

**Week 6**  
**CHE 3332 - Organic Chemistry 2**

**Hello and Welcome to the weekly resources for CHE 3332 – Organic Chemistry 2!**

**This week is Week 6 of class, and typically in this week of the semester your professors are covering these topics below.** If you do not see the topics your particular section of class is learning this week, please take a look at other weekly resources listed on our website for additional topics throughout the semester.

We also invite you to **look at the group tutoring chart on our website to see if this course has a group tutoring session offered this semester.** If you have any questions about these study guides, group tutoring sessions, private 30 minute tutoring appointments, the Baylor Tutoring YouTube channel or any tutoring services we offer, please visit our website [www.baylor.edu/tutoring](http://www.baylor.edu/tutoring) or call our drop in center during open business hours. M-Th 9am-8pm on class days 254-710-4135.

**Keywords:** Molecular Orbital (MO), Conjugation, Diene, Diels Alder

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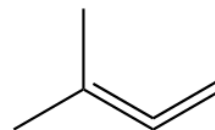
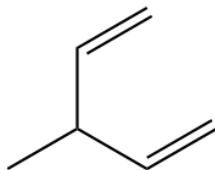
**TOPIC OF THE WEEK: Conjugated Pi Systems and Pericyclic Reactions**  
(Ch16)

**What is a Conjugated Pi System?**

Since we covered this topic slightly, I will give a short recap on all the important info. Basically a conjugated system consists of a molecule with multiple double ( $\pi$ ) bonds, spaced **apart by one carbon**. These evenly spaced  $\pi$  bonds can then interact with each other, boosting the stability of the molecule. **Any  $\pi$  bond directly connected or spaced too far**, does not count within the conjugated system.



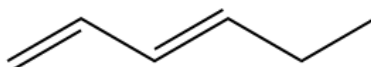
3 conjugated pi bonds



Not conjugated systems, pi bonds are not spaced correctly

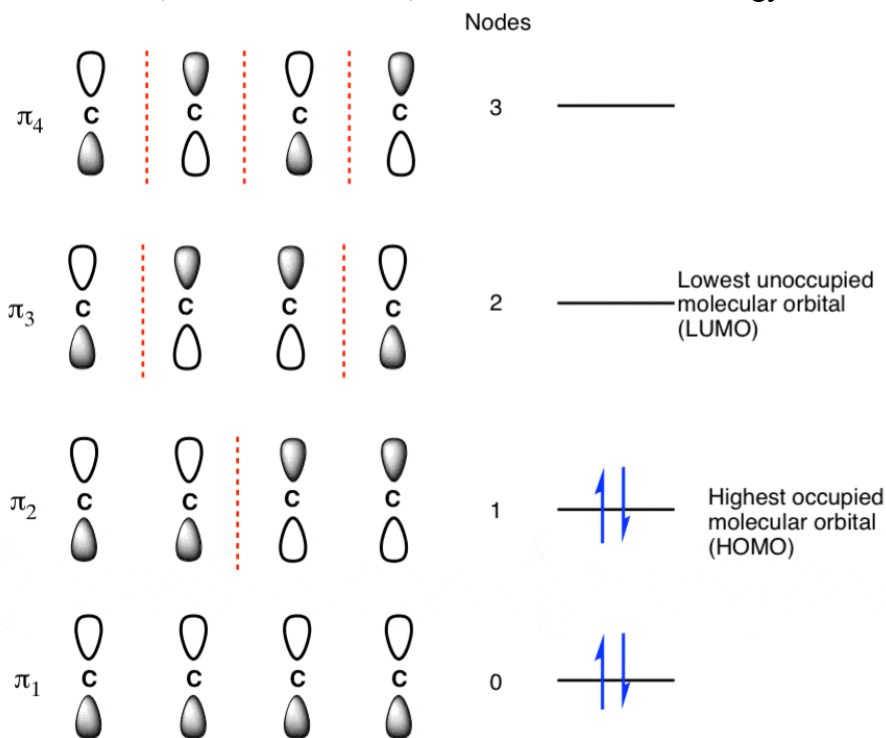
**Molecular Orbital (MO) Diagram:**

Using our conjugated system, we can make a MO Diagram, to help explain the ability for these systems to react. It will also provide a good visual of the phases of the bonds. To do so, let's use an example molecule, hex-1,3,-diene:



hex-1,3-diene

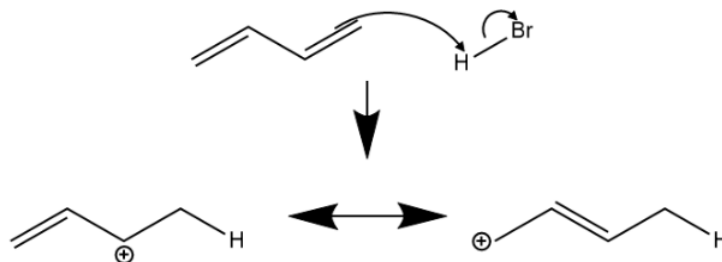
1. Count the number of carbons **participating in the  $\pi$  system**, **NOT** in the entire molecule. This molecule only has 4 carbons in the system, so 4 evenly spaced dots, and 4 energy levels are drawn.
2. Draw nodes (dashed lines) in between the carbon dots, starting with zero nodes, then one and so on.
3. Mark each carbon dot with a phase (either + or -). Initially, each orbital will be in phase (all +), but after every node, the phase will change to - or back to +.
4. Now we will determine both our highest occupied, and lowest unoccupied molecular orbital (HOMO and LUMO). To do so, each energy level should be assigned  $2\pi$  electrons. Because our molecule only has 4  $\pi$  electrons, we will only go up to the second energy level. Thus, this is our HOMO, and the next unfilled energy level is our LUMO.



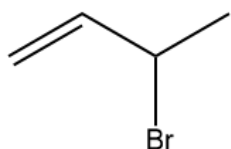
Now that we have covered some of the important basics of conjugated systems, we can now talk about the different types of reactions that involve them (there are quite a few!).

### Electrophilic Addition:

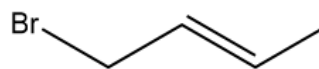
One type of reaction that is important within the context of conjugated systems is electrophilic addition. Similarly to how we can add HBr to a single double bond, we can also add HBr (or any HX halide), to a conjugated system, yielding interesting results. Because of the two double bonds, when the H atom is added, we can form two carbocation resonance structures.



The carbon to which Br<sup>-</sup> will now attach to is dependent on the energetics of the system. Addition of Br to the terminal carbocation is difficult to achieve because of the **high activation energy** the reaction must overcome. At **low temperatures, it is not possible**, but if we were to increase the heat, it is the dominant product, and thus the **thermodynamic product**. Addition to the middle carbocation will yield a less stable product, but the reaction has a much lower activation energy, and will thus be the dominant product at room temperature. This gives us the **kinetic product**.



1,2- Product, Kinetic Product

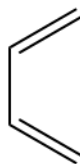


1,4 - Product, Thermodynamic Product

### Pericyclic Reactions:

#### Cycloaddition:

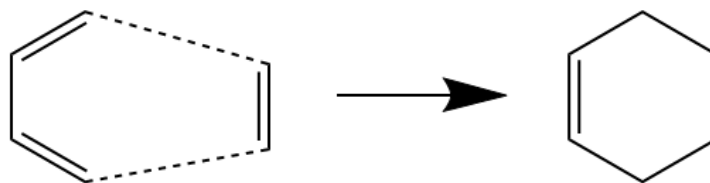
This reaction (commonly referred to as the **Diels-Alder** reaction), involves both a dienophile and a diene reacting together to form a ring structure. Simply put, **a diene is a molecule which has two double bonds**. Thus, a dienophile, will be a molecule attracted to a diene. In order to create a new ring,  $\pi$  bonds are moved and destroyed, in order to form  $\sigma$  bonds. For every Diels-Alder reaction, **two  $\sigma$  bonds** are formed, and **two  $\pi$  bonds** are destroyed.



Diene

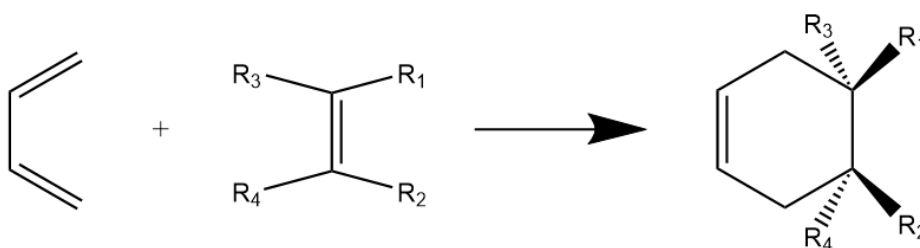


Dienophile



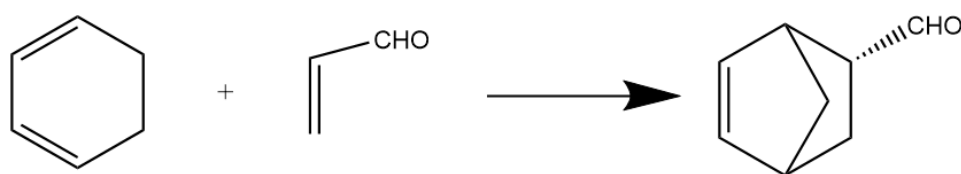
Notice here that two  $\pi$  bonds (one from both the diene and dienophile) were used to link the two molecules together (becoming  $\sigma$  bonds), while the other was simply moved around.

It is important to know that the dienophile can take on many different forms, and is usually not just a single double bond. For instance, it may be a triple bond, although it still behaves the same as a regular double bond. Additionally, many dienophiles will have added substituents. While they do not change the mechanism of the reaction, the stereochemistry of the substituents will be important to determine.



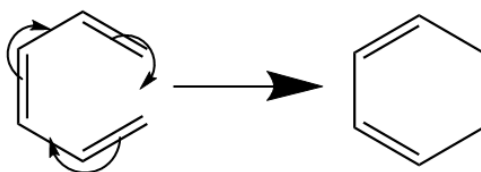
General Stereochemistry Rule for Diels-Alder Reactions

Sometimes, the substituents will not follow the pattern above. This is because bulky substituents may be forced to favor the **endo** (downward or dashed) position. If the Diels-Alder reaction happens to create a **bicyclic ring with bridgehead carbon**, the resulting steric hindrance will lead to an endo preference.

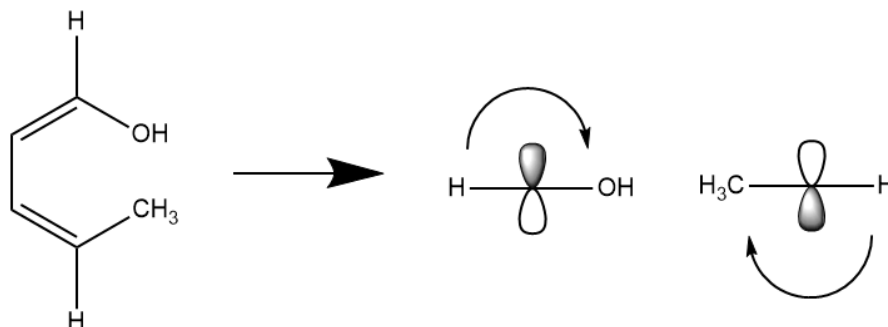


### Electrocyclic Reactions:

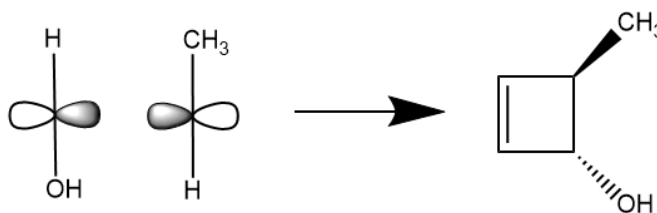
Similarly to cycloaddition, this type of reaction involves the creation of a carbon ring, using a single molecule which uses its  $\pi$  bonds to create a ring structure. Because of this, **one  $\pi$  bond** is destroyed, and **one  $\sigma$**  is formed in its place.



It is very important to keep track of any substituents during electrocyclic reactions, as the stereochemistry may change depending on the reagents used to perform the reaction. To perform this reaction, there needs to be an energy source, in the form of **heat** or **U.V. light** (or  $h\nu$ ). If **heat is used, the HOMO is used to determine stereochemistry, and if U.V. is used, the LUMO will determine the substituent stereochemistry**. While you can memorize certain patterns, it is best to refer to our M.O. diagrams when solving these problems. We need to rotate our p-orbitals so that the same phases meet with each other.



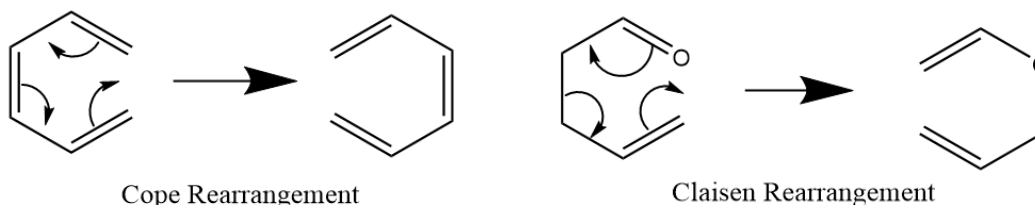
If we look at the orbital for the two ends (with the -OH and CH<sub>3</sub> substituents) we can see that the p-orbitals are out of phase, so we want to rotate them so that they are in the same phase (i.e. the same colored orbitals line up with each other).



With the two orbitals in phase, we can see that the two substituents are facing in opposite directions.

### **Sigmatropic Rearrangement:**

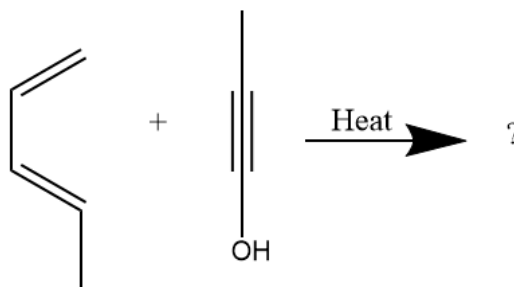
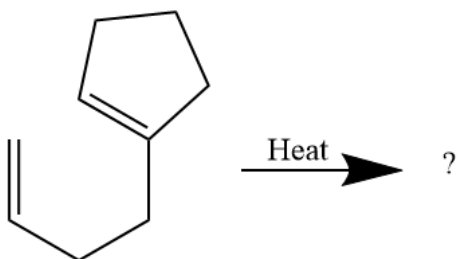
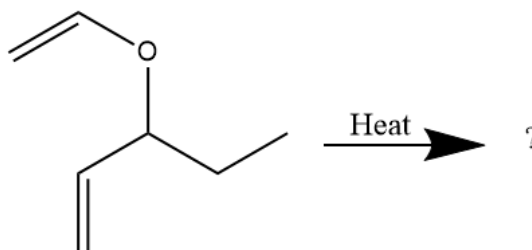
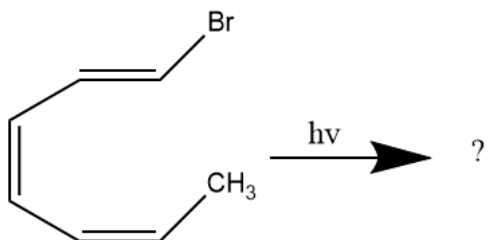
As the name suggests, this type of reaction involves the movement of one  $\sigma$  bond within a molecule. No other bonds ( $\sigma$  or  $\pi$ ) are created, but are instead moved around the molecule. There are two types of sigmatropic rearrangement, the Cope and the Claisen rearrangement. The first reaction involves a molecule whose atoms are all carbon atoms, whereas in a Claisen rearrangement, one atom is an oxygen, usually in the form of an ether or ketone.



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### CHECK YOUR LEARNING:

Provide the product for each reaction:



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### THINGS YOU MAY STRUGGLE WITH!

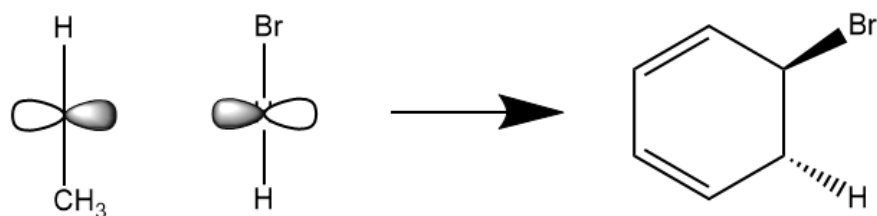
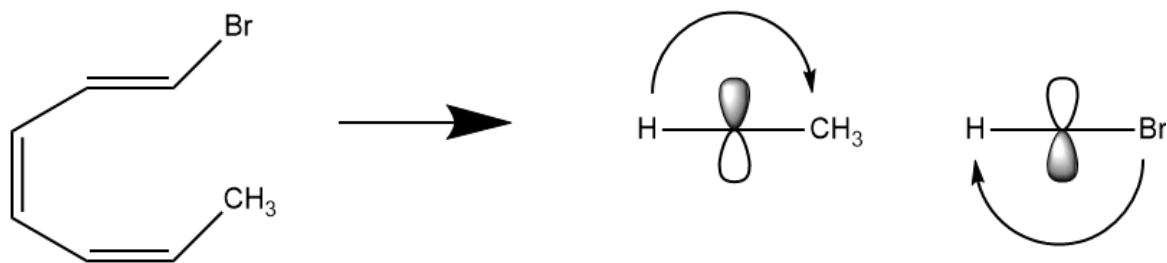
- Also remember to keep track of stereochemistry when doing Diels Alder reactions. Because of how many things you need to deal with, and the exceptions, and can be a bit tricky to keep track of all the substituents.
- Similarly, for both Electrocyclic and Sigmatropic reactions, remember to accurately keep track of the double bonds that are moving around. Also don't move them too far, remember they can only jump 1 carbon!
- M.O. diagrams can be a bit tricky. They are also important in electrocyclic reactions, so any inaccuracies can cause problems.

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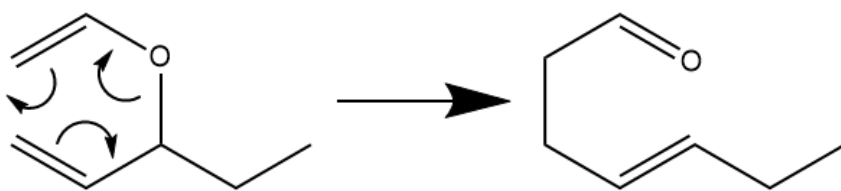
Thanks for checking out these weekly resources!

Don't forget to check out our website for group tutoring times, video tutorials and lots of other resources: [www.baylor.edu/tutoring](http://www.baylor.edu/tutoring)! Answers to check your learning questions are below!

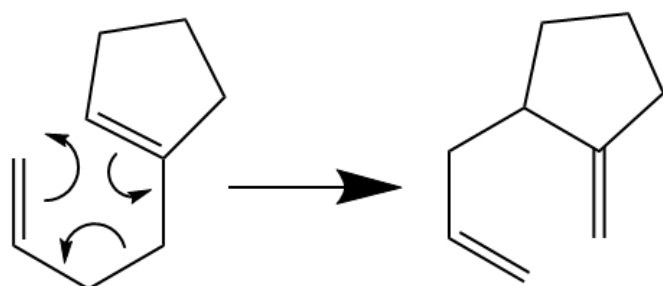
ANSWERS FOR THE PRACTICE PROBLEMS:



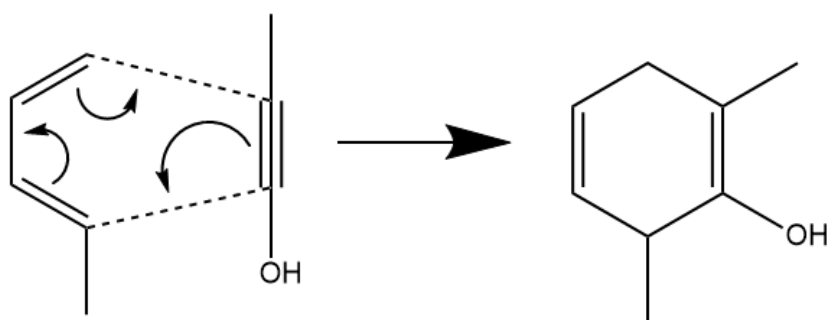
1.



2.



3.



4.

*All drawings of molecules and mechanisms are made by me. The MO Diagram is courtesy of Master Organic Chemistry*