

## 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?

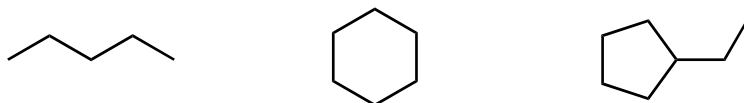
What if there are more than 2?

What are the three kinds of dienes you can have?

#### Isolated Dienes

What is an isolated diene? How do they behave?

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



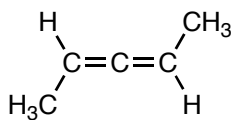
#### Cumulated Dienes

What is a cumulated diene?

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?

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



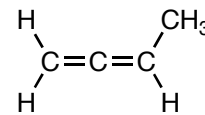
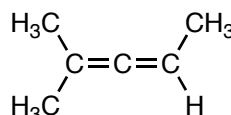
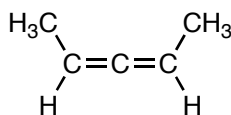
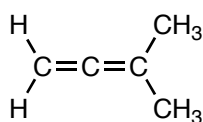
Is this compound chiral?

Is there a plane of symmetry?

Which carbons are stereocenters?

How many stereoisomers are possible?

Which of the following allenes are chiral?

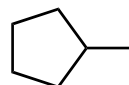
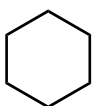
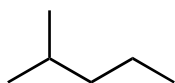


How can you tell without making a model which ones will be chiral?

### Conjugated dienes

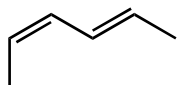
What is a conjugated diene? two or more C=C connected by C-C

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



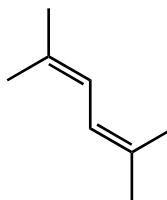
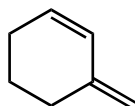
What orientation of the pi bonds gives the lowest energy?

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?



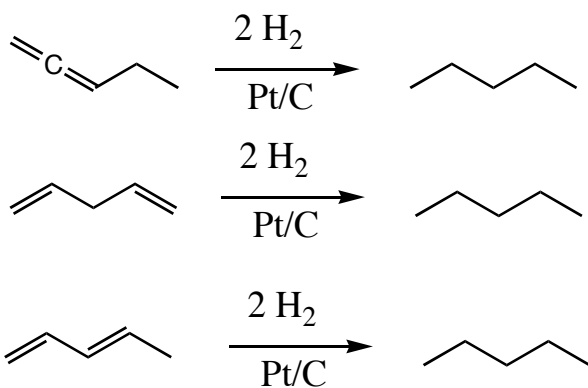
What is the difference between an s-trans diene and a trans C=C?

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



### Energies of dienes

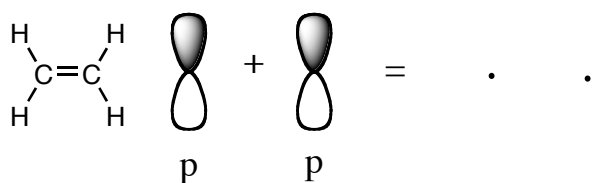
What do the heats of hydrogenation tell us about the relative energies of isolated, cumulated, and conjugated dienes?



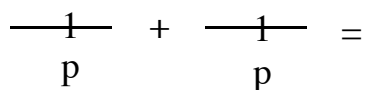
## II. Reactions involving allylic intermediates

### Molecular orbitals of compounds with multiple p orbitals

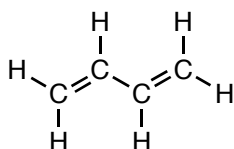
What molecular orbitals are formed when two p orbitals combine?



How can the energy of these orbitals be represented?



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



Why are conjugated dienes lower in energy than isolated ones?

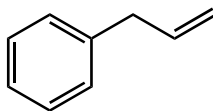
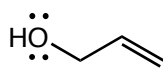
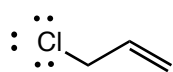
What do these orbitals look like?



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

# Allylic cations, radicals, and anions

What is an allyl group?



What would the following look like?

allyl cation:

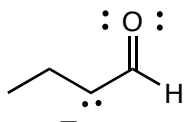
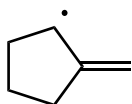
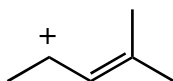
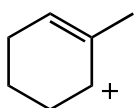
allyl radical:

allyl anion:

Why are each of these unusually stable?

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

Give the other resonance structure for the following:



Which of the structures above have a greater resonance contributor?

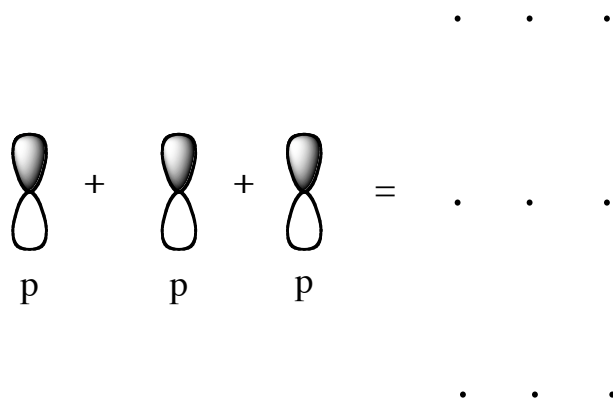
How does the stability of allyl and allylic cations compare to 1°, 2°, and 3° cations?



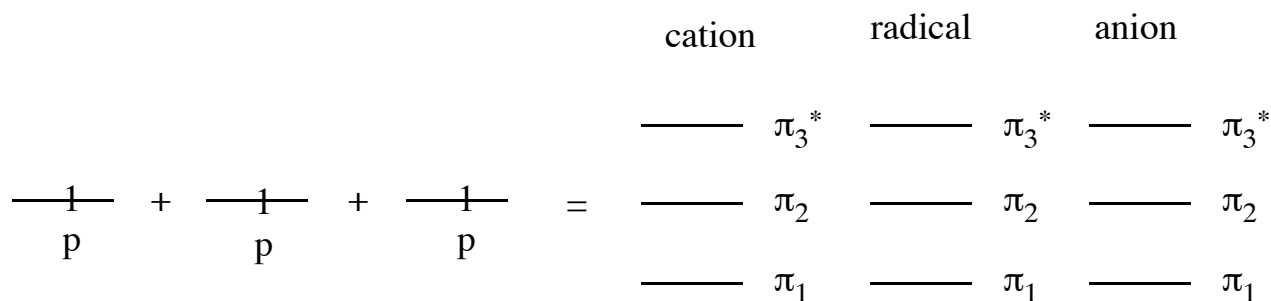
How does the stability of allyl and allylic radicals compare to 1°, 2°, and 3° radicals?



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



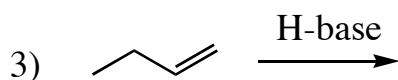
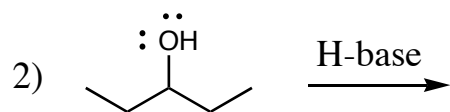
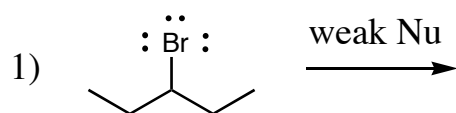
Which orbitals contain electrons in a allylic cation, radical, and anion?



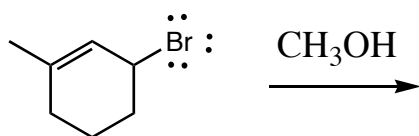
Do the molecular orbitals and the resonance structures agree on where the positive charge, radical, and negative charge are?

Reactions involving allylic cations as intermediates

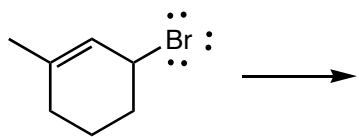
What reactions do we know that involve carbocation intermediates?



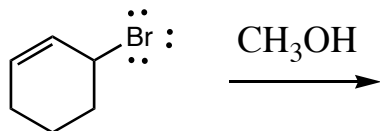
What products are formed when the following allylic alcohol undergoes an  $S_N1$  reaction?



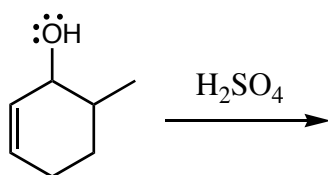
How can we explain this by looking at the mechanism?



What products would be formed by the following reaction?



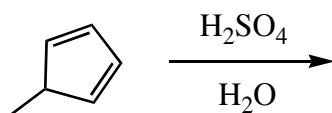
What two products would be formed by the following reaction?



How can you choose between two possible H's on either side of the  $\text{C}^+$ ?

Why doesn't a rearrangement occur?

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

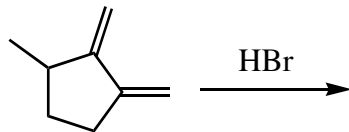


How are these two products labeled?

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



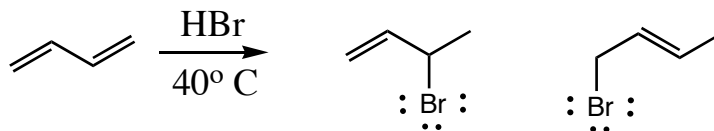
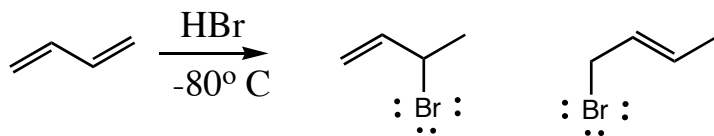
How many products would be formed by the following reaction?



Why are there four products instead of two?

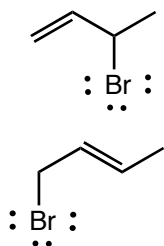
What is the relationship between the two carbocations?

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?

How does the energy of the final products compare?



What do the energy diagrams look like?

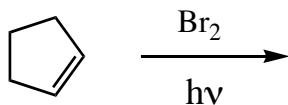
How does this explain the results?

at low temperatures:

at higher temperatures:

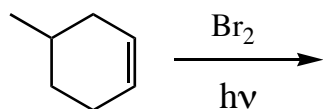
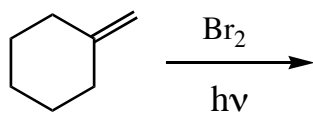
### Reactions using allylic radicals as intermediates

Why do alkenes give allylic bromides when reacted with  $\text{Br}_2$  and light?

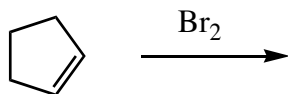


Why is a H taken only from the C next to the C=C?

What products will be formed by the following reactions?

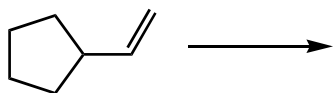


What other reaction can an alkene and  $\text{Br}_2$  undergo?



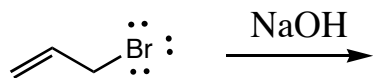
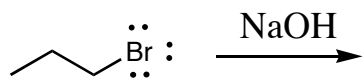
What conditions favor the two kinds of product?

What reagent is commonly used to favor the substitution product?



S<sub>N</sub>2 reactions of allylic halides

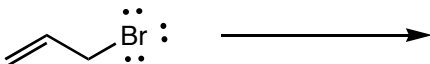
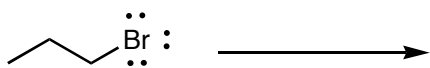
How do allylic halides compare with regular alkyl halides as electrophiles in S<sub>N</sub>2 reactions?



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

How do the transition states of the two reactions compare?

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



How could this reaction be used to make allylbenzene?

### III. The Diels-Alder Reaction

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

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

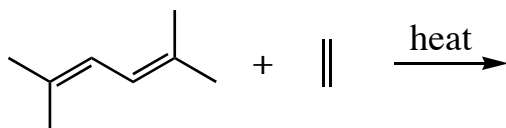
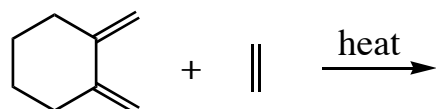
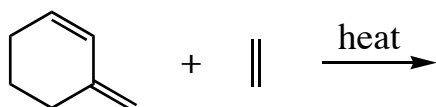
What reagents are needed?

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

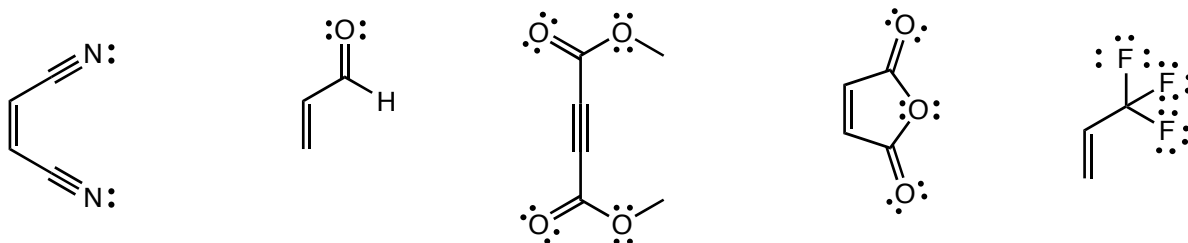


What conformation does the diene need to be in for the reaction to proceed?

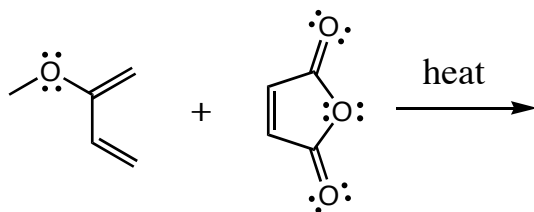
What happens if the diene is unable to rotate?



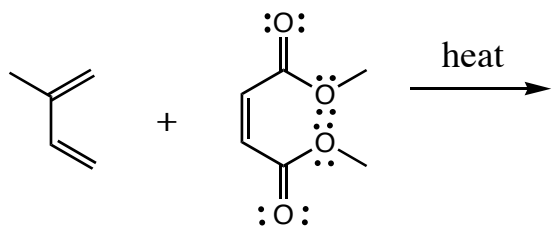
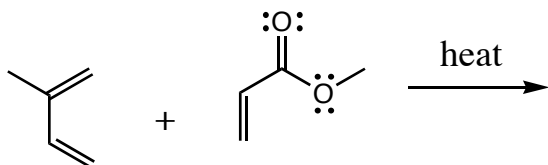
In order for this reaction to proceed at a reasonable rate, the dienophile must have some substituents. Below are some that work well. What kind of substituents do they have?



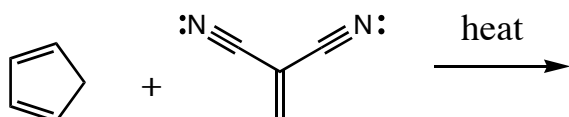
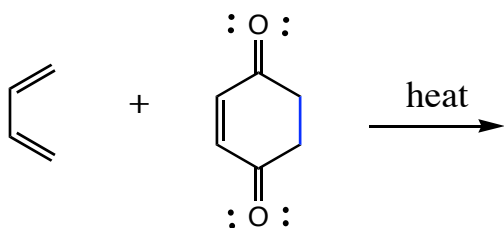
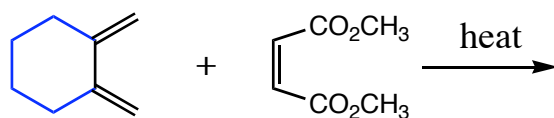
Sometimes the diene is also substituted. What kind of substituents work well? What role does this give the diene and dienophile?



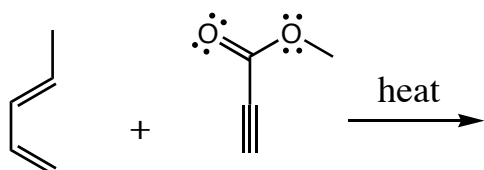
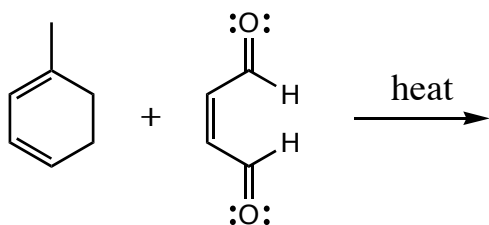
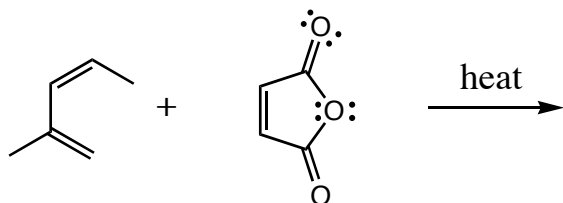
Under what conditions will two constitutional isomers be formed?



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

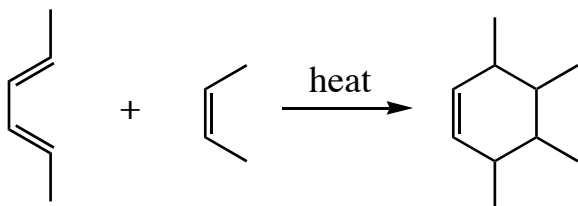


Practice:

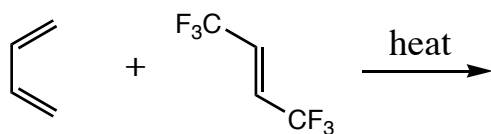
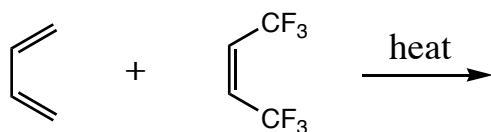


Stereochemistry of the Diels-Alder reaction

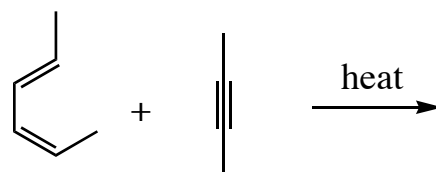
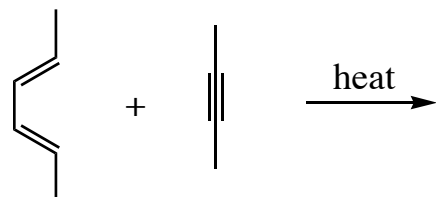
How many atoms make new bonds in the Diels-Alder reaction?



What happens to the substituents that come from the dienophile?

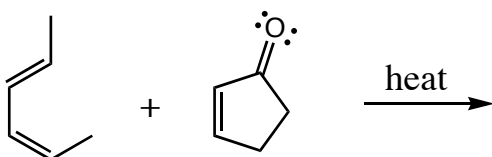
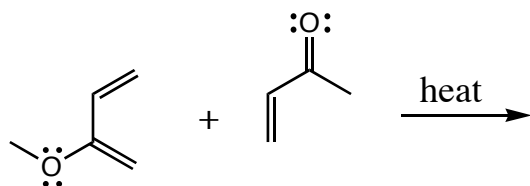
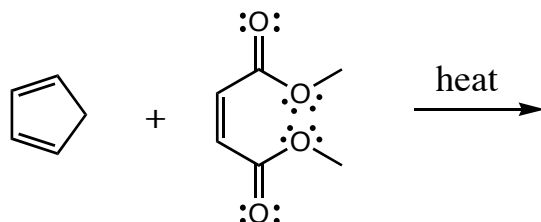
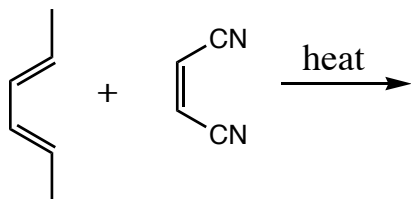


What happens to the substituents that come from the diene?





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?

