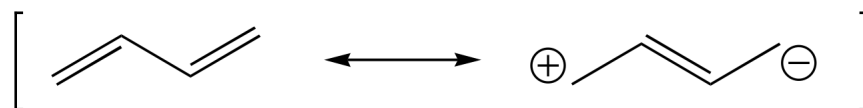


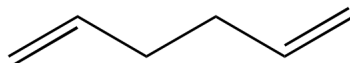
Conjugated Systems

Double bonds in conjugation behave differently than isolated double bonds

With conjugated double bonds resonance structures can be drawn

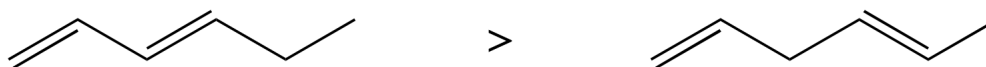


With isolated double bonds cannot draw resonance structures including both alkenes



Leads directly to energy differences

As expected, those structures that can draw resonance structures are more stable, therefore conjugated double bonds are more stable than isolated double bonds



More stable

Remember that internal double bonds are more stable than terminal double bonds
-in addition we can classify dienes, and other multiple alkene structures,
by whether the alkenes are in conjugation

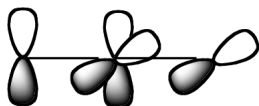
Another type of multiple alkene is an allene

Allenes, shortest form of a cumulene (parent name), have two double bonds with common carbon atom in both alkenes



Cumulenes are less stable than both conjugated and isolated double bonds

The double bonds are orthogonal to each other



Leads to a less stable structure

Molecular Orbitals

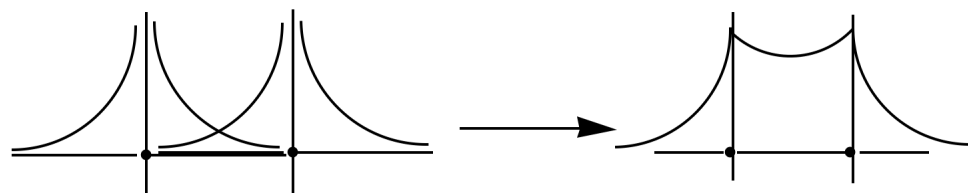
We can understand, and predict, many properties of conjugated systems by considering the molecular orbitals

Remember when we discussed bonding in organic compounds we formed bonds by combining atomic orbitals

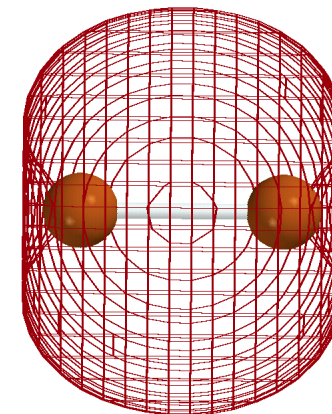
Either sigma (σ) or pi (π) bonds were formed depending upon the symmetry of the resultant bond upon addition of the atomic orbitals

Sigma Bonds

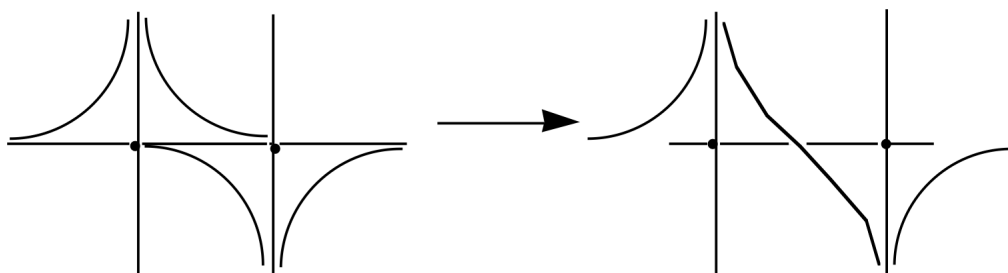
Formed by combining two atomic orbitals
(shown here with two atomic s orbitals)



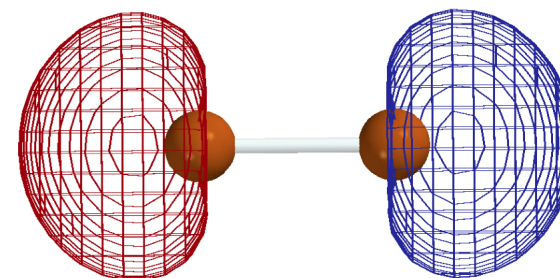
Sigma (bonding)



If combine two atomic orbitals **MUST** obtain two molecular orbitals



Sigma* (antibonding)



The same process occurs when considering conjugated dienes

Rules for combining orbitals:

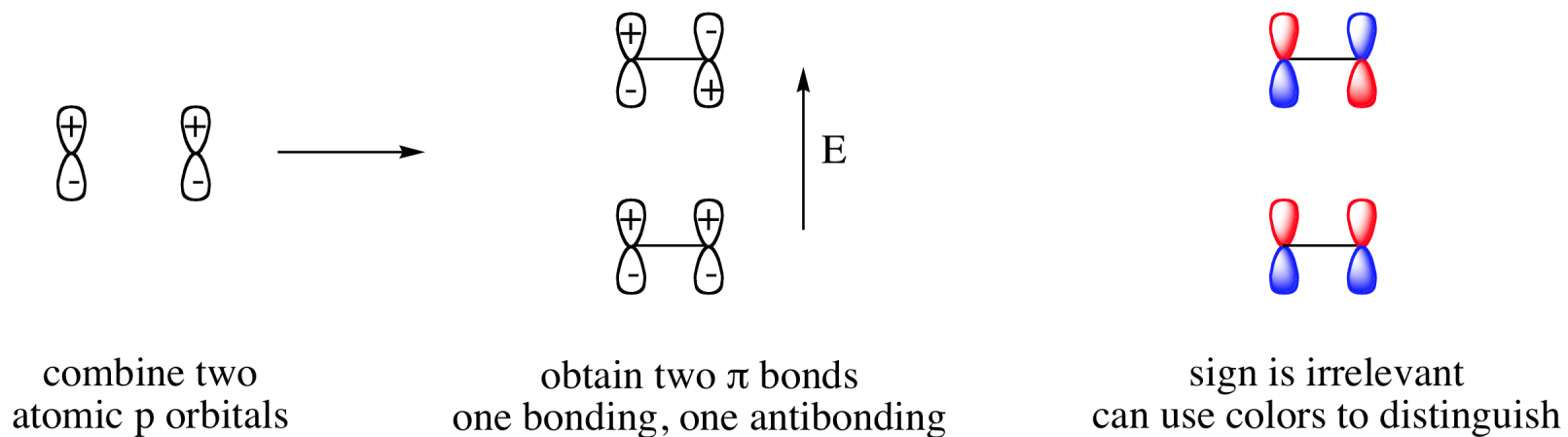
- 1) Always get the same number of molecular orbitals as number of atomic orbitals used to combine
- 2) As the number of nodes increase, the energy of the molecular orbital increases
- 3) The molecular orbitals obtained are the region of space where the electrons may reside (on time average)

First consider an isolated alkene

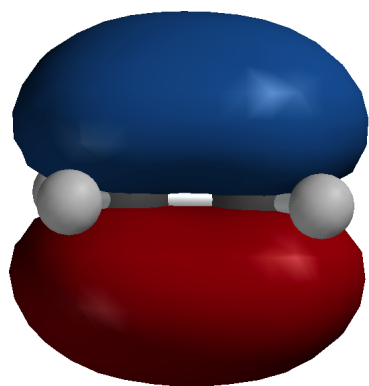
Simplest is ethylene

We can separate the sigma and pi framework

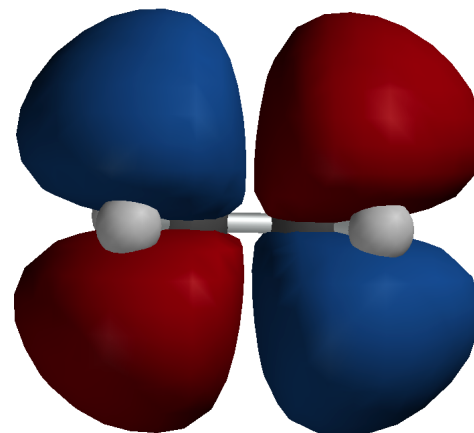
With alkenes, we are interested in the pi framework
since this is what controls the reactivity



The molecular orbitals obtained computationally appear same as the approximation used by combining atomic p orbitals



π bond



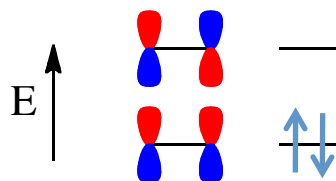
π^* bond

Can draw electronic configuration for the π system

Again consider ethylene

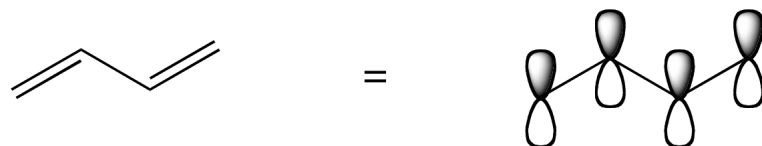
Since there are 2 π electrons in this molecule, will place 2 electrons in MO diagram

Always place electrons in lowest energy orbital first
Each orbital can accommodate two electrons



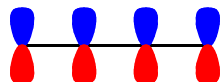
Use same procedure for larger conjugated systems

With butadiene there are 4 p orbitals in conjugation



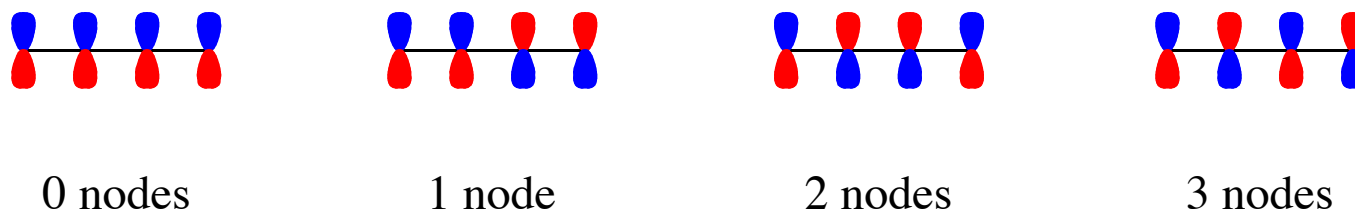
Realize if we add 4 p orbitals then we must obtain 4 molecular orbitals

The difference between the 4 orbitals will be the sign of adjacent atomic orbitals

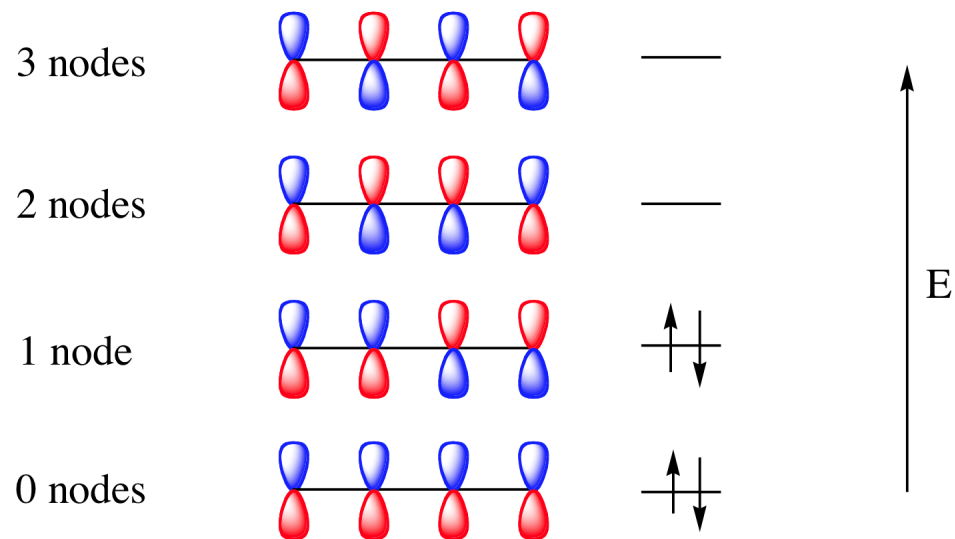


Lowest energy molecular orbital for butadiene
-has three bonding interactions between adjacent orbitals

We will obtain 4 molecular orbitals with different number of nodes



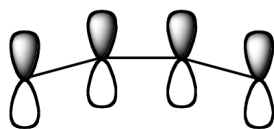
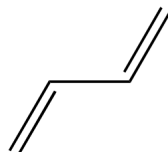
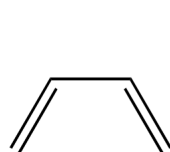
We can also predict the relative energy levels of these molecular orbitals by the number of nodes (as nodes increases, energy increases)



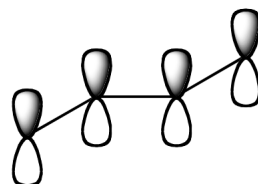
The electronic configuration can thus also be determined by knowing there are 4 π electrons

In order to allow electron delocalization the p orbitals must be aligned

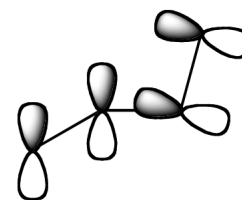
This constrains the geometry of conjugated systems
The p orbitals must be in the same direction – thus the carbon framework is planar



s-cis



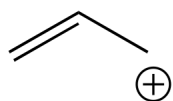
s-trans



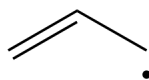
poor
overlap

Molecular Orbital Picture for Allylic Systems

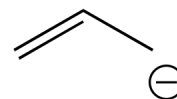
An allylic system refers to 3 conjugated p orbitals



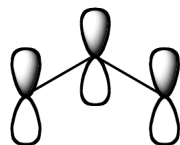
allylic cation



allylic radical

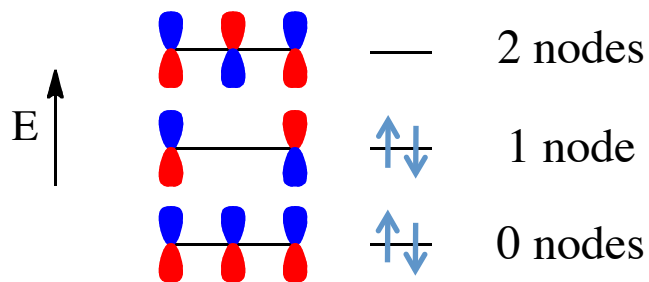


allylic anion



all allylic systems
have 3 p orbitals
in conjugation

With 3 conjugated p orbitals, must obtain 3 molecular orbitals



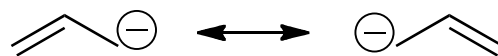
Depending upon number of π electrons the electronic configuration can be determined

Allyl cation has 2 π electrons

Allyl radical has 3 π electrons

Allyl anion has 4 π electrons

Implies that excess negative charge of anion is located on the terminal carbons
(size of coefficients correlates with probability of electron density)

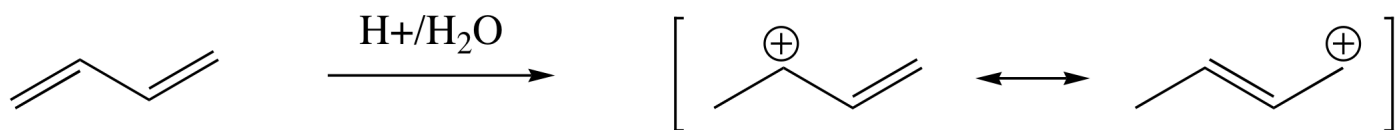


Similar to resonance description

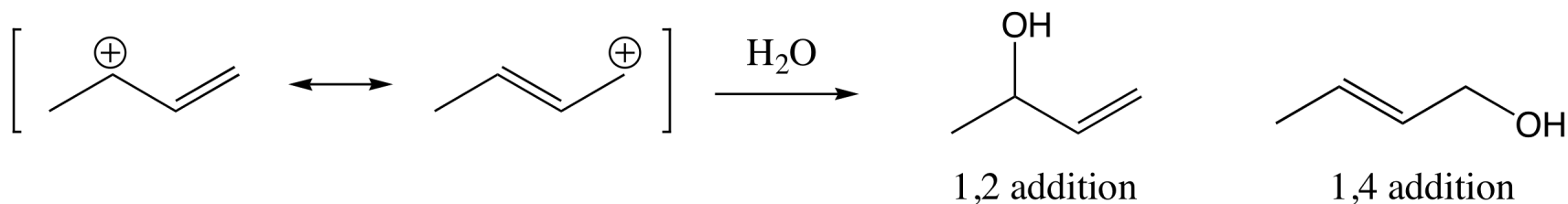
Addition to Conjugated Dienes

As we have already seen, alkenes can react with electrophiles to create a carbocation

With conjugated dienes this reaction will create an allylic carbocation



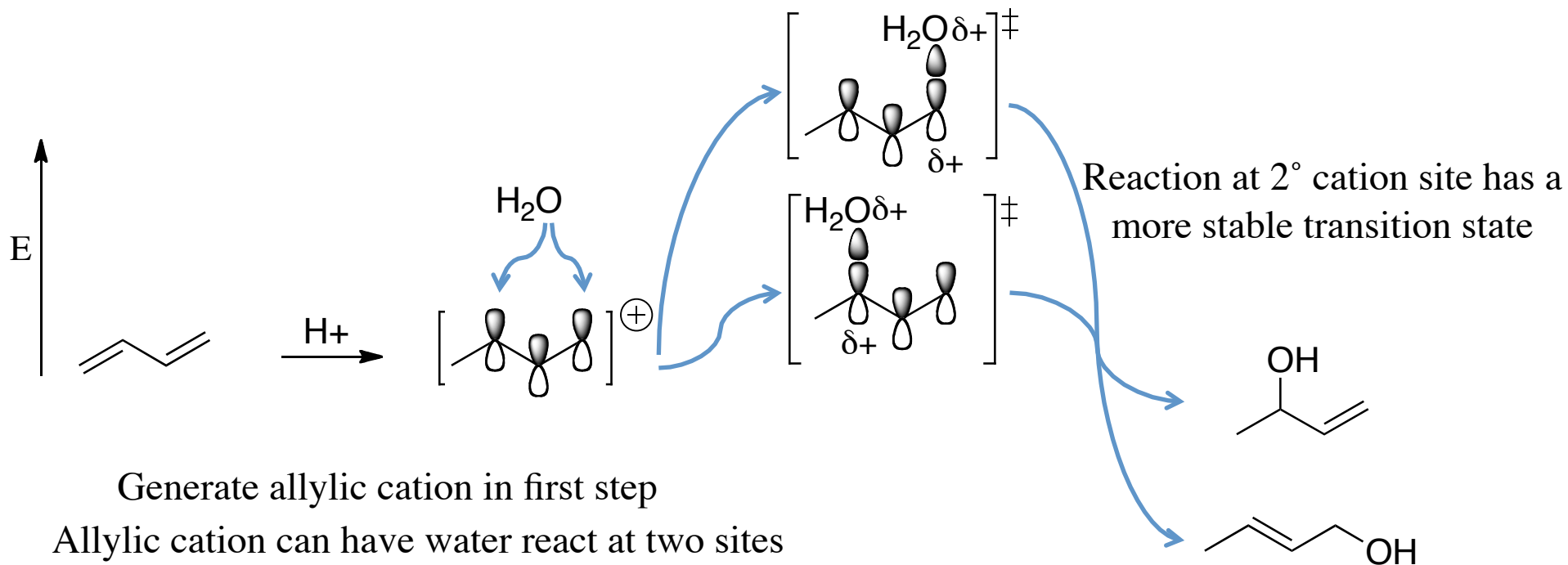
The nucleophile can then react with either resonance form in the second step



Kinetic versus Thermodynamic Control

What forms faster (kinetic product) and what is more stable (thermodynamic product) need not be the same

Consider the addition to conjugated dienes



Generate allylic cation in first step

Allylic cation can have water react at two sites

Reaction at 2° site

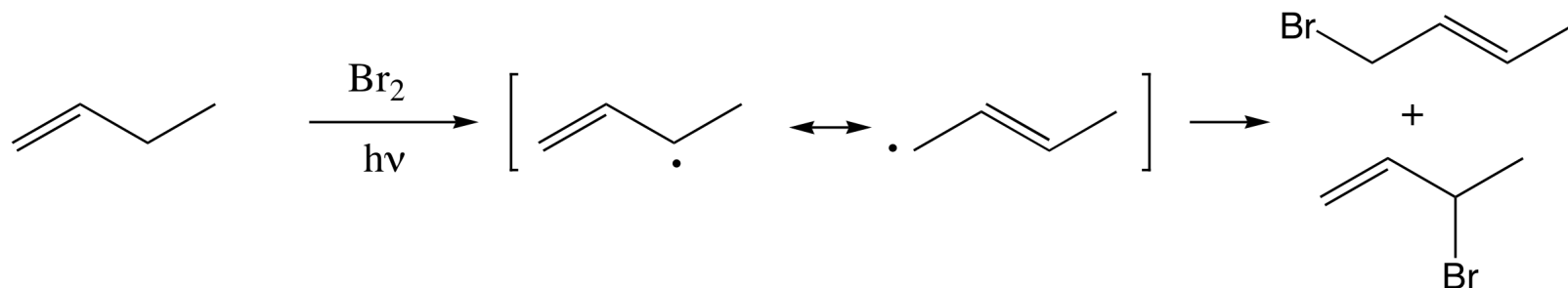
Reaction at 1° site

Thus the kinetic product has water reacting at 2° site

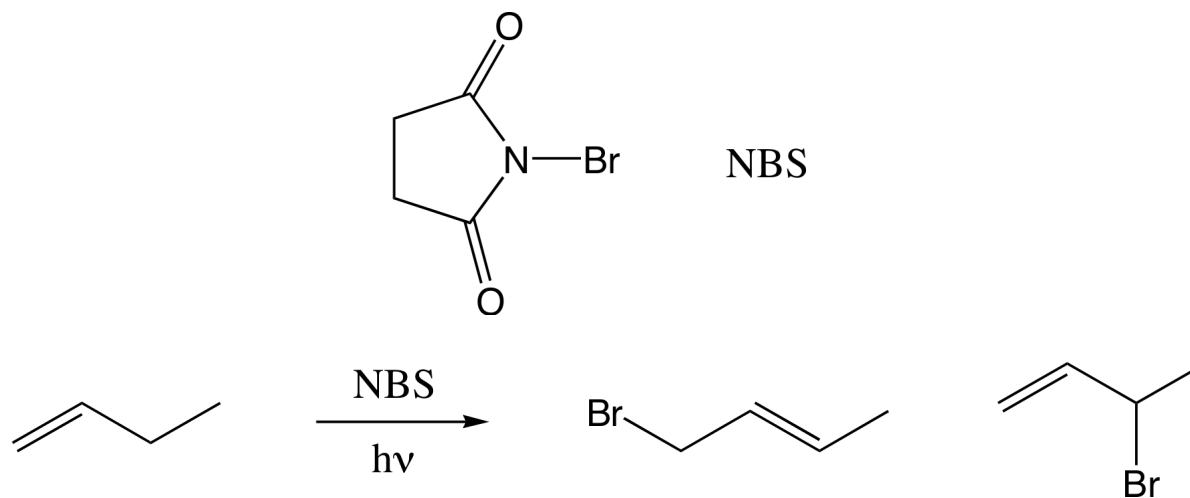
The thermodynamic product has water reacting at 1° site

Formation of Allylic Radical

Remember that we form allylic radicals with free radical halogenation with an alkene



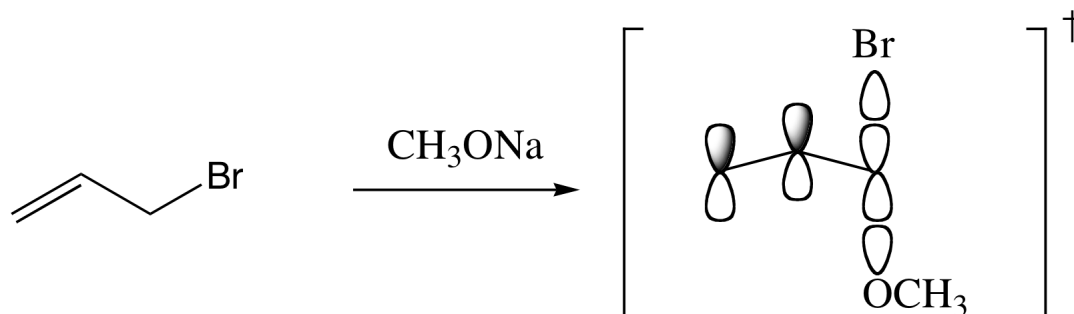
Another way to generate the bromine radical is to use NBS (N-bromosuccinimide)



S_N2 Reactions of Allylic Halides

Allylic halides react faster with a nucleophile in a S_N2 reaction than halides without allylic stabilization

The conjugated π system stabilizes the developing charge in the transition state



Due to this enhancement, allylic halides react with Grignard reagents well, remember that Grignard reagents often have poor yields with unactivated alkyl halides

Pericyclic Reactions

Reactions involving concerted bond formation, or bond breakage,
with a ring of interacting orbitals

Ring of interacting orbitals
-Orbitals must form a continuous loop

Therefore each orbital must be able to interact with the adjacent orbital

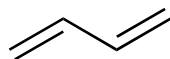
Interactions between orbitals on different reactants

Electrons are located in Molecular Orbitals (MO's)

When two molecules react, a molecular orbital on one molecule interacts with a molecular orbital on the second molecule which causes an energy gain (if reaction is favorable)

With conjugated π systems we can consider only the π framework

Butadiene



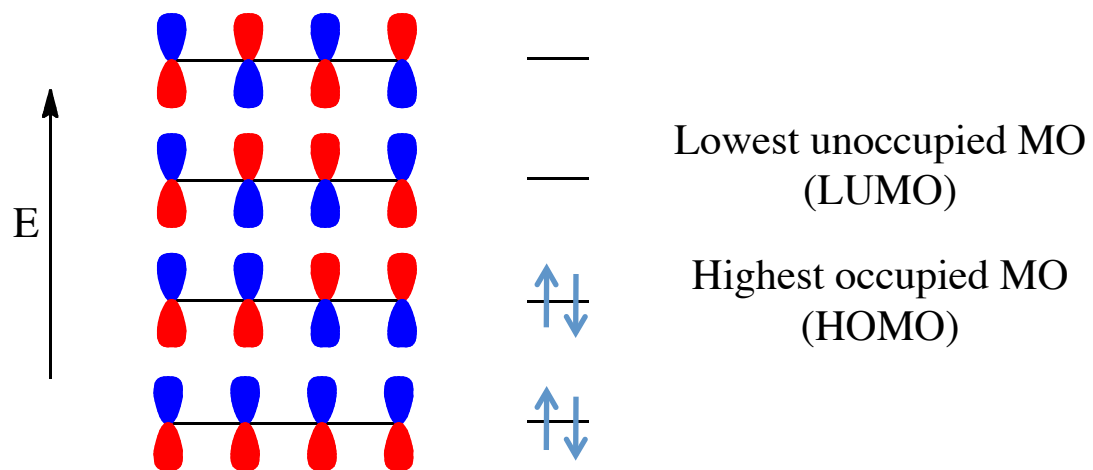
Consists of four interacting p orbitals which form the π framework



4 π electrons in 4 continuous p orbitals

As we learned in forming σ bonds – the energy of a MO (or a bond) is dependent upon the symmetry of the interacting orbitals

Molecular Orbitals for Butadiene



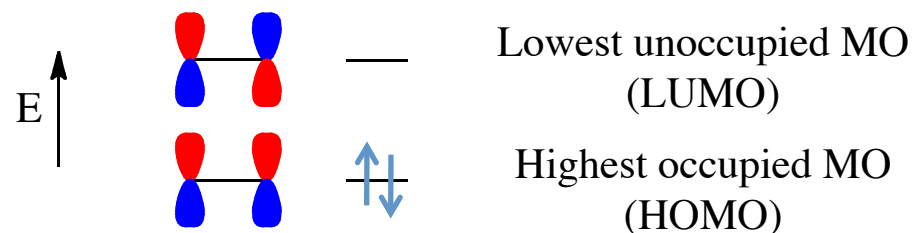
4 electrons are placed in these molecular orbitals by pairing the lowest energy MO's until all electrons are placed in orbitals

The molecular orbital that is highest in energy that contains electrons is called the highest occupied molecular orbital (HOMO)

The molecular orbital that is lowest in energy that does not contain electrons is called the lowest unoccupied molecular orbital (LUMO)

Ethylene

The molecular orbitals for ethylene can be obtained in a similar manner



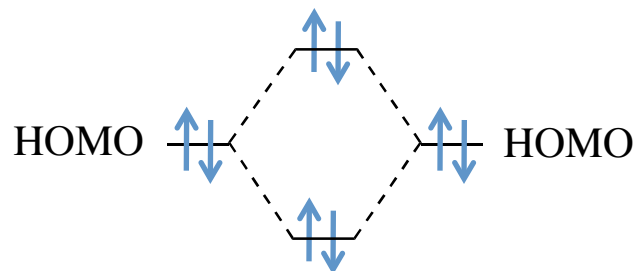
2 electrons are placed in 2 MO's
derived from the two conjugated p orbitals

After determining the electronic configuration,
the HOMO and LUMO orbitals can be determined

Energy Gain in a Reaction

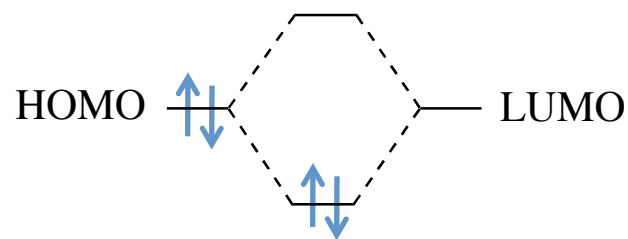
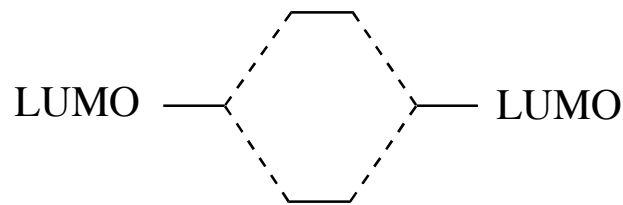
Remember that these molecular orbitals on two molecules combine to form new orbitals in a reaction

Consider the interaction of HOMO and LUMO orbitals on different molecules



If two HOMO orbitals react then two new MO's will be obtained (one lower and one higher in energy)

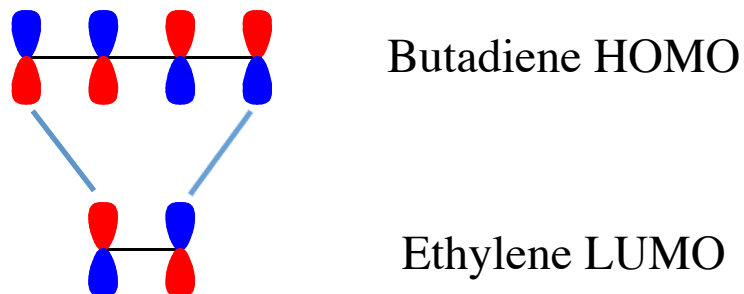
The 4 electrons will be placed and thus there is no energy gain



The only energy gain is when a HOMO from one molecule reacts with a LUMO from the other molecule

In order for the HOMO of one molecule to interact with the LUMO of another molecule the SYMMETRY of the orbitals must be correct

If the symmetry is wrong, then we cannot have interacting orbitals

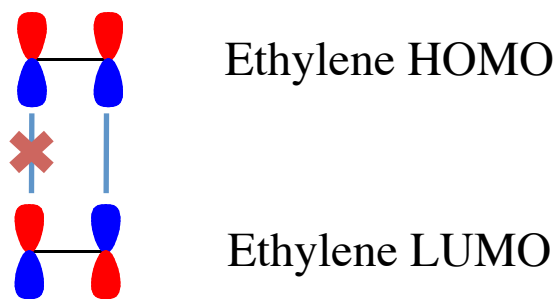


Consider butadiene reacting with ethylene

The symmetry of the interacting orbitals is correct,
therefore butadiene reacting with ethylene is symmetry allowed

Ethylene, however, cannot react with itself

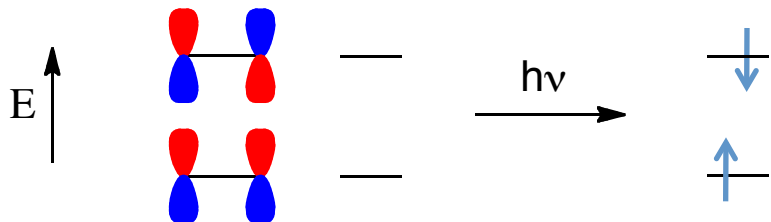
The orbitals cannot align themselves with proper symmetry



Therefore this reaction is symmetry forbidden

Excitation

Photolysis (if the energy of light is correct!) can excite an electron to a higher MO



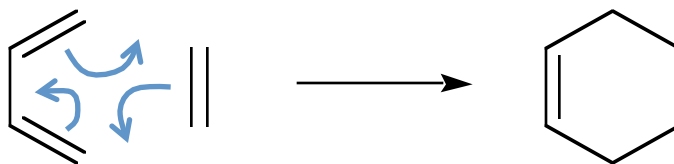
This process changes the symmetry of the HOMO

Therefore a reaction can be made “symmetry allowed” by photolysis

Ethylene, for example, will react under photolysis but not thermally

Diels-Alder Reaction

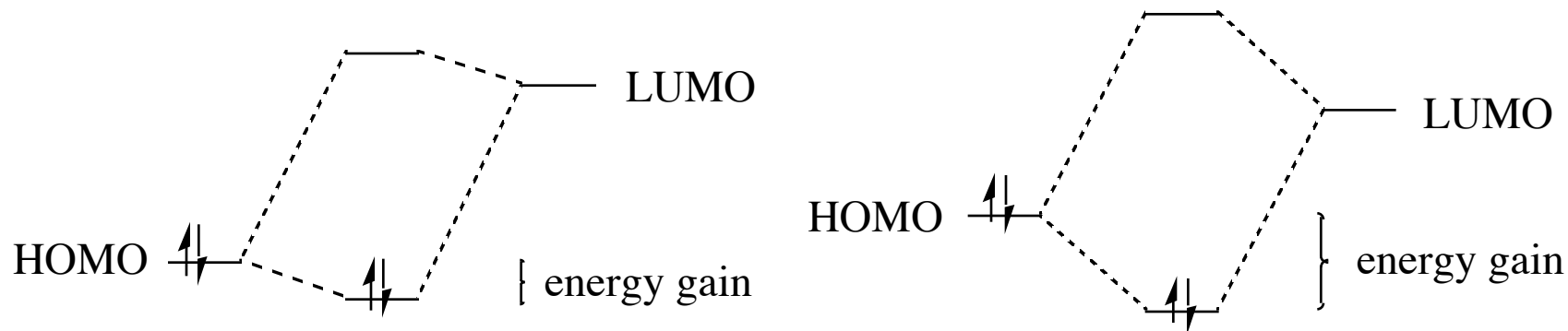
The reaction between butadiene and ethylene is called a Diels-Alder reaction



Obtain cyclohexene functional units after a Diels-Alder reaction

Diels-Alder Reaction is favored by a lower HOMO-LUMO energy gap

In addition to requiring the correct symmetry, the energy gap between the HOMO and LUMO orbitals determines the amount of energy gain in a reaction



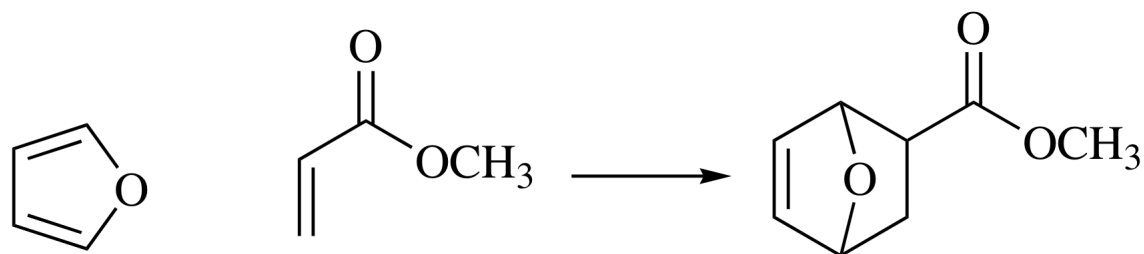
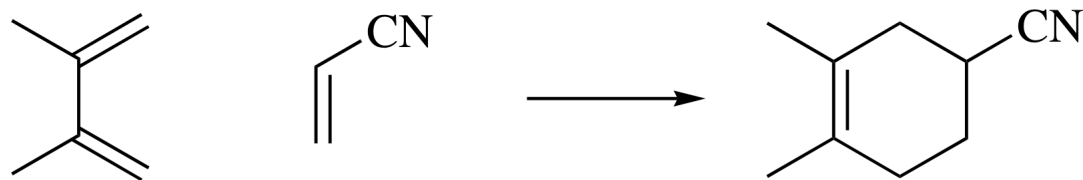
As the energy gap between the HOMO and LUMO becomes smaller
the reaction rate is favored

Adjusting Energy Levels

Electron withdrawing groups lower the energy of a molecular orbital,
Electron donating groups raise the energy of a molecular orbital

Usually the butadiene reacts through the HOMO and ethylene reacts through the LUMO,
therefore a Diels-Alder reaction is favored with electron withdrawing groups on ethylene and
electron donating groups on butadiene

Reaction Products



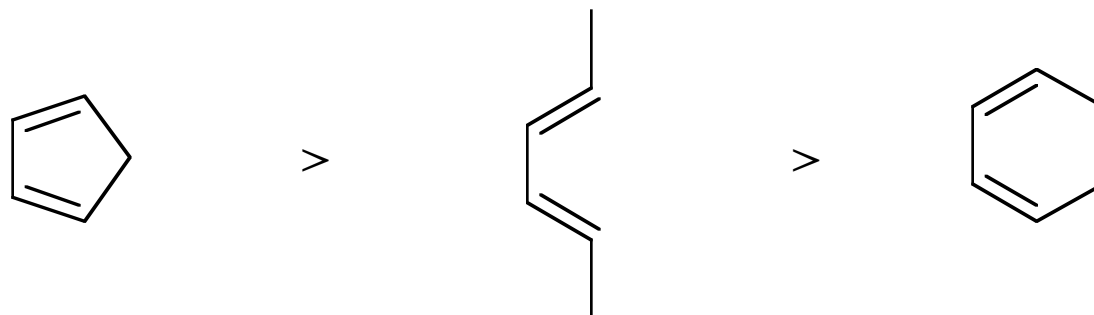
Always try to find the cyclohexene unit in the product,
this will indicate what was the initial butadiene and ethylene parts

Stereochemistry of Addition

Butadiene must be in a s-cis conformation,
not s-trans

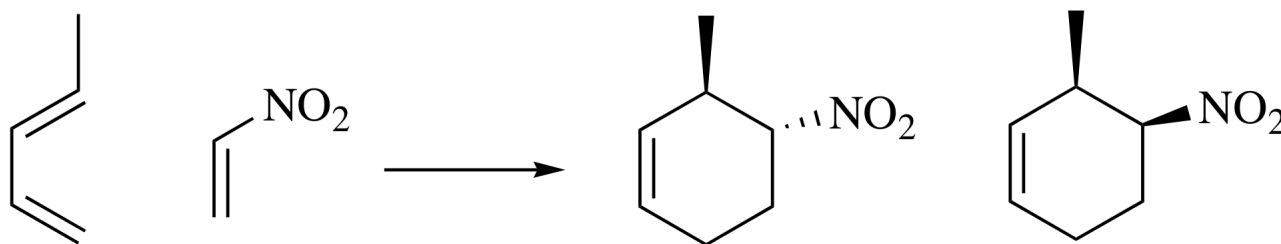


Therefore the rate of the reaction will be affected by diene substituents



Orientation Between the Diene and Alkene

The two components can react to form two different stereoproducts

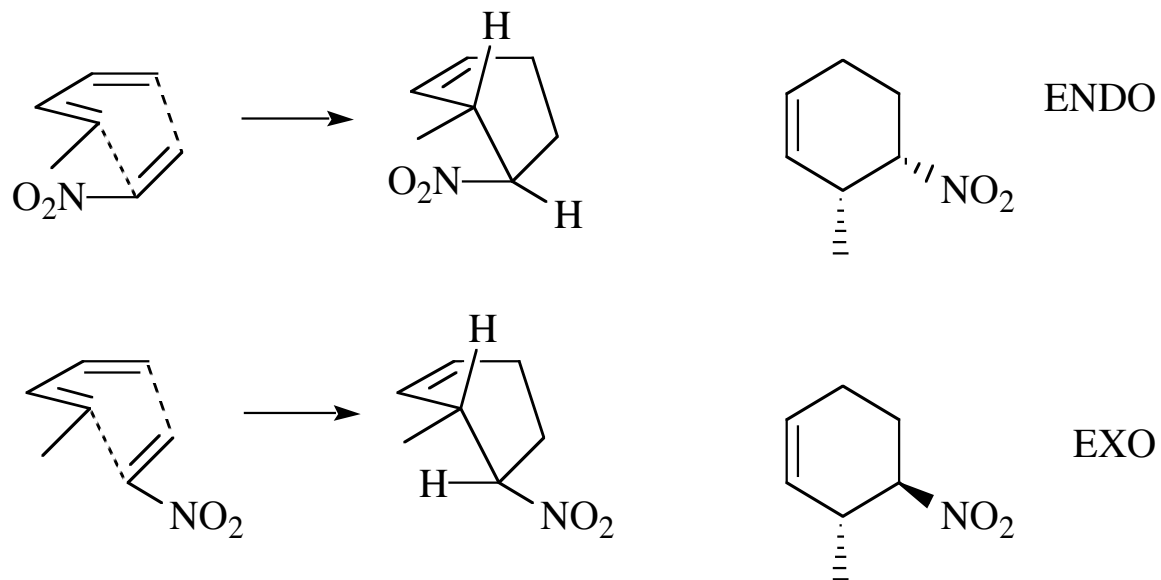


These two products are diastereomers

Which is favored?

Endo Rule

The Diels-Alder reaction favors the endo product

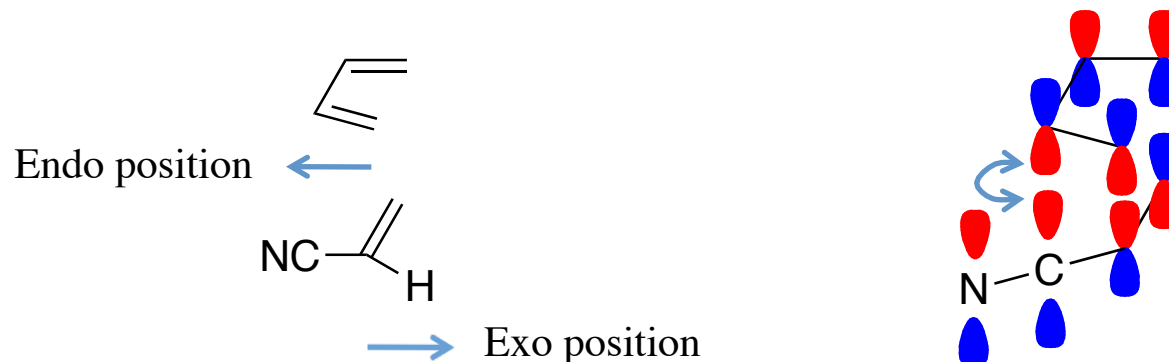


Endo means “inside” the pocket formed by the Diels-Alder reaction,
exo is “outside” of this pocket

Energetic Basis of Endo Rule

This stereochemical preference is due to ENERGY

In the endo position the orbitals on the electron withdrawing group can favorably interact with the orbitals of the diene

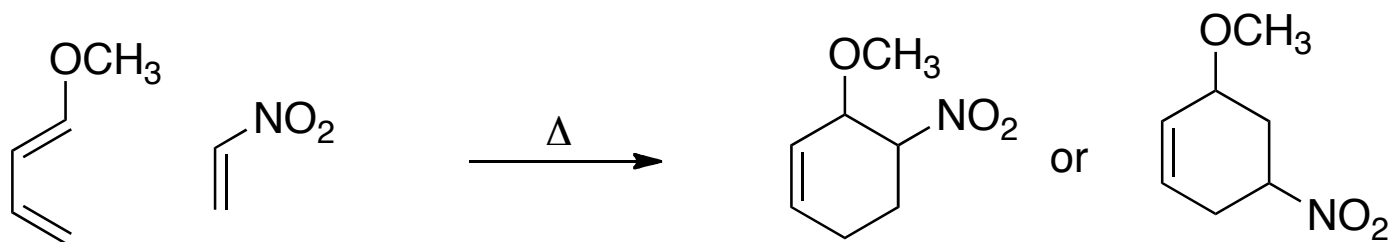


In endo position, orbitals on alkene substituents can interact with p orbitals of butadiene

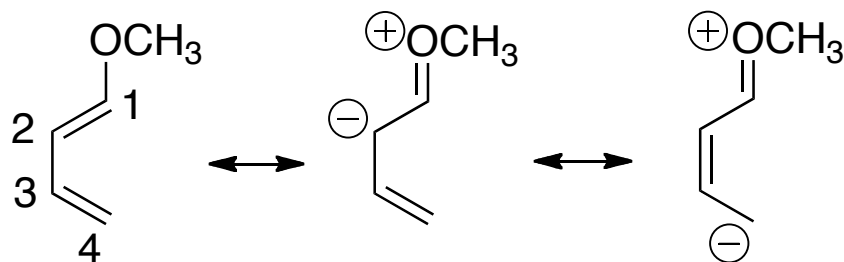
In exo orientation this interaction is not present

Regiochemistry of Unsymmetrically Substituted Diels-Alder Products

When a monosubstituted butadiene and a monosubstituted alkene react, different regioproducts can be obtained

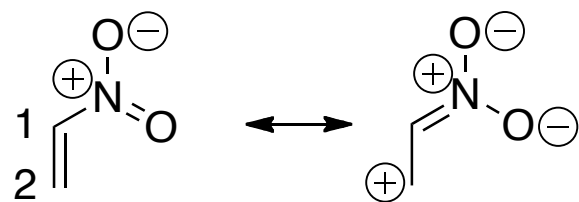


Can predict favored product by understanding location of charge in molecules



Consider resonance forms

Negative charge is located on C2 and C4

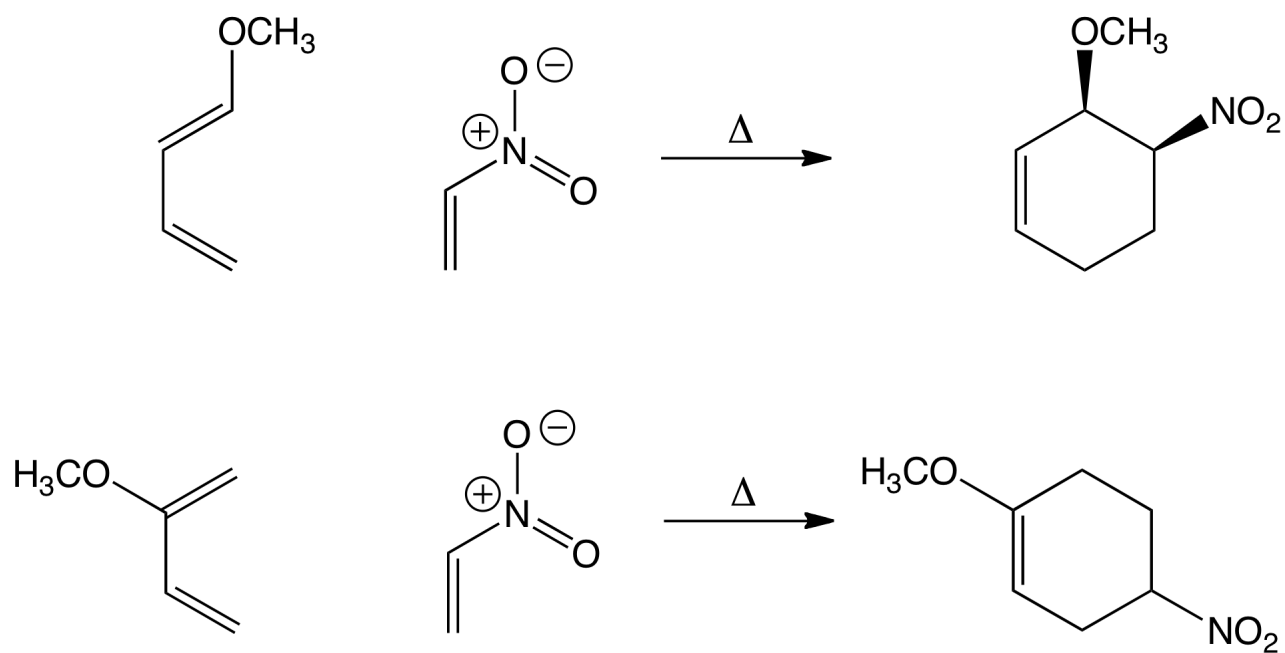


Consider resonance forms

Positive charge located on C2

The negative charge will react preferentially with the positive charge to obtain one regioproduct

Using this analysis we can predict regioproducts



A Diels-Alder reaction can therefore control both regio- and stereochemistry

Ultraviolet-Visible Spectroscopy (UV-VIS)

Another analytical tool to determine organic structures is UV-VIS spectroscopy

Similar to IR, this is another spectroscopic technique,
therefore a sample is irradiated with light of a particular wavelength

If the compound absorbs the light, the detector will record the intensity of absorbance

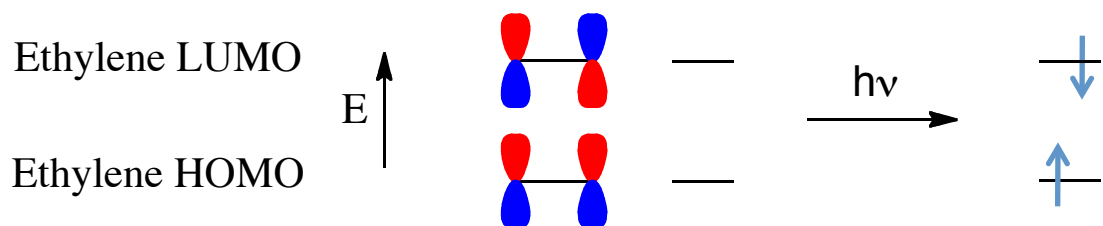
In an UV-VIS spectrum the light used is between ~200 nm to ~700 nm
(UV range is ~200 nm to ~370 nm, while visible light is ~370 nm to 700 nm)

Remember that in IR the wavelength of light used was 2.5 – 25 μm
(between one to two orders of magnitude larger than UV light)

UV light is thus much higher in energy than IR light

Instead of causing molecular vibrations,
UV-VIS light causes electronic excitations

An electron is excited from the HOMO to the LUMO



If the correct amount of energy is applied (i.e. the correct wavelength of light),
the excitation of one electron from the HOMO to the LUMO will occur

The amount of energy required is thus the energy gap between the HOMO and LUMO

As the HOMO-LUMO gap changes, the wavelength required for excitation changes
(remember that a lower wavelength is higher in energy)

The HOMO-LUMO energy gap is affected by the amount of conjugation

A conjugated diene system has a lower HOMO-LUMO energy gap
than an isolated double bond

Therefore a more conjugated system has a higher wavelength of absorbance
(higher wavelength is lower in energy, therefore smaller energy gap)

Information Obtained from a UV-VIS

The major piece of information is the point of maximum absorbance
(called λ_{max})

In addition an absorbance is characterized by how strongly the molecule absorbs

Beer's law: $A = \epsilon \cdot c \cdot l$

c = concentration of sample

l = path length of sample

ϵ = molar absorptivity (extinction coefficient)

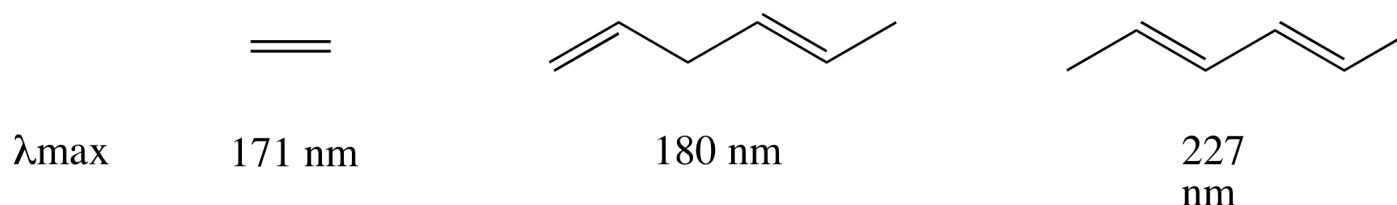
*characteristic of sample

If the molecule absorbs more strongly, it has a higher ϵ

$$\lambda_{\text{max}}$$

As seen earlier, the position of the λ_{max} indicates the HOMO-LUMO energy gap

A more conjugated system has a lower HOMO-LUMO energy gap,
therefore the λ_{max} will be of a longer wavelength



Only conjugated alkenes will cause a shift in λ_{max}

As the conjugation increases, the shift will increase

Compounds that are colored to our eye therefore must be very conjugated
(the lowest wavelength human eyes detect is ~ 370 nm)