

Learning Guide for Chapter 17 - Dienes

- I. Isolated, conjugated, and cumulated dienes
- II. Reactions involving allylic cations or radicals
- III. Diels-Alder Reactions
- IV. Aromaticity

I. Isolated, Conjugated, and Cumulated Dienes

What is a diene? a compound with two C=C

What if there are more than 2? compounds with lots of C=C are basically like dienes

What are the three kinds of dienes you can have?

isolated, conjugated, cumulated

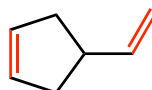
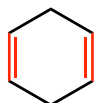
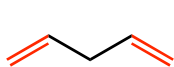
Isolated Dienes

What is an isolated diene? How do they behave?

a compound with 2 or more C=C that are separated by an sp^3 C

just like regular alkenes

Draw double bonds to make the following compounds into isolated dienes.

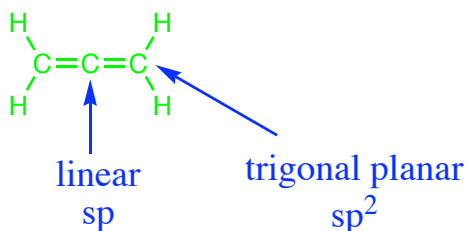


Cumulated Dienes

What is a cumulated diene?

a compound with two C=C's right next to each other (share a C)

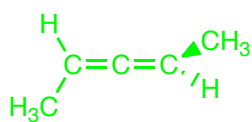
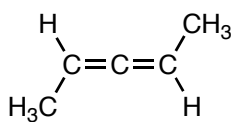
Draw the smallest cumulated diene possible. What is the geometry and hybridization of each C? What is it called?



What is the name of this compound? How else can it be used?

allene; it is used as a common name for other cumulated dienes

Make a model of the compound below. Then draw it in three dimensions. How are the substituents oriented to each other?



the pi bonds and substituents are at 90° to each other

Is this compound chiral? **yes! its mirror image is not the same**

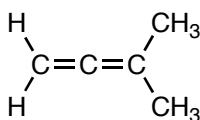
Is there a plane of symmetry? **no**

Which carbons are stereocenters? **both sp² C's**

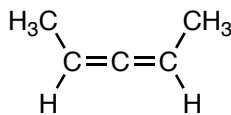
it's sort of like a stretched out tetrahedral carbon...

How many stereoisomers are possible? **2**

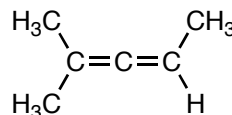
Which of the following allenes are chiral?



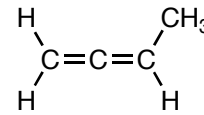
no



yes



no



no

How can you tell without making a model which ones will be chiral?

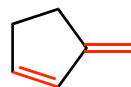
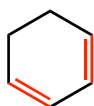
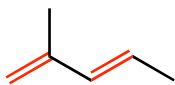
substituents have to be different from each other on both ends

if either end has two which are the same, there will be a plane of symmetry

Conjugated dienes

What is a conjugated diene? two or more C=C connected by C-C

Draw double bonds to make the following compounds into conjugated dienes.

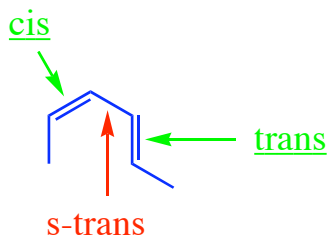
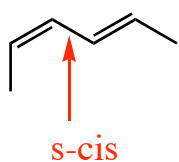


What orientation of the pi bonds gives the lowest energy?

pi bonds in the same plane have the lowest energy

If a conjugated diene is free to rotate, how many conformations will allow the pi bonds to be in the same plane? What are they called?

two possibilities:



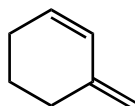
this molecule can change from s-trans to s-cis, but the cis and trans C=C can't change

What is the difference between an s-trans diene and a trans C=C?

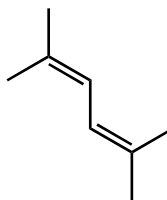
s-cis is a conformation - a position of the molecule as a bond rotates

a cis C=C is a stereoisomer - can't rotate

Why don't the conjugated dienes below have two different conformations?



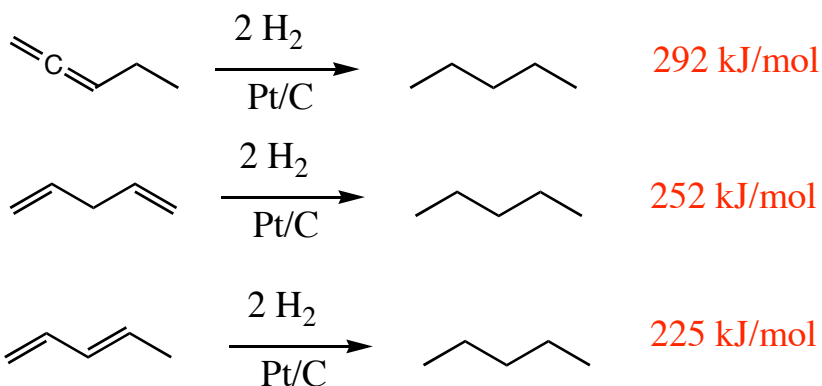
cyclic - can't rotate



too much steric hindrance

Energies of dienes

What do the heats of hydrogenation tell us about the relative energies of isolated, cumulated, and conjugated dienes?



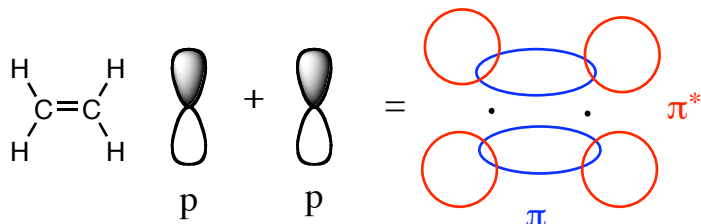
highest energy - cumulated

lowest energy - conjugated

II. Reactions involving allylic intermediates

Molecular orbitals of compounds with multiple p orbitals

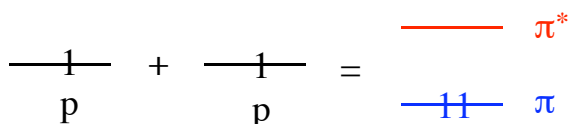
What molecular orbitals are formed when two p orbitals combine?



2 p orbitals = 2 pi orbitals
1 bonding, 1 antibonding

we usually only worry about the bonding orbital because it is the only one occupied

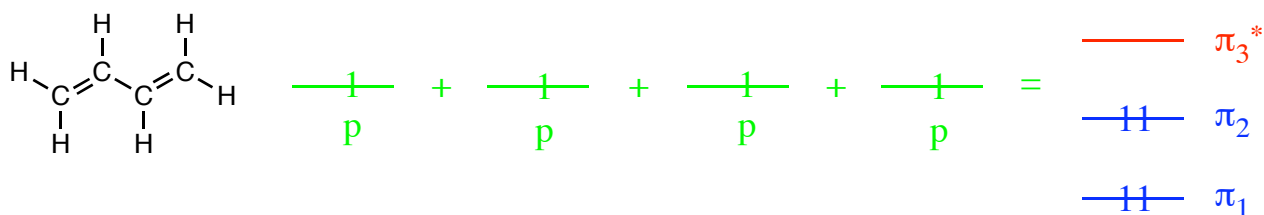
How can the energy of these orbitals be represented?



the bonding orbital is lower in energy than the p orbitals, while the antibonding orbital is higher

When more than 2 p orbitals are on neighboring carbon atoms, what happens?

all of the p orbitals combine

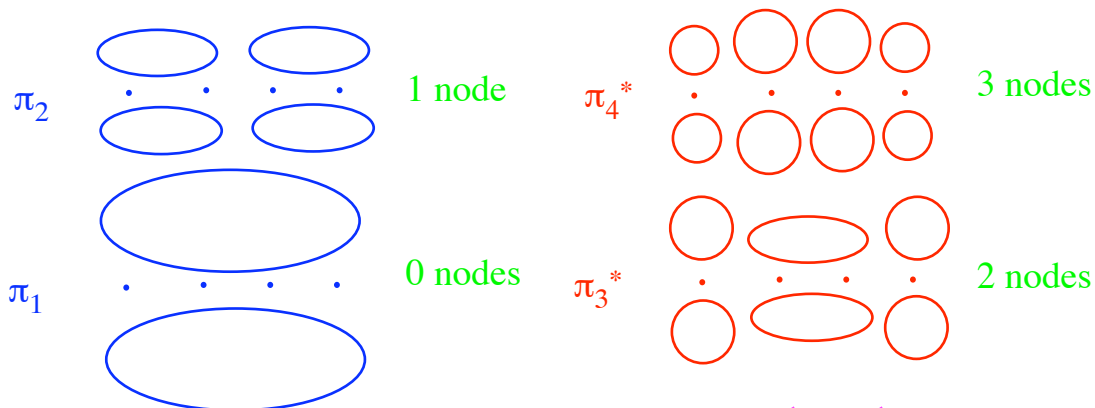


Why are conjugated dienes lower in energy than isolated ones?

the lowest pi bond is even more stable

2 bonding
2 antibonding

What do these orbitals look like?



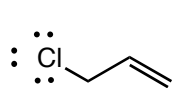
Is the bond in the middle a single or double bond?

midway between C-C 153 ppm; C2-C3 148 ppm; C=C 134 ppm

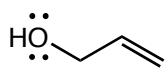


Allylic cations, radicals, and anions

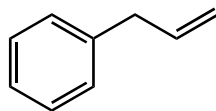
What is an allyl group? 3 C's in a row, last two with a C=C



allyl chloride

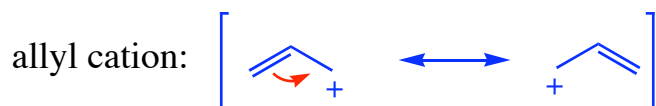


allyl alcohol



allyl benzene

What would the following look like?

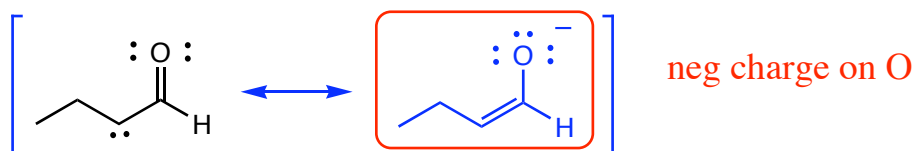
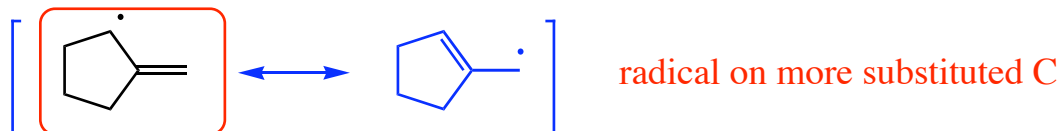
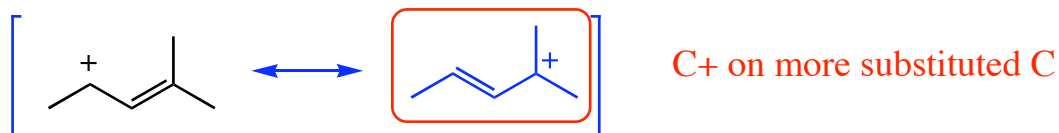
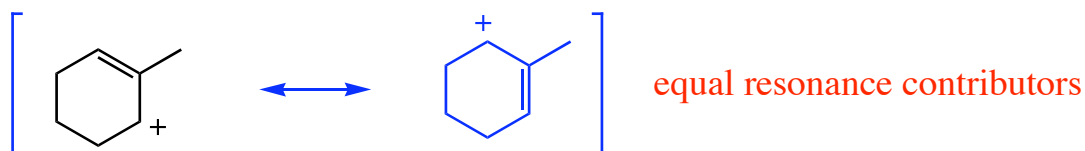


Why are each of these unusually stable? resonance

What are compounds called if they contain an allyl cation, but with substituents?

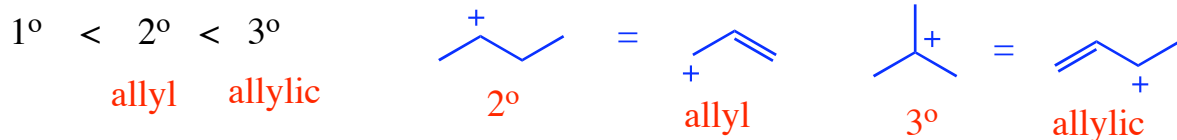
allylic cations

Give the other resonance structure for the following:

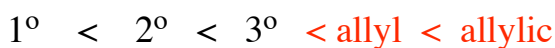


Which of the structures above have a greater resonance contributor?

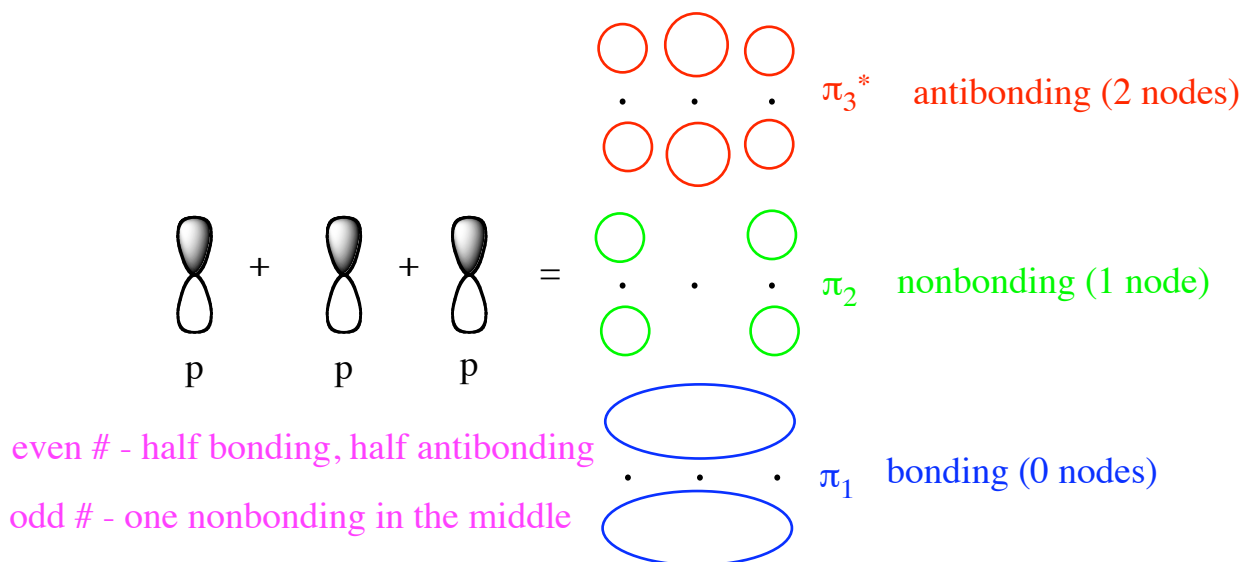
How does the stability of allyl and allylic cations compare to 1°, 2°, and 3° cations?



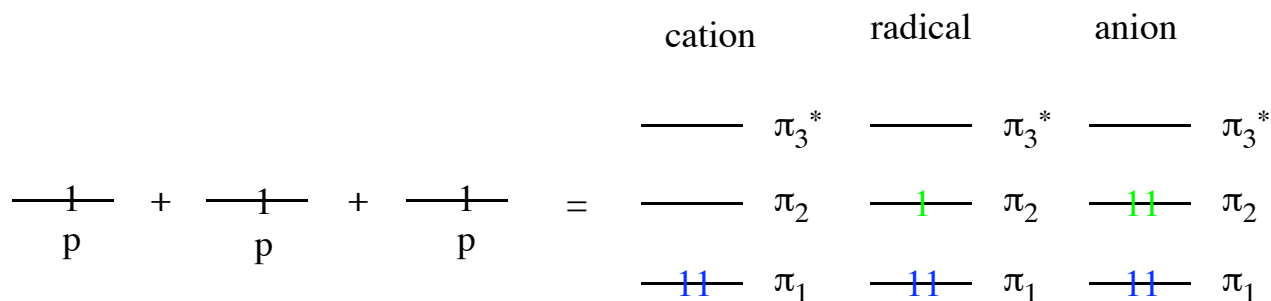
How does the stability of allyl and allylic radicals compare to 1°, 2°, and 3° radicals?



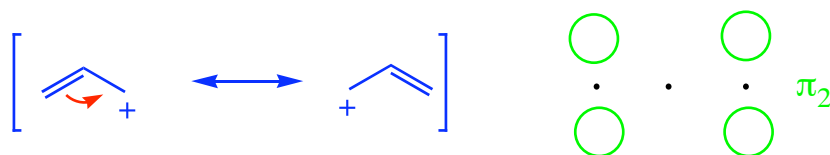
What do the molecular orbitals of an allylic system look like?



Which orbitals contain electrons in a allylic cation, radical, and anion?



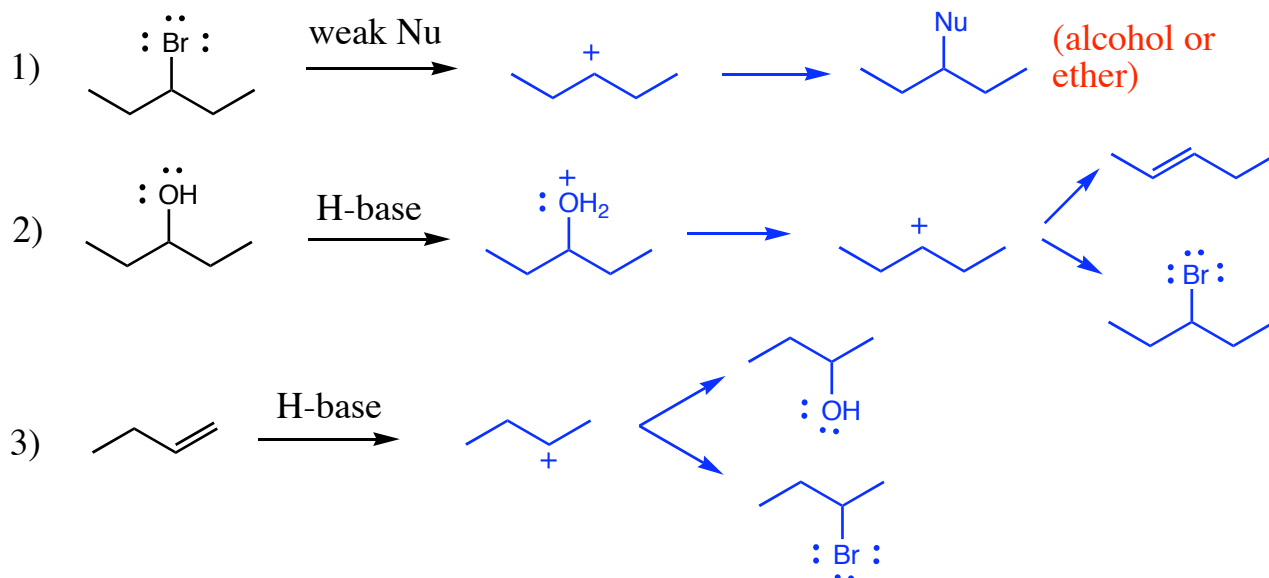
Do the molecular orbitals and the resonance structures agree on where the positive charge, radical, and negative charge are?



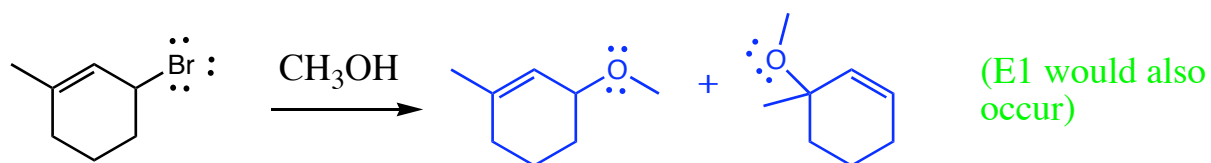
both show it is shared by the two outside C's

Reactions involving allylic cations as intermediates

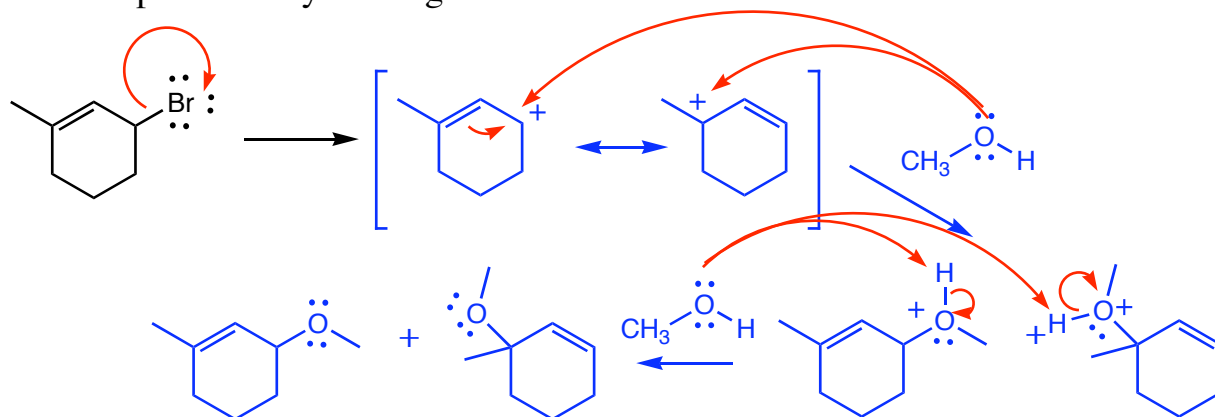
What reactions do we know that involve carbocation intermediates?



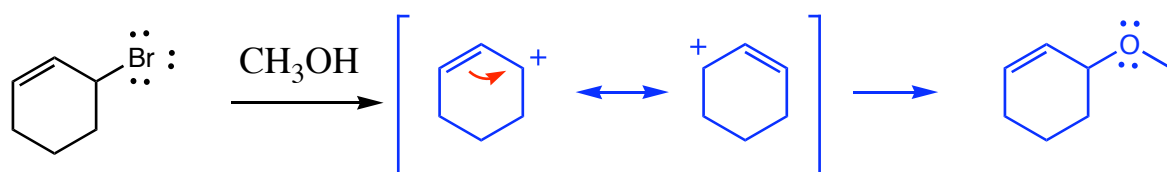
1) What products are formed when the following allylic alcohol undergoes an S_N1 reaction?



How can we explain this by looking at the mechanism?

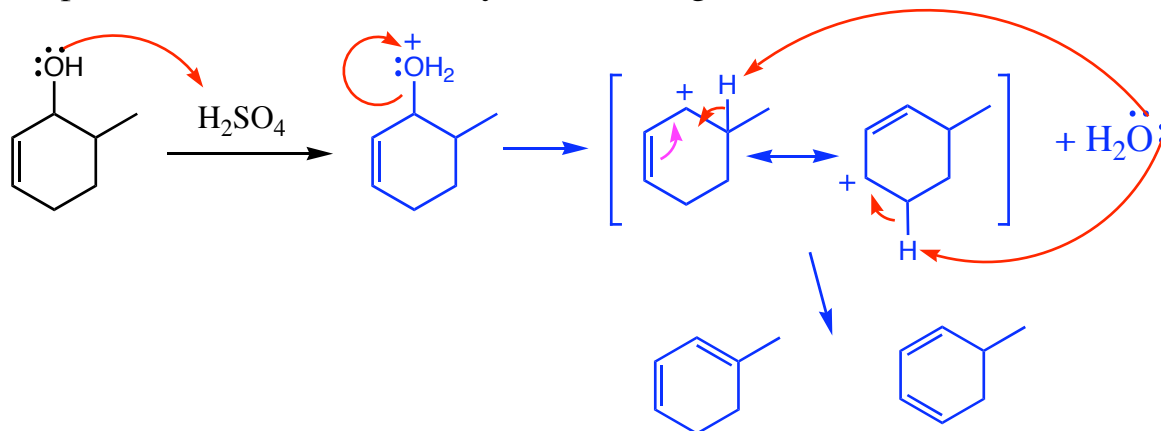


What products would be formed by the following reaction?



if the two resonance structures are symmetrical, only one product forms

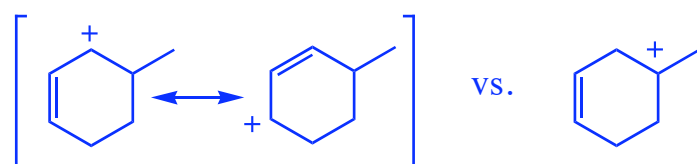
2) What two products would be formed by the following reaction?



How can you choose between two possible H's on either side of the C+?

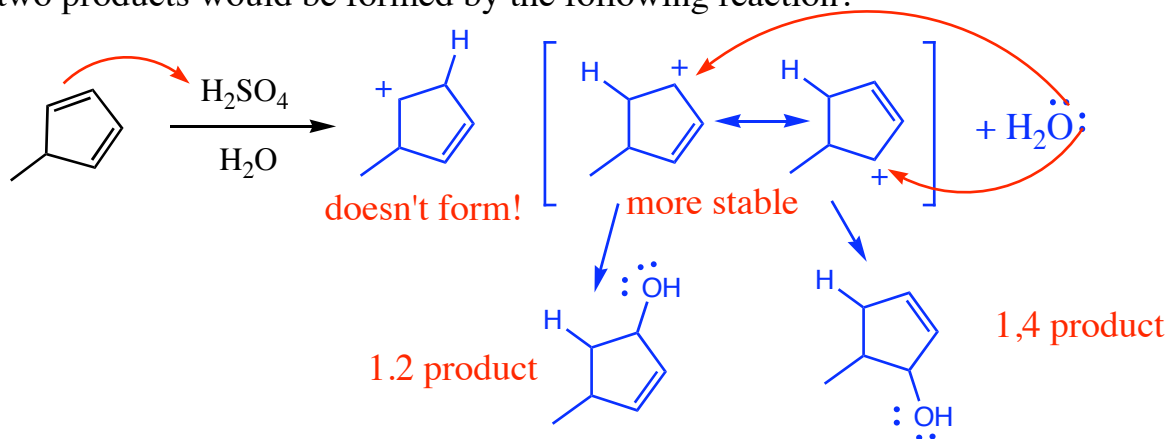
conjugated dienes are much more stable than cumulated dienes (especially in a ring)

Why doesn't a rearrangement occur?



1/2 + on two different C's is more stable than + charge on one C
resonance stabilized C+ don't rearrange

3) What two products would be formed by the following reaction?

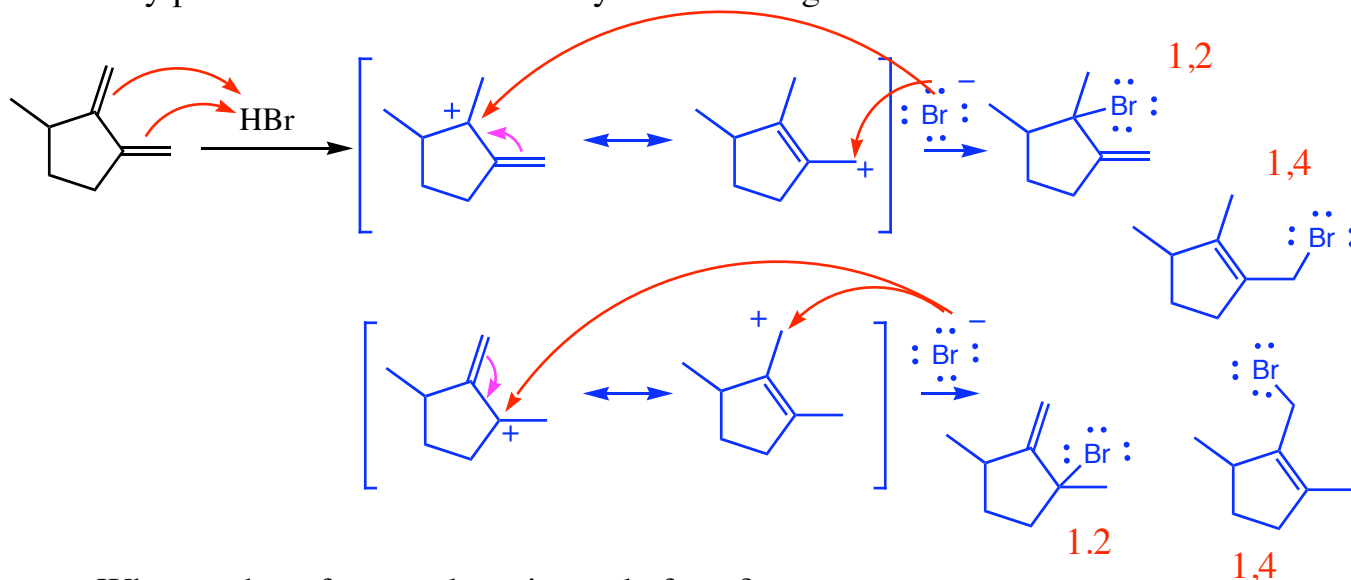


How are these two products labeled?

Why does the carbocation always form next to the other bond?

so that it can be resonance stabilized

How many products would be formed by the following reaction?



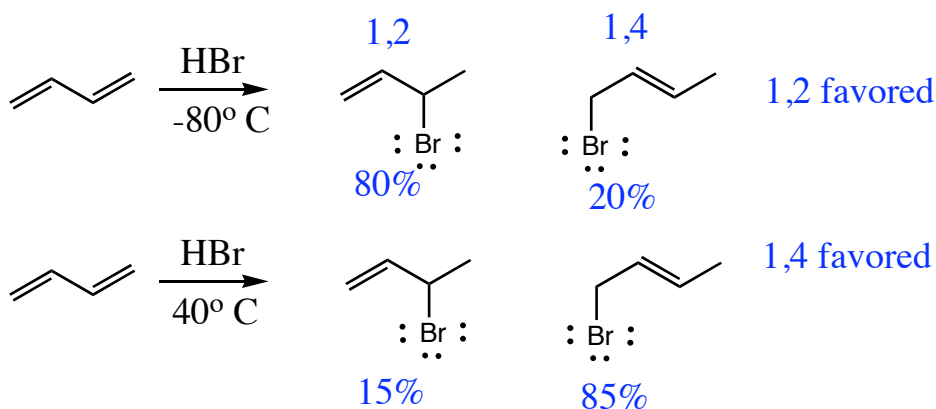
Why are there four products instead of two?

the two C=C's are not the same - they give different C+ if they attack

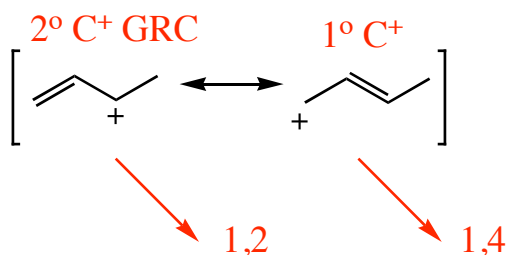
What is the relationship between the two carbocations?

constitutional isomers (each with their own resonance structures)

How will the ratio of products in the addition of HBr with 1,3-butadiene be different depending on the temperature of the reaction?



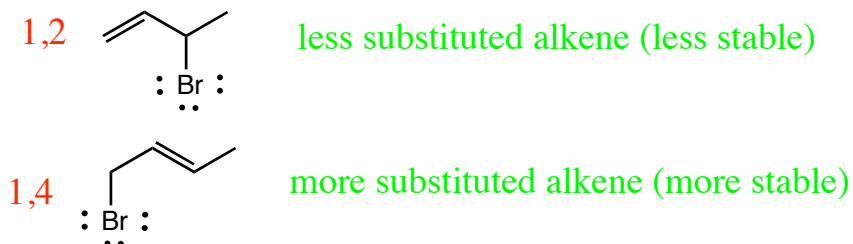
How does the energy of the resonance structures of the carbocation intermediates compare?



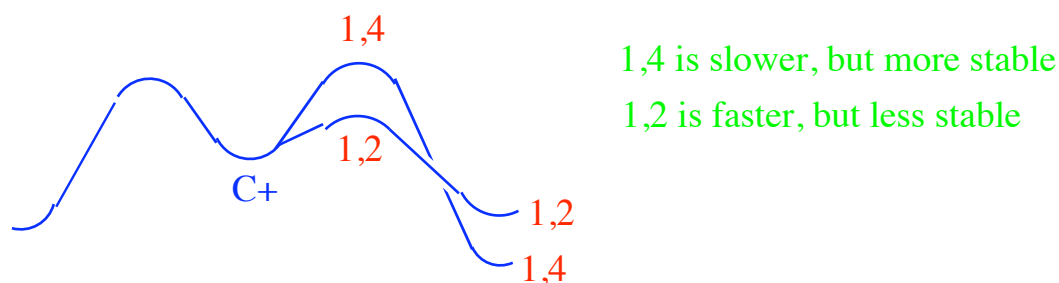
transition state for forming 1,2 product is lower than for forming 1,4 product

1,2 product forms faster

How does the energy of the final products compare?



What do the energy diagrams look like?



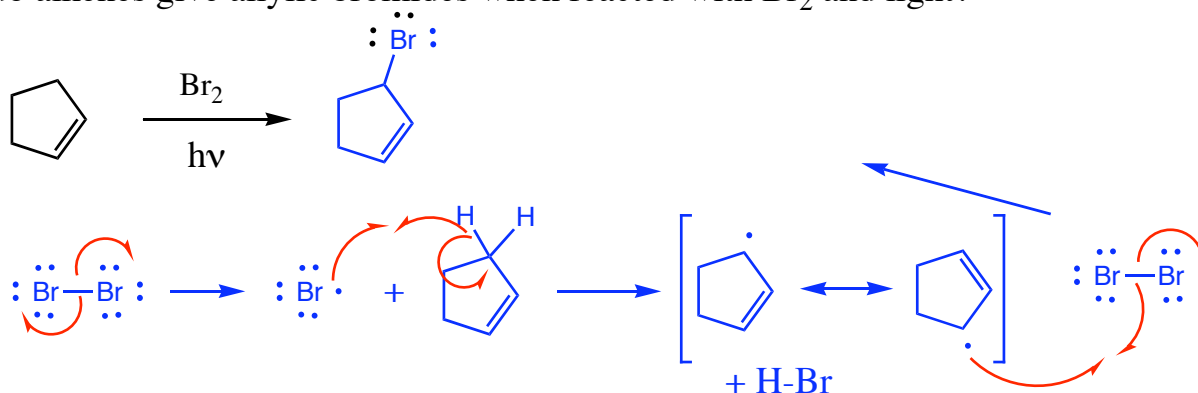
How does this explain the results?

at low temperatures: the 1,2 product forms faster
not enough energy for the reaction to go backward
the 1,2 product is favored
(kinetic control)

at higher temperatures: the 1,2 product is formed faster
enough energy for the reaction to go backward, equilibrium established
1,2 product has lower activation energy to reverse
over time, more of the 1,4 product is formed
(thermodynamic control)

Reactions using allylic radicals as intermediates

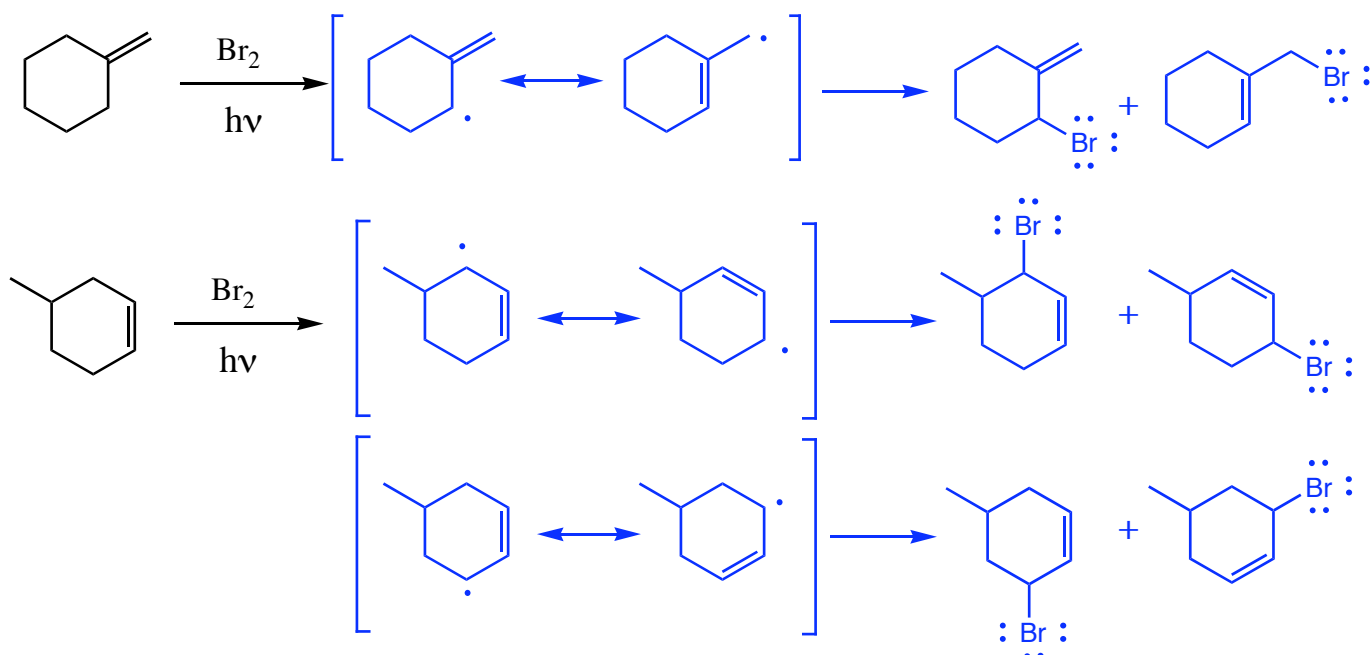
Why do alkenes give allylic bromides when reacted with Br₂ and light?



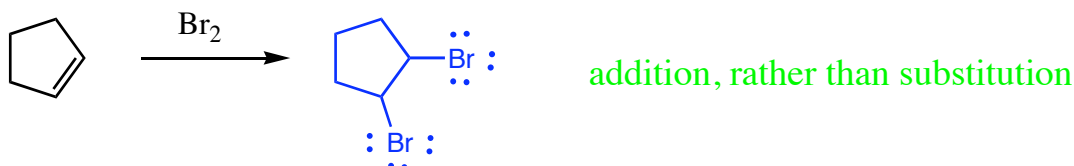
Why is a H taken only from the C next to the C=C?

it forms an allylic radical - more stable than other radicals

What products will be formed by the following reactions?



What other reaction can an alkene and Br₂ undergo?



What conditions favor the two kinds of product?

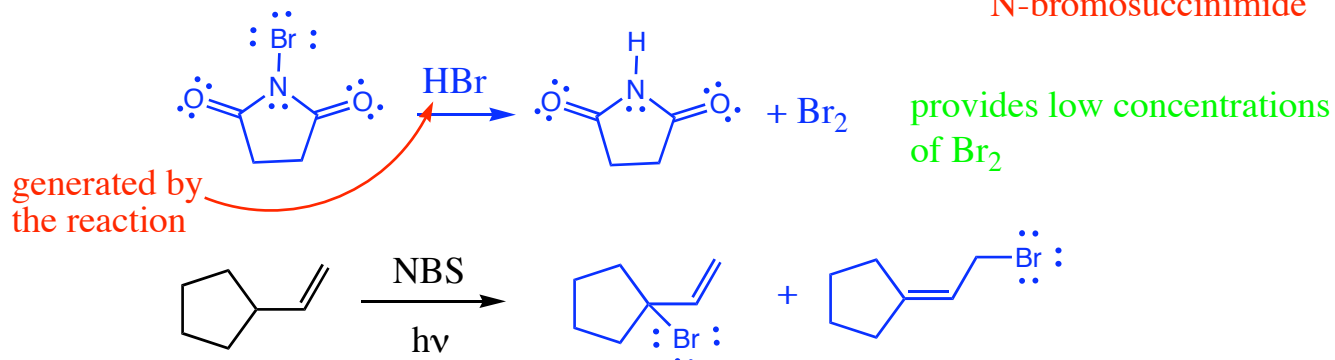
addition product: high concentration of Br₂, cold, dark

substitution product: low concentration of Br₂, heat or light

What reagent is commonly used to favor the substitution product?

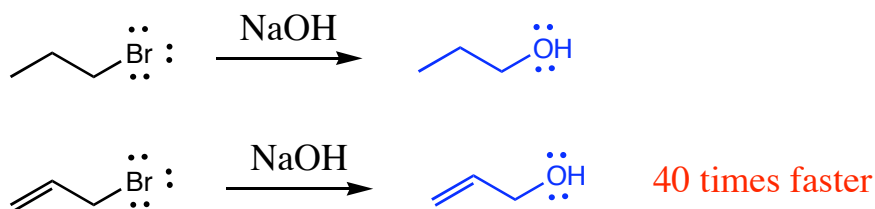
NBS

N-bromosuccinimide



S_N2 reactions of allylic halides

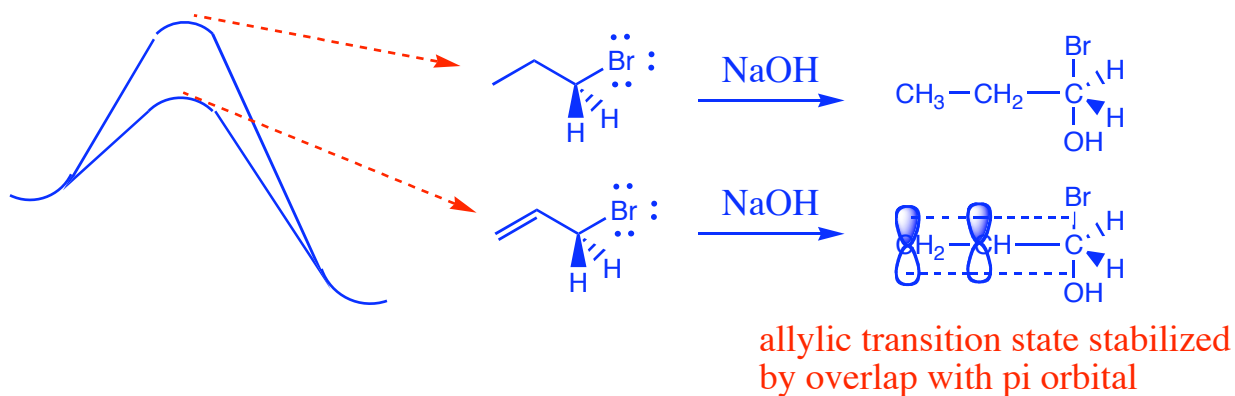
How do allylic halides compare with regular alkyl halides as electrophiles in S_N2 reactions?



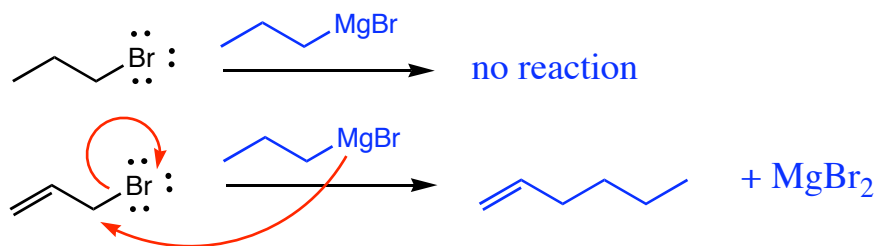
Can this be explained by having an allylic carbocation as an intermediate?

no - the reaction takes place in one step

How do the transition states of the two reactions compare?

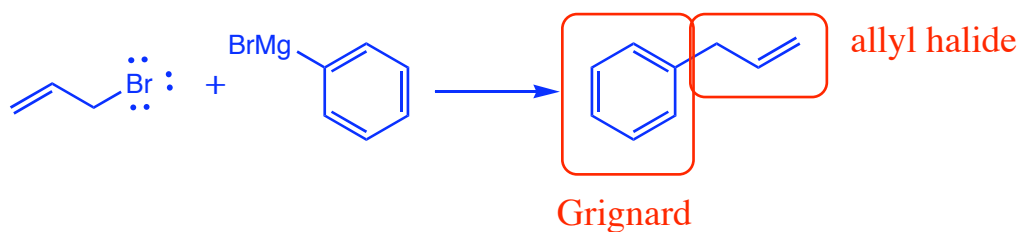


What reaction does this allow allylic halides to do that alkyl halides will not?



allylic halides will react in S_N2 substitutions with Grignards and organolithium reagents

How could this reaction be used to make allylbenzene?



III. The Diels-Alder Reaction

What starting materials are needed for a Diels-Alder reaction?

diene + alkene or alkyne

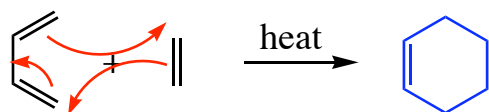
In order to avoid saying "alkene or alkyne" every time, what name is given to the reagent that is not the diene?

dienophile

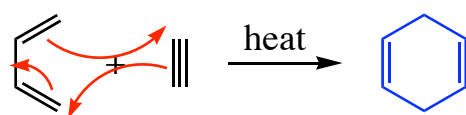
What reagents are needed?

none - just heat it up

How does the reaction occur? What kind of product does it form?



six-membered ring w/C=C



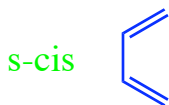
six-membered ring w/ 2 C=C's

one step

electrons flow in a circular motion

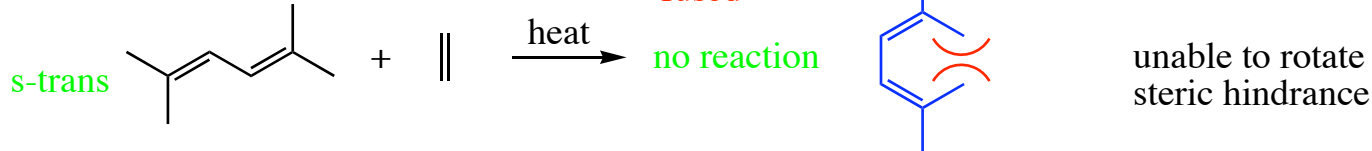
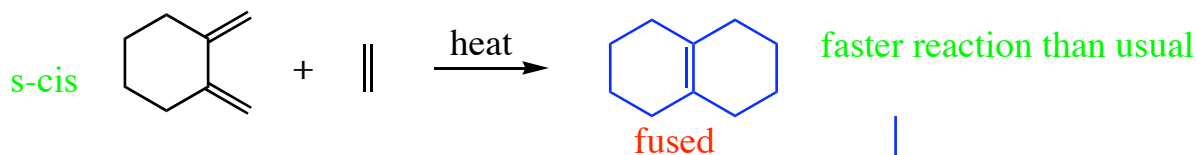
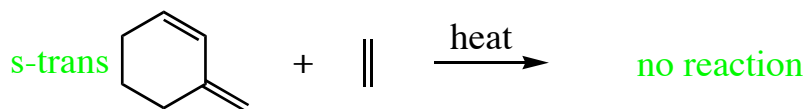
arrows can be drawn clockwise or counterclockwise

What conformation does the diene need to be in for the reaction to proceed?

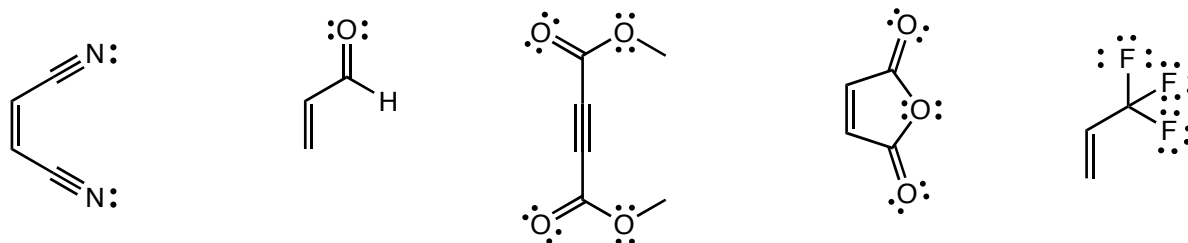


s-trans has to rotate before it can react

What happens if the diene is unable to rotate?



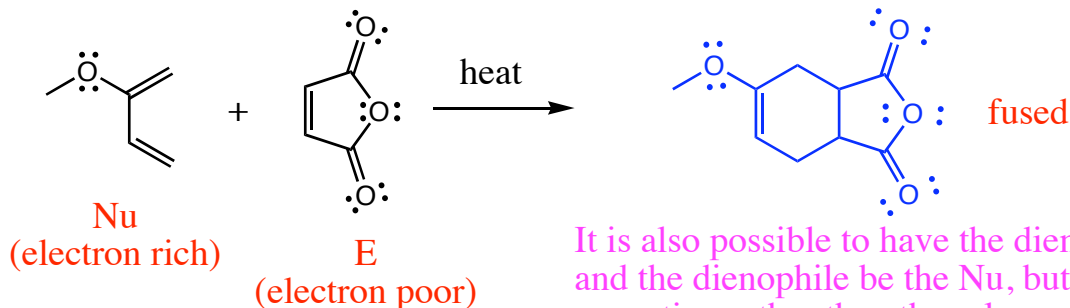
In order for this reaction to proceed at a reasonable rate, the dienophile must have some substituents. Below are some that work well. What kind of substituents do they have?



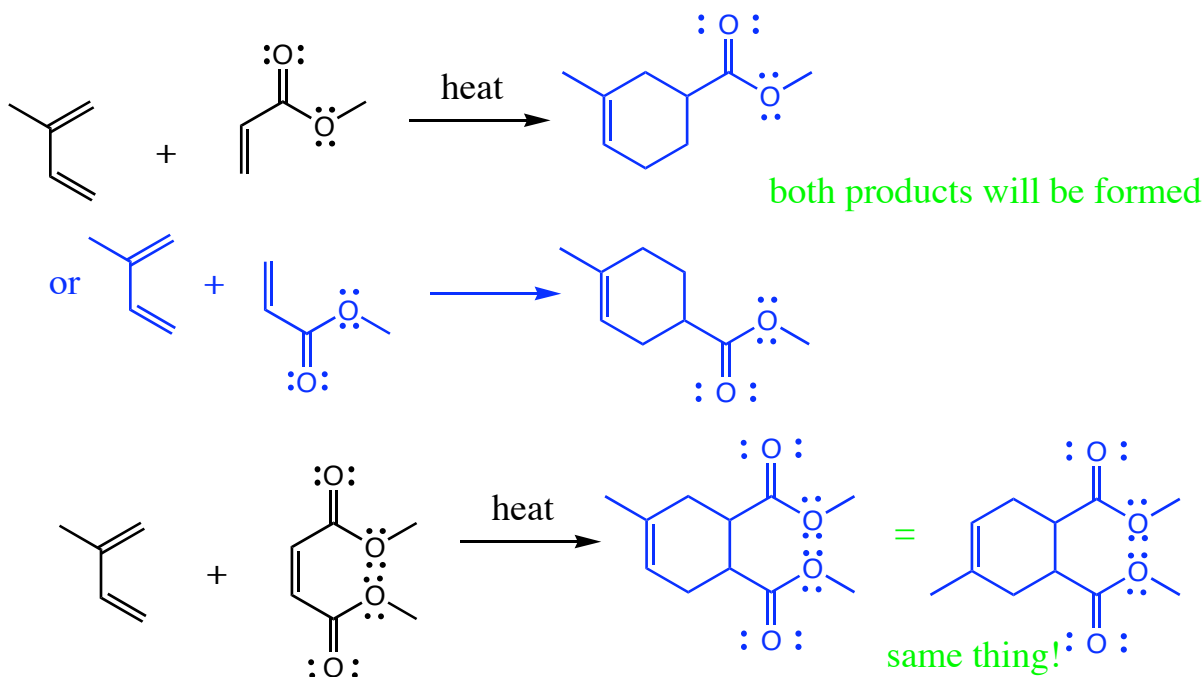
dienophiles need electron withdrawing groups - electronegative atoms or partially positive atoms.

Sometimes the diene is also substituted. What kind of substituents work well? What role does this give the diene and dienophile?

dienes sometimes have electron-donating groups - atoms with lone pairs



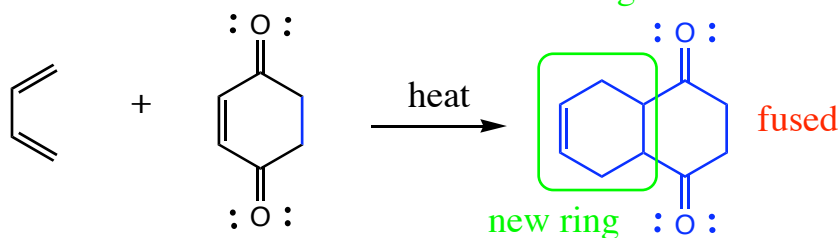
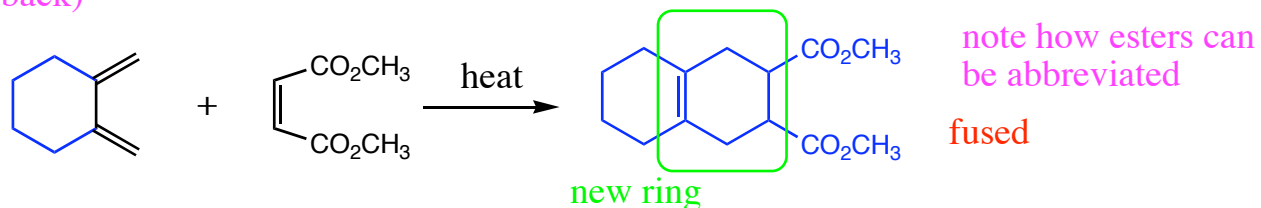
Under what conditions will two constitutional isomers be formed?



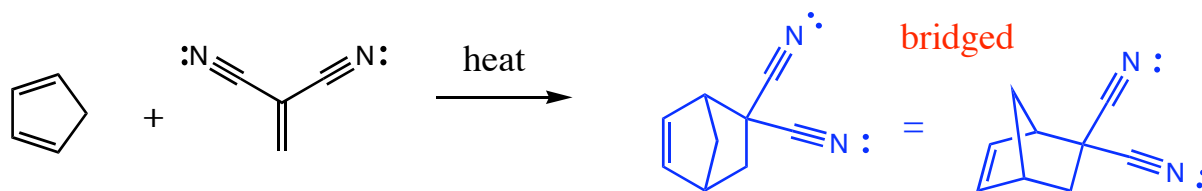
if both the diene and dienophile are unsymmetrical, you will get constitutional isomers; if only one is unsymmetrical, only one isomer is possible

When will fused bicyclic rings occur? When will bridged bicyclic rings form?

look for fused rings on previous pages (middle of previous page, bottom of next page back)



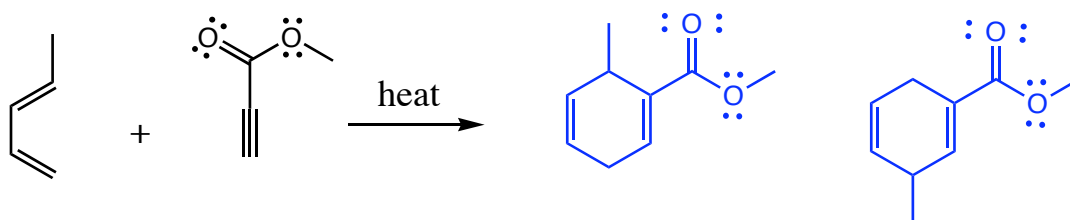
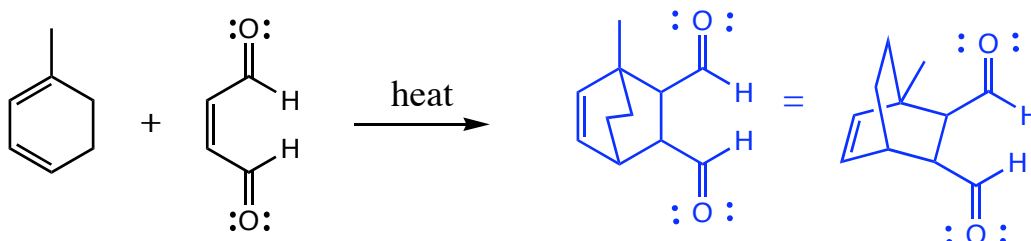
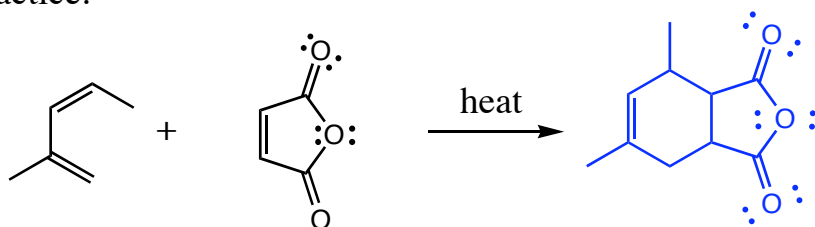
if the dienophile is in a ring, or the diene has a ring on the outside of it = fused



if the diene is in a ring = bridged

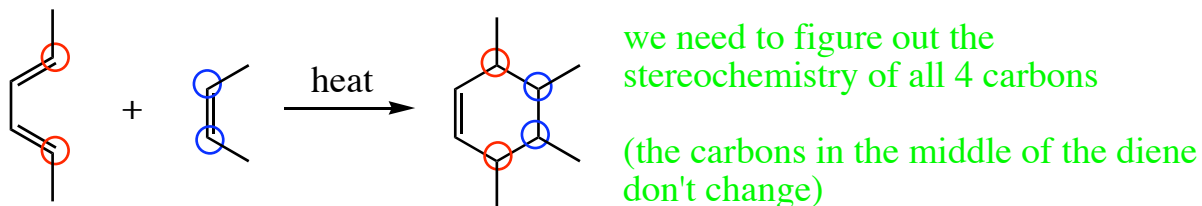
make a model

Practice:

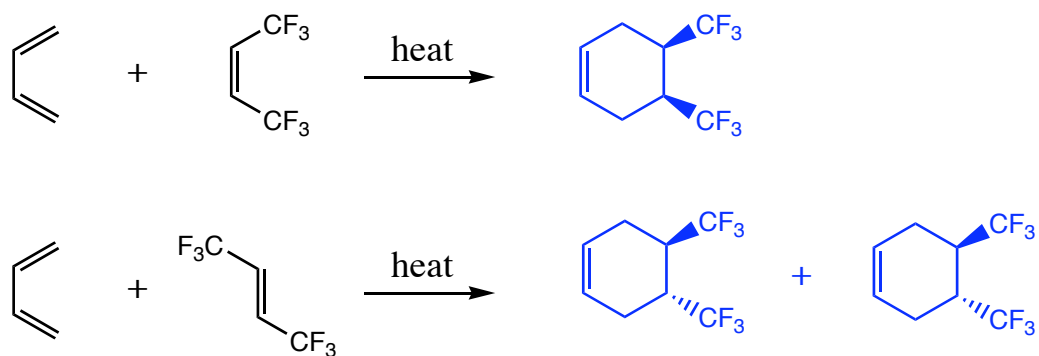


Stereochemistry of the Diels-Alder reaction

How many atoms make new bonds in the Diels-Alder reaction? 4

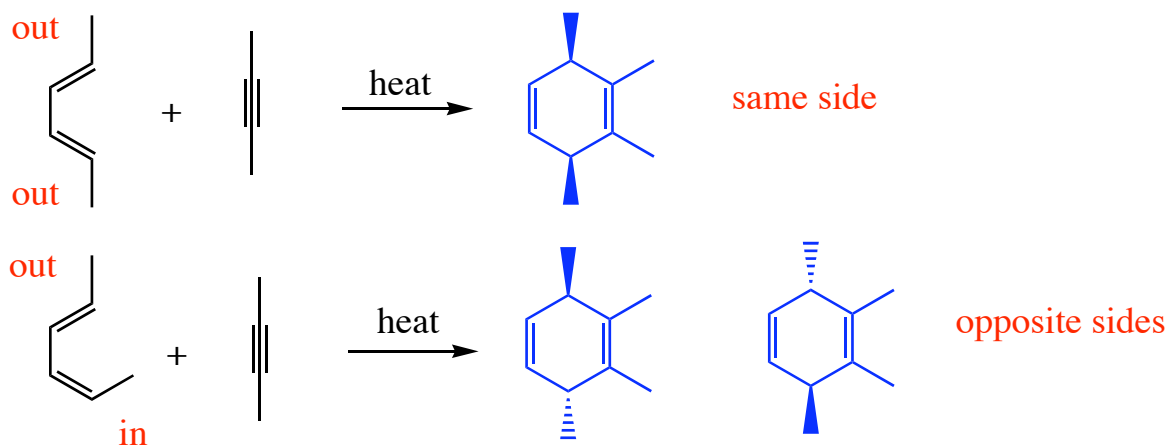


What happens to the substituents that come from the dienophile?



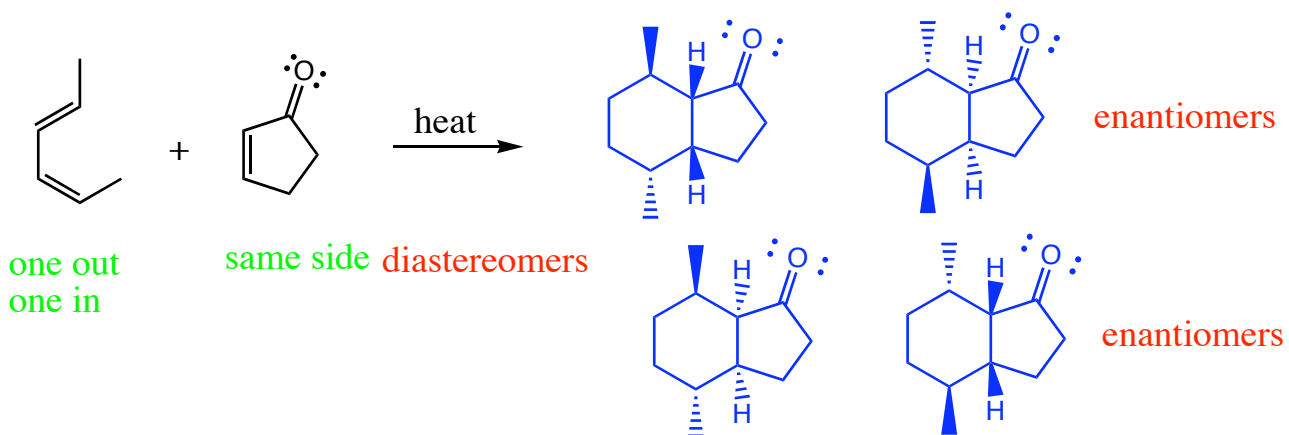
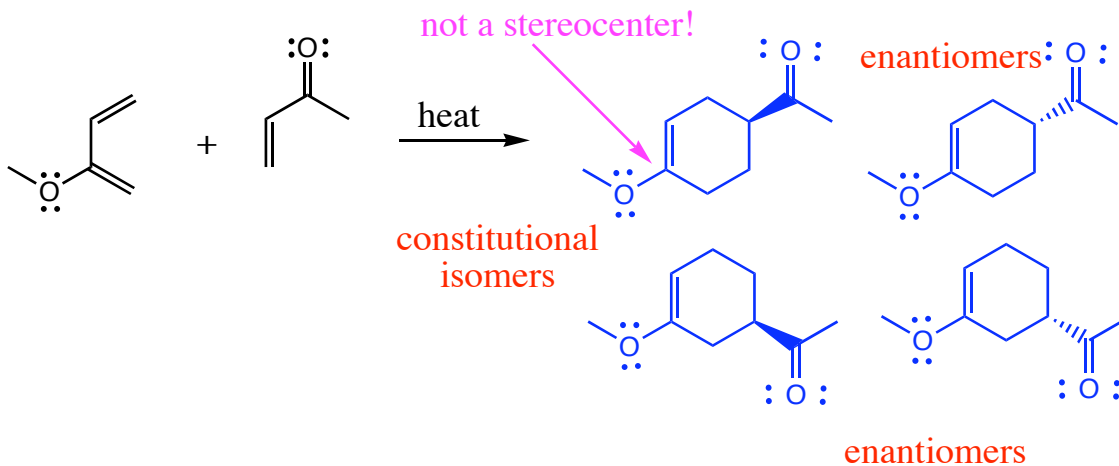
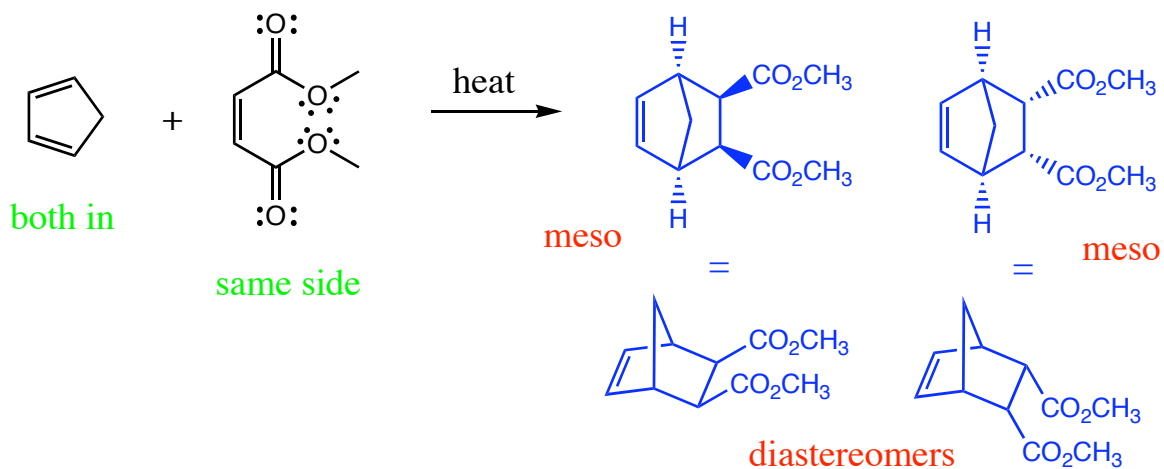
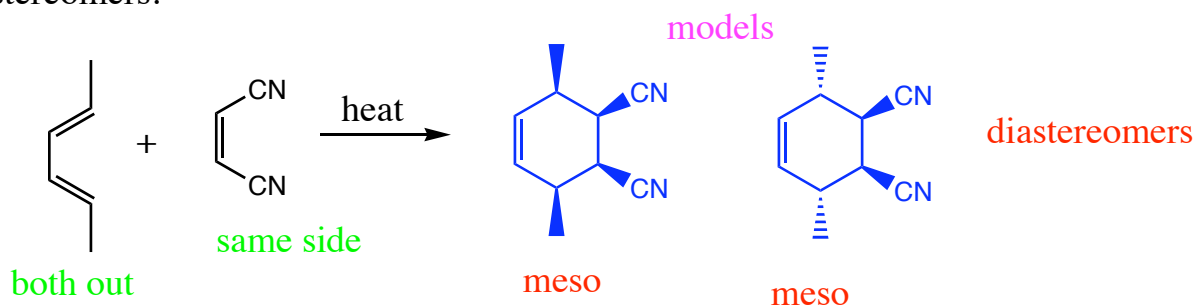
cis - same side; trans - opposite sides (syn addition)

What happens to the substituents that come from the diene?



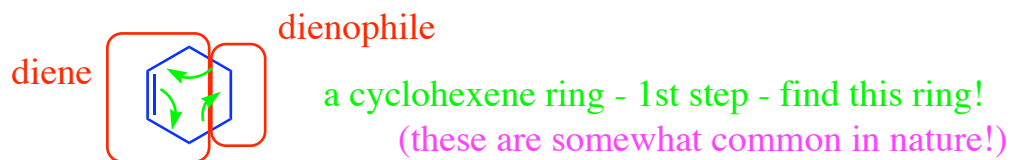
if they are both pointed out, they end up on the same side;
if one is pointed out and the other in, they end up on opposite sides

Give all isomers that will be formed in the following reactions. Label enantiomers and diastereomers.



Using the Diels-Alder reaction for synthesis

What structure must be present in the product in order to use the Diels-Alder reaction?



Where on this structure was the diene? Where was the dienophile?
How would the electrons have to flow to reverse the reaction?

From what diene and dienophile could the following compounds be made?

