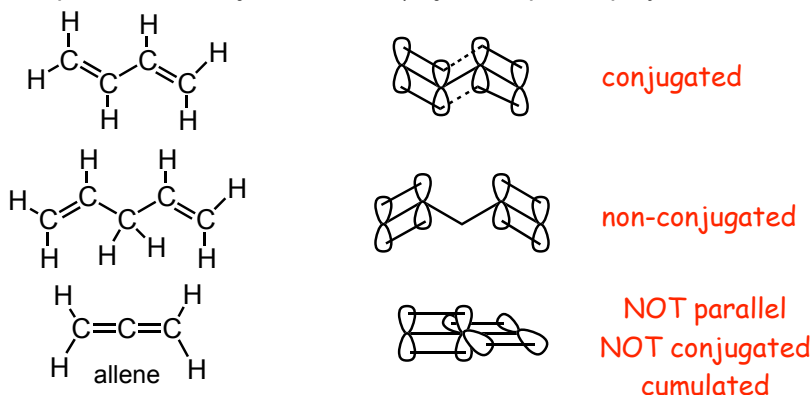


1 Conjugated Systems and Resonance

The requirements for conjugation are the same as for resonance.

- A parallel array of atomic p orbitals on adjacent atoms (adjacent sp² or sp hybridized atoms):

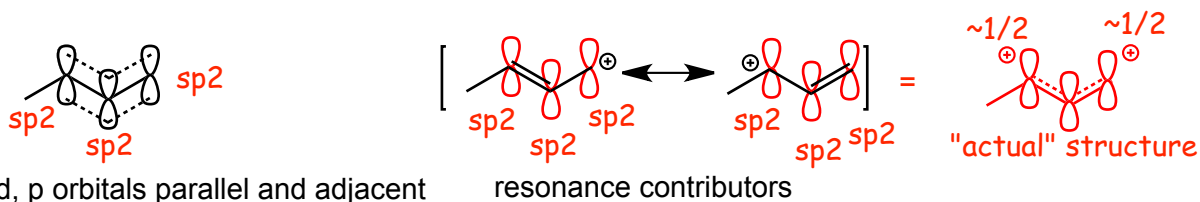


- The two π-bonds in allene (the lower structure above) are **not** conjugated because the formal p atomic orbitals do not overlap across both double bonds, the 2 p A.O.s on the central carbon are at **right angles** (are orthogonal) to each other, this situation is called cumulative.

The Significance of Conjugation

- Conjugation allows reactions to be explained which cannot be explained using simple Lewis structures, since under these conditions simple two-atom Lewis bonding does not occur, π-bonding can occur over the entire length of the conjugated system, bonds including multiple atoms.

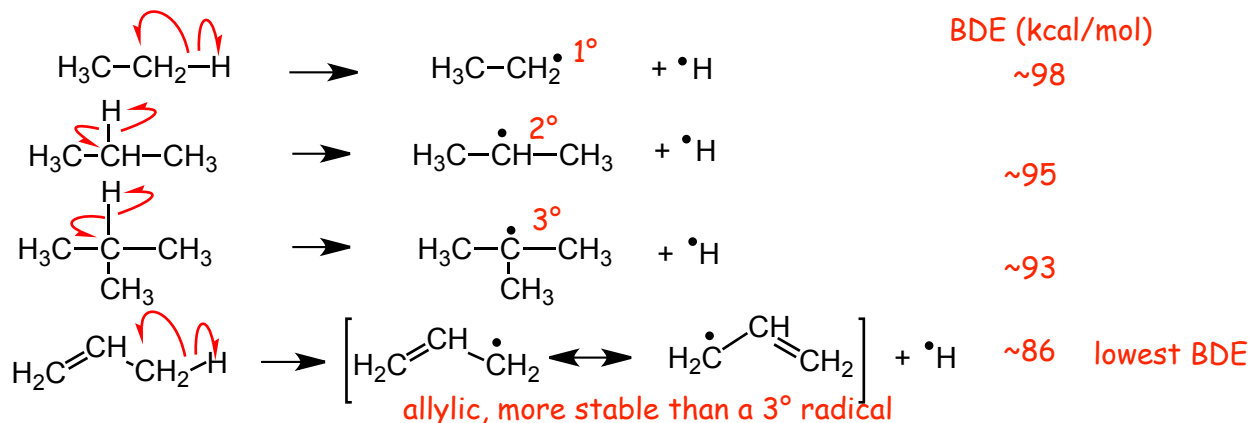
Conjugation & Resonance are different Ways of describing Electron Delocalization in π-systems!



All conjugated systems involve resonance delocalization, and vice versa; you can draw resonance contributors for any conjugated system

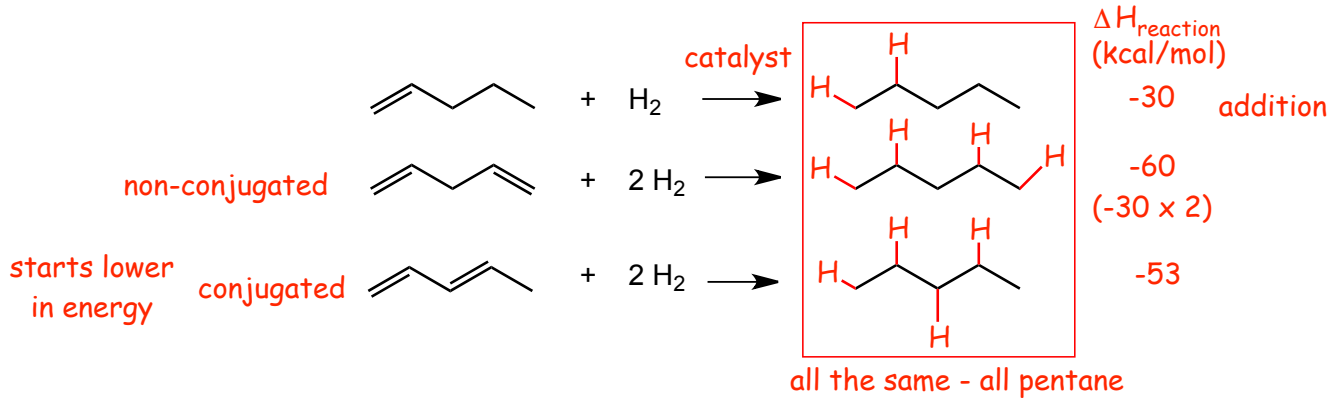
Our discussion of conjugated systems is simply a more detailed and complete look at systems that have resonance, their underlying structural properties, and their chemical reactions, **and** a look at some reactions that **cannot** be explained using only the resonance model (remember chemical models!).

Examples of Conjugated Systems: the allyl radical:



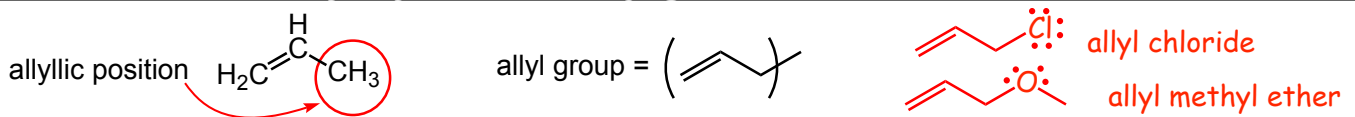
- Lower BDE means higher radical stability (lower energy electrons in the radical)
- **Resonance delocalization** in a **conjugated system** stabilizes (lowers the energy of the electrons in) the radical due to delocalization of electrons (the electrons “see” more nuclei).

Example



- The **less exothermic** the reaction, the **more stable** the diene (since it starts lower in energy).
- The conjugated diene has lower energy electrons due to delocalization compared to the non-conjugated diene.

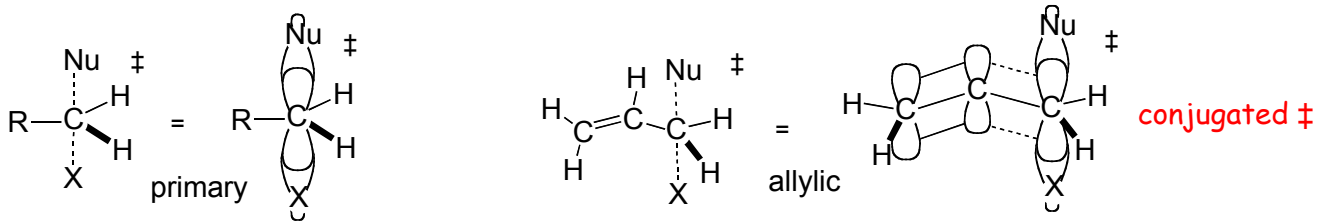
2 Reactions of Allyl Systems : Conjugated Intermediates



- Allyl systems often react via conjugated (resonance stabilized) intermediates.

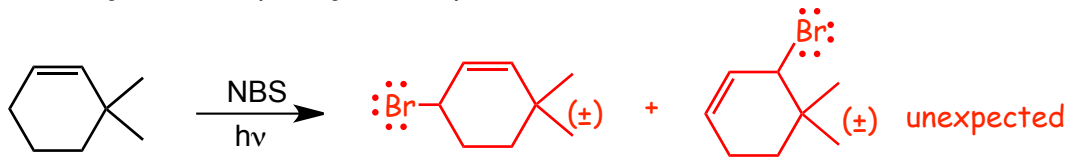
Allylic Substitution via S_N2 (Review, seen before!)

Recall: S_N2 reactivity: 3° < 2° < 1° < allylic (fastest of all, because the transition state is conjugated!)



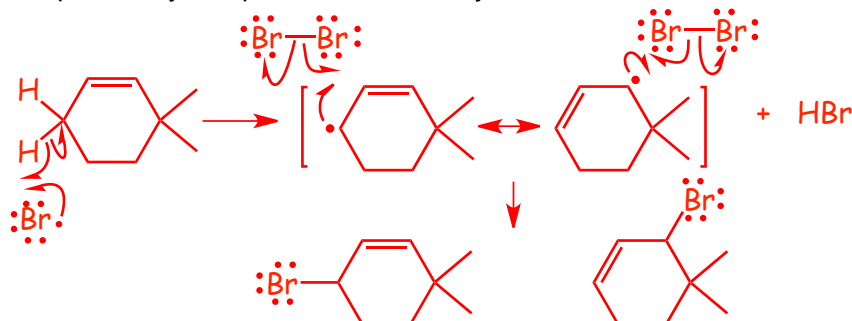
- Conjugation (resonance) stabilizes the electrons in the transition state for SN2 reactions at an **allylic** carbon.

Bromination via Allyl Radicals (Mainly Review!)



- Where does this "unexpected" product come from?

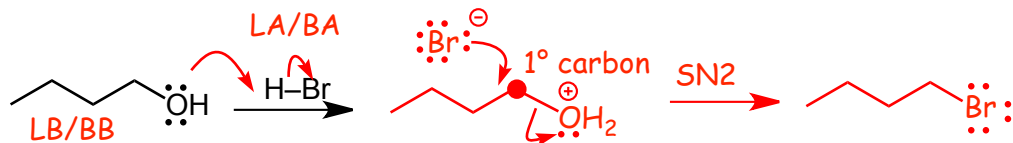
A Partial Mechanism explains why **two** products are actually formed:



- Remember the resonance contributors are telling us what the real structure of the radical is, i.e. that the non-bonding electron is not localized on a single carbon atom, but that it is delocalized over two carbon atoms, the two atoms where the substitution takes place, which is why we get two products.
- The resonance contributors are not two different things, but the same thing drawn two different ways.
- The "other" product was always formed in allylic brominations, until now we have always tried to simply give examples where reaction at the two carbons with radical electron density gave the same product.

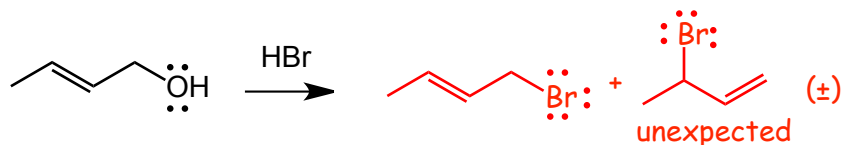
Substitution via S_N1 (Mainly Review)

Recall

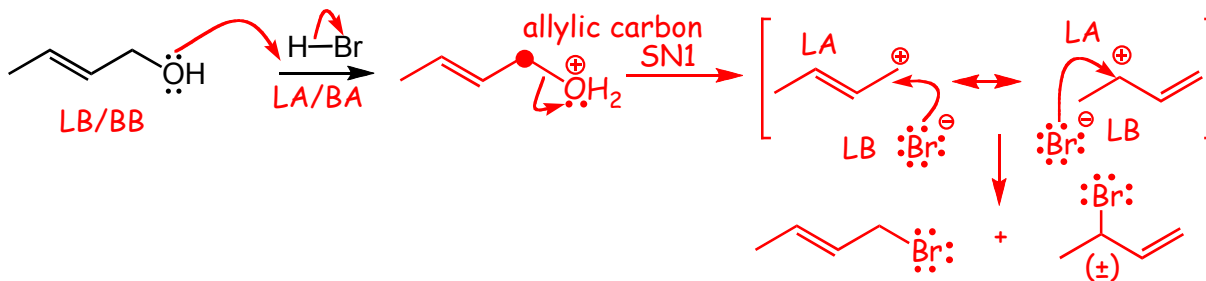


- Substitution occurs at the **primary** carbon by an S_N2 mechanism.

However:

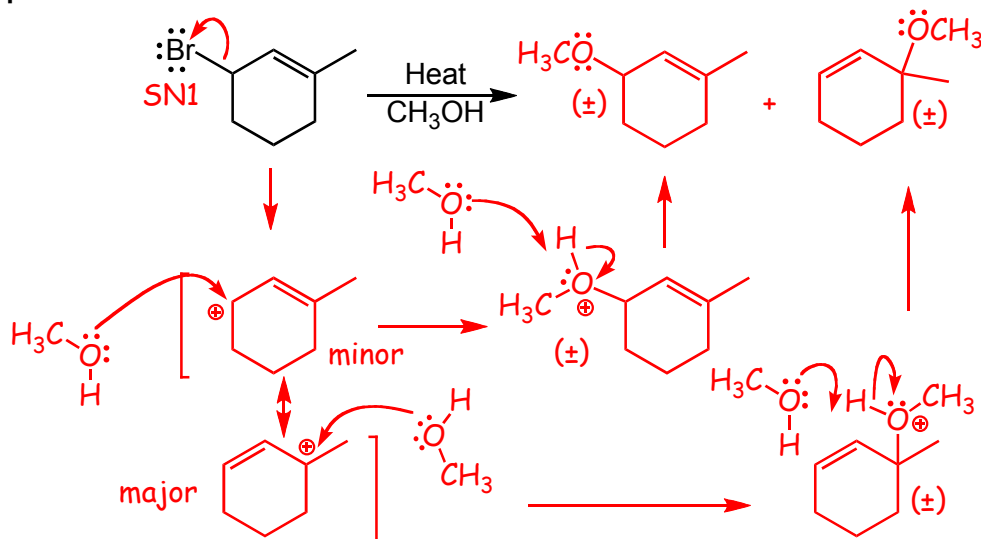


The Mechanism:



- Recall, protonation of an -OH group converts it from a poor to a good leaving group.
- In this case, substitution occurs via an S_N1 mechanism at the **allylic** carbon (bromide is a weak nucleophile and a resonance stabilized (conjugated) cation intermediate can be formed via S_N1).

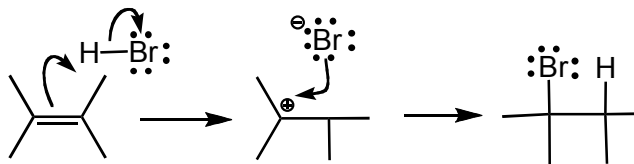
Another Example:



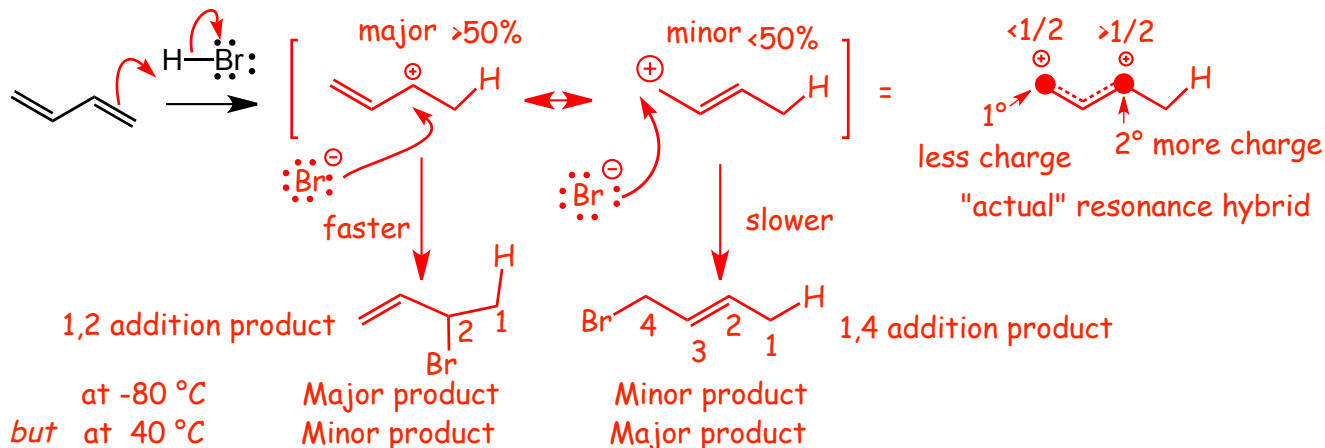
- These are classic S_N1 reaction conditions, an allylic bromide, a polar protic solvent, a weak nucleophile, heat
- Q. Which is the major and which is the minor product?**
A. This depends upon the conditions, i.e. whether the reaction is under kinetic or thermodynamic control.

3 Reactions of Dienes : Kinetic versus Thermodynamic Control

Addition of HBr: Recall:

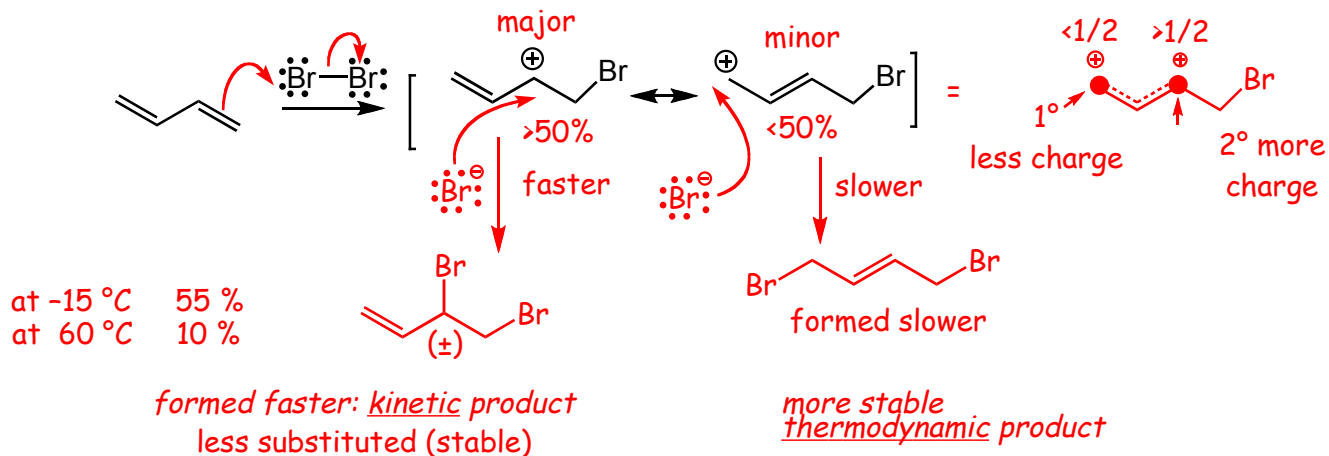


Analogously:



- The charge is not evenly distributed in the resonance stabilized cation intermediate, shown above are two **different** ways of indicating the differing amounts of positive charge on the carbons, either in terms of the "actual" resonance hybrid cation structure, or as an unequal resonance mixture (both models say the same thing).
- Reaction is **slower** at the primary carbon, there is less positive charge there, but reaction there forms the more substituted (more stable) alkene isomeric product.
- Reaction is **faster** at the secondary carbon, there is more positive charge there, but reaction there forms the less substituted (less stable) alkene isomeric product.
- **You can make good arguments for both of the products**, a **kinetic** argument says that the 1,2-product is formed faster and should be the major product, a **thermodynamic** argument says that the 1,4-product is more stable and should be the major product.

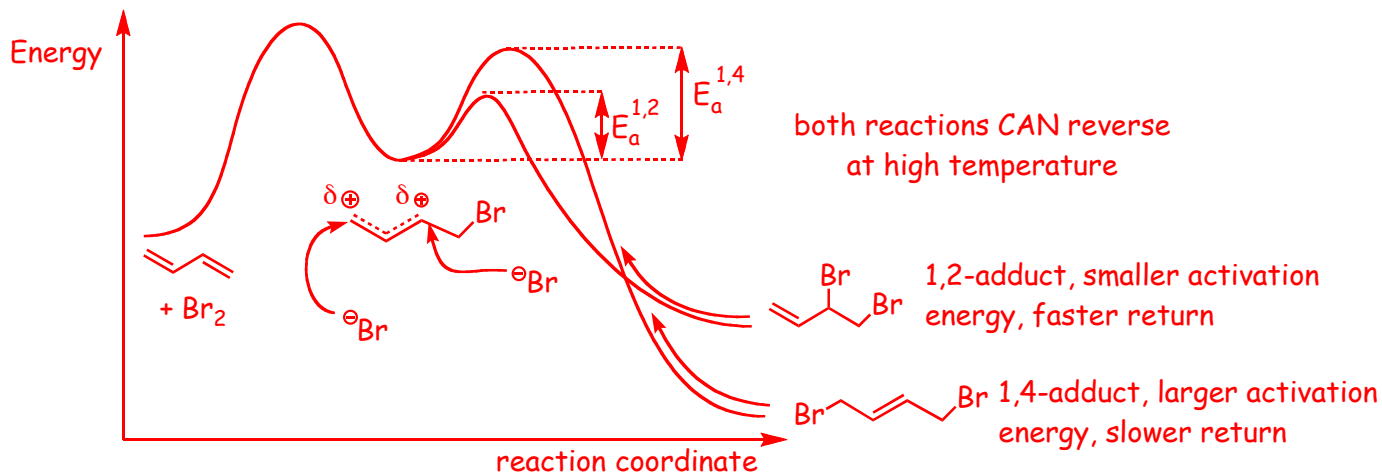
Another Example:



- Note, a bromonium ion intermediate is **not** formed here, as it would have been for Br₂ addition to a simple alkene, a more stable, resonance stabilized allyl cation intermediate is formed instead.
- As in the previous example, the **faster** reaction at the carbon that has a larger partial positive charge forms the **less stable** 1,2-addition product, the **kinetic** product, and the **slower** reaction at the carbon that has a smaller partial positive charge forms the **more stable** 1,4-addition product, the **thermodynamic** product.

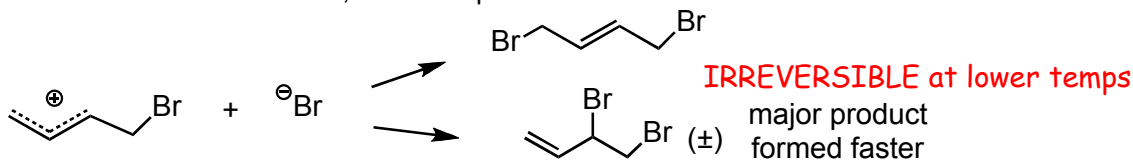
• **What Determines Kinetic and Thermodynamic Control of Products?**

• This is best explained in terms of a reaction energy diagram

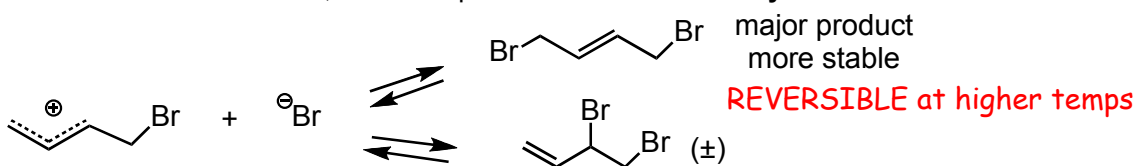


- At all temperatures, the less stable 1,2-adduct is formed **faster** from the primary resonance stabilized intermediate.
- At low temperatures, the initially formed 1,2-product and 1,4-products "stay there", reverse reaction is not possible, there is not enough thermal energy to return (the reactions are **irreversible**), more 1,2-product is formed because this product is formed faster.
- At high temperatures, the 1,2-product and the 1,4-products can return to the intermediate (**reversible**), although return of the 1,2-product is faster (requires less energy) and return of the 1,4-product is slower (requires more energy).
- Eventually the more stable 1,4-product accumulates and becomes the major product.

• When the reactions are **irreversible**, the entire process is under **kinetic control**:

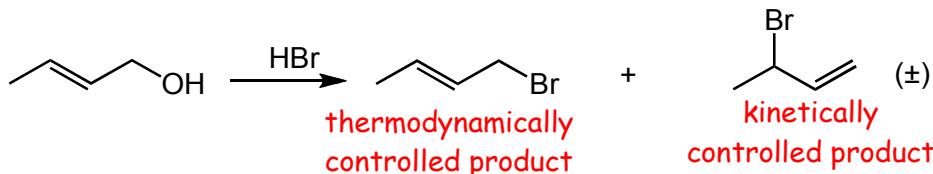


• When the reactions are **reversible**, the entire process is under **thermodynamic control**:



• **Most organic reactions are under kinetic control** (think about the lowest energy transition state, lowest energy intermediate resulting in the fastest reaction "winning"), **examples of thermodynamic control are rare.**

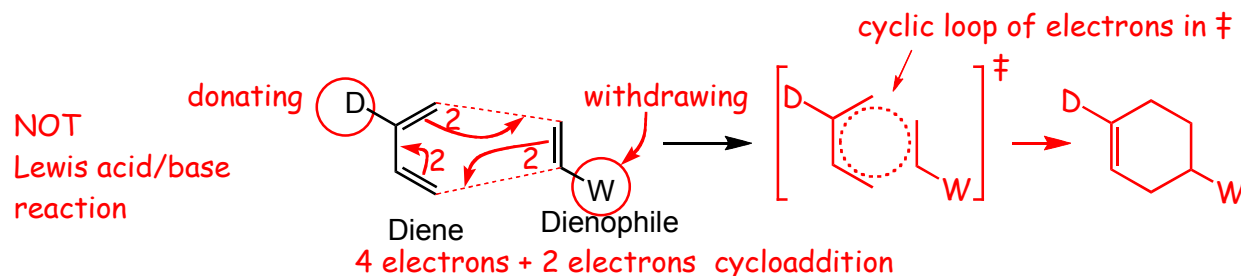
An example in reactions of alkenes:



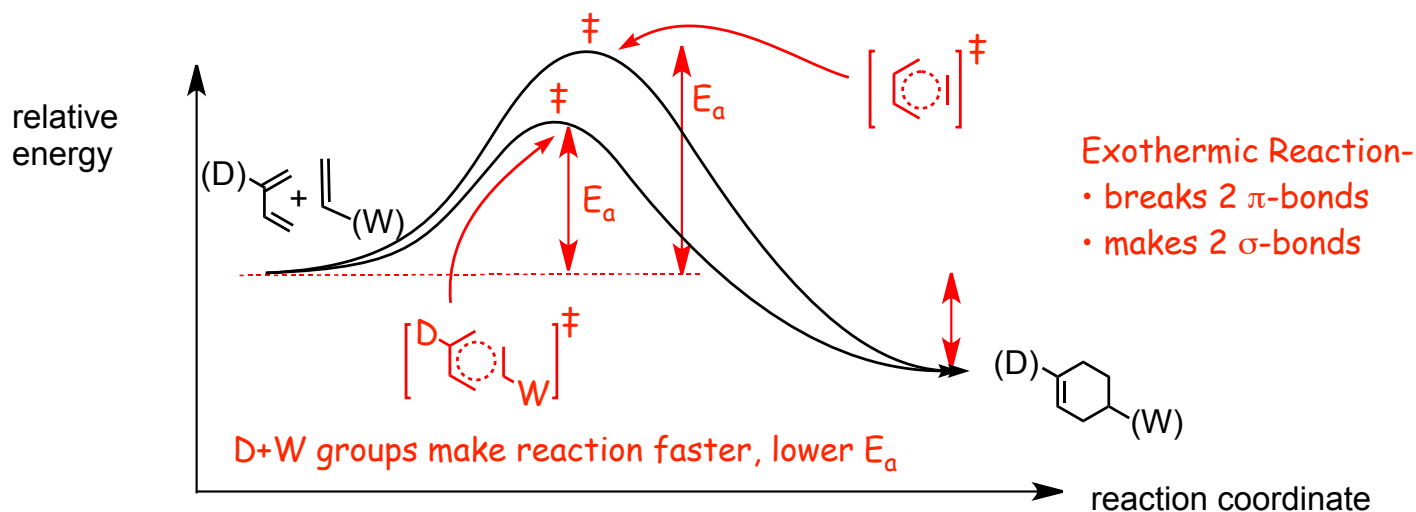
4 The Diels-Alder Reaction : Cycloaddition

• The Diels-Alder reaction is a **cycloaddition reaction** (makes a cyclic structure)

D = π -donating group; W = π -withdrawing group

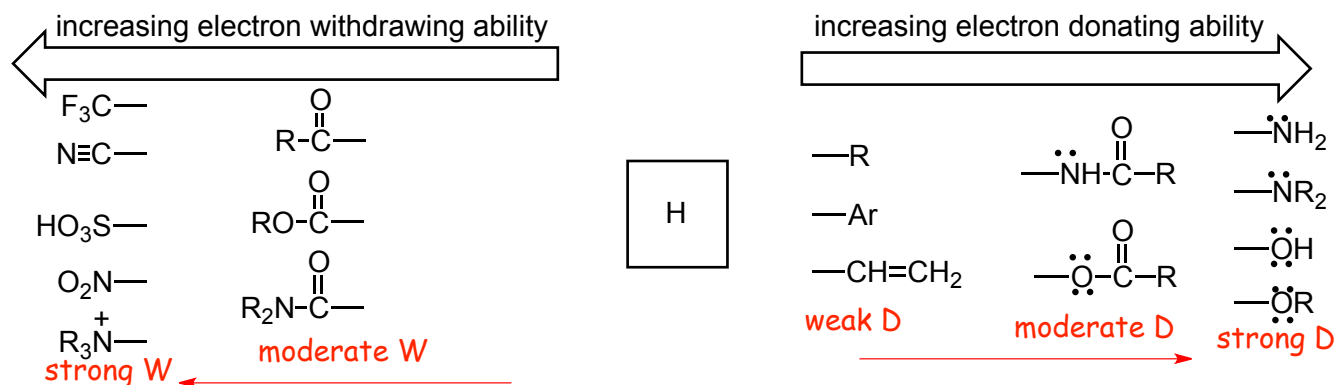


- This is an Addition reaction that makes two new C-C σ -bonds and a ring: a cycloaddition reaction.
- All bonds made and broken at the same time: **A Concerted reaction** (like SN2 and E2).
- **4** Electrons from diene and **2** electrons from dienophile, thus **4 + 2 cycloaddition reaction**.
- **This is not a Lewis acid/base nucleophile/electrophile reaction**, both reactants provide a pair of electrons to make a new bond to each other, **and**, the reaction has an interesting "electrons in a loop" transitions state that is important.
- The reaction goes faster (has a lower activation energy) with an electron donating group (-D) on the diene and an electron withdrawing group (-W) on the dienophile.

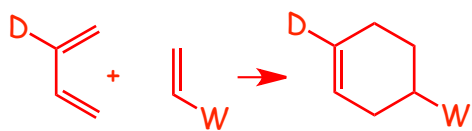


Reminder of Electron Donating and Withdrawing Groups on π -Systems

• Donating and withdrawing ability of substituents is measured relative to hydrogen:



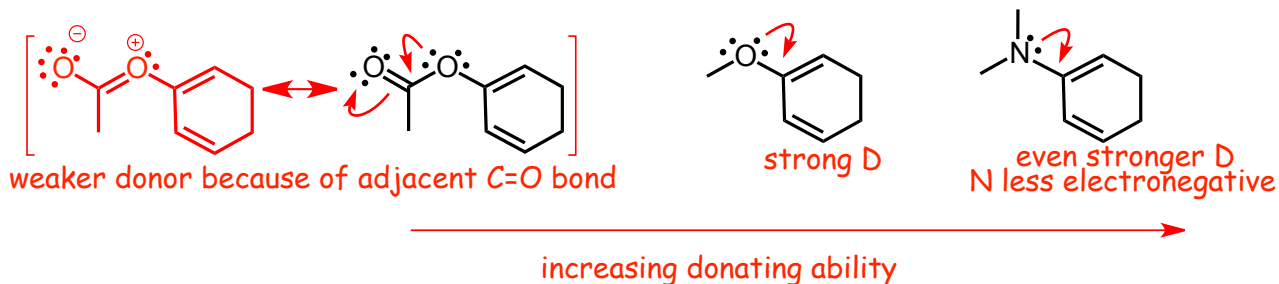
- Remember, distinguishing the donating and withdrawing groups is fairly easy - **No Memorization!**
- With the exception of the simple alkyl and aryl substituents, all of the donating groups all have non-bonding electrons on the atom that is attached to the π -system.
- Just about everything else is a withdrawing substituent due to the inductive effect.



Diels-Alder reactions are increasingly faster with increasingly stronger donating groups (D) on the diene

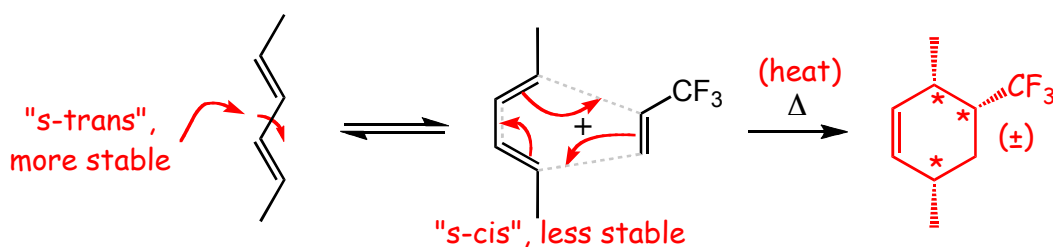
Diels-Alder reactions are increasingly faster with increasingly stronger withdrawing groups (W) on the dienophile

Some More on Donating Groups:



- Non-bonding electrons on the less electronegative element N are higher in energy and more "available" for resonance donation than those on oxygen.
- Non-bonding electrons that are resonance delocalized into other π -systems, e.g. part of an ester, above left, are lower in energy and less "available" for resonance donation into a diene.

The diene needs to be in the correct conformation to react:

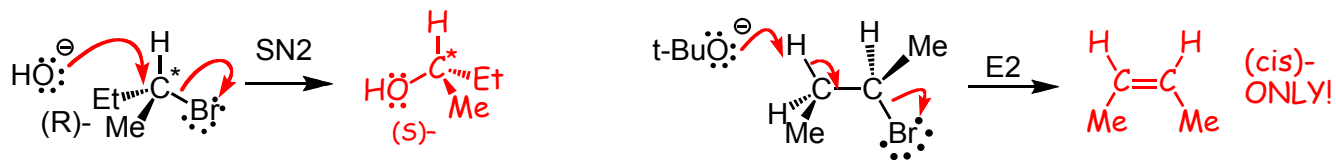


- The terms "s-cis" and "s-trans" refer to the different **conformers** corresponding to rotation around the **central** C-C bond, they are related to cis-/trans- isomers of alkenes, but the restricted rotation is around a single bond
- The Diels-Alder reaction needs an "s-cis" conformation of the diene for reaction.
- The reaction is **also stereospecific**, it is concerted, and generally needs (some) heat.

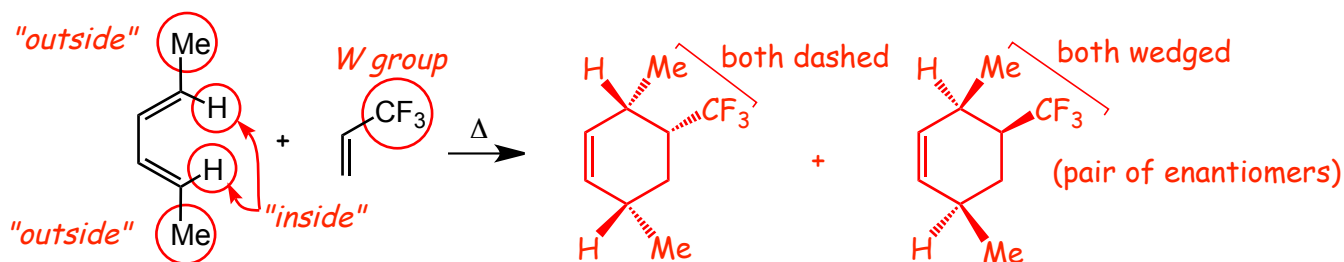
Explanation for the Stereochemistry:

Concerted reactions are often **stereospecific**.

Recall: The following **concerted** reactions (all bonds broken and made at the same time):



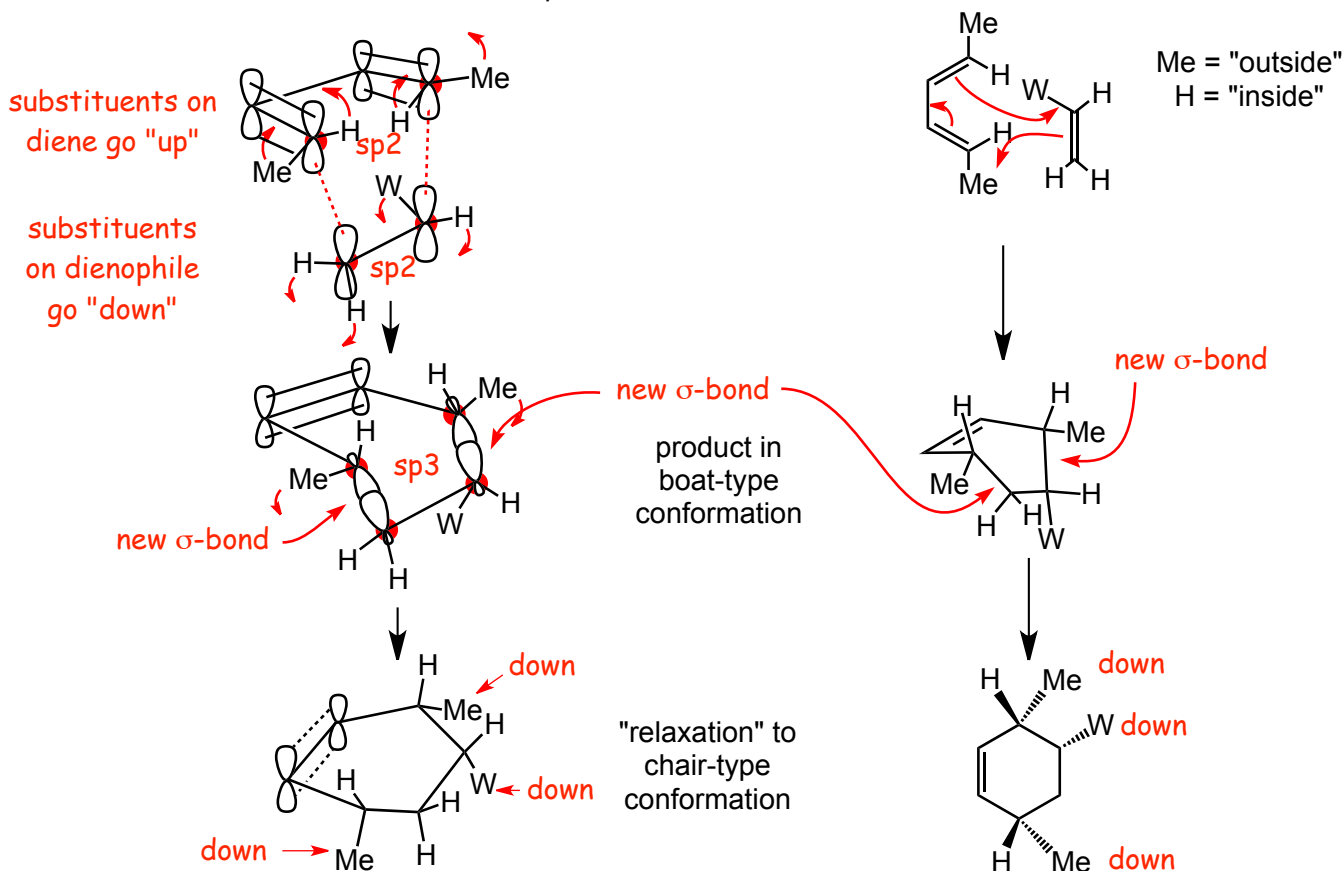
The stereochemistry of the Diels-Alder reaction is centered around the substituents, specifically:



- Both the "outside" substituents on the diene end on the same side in the cyclohexene product (i.e. both have wedged or dashed bonds).
- Both "inside" groups on the diene end on the opposite side to the "outside" groups on the diene.
- The W groups on the dienophile end on the same side as the "outside" groups on the diene: **the endo rule**.

The Concerted Reaction:

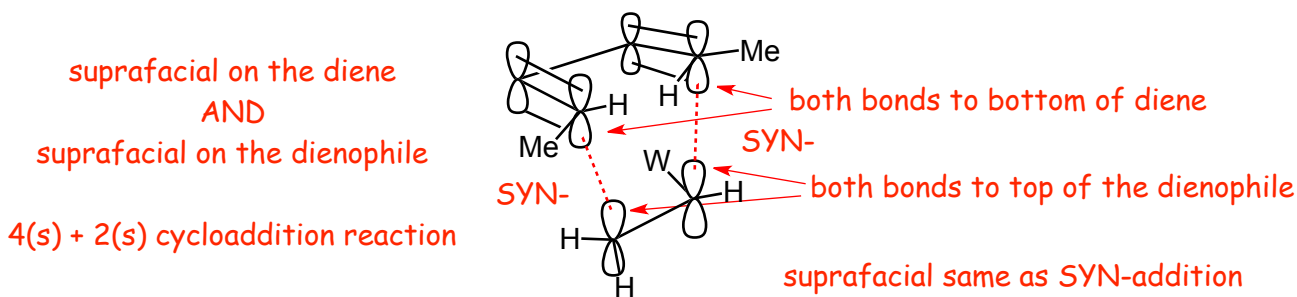
- The p A.O.s at the end of the diene and the dienophile have to transform into sp³ atomic orbitals as the new σ-bonds are formed, the substituents on these atoms will "move" in response to the change in hybridization.
- This is illustrated below for the case of dienophile addition from the "bottom".



- **Both** new bonds made at the same time on **same side of the diene** (the bottom in this example), the reaction is thus **suprafacial** with respect to the diene.
- **Both** new bonds made at the same time on **same side of the dienophile** (the top in this example), the reaction is also **suprafacial** with respect to the dienophile.
- The Diels-Alder reaction is a 4(s) + 2(s) cycloaddition, where (s) refers to suprafacial.

Suprafacial Reaction: Definition.

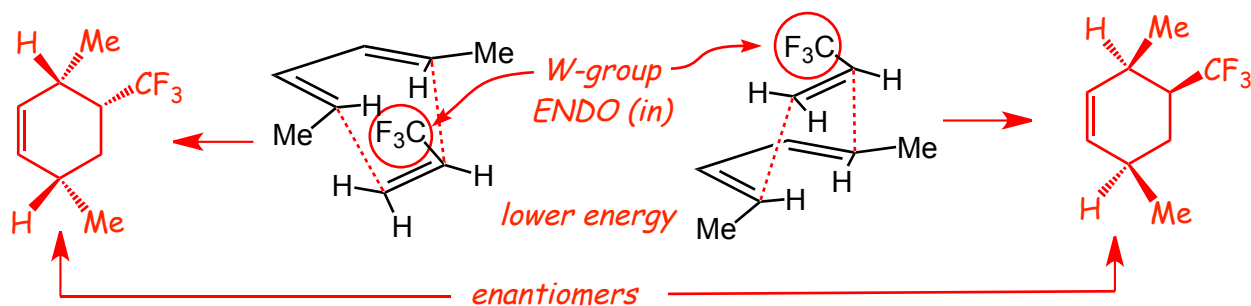
- Both bonds are made to the same "face" of the reactant, i.e. for a flat π-system this means both bonds made to the bottom face or both bonds made to the top face:



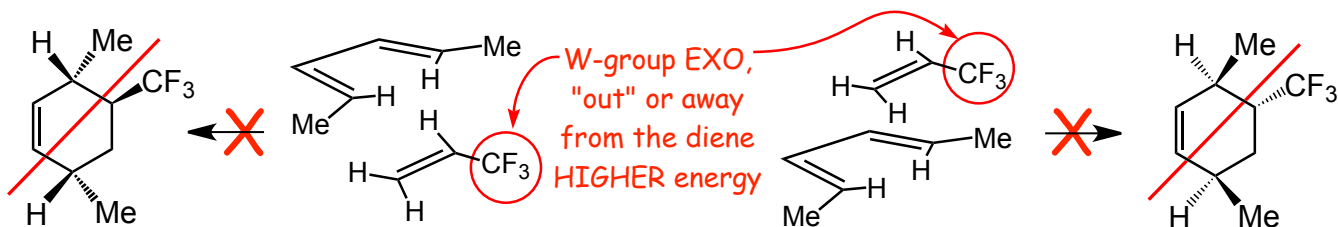
- If a reaction is **suprafacial** on one of the reactants, then this is the same as **syn-addition** on that reactant.

Origin of the Endo Rule

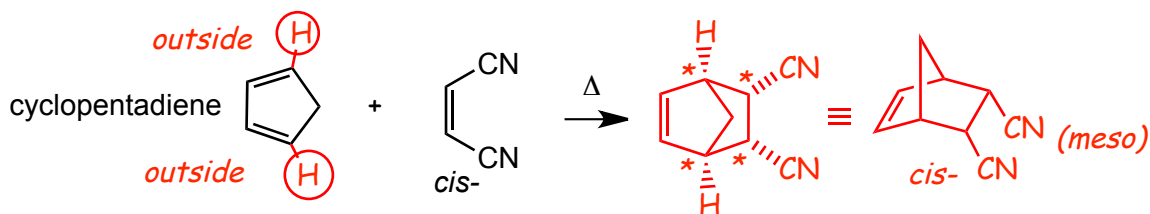
- **Endo** means "in", as opposed to **Exo** which means "out".
- The dienophile can approach the diene in one of two different ways, i.e. with the withdrawing groups "in", towards the diene (**endo**), or with the withdrawing group "out", away from the diene (**exo**). The **endo** reaction is shown below, you can see that in this case the withdrawing group will either be below or above the diene.



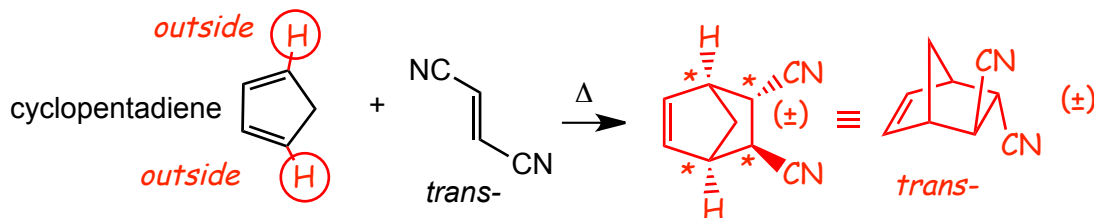
- The **endo** approach of the dienophile usually leads to the lower energy transition state because the electronegative elements in the W-group can stabilize the relatively high energy electrons in the diene, this is called a secondary orbital interaction.
- The **endo** approach results in the -W group and the substituents in the "outside" of the diene (both -Me in the example above) being on the same side of the cyclohexene ring in the product, i.e. these bonds are both dashed (when reaction occurs from below) or they are both wedged if reaction occurs from above.
- In the alternative **exo** approaches, the W-group is "out" with respect to the diene (it points "away" from the diene), and the electronegative elements in the -W group cannot stabilize the higher energy electrons in the diene. Reaction **exo** would proceed via a higher energy transition state, i.e., slower.



Examples: On the dienophile:

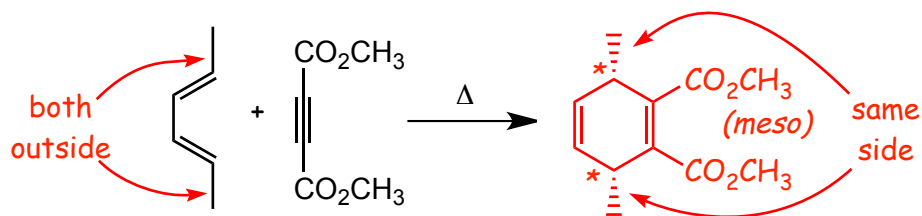


- **Four** chiral/asymmetric centers are generated, but the structure has a mirror plane of symmetry, thus it is an achiral meso compound.

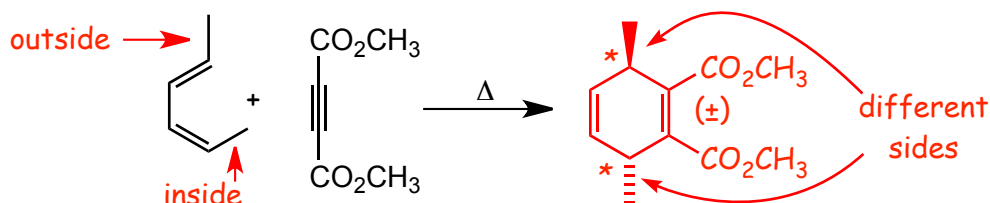


- **Four** chiral/asymmetric centers are generated, the structure has **no** mirror plane of symmetry, it is thus formed as a racemic mixture.

Examples: On the diene:

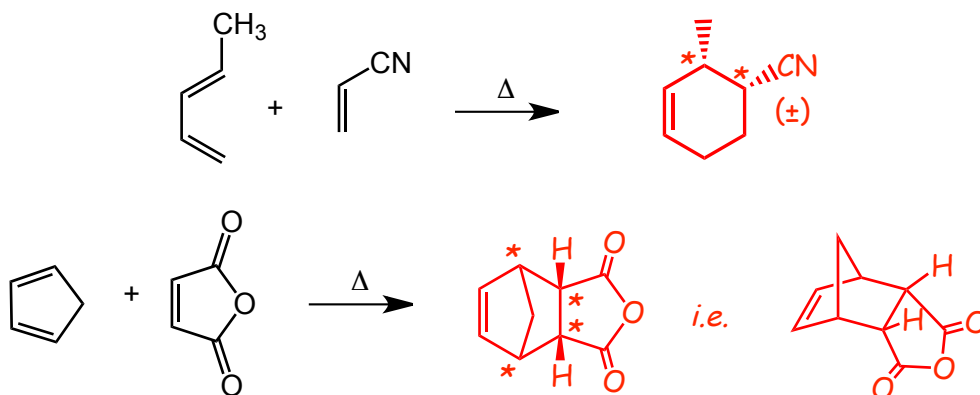


• **Two** chiral/asymmetric centers are generated, but the structure has a mirror plane of symmetry, thus it is an achiral meso compound.



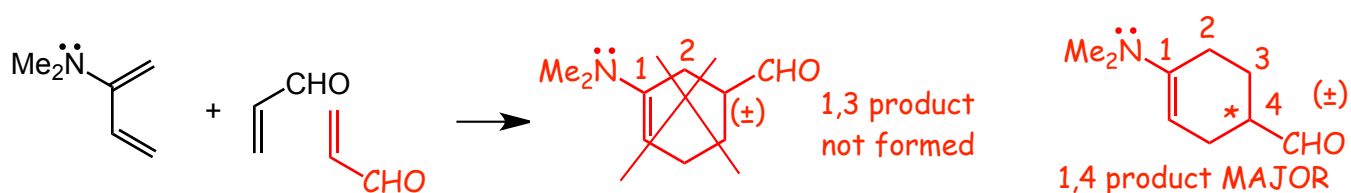
• **Two** chiral/asymmetric centers are generated, the structure has **no** mirror plane of symmetry, it is thus formed as a racemic mixture.

Mixed Examples



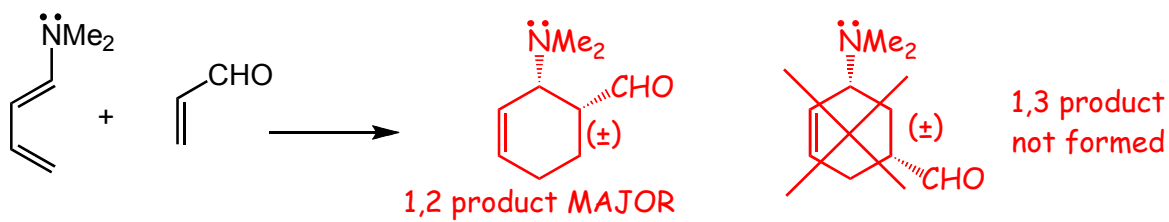
Orientation of addition: The Regiochemistry.

• The reaction is also **regiospecific** (one structural isomer is favored over others, c.f. Markovnikov).



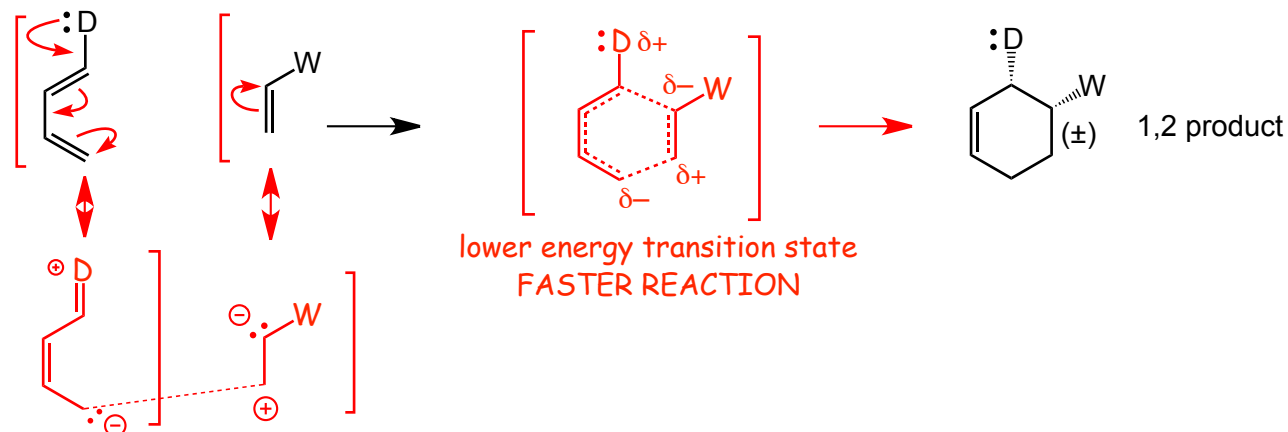
• There is only **one** chiral center formed (*), and so there is no need to draw the bond as wedged or dashed, in fact doing so would have no meaning in this case, we don't need to specify that this bond is wedged or dashed with respect to any other bond in the product structure, therefore this bond should be drawn as **plain**, with the racemic mixture symbol (±) to show that we made two enantiomers.

• The 1,4-product is the major product, **not** the 1,3-product. These are structural isomers and shows that the reaction has **regiospecificity**. (Remember, the way that we draw the molecules on paper isn't necessarily the way that they are when undergoing a reaction, don't be fooled by the way the structures are drawn on paper).

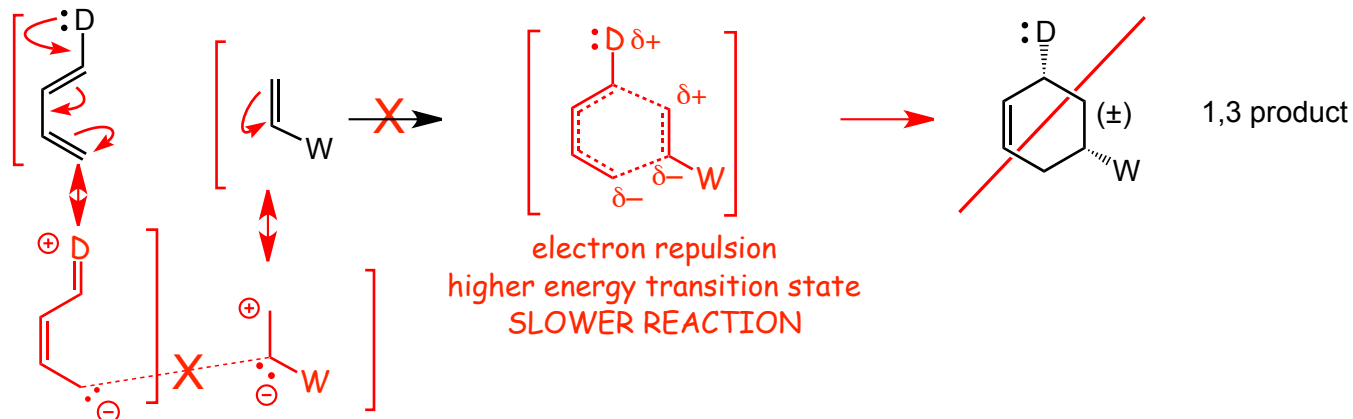


- These reactions can be explained using the following **minor resonance contributors**.
- Formation of the 1,3-product is always disfavored due to electron repulsion.
- Let's look at this for **generic** donating (-D) and withdrawing (-W) groups:

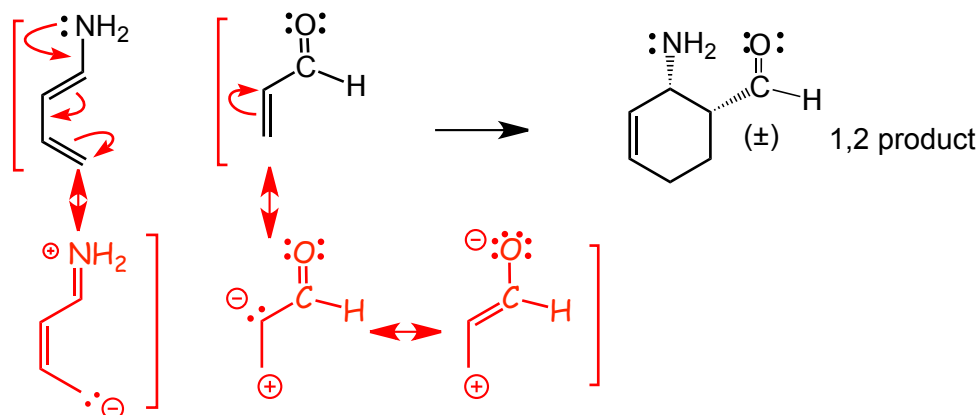
1,2-Addition: This Product is formed faster, it is the **major** organic product.



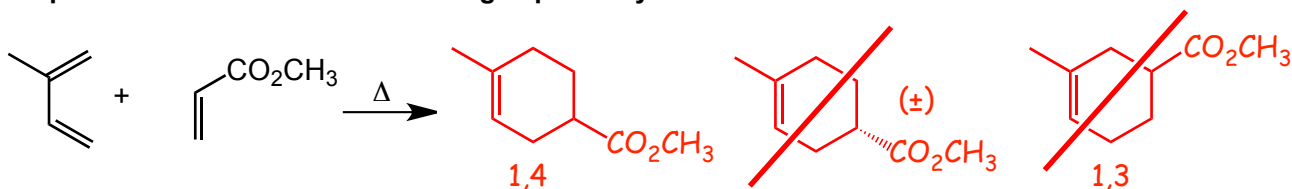
1,3-Addition: This product is formed **slower**, it is the **minor** organic product.



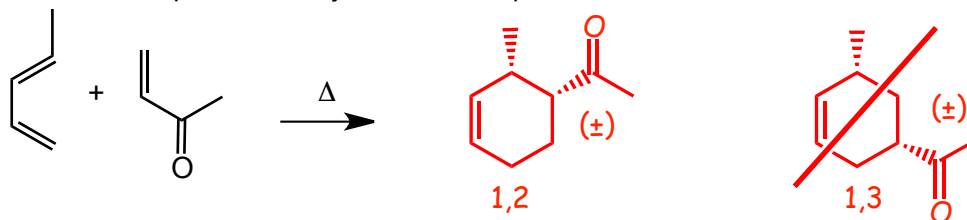
Example: With actual donating and withdrawing groups:



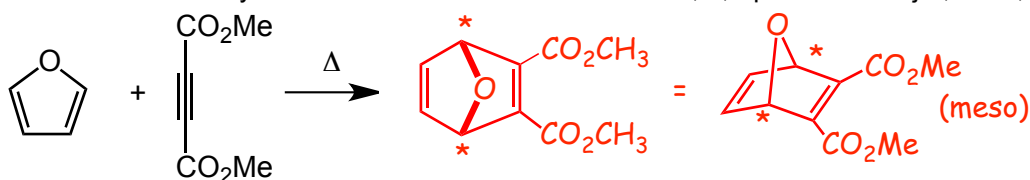
Example Reactions with Stereo- and Regiospecificity:



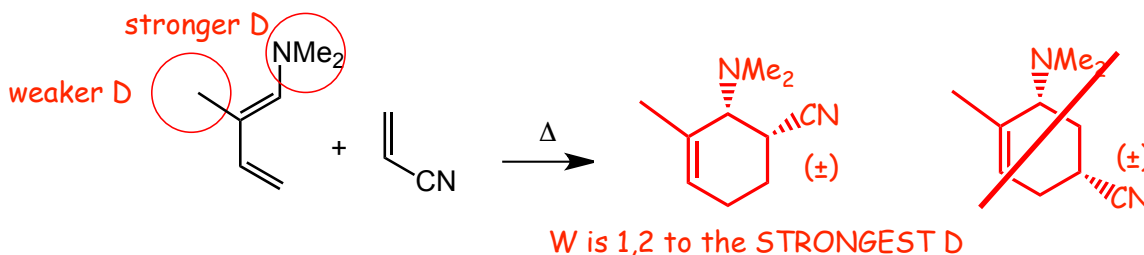
- **One** chiral center, no wedged/dashed bonds (only \pm), wedged/dashed bonds have no meaning if a racemic mixture is specified, **and**, 1,4-product is major, not the 1,3-product.



- **Two** chiral centers, need **both** dashed bonds to illustrate the relative stereochemistry of the -D and the -W group, **and** the racemic mixture symbol to indicate the other enantiomer, 1,2-product is major, not 1,3-product.



- There are chiral centers in the product (*), but the product has a mirror plane of symmetry, it is an achiral meso compound.



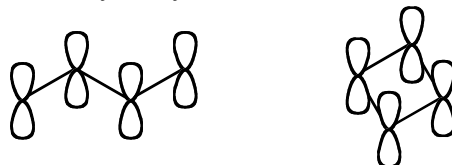
- The product that has the -W group 1,2- with respect to the strongest donating group is the major product.

5 π -Molecular Orbitals : Pericyclic Reactions

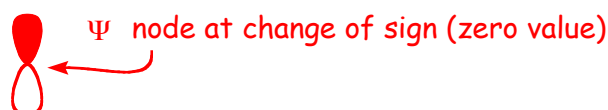
Molecular orbitals - Where **are** the electrons in a molecule?

- Build molecular orbitals by combining appropriate atomic orbitals.
- Build pi-molecular orbitals by combining p atomic orbitals.
- The number of molecular orbitals we must make is equal to the number of p atomic orbitals that we combine.

First, we are concerned with linear systems, cyclic systems come later.



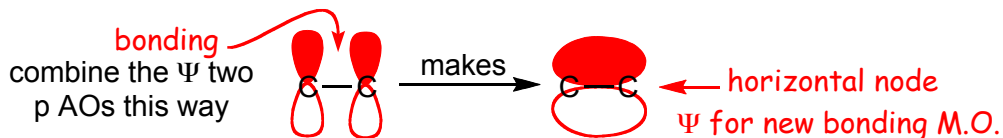
We need to (briefly) revisit concept of orbital wavefunction: example of a p-A.O.



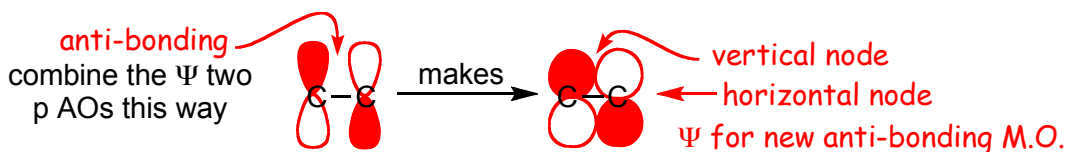
- Shown above is a graphical representation of waveform of an atomic p orbital.
- The waveform is a mathematical function which evaluates to positive value, negative value, or zero.
- Only the relative sign of the wavefunction is important (+ or -), we distinguish using shading (black/white).

Revisit concept of bonding and making Molecular Orbitals by Combining Atomic Orbitals

- For the case of two p atomic orbitals (AOs) on two adjacent carbon atoms, overlap of the orbital wavefunctions results in simultaneous constructive (in-phase) **and** destructive (out of phase) interference of the wavefunctions to generate two new wavefunctions.
- Overlap of the wavefunctions of atomic orbitals of same sign (in-phase, constructive interference) generates a new bonding wavefunction, the new bonding molecular orbital.
- The new bonding wavefunction builds electron density between the nuclei, allows electrons to "see" both nuclei
- An electron in the new bonding wavefunction is lower in energy compared to being in the original atomic orbital.



- The wave nature of orbital wavefunctions means that if the atomic wavefunctions can overlap in-phase (as above), then they must simultaneously overlap out of phase (whether we like it or not(!), shown below) which results in **destructive** interference of the atomic orbital wavefunctions between the atoms, which generates a new **anti-bonding** wavefunction.
- The new anti-bonding wavefunction eliminates electron density between the nuclei.
- An electron in the new anti-bonding wavefunction would be **higher** in energy compared to being in the original atomic orbital.

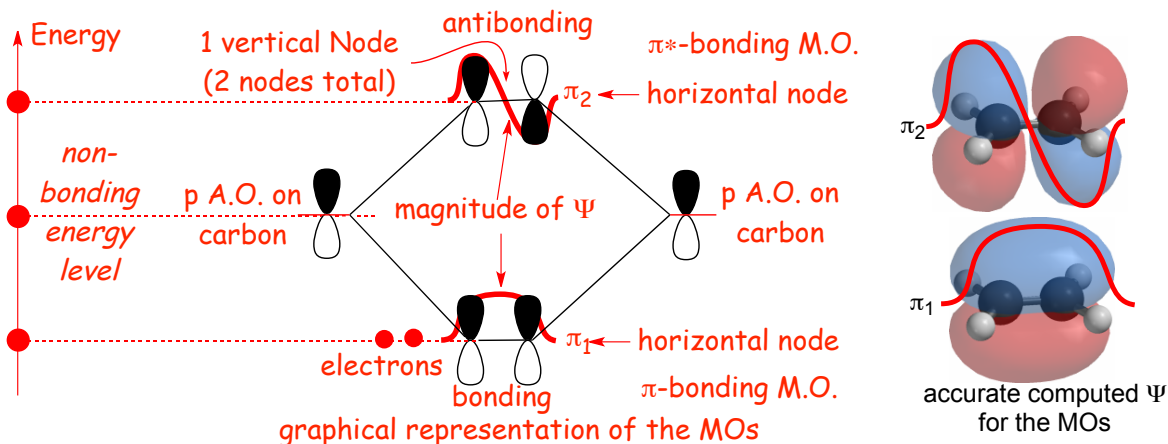


5.1 Rules for Constructing Molecular Orbitals

You will not memorize these rules, you will learn them very quickly by using them

- 1) The number of M.O.'s = the number of A.O.'s, **because**, orbitals can't "disappear".
- 2) 2 electrons per M.O., **because**, of the **Pauli** principle.
- 3) The lowest energy M.O. has zero vertical nodes, **therefore** it is the most "bonding".
- 4) Increasing vertical nodes means increasing energy, **because**, they become less "bonding".
- 5) Symmetry of nodes determined by molecular symmetry, **because**, they are standing waves.

5.2 pi-Molecular Orbitals of Ethylene

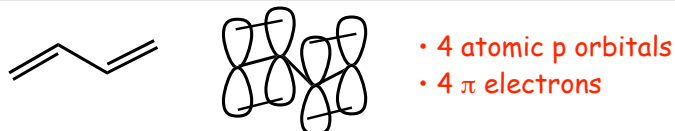


- 1) 2 A.O.'s, therefore, 2 M.O.'s must be formed when they combine ($\pi-1$ and $\pi-2$)

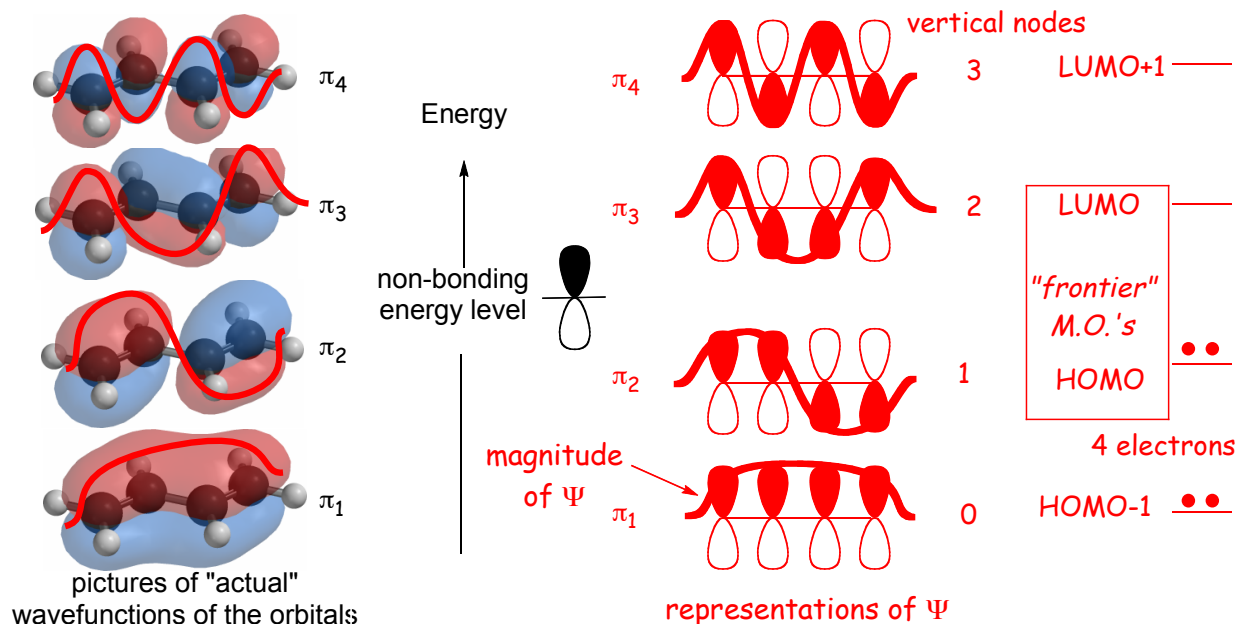
- 2) 2 Electrons (max.) per M.O. - 2 electrons in bonding π -1 M.O.
- 3) π -1 has **no vertical** nodes.
- 4) π -2 has **one vertical** node (wavefunction changes sign, goes through zero).
- 5) The node position determined by molecular symmetry (in the middle!), wavefunctions are **standing waves**.

- The p-A.O.'s do not actually exist in the molecule, the M.O.s are drawn using a "cartoon" or "digital" approximate p A.O. method because it is too hard to draw the actual orbitals accurately.
- The wavefunctions really look like waves!

5.3 π -Molecular Orbitals of Butadiene



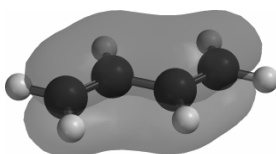
- Here we consider the **π -molecular orbitals only** (ignore the σ -MOs).
- There are 4 p A.O.'s, therefore 4 pi-M.O.'s must be formed when they combine, π 1, π 2, π 3, π 4
- 2 electrons in each M.O. (π -1, π -1)
- Lowest, π -1, has no vertical nodes (all have one horizontal node).
- Increasing vertical nodes = increasing energy.
- The nodes are symmetrical because the wavefunctions of the M.O.s describe **standing waves**.



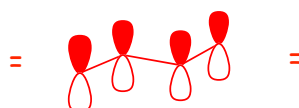
HOMO = Highest Occupied Molecular Orbital

LUMO = Lowest Unoccupied Molecular Orbital

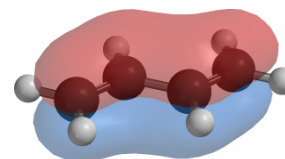
The Wavefunction Squared give the probability of finding the electrons in the orbitals



Ψ^2 for π_2 M.O., gives probability of finding the electrons, hard to draw!



"representation" of Ψ for π_2 M.O. using A.O.'s what WE draw

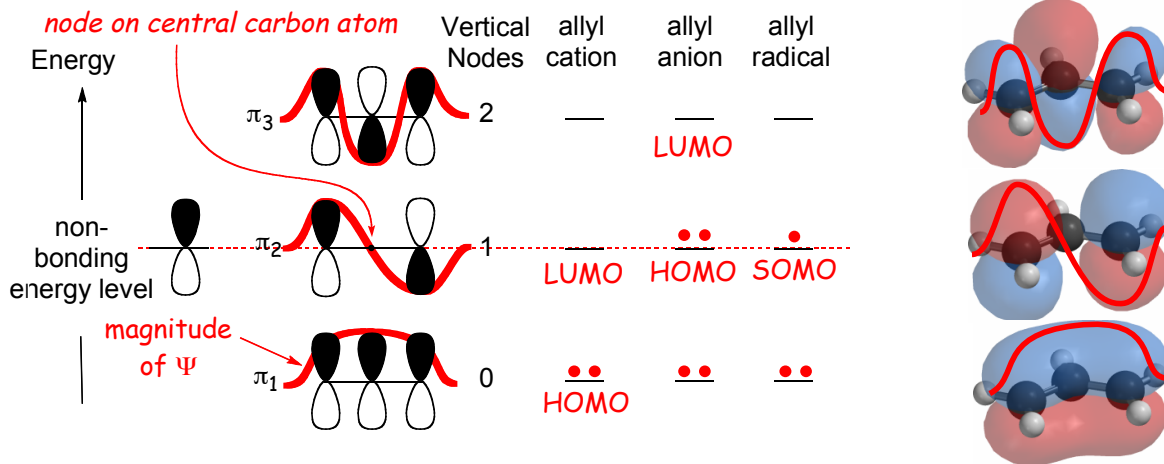
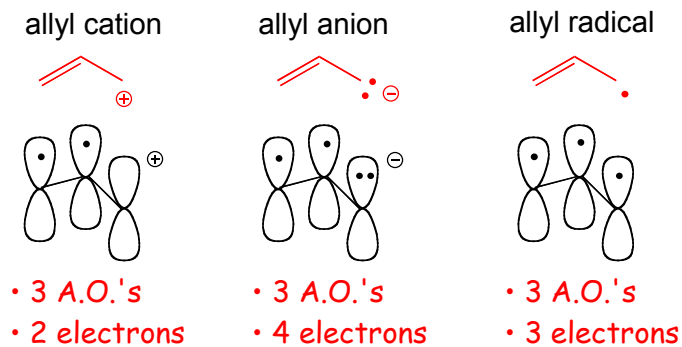


accurate computed Ψ for π_2 M.O. too hard to draw!

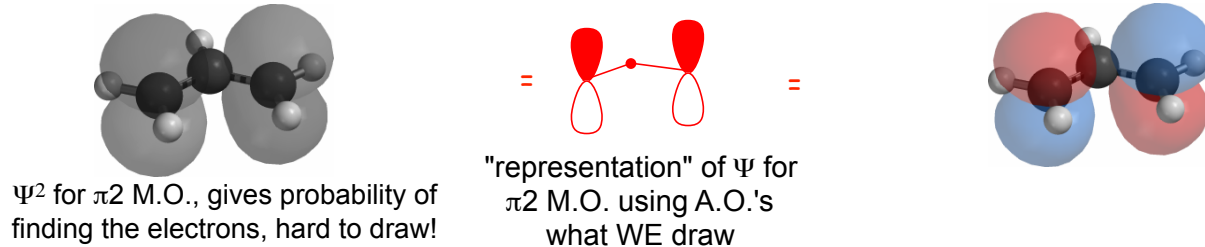
- The electrons are distributed over all 4 carbon atoms, but never found at a node (horizontal in this case).

5.4 pi-Molecular Orbitals of The Allyl System

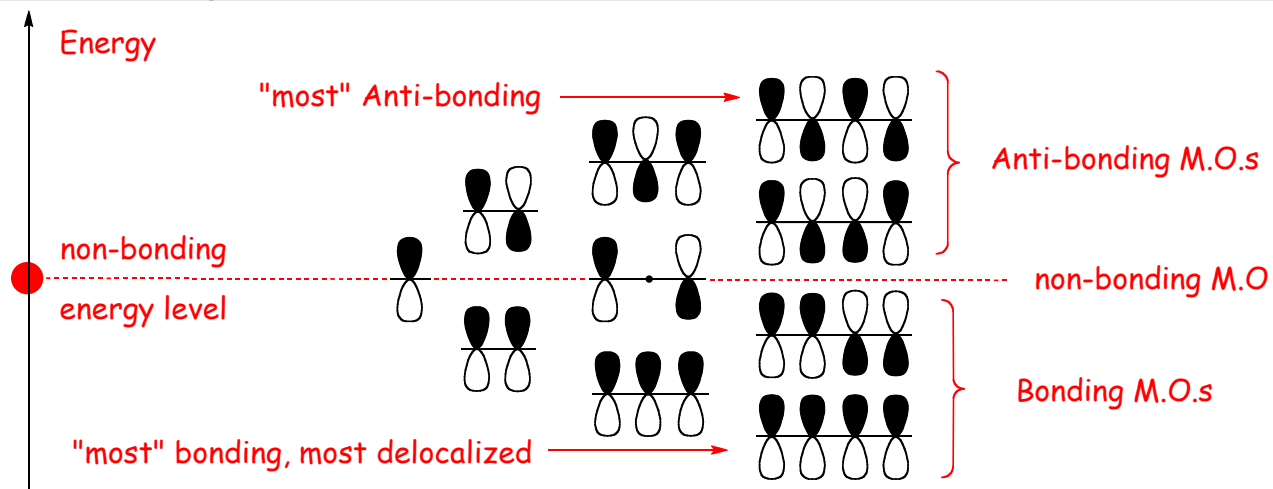
The allyl system describes the simplest resonance stabilized ion and radical intermediates in organic chemistry, shown below are the simplest allyl anion, allyl cation and allyl radical, each are conjugated systems, each have 3 carbon atoms involved in the conjugated system (resonance), but they have different numbers of electrons associated with the conjugated system (involved in resonance).



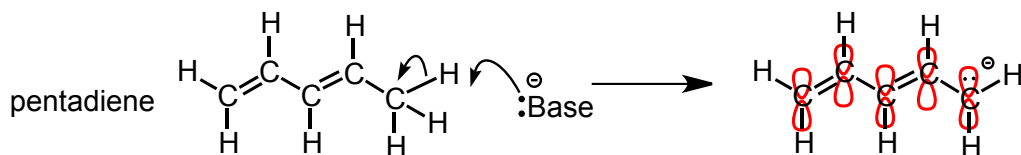
The Wavefunction Squared give the probability of finding the electrons in the HOMO of the allyl anion



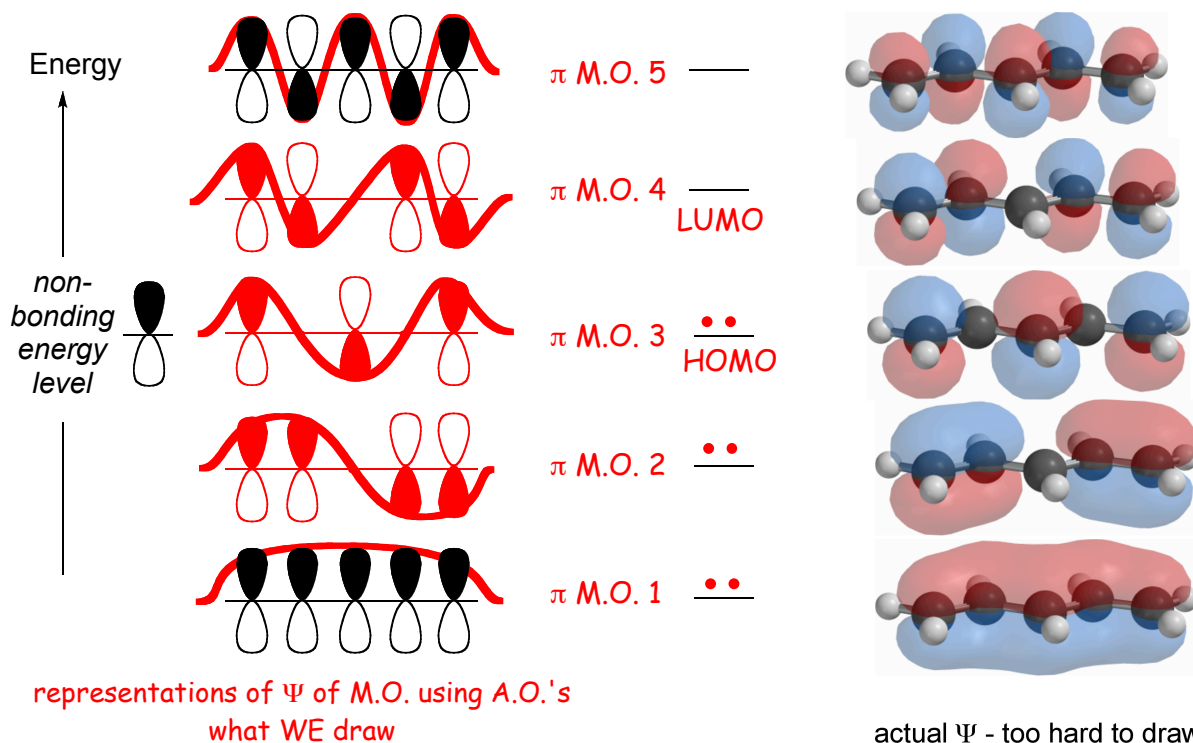
5.5 Relative Energies of Pi-Molecular Orbitals



Example problem: What is the HOMO & LUMO of the pentadienyl anion?



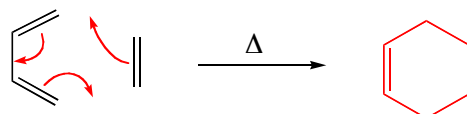
1. How many p A.O.'s do we have to work with? Answer = **five**
2. How many M.O.'s will we have? Answer = **five**
3. How many electrons do we have? Answer = **six**
4. How many nodes will the HOMO have? Answer = **two**
5. How many nodes will the LUMO have? Answer = **three**



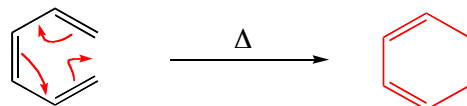
6 Frontier Molecular Orbital Theory : Pericyclic Reactions

- All pericyclic reactions are **concerted** and involve cyclic transition states and we need M.O.'s to understand them.
- There are several kinds of pericyclic reaction, we look at **only** two of them:

1. Cycloadditions



2. Electrocyclic reactions



There are three different theories for pericyclic reactions, we will look at two of them:

1. Frontier Molecular Orbital Theory.
2. Aromatic Transition State Theory.

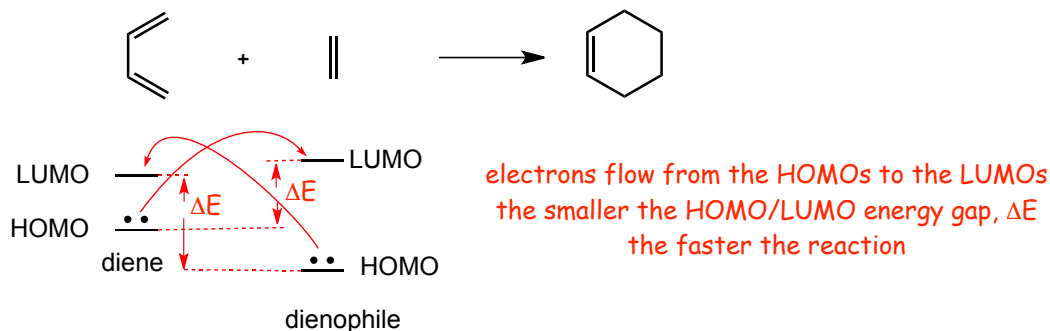
The other theory is conservation of orbital symmetry, it is more complete than the other two, but is beyond the scope of a General Organic Chemistry course.

FMO Theory: (Approximate, but it works!)

- The fundamental principle for understanding Pericyclic Reactions.....

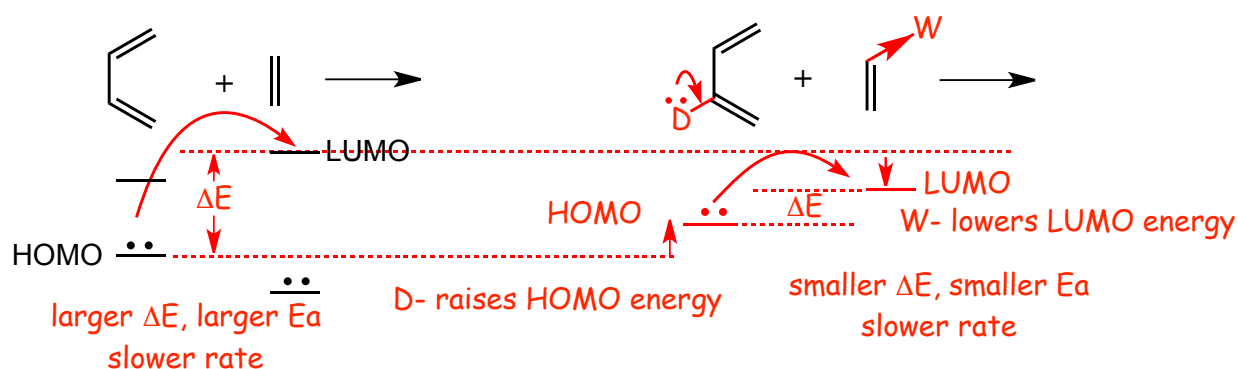
donated electrons come from the **highest energy occupied orbital, i.e. HOMO**
electrons are **accepted** into the **lowest energy unoccupied orbital, i.e. LUMO**

Example: The Diels-Alder Reaction



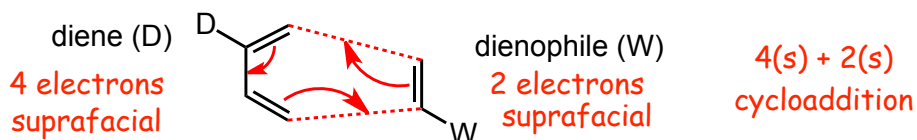
- The smaller the energy gap between where the electrons come from (HOMO) and are going to (LUMO), the faster the reaction.
- A **donating** substituent on the diene **raises** the energy of the electrons, specifically in the **HOMO**.
- A **withdrawing** substituent on the dienophile **lowers** the energy of electrons, specifically in the **LUMO**.

Compare: HOMO/LUMO Energy Gap in Diels-Alder reaction with the addition of D- and W- Substituents:



- Electrons “flow” from the HOMO to the LUMO is determined by the HOMO/LUMO energy “gap”, ΔE .
- There is a **smaller HOMO/LUMO energy gap** with D- and W- substituents, ΔE becomes smaller, resulting in a **faster reaction**
- FMO theory explains the substituents effects on the rate of the Diels-Alder reaction!

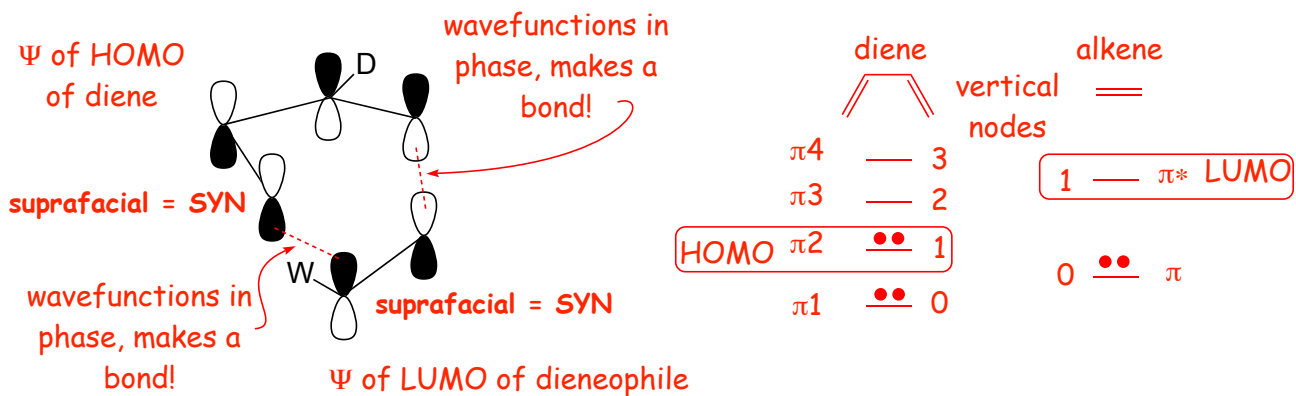
Revisit Diels-Alder Reaction - 4 + 2 Cycloaddition Reaction



- When **atomic** wavefunctions overlap in phase - they make a bond.
- When **molecular** wavefunctions overlap in phase - they make a bond!
- we now ask the following question: Can overlap the molecular orbitals of both reactants, **suprafacial/suprafacial** occur **in-phase** and therefore **make both bonds at the same time?**
- If it can then the 4(s) + 2(s) **concerted reaction** is allowed.

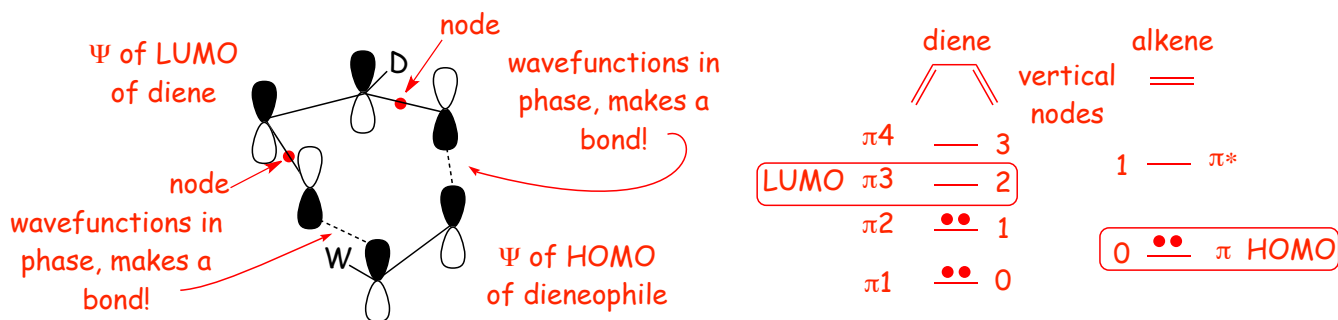
First: consider suprafacial/suprafacial overlap of the **HOMO of the diene** + the **LUMO of the dienophile**

- Recall, suprafacial is equivalent to syn-addition.



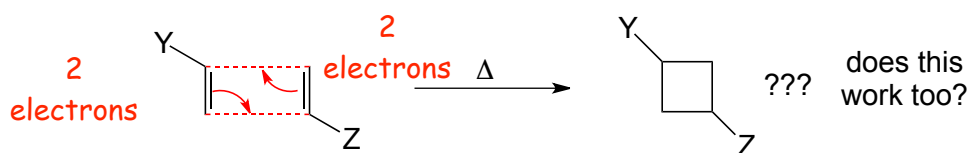
- Overlap of the **HOMO** of the diene **suprafacial** and the **LUMO** of the dienophile **suprafacial** results in **in-phase and bonding interactions** to make **both** of the new σ -bonds at the same time.
- Therefore, a concerted Diels-Alder reaction **4(s) + 2(s) cycloaddition is allowed, according to F.M.O. theory.**

Now: Consider reaction "other way round", **HOMO of dienophile & LUMO of diene:**

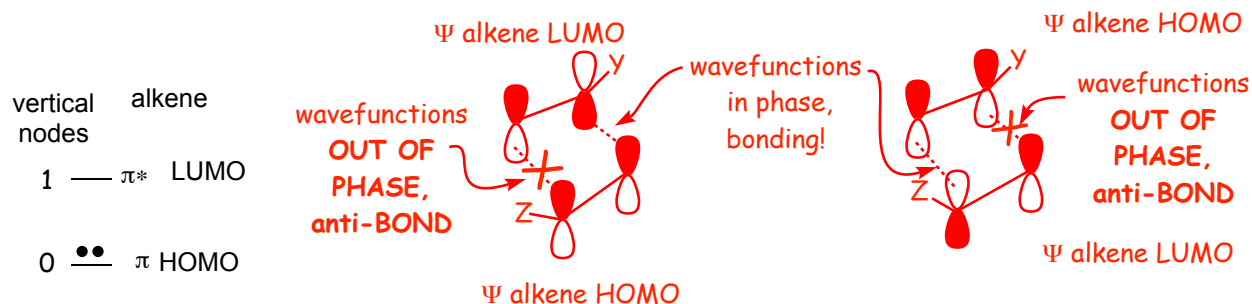


- Overlap of the **LUMO** of the diene **suprafacial** and the **HOMO** of the dienophile **suprafacial** also results in **in-phase and bonding interactions** to make **both** of the new σ -bonds at the same time.
- Therefore, a concerted Diels-Alder reaction **4(s) + 2(s) cycloaddition is allowed** according to F.M.O. theory **using either analysis, i.e. HOMO/LUMO or LUMO/HOMO.**
- When considering whether a concerted cycloaddition reaction is allowed it doesn't matter which HOMO/LUMO combination we consider.

What About a 2(s) + 2(s) Cycloaddition Reaction?

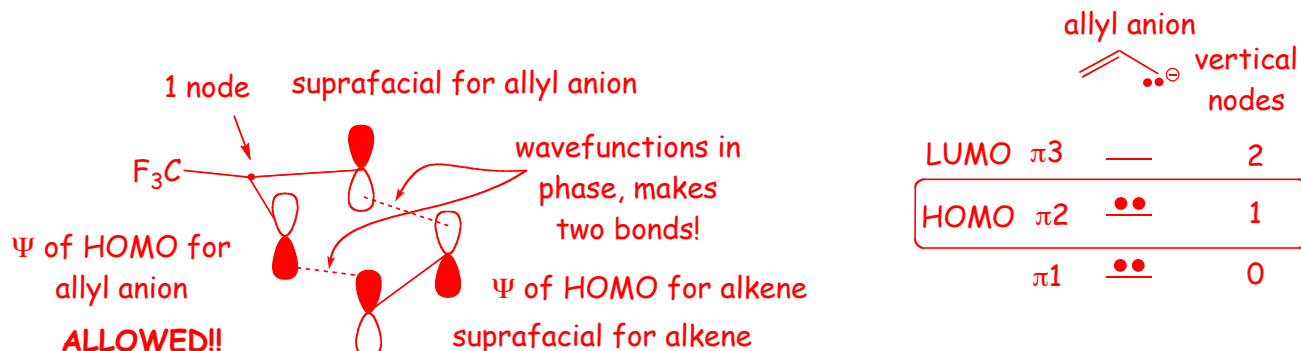
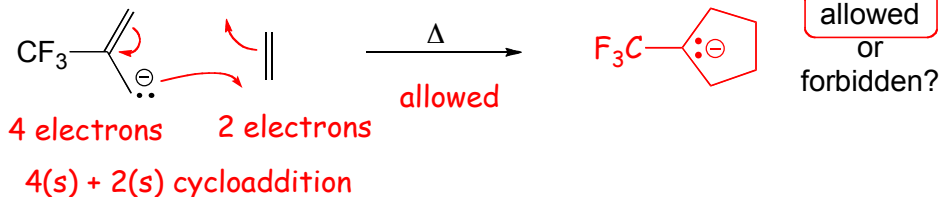


- Consider overlap of the **HOMO and LUMO** of the two alkenes **suprafacial/suprafacial** (add to both sides of both molecules at the same time):



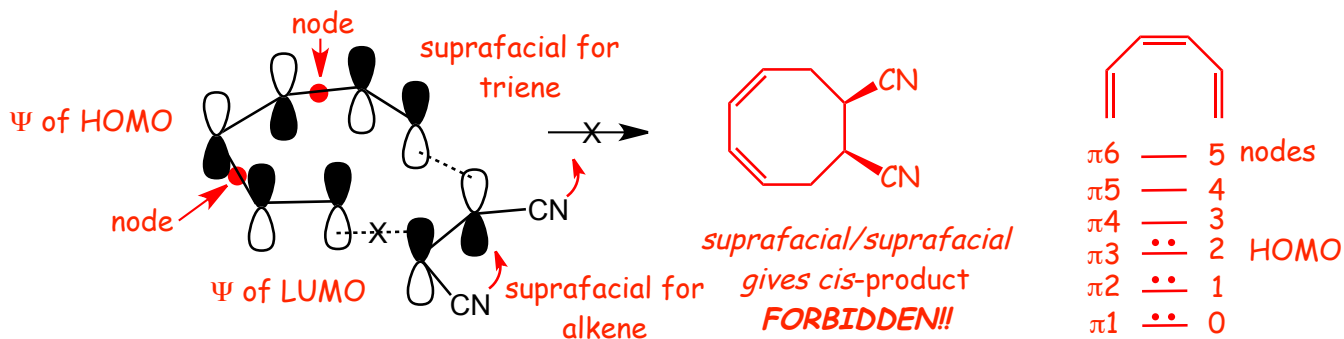
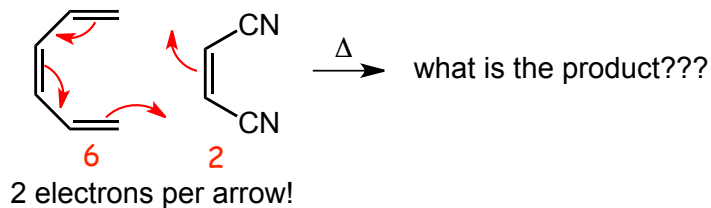
- This results in **one anti-bonding** interaction for both HOMO/LUMO combinations.
- A **suprafacial/suprafacial 2(s) + 2(s) cycloaddition reaction is forbidden** according to F.M.O. theory.

Example: A different 4 + 2 cycloaddition:

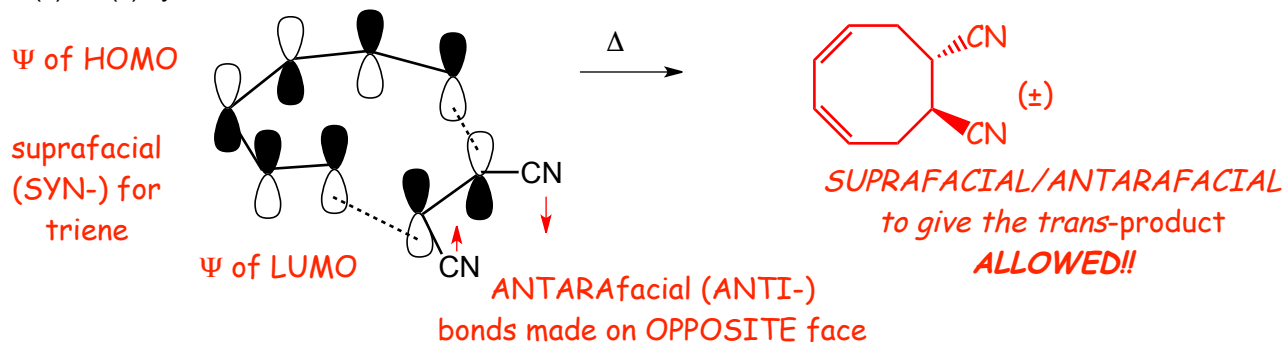


- When this reaction is **suprafacial/suprafacial**, 4(s) + 2(s), then reaction is allowed.
- **Only** a suprafacial/suprafacial reaction is possible in this case because the cyclic system is not large enough to have bonding occurring any other way.

Example: A 6 + 2 cycloaddition reaction:



- A 6(s) + 2(s) cycloaddition reaction is **forbidden**.



- **Antarafacial**, opposite of suprafacial - it means making the one bond on **opposite** sides of the two reactants.
- A 6(s) + 2(a) cycloaddition reaction is **allowed** (suprafacial/antarafacial).
- A 6(a) + 2(s) cycloaddition would also be **allowed** (antarafacial/suprafacial).
- Antarafacial cycloadditions are possible when there are enough atoms (usually at least seven or eight) atoms involved in the cycloaddition to make a large enough ring to allow antarafacial overlap.
- In this example above there were eight atoms, but (s) + (a) cycloadditions are actually quite rare.

Electrocyclic Reactions



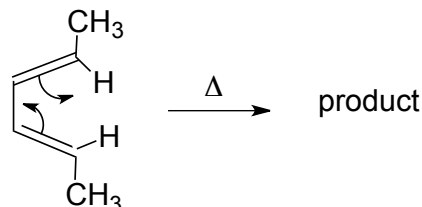
- We need to consider **two** ways that the ring can be closed:

Conrotatory: The sigma-bonds and orbitals rotate in the **same direction** (in concert).

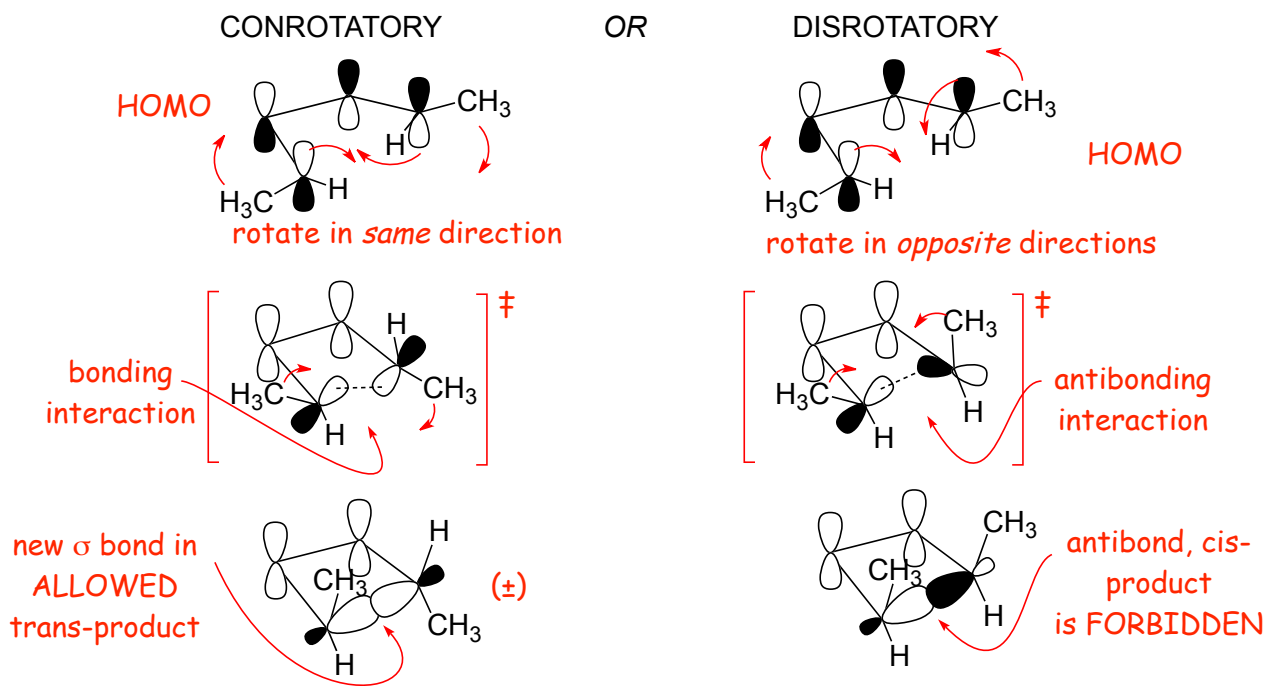
Disrotatory: The sigma-bonds and orbitals rotate in **opposite directions**.

Example:

- Show how you would determine the product of the reaction below using F.M.O. theory:



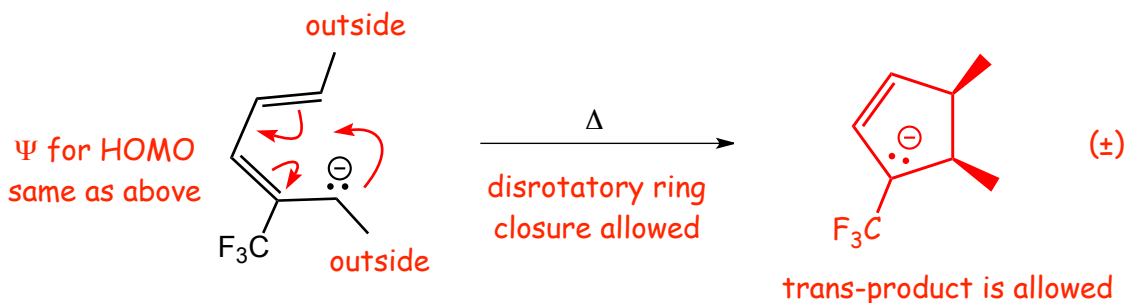
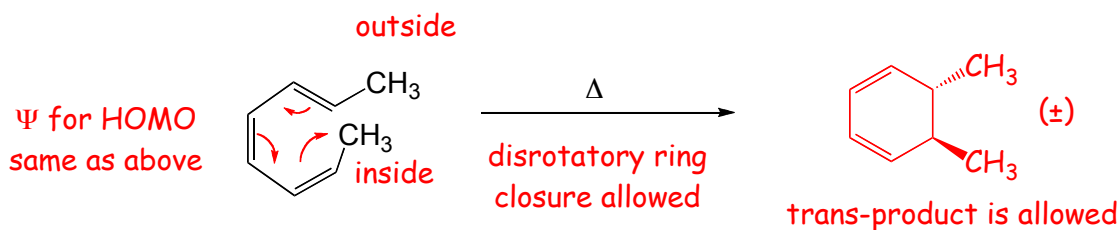
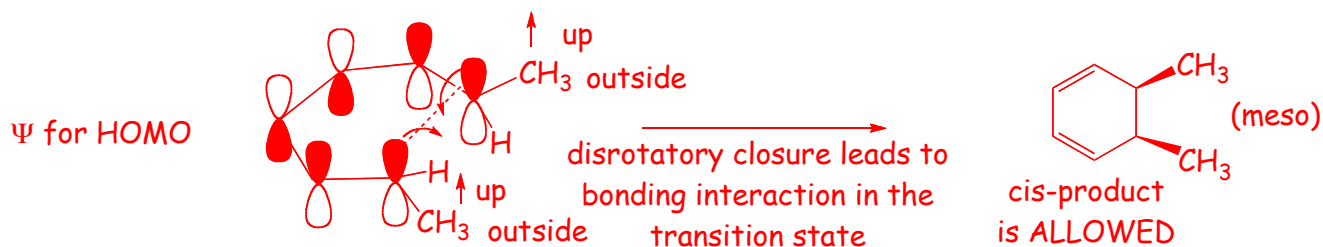
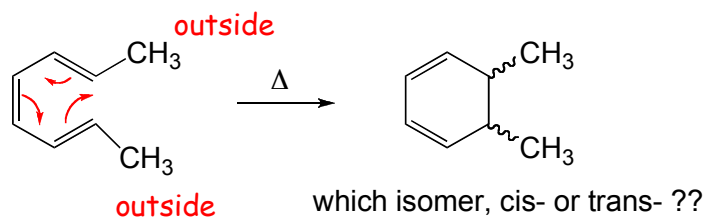
- In this case the reaction is **unimolecular** (one molecule, not bimolecular), electron flow is not from one molecule to another, we are concerned with the highest energy (most reactive) electrons in the starting structure only, these are contained in the Highest Occupied Molecular Orbital, the HOMO.



- As the ring closes, the important orbitals are those at the end of the conjugated system, they transform from formal p atomic orbitals into sp³ hybridized atomic orbitals, and at the same time they rotate 90 degrees so that they are pointing towards each other so that they can overlap and make the new sigma-bond.

- Conrotatory ring closure results in a bonding (in-phase) interaction between these orbitals, both in the transition state and in the final product, conrotatory ring closure is **allowed**.
- Disrotatory ring closure results in anti-bonding (out of phase) orbital overlap, disrotatory ring closure results in a higher energy transition state, this reaction is **forbidden** in the language of F.M.O. theory.

Examples



- The enantiomer is the product that is obtained by doing disrotatory ring closure in the "other direction", which results in the product with the upper CH₃ wedged and the lower one dashed

What we just did is amazing (you should be amazed!)

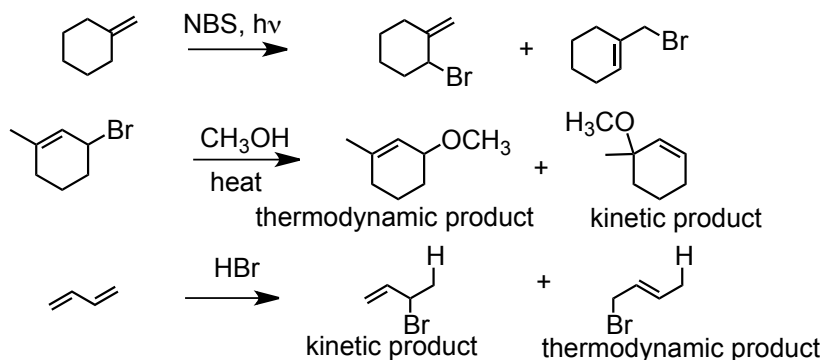
mind = blown



- These reactions can **only** be explained and understood by taking the **wave properties** of the electrons in the molecular orbitals into account.
- Understanding the wave nature of electrons is difficult, but **without this there is no understanding of pericyclic reactions**.

- The wavefunctions **have** to overlap in phase in order to get the reactions to go, at least as the concerted reactions discussed here.
- These reactions represent **quantum mechanics** in **organic chemistry**.
- The quantum/wave nature of electrons is difficult to understand, **however**:
- **Explain the presence of orbitals any other way!**
- **Explain pericyclic reactions any other way!** (*you can't!*)

8 Summary of Conjugated Reaction Types



The Diels-Alder reaction is stereochemical and regiochemical controlled

