

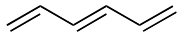
Conjugation and Pi Molecular Orbitals
Learning Objectives

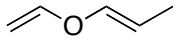
Here are the skills you should have for these topics:

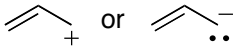
1) Be able to construct π molecular orbitals (MOs) for conjugated compounds:

π MOs of conjugated compounds are the primary orbitals involved in cycloaddition reactions (e.g. the Diels-Alder reaction). **π MOs** are constructed as follows:

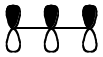
1) for every p orbital, there exists a π MO...

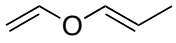
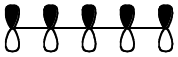
 = 6 p orbitals, therefore 6 π MOs

 = 5 p orbitals, therefore 5 π MOs

 = 3 p orbitals each, therefore 3 π MOs each

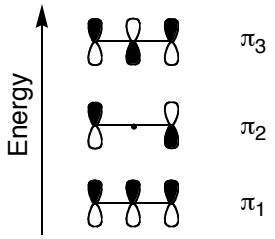
2) draw π MO #1 (the lowest energy π MO) by drawing a linear chain of p orbitals, coloring in the lobes such that there are no nodes (i.e. no break in color) between the p orbitals...

for  , π MO #1 has 3 p orbitals shaded as follows: 

for  , π MO #1 has 5 p orbitals shaded as follows: 

3) draw the remaining π MOs by drawing a linear chain of p orbitals, coloring in the lobes such that there are 1, 2, 3, etc. nodes (i.e. a break in color) in that MO. *Note: the location of the node(s) must be symmetrical about the molecule.* For MOs with an odd number of p orbitals, the node will fall on a p orbital and "obliterate" that p orbital.

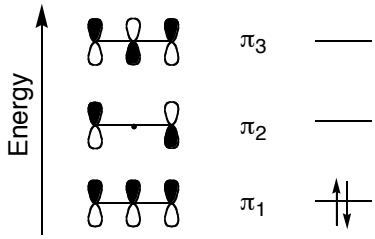
for 

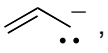


4) each π MO can contain two electrons. Fill up the π MOs using the total number of electrons from the individual p orbitals.

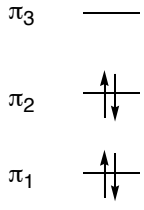
for  ,

there are only 2 π electrons



for  ,

there are 4 π electrons

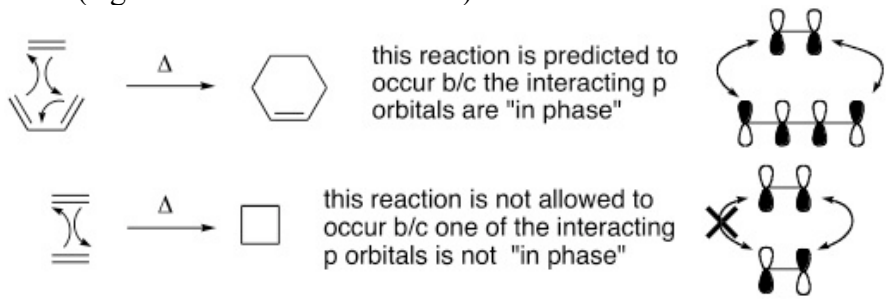


5) determine the HOMO (Highest Occupied Molecular Orbital) and LUMO (Lowest Unoccupied MO) based on where the electrons end up.

2) Understand the theory behind thermodynamic and kinetic control of addition reactions to conjugated systems and be able to predict the products of such reactions.

3) Be able to use π MOs to predict whether a cycloaddition reaction will proceed thermally or photochemically:

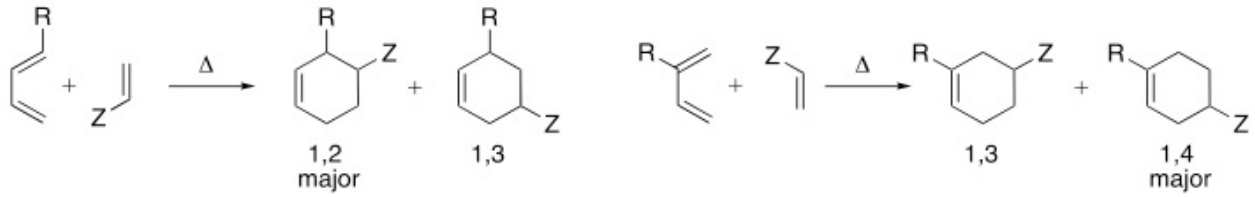
The **π MOs**, specifically the **HOMOs** and **LUMOs** can be used to determine the reactivity of polyenes in cycloaddition reactions (e.g. the Diels-Alder Reaction).



4) Know the mechanism of the Diels-Alder reaction, be able to predict its products, and be able to use the reaction in a synthesis. Here are the details that you need to remember for the reaction:

a) the diene must be in the s-cis conf ormation to react. If it isn't, rotate about the σ-bond if possible.

b) in Diels-Alder reactions where disubstituted cyclohexenes are formed, 1,2 or 1,4 products are formed preferentially over 1,3 products.



c) the endo rule states that electron withdrawing groups on the dienophile prefer to point toward the diene.

d) the stereochemistry of addition follows the following pattern: