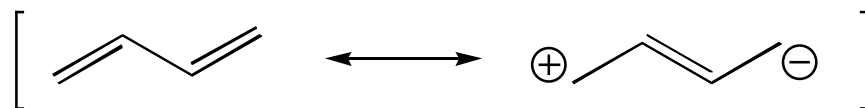


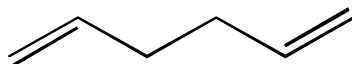
Conjugated Systems

Double bonds in conjugation behave differently than isolated double bonds

With conjugated double bonds resonance structures can be drawn



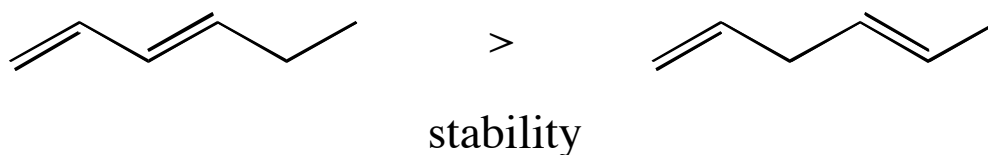
With isolated double bonds cannot draw resonance structures including both alkenes



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

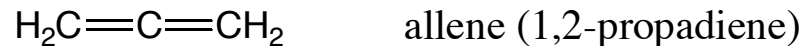


remember that internal double bonds are more stable than terminal double bonds

-in addition we can classify dienes, and other multiple alkene structures, by whether the alkenes are in conjugation

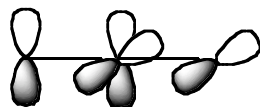
Another type of multiple alkene is an Allene

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



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

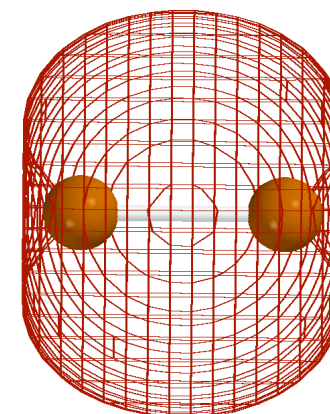
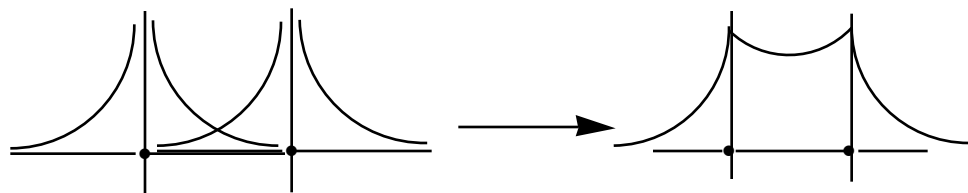
We can understand, and predict, many properties of conjugated systems by considering the molecular orbital picture

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

This lead to either sigma, σ , or pi, π , bonds depending upon the symmetry of the bond formed upon addition of the atomic orbitals

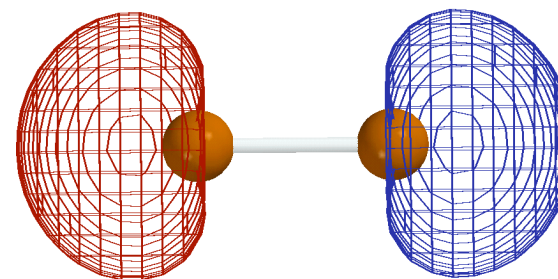
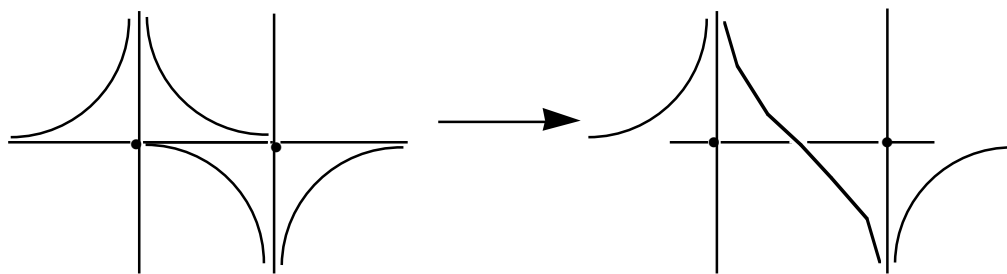
σ BONDS

formed by combining two atomic orbitals (here we have 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

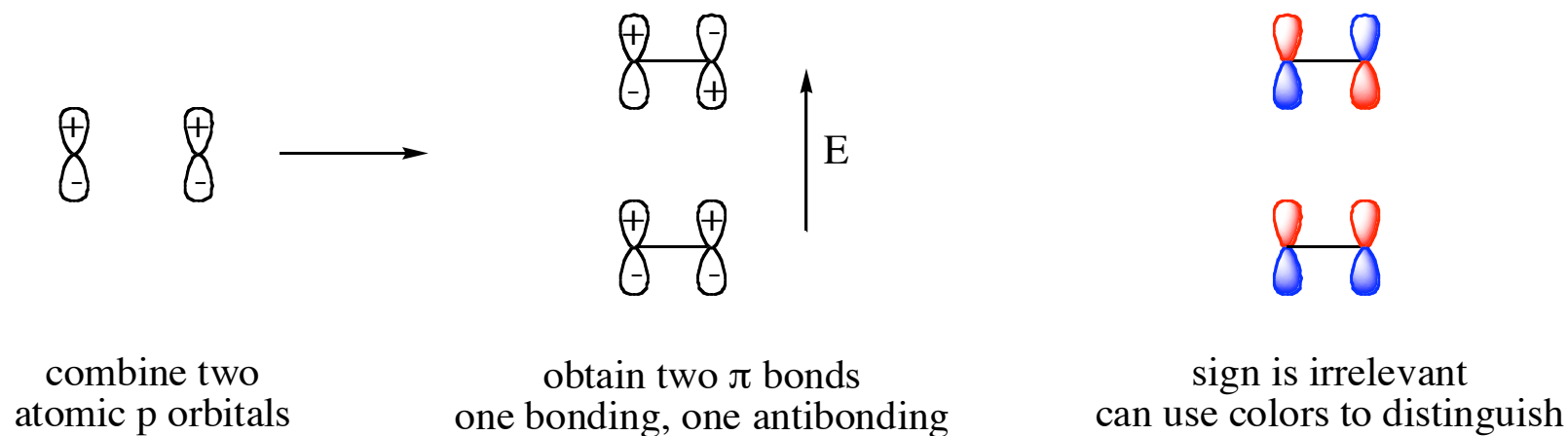
Rules for combining orbitals:

- 1) ALWAYS get the same number of molecular orbitals as 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)

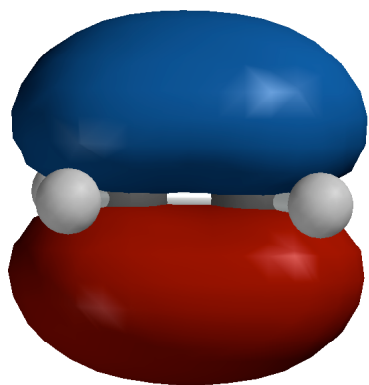
First consider an isolated alkene

Simplest is ethylene

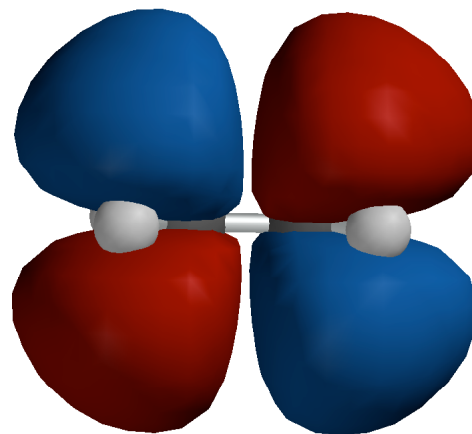
We can separate the sigma and pi framework
With alkenes we are interested in the π framework
since this is what controls the chemistry



if we look at computational obtained molecular orbitals we see same pattern



π bond



π^* bond

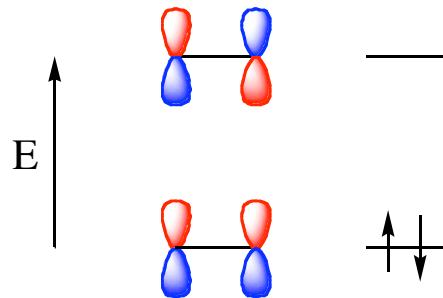
Can draw electronic configuration for the π system

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 fit two electrons



Can follow same procedure for conjugated systems

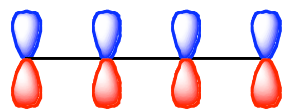
With butadiene there are 4 p orbitals in conjugation



realize if we add 4 p orbitals then we will obtain 4 molecular orbitals

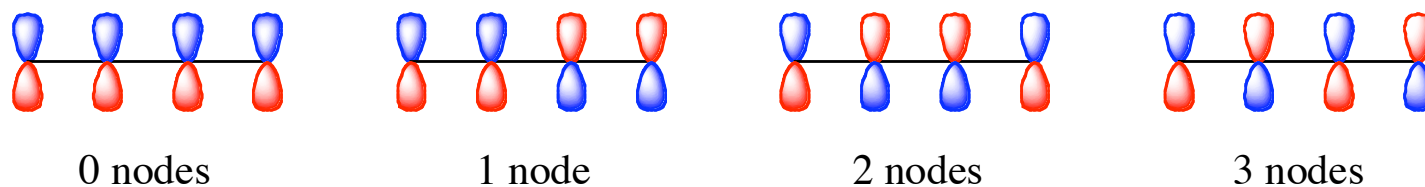
the difference between the 4 orbitals will be sign of the adjacent atomic orbitals

one molecular orbital



three bonding interactions
between adjacent atoms

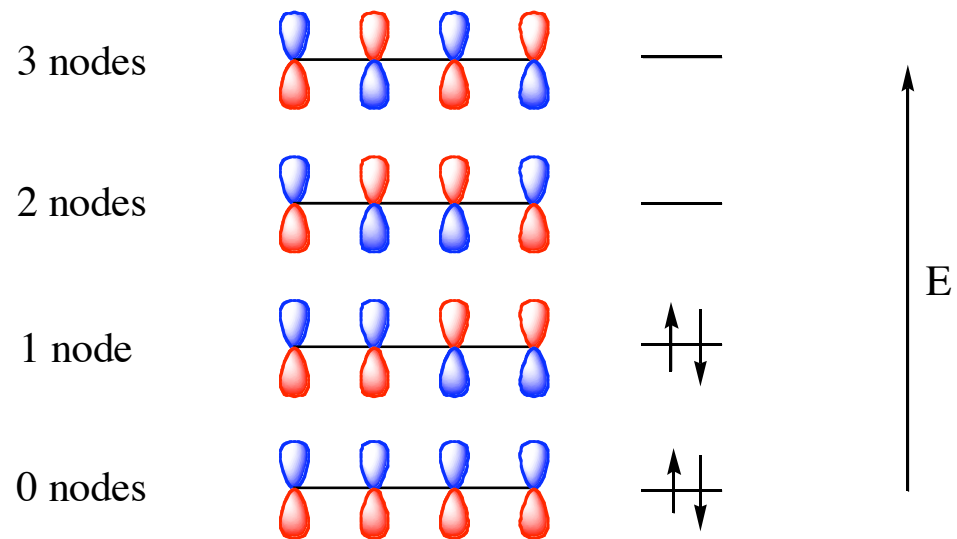
We can obtain the 4 molecular orbitals



we can also predict the relative energy levels of these molecular orbitals
by the number of nodes

as the number of nodes increase the energy increases

Electronic Configuration of Butadiene

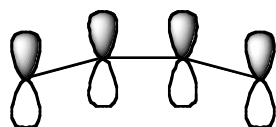
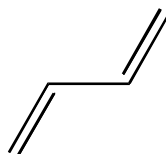
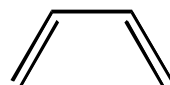


butadiene has 4 π electrons

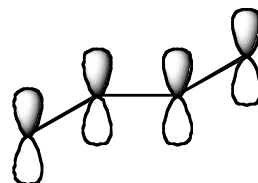
In order to allow electron delocalization the p orbitals must align

This constrains the geometry of conjugated systems

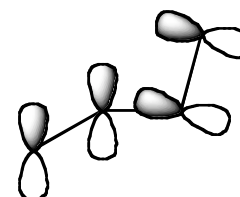
The p orbitals must be in the same direction - thus the carbon framework is planar



s-cis



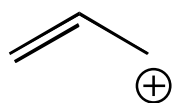
s-trans



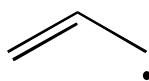
poor
overlap

Molecular Orbital Picture for Allylic Systems

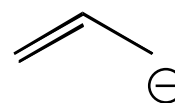
Allylic refers to systems with 3 conjugated p orbitals



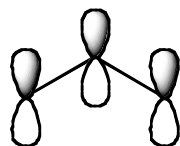
allylic cation



allylic radical

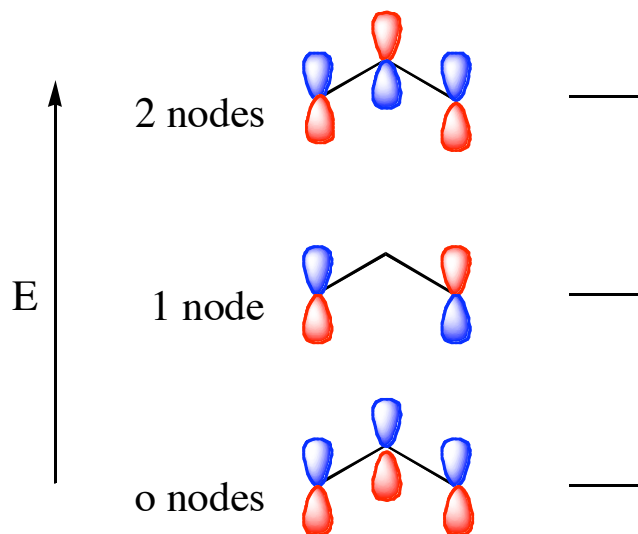


allylic anion



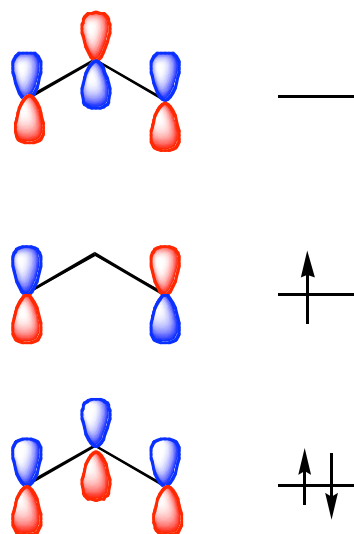
all allylic systems
have 3 p orbitals
in conjugation

with 3 conjugated p orbitals must obtain 3 molecular orbitals



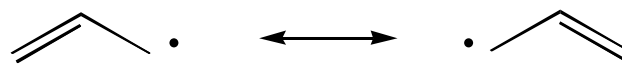
depending upon # of π electrons the electronic configuration can be determined
(allylic cation has 2, allylic radical 3, allylic anion 4)

Electronic Configuration for Allyl Radical



implies that radical is on the terminal carbons

(size of coefficients correlates with probability of electron density)

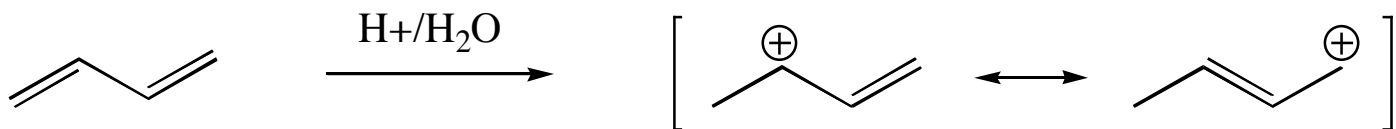


similar to resonance description

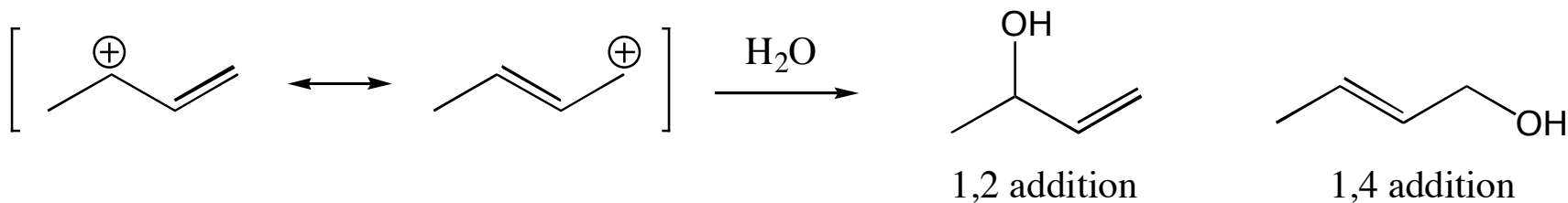
Addition to Conjugated Dienes

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

With conjugated dienes this reaction will create an allylic carbocation



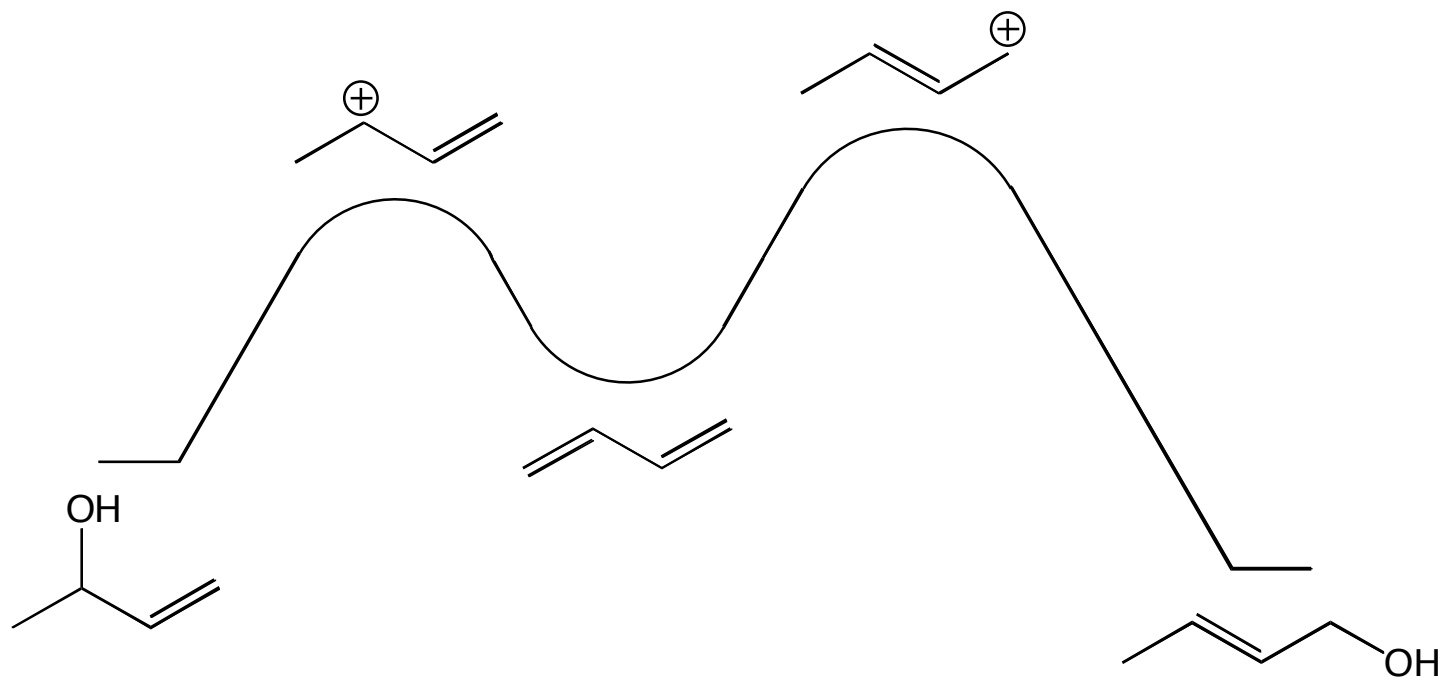
the nucleophile can then react with either of these resonance forms



Kinetic vs. Thermodynamic Control

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

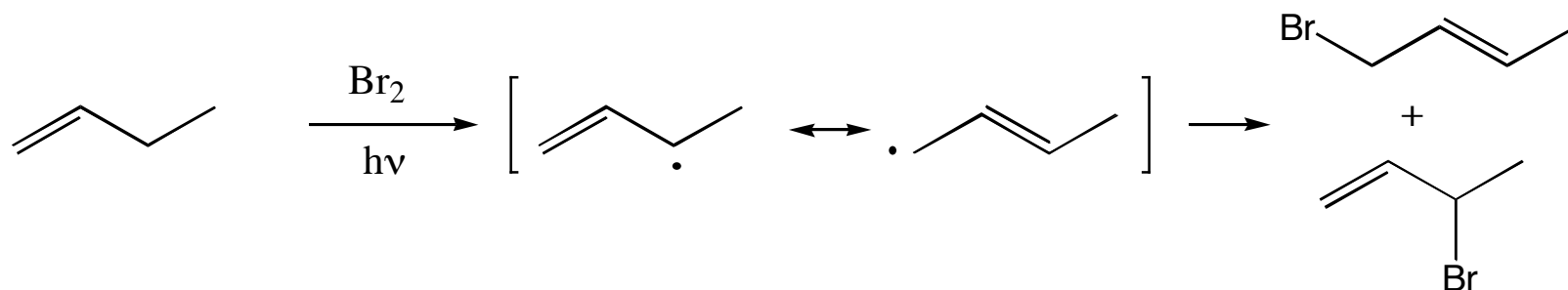
secondary carbocation is more stable than primary



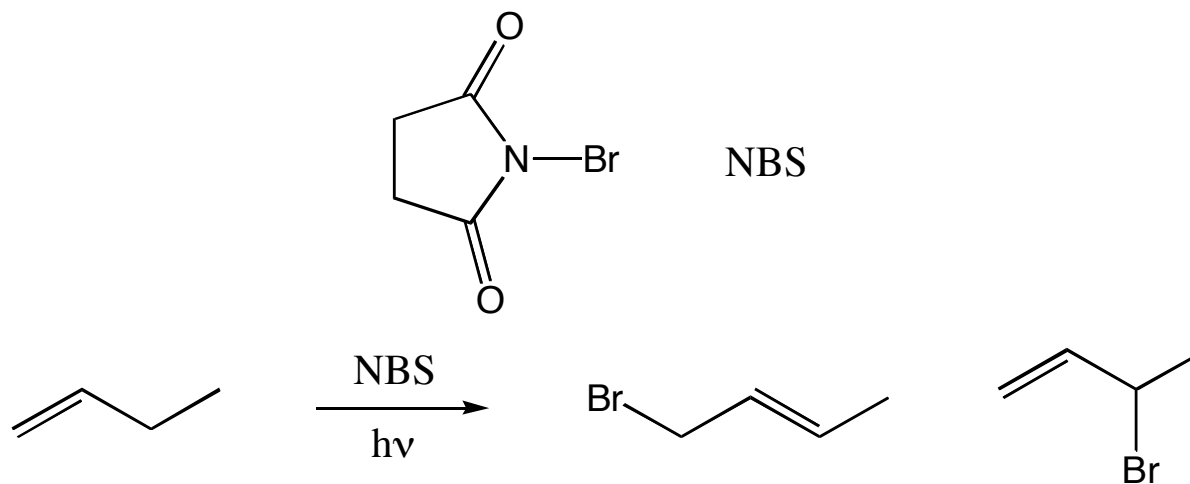
internal double bond is more stable than terminal double bond

Formation of Allylic Radical

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



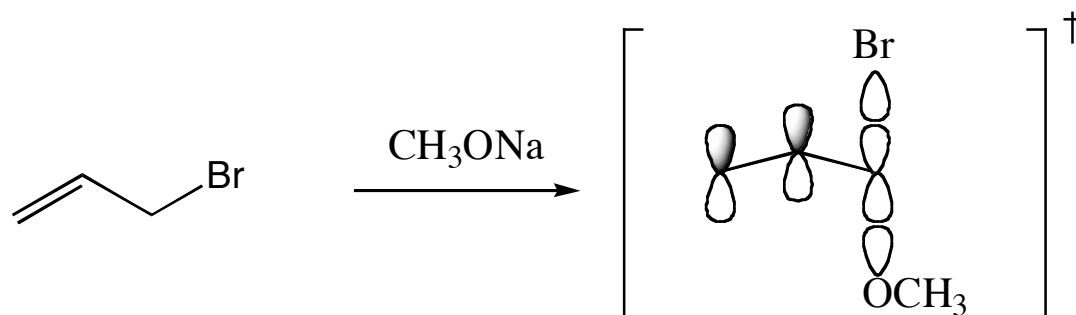
another way to generate the bromine radical is to use NBS (N-bromosuccinimide)



S_N2 Reactions of Allylic Halides

Allylic halides react faster with a given nucleophile

The p 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

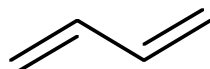
Interactions Between Orbitals on Different Reactants

electrons are located in Molecular Orbitals (MO's)

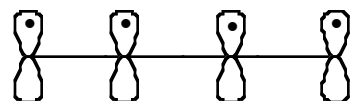
when two molecules react a molecular orbital on one interacts with a molecular orbital on the second which causes an energy gain
(if reaction is favorable)

with conjugated π systems we can consider only the π framework

Butadiene



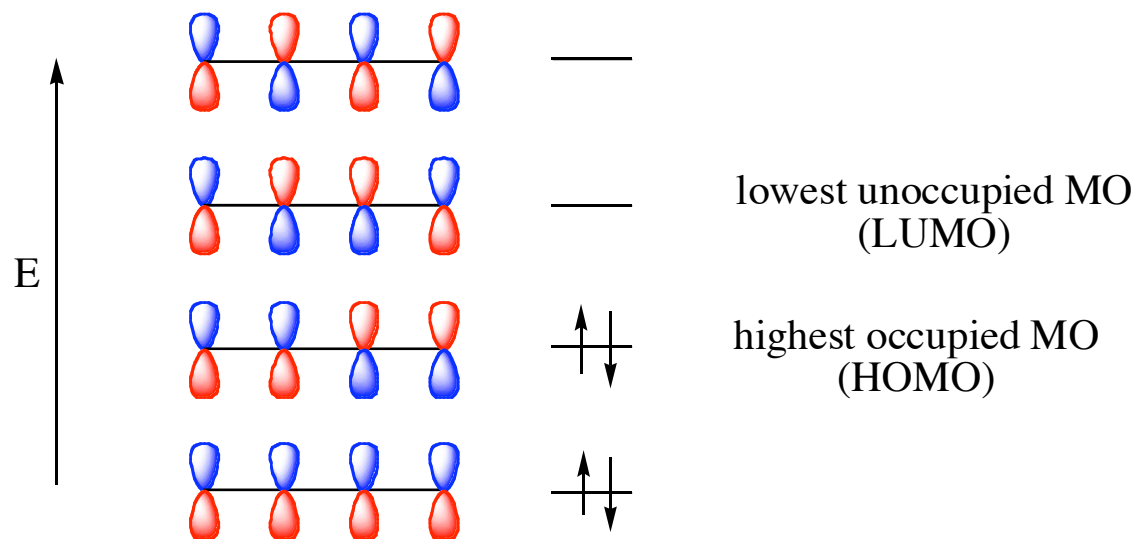
consists of four interacting p orbitals which form the π framework



4 π electrons
in 4 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

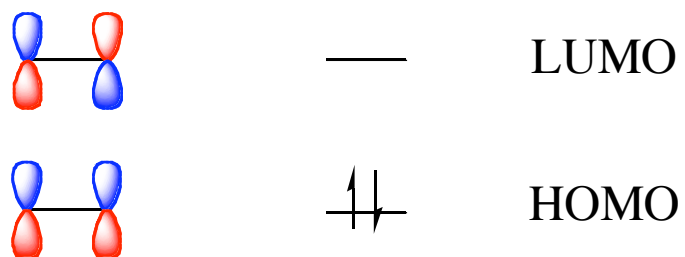
Molecular Orbitals for Butadiene



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

Ethylene

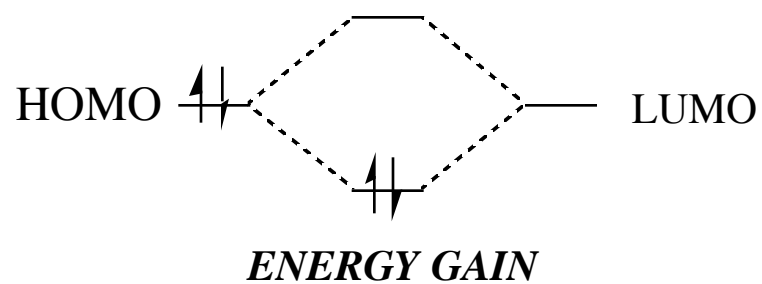
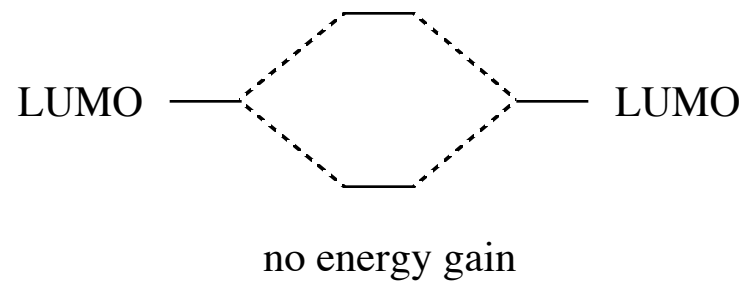
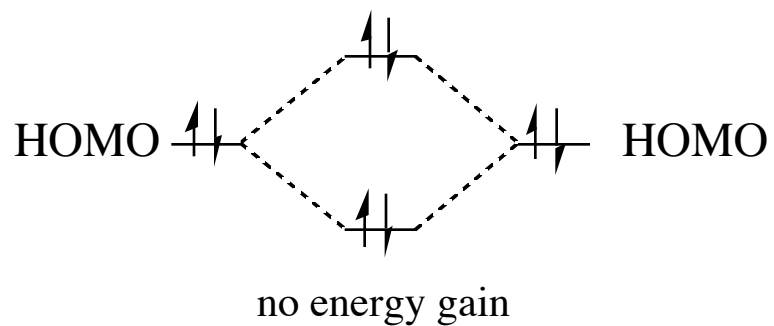
likewise we can obtain orbital symmetry for ethylene



2 electrons in 2 MO's derived from 2 p orbitals

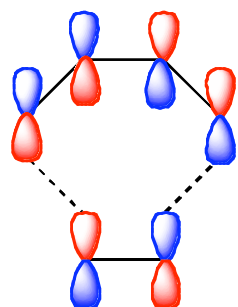
Energy Gain in a Reaction

remember these molecular orbitals combine to form new orbitals in a reaction



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

if the symmetry is wrong then we do not have interacting orbitals



butadiene HOMO

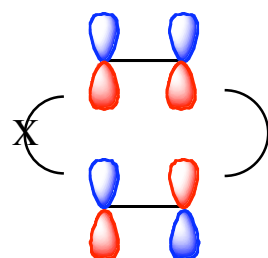
ethylene LUMO

therefore butadiene reacting with ethylene is symmetry allowed

*consider symmetry where bonds are being formed

Ethylene, however, cannot react with itself

The orbitals cannot align themselves with proper symmetry



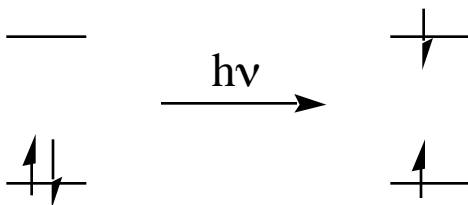
ethylene HOMO

ethylene LUMO

therefore this reaction is symmetry forbidden

Excitation

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

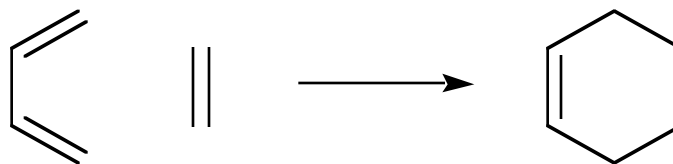


this process changes the symmetry of the HOMO

therefore a reaction can be made "symmetry allowed" by photolysis

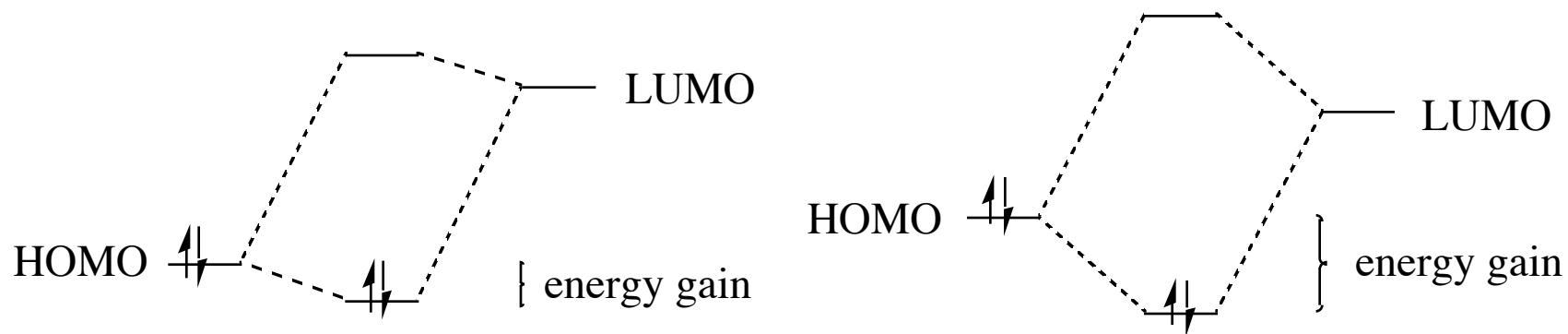
Diels - Alder Reaction

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



Reaction is favored by a lower HOMO-LUMO Gap

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



as the energy gap between HOMO and LUMO becomes smaller
there is more interaction between the orbitals

Adjusting energy levels

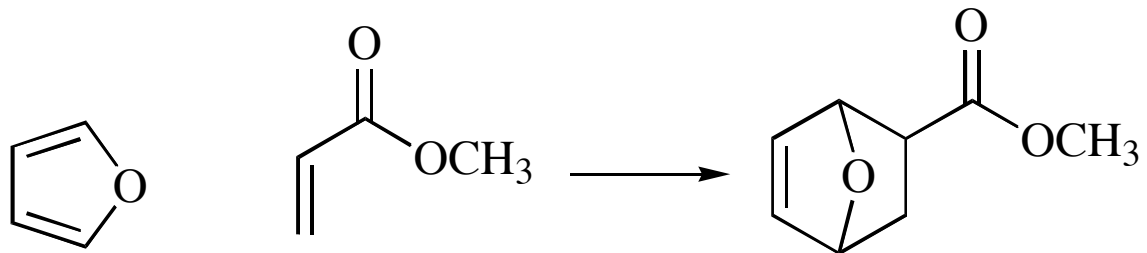
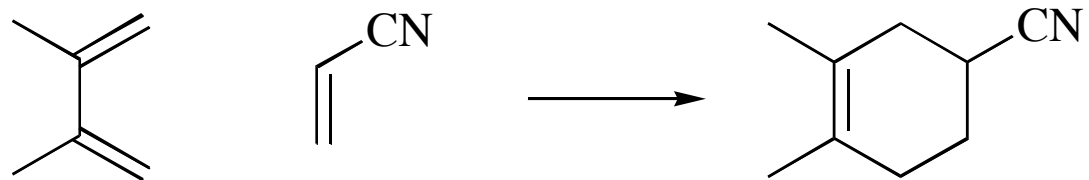
electron withdrawing groups lower the energy of a molecular orbital

electron donating groups raise the energy of a molecular orbital

therefore a Diels - Alder reaction is favored by

electron withdrawing groups on ethylene and electron donating groups on butadiene

Reaction Products

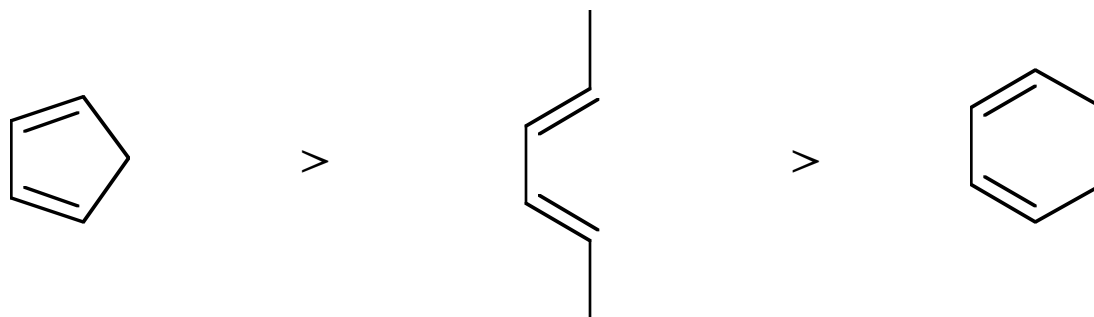


Stereochemistry of Addition

butadiene must be s-cis NOT s-trans

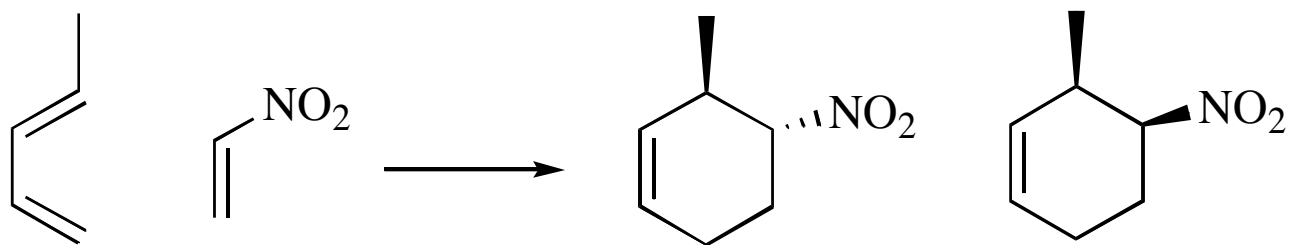


therefore the rate of reaction will be affected by diene orientation



Orientation Between the Diene and Alkene

the two components can react to form two different stereoproducts

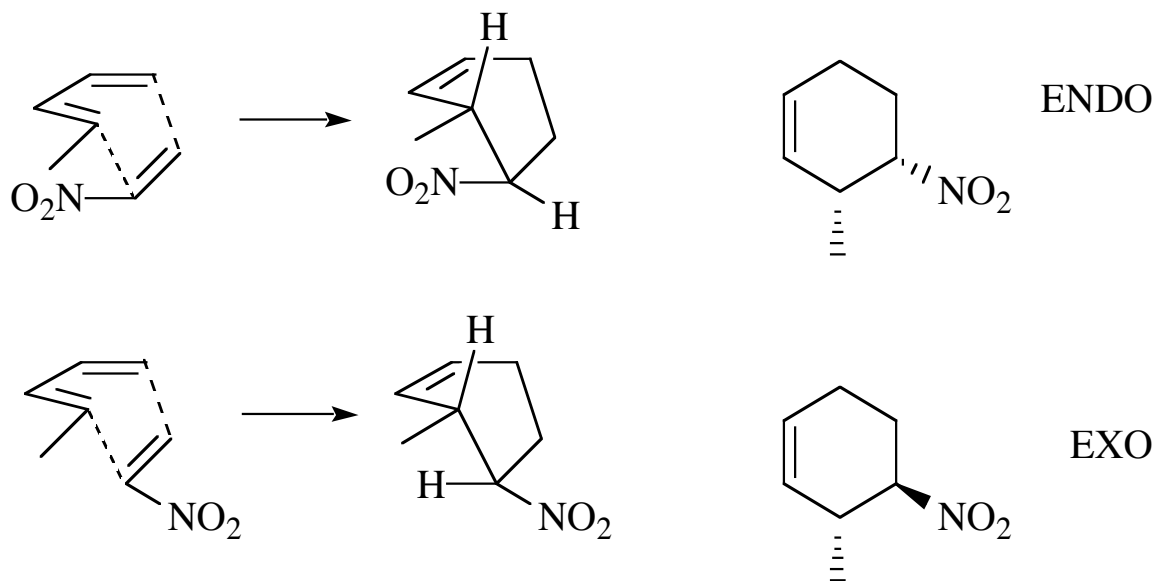


these two products are diastereomers

which product 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

Again this stereochemical preference is due to ENERGY

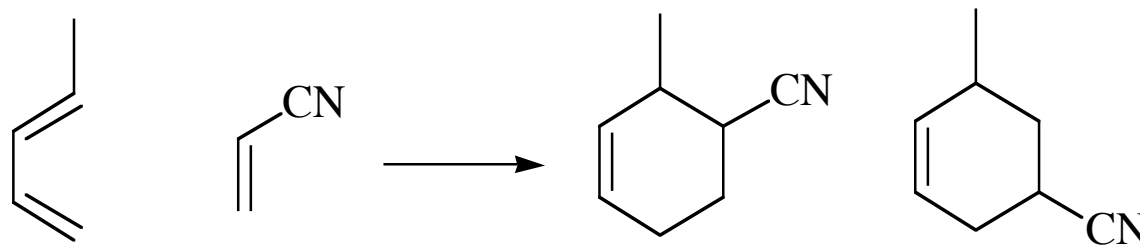
in the endo position the orbitals on the electron withdrawing group
can favorably interact with the orbitals of the diene



in exo orientation this interaction is not present

Regiochemistry of Unsymmetrically Substituted Diels - Alder Products

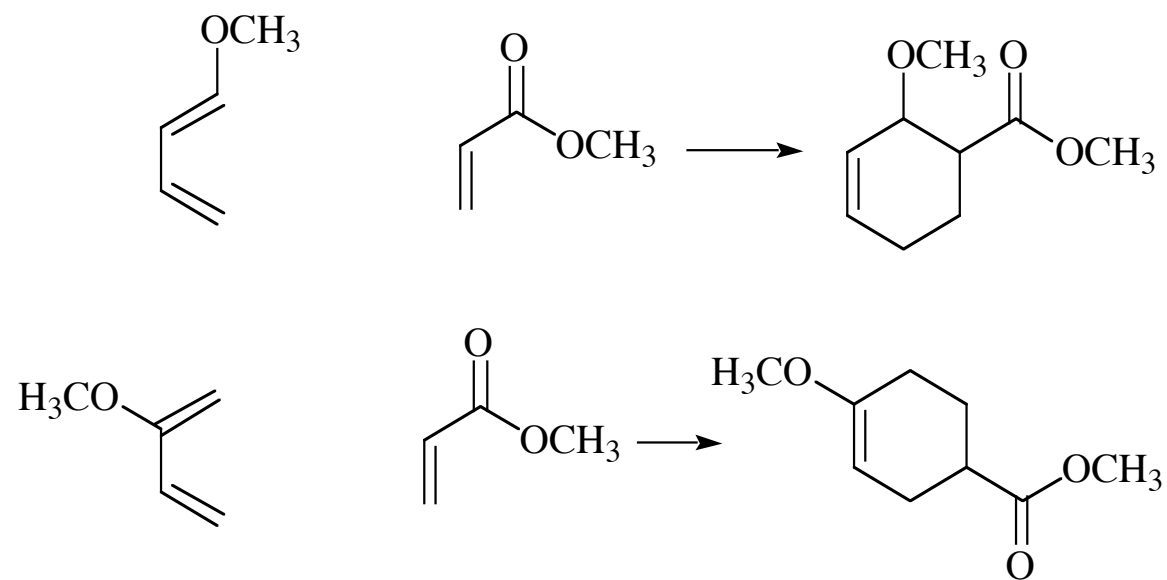
when a monosubstituted butadiene or a monosubstituted alkene react
different regioproducts can be obtained



can predict by understanding charge location in molecules



Using this analysis we can predict regioproducts



Ultraviolet-Visible Spectroscopy

(UV-Vis)

another analytical tool to determine organic structures is UV-Vis spectroscopy

like 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 amount of absorbance

in an UV-Vis spectrum the light used is between ~200 nm - 700 nm

UV range is ~200 nm to ~370 nm while visible light is ~370 nm to 700 nm

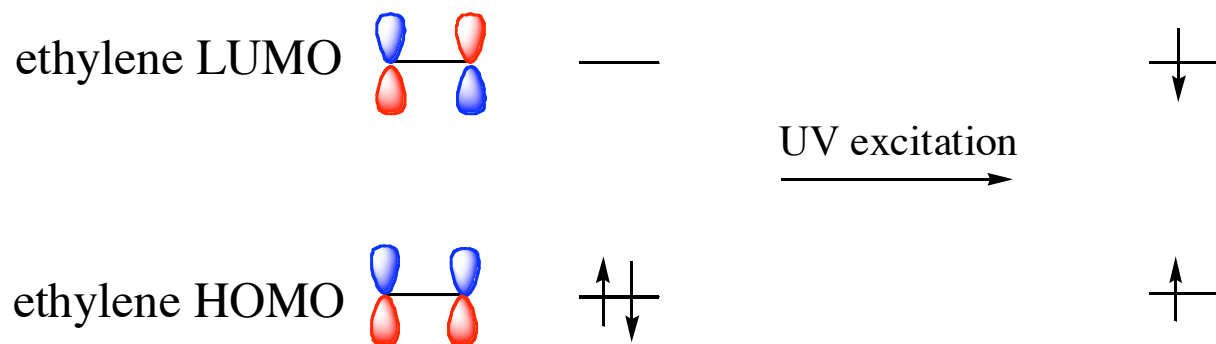
Remember that IR the wavelength of light used was 2.5 - 25 μm

(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 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 this energy gap changes the wavelength required for excitation changes
(remember a lower wavelength is a higher 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 conjugated system has a higher wavelength of absorbance
(higher wavelength is lower energy)

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: $A = \epsilon cl$

c = concentration of sample

l = path length of sample

ϵ = molar absorptivity (extinction coefficient)

*characteristic of the sample

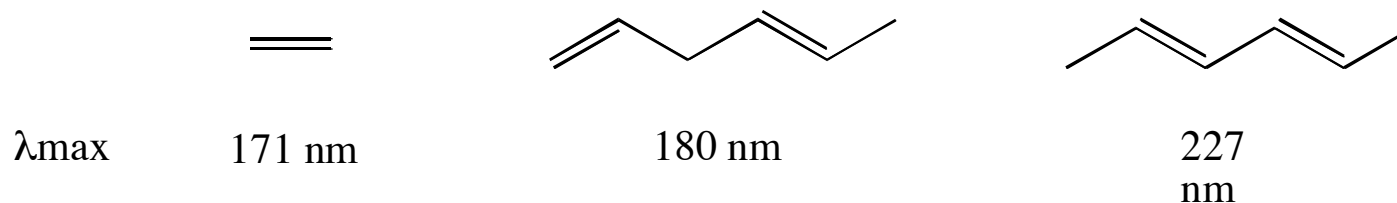
if the molecule absorbs strongly it has a higher ϵ

λ_{\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 gap

therefore the λ_{\max} will be of a longer wavelength (less energy)



only conjugated alkenes will cause a shift in λ_{\max}

as the conjugation increases the shift will increase