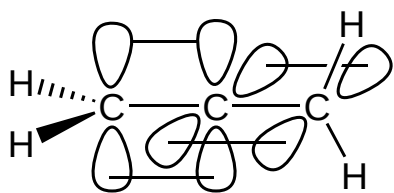


Problem Set 1

Answer Key

1. Using the incomplete structure shown for allene ($\text{H}_2\text{C}=\text{C}=\text{CH}_2$), draw the p orbitals in their proper orientation and indicate which of these orbitals are interacting to form π bonds. Indicate the hybridization of each of the carbon atoms. Can allene properly be described as a conjugated system?



Carbons at ends are sp^2 -hybridized.

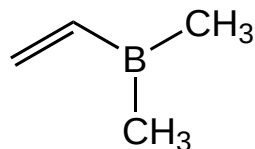
Middle carbon is sp -hybridized.

Allene **cannot** be described as a conjugated system; the two π bonds are orthogonal to each other.

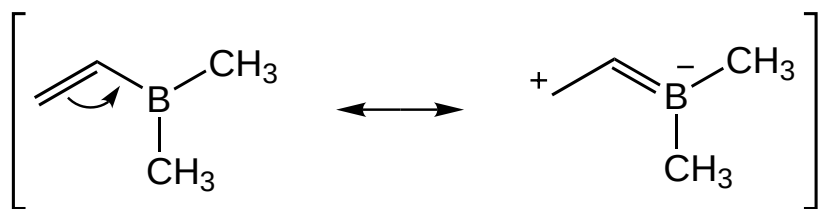
2. If you were to view 1,3-butadiene as 2 connected but *non-interacting* double bonds, what prediction would you make about the relative energy levels of the two pairs of π electrons? Is your prediction consistent with the molecular orbital picture we discussed in class?

If it were two connected but non-interacting double bonds, we would predict that the two pairs of π electrons are at the same energy level or are degenerate. This is not consistent with our molecular orbital picture for butadiene, which predicts that the two pairs of π electrons are of different energy.

3. Consider the molecule shown at right, dimethylvinylborane:

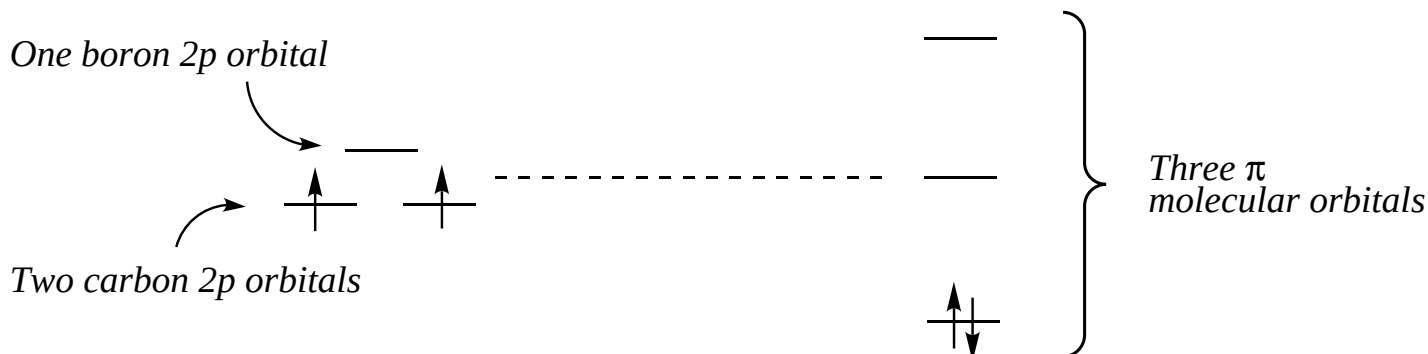


a. What reasonable resonance structure(s) can you draw, if any?



Boron only has three electrons available for bonding, and all three are already in use in the three σ bonds. If the boron is sp^2 hybridized, there is an empty p orbital left over for conjugation with the double bond.

b. Starting from the relevant atomic orbitals, construct molecular orbitals (as we have done in class) that best match your answer to part a.

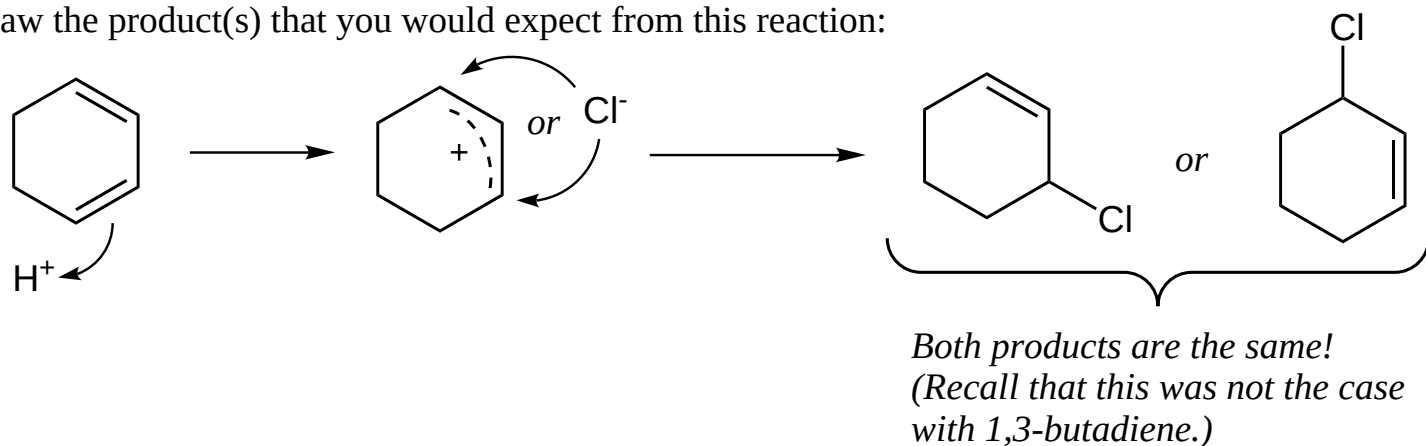


c. The electronic structure of dimethylvinylborane most closely resembles that of which of the following: allyl cation; allyl radical; allyl anion; none of the above?

The allyl cation. An atom with an empty p orbital directly bonded to a π bond. As with methylvinyl ether, the overlap is not as good when different atoms are mixed.

4. You are a brilliant organic chemist, and you have just developed the theory of delocalization in 1,3-dienes. You decide to try to prove your theory to your disbelieving colleagues by reacting 1,3-butadiene with HCl. Unfortunately, the only diene you have available is 1,3-cyclohexadiene.

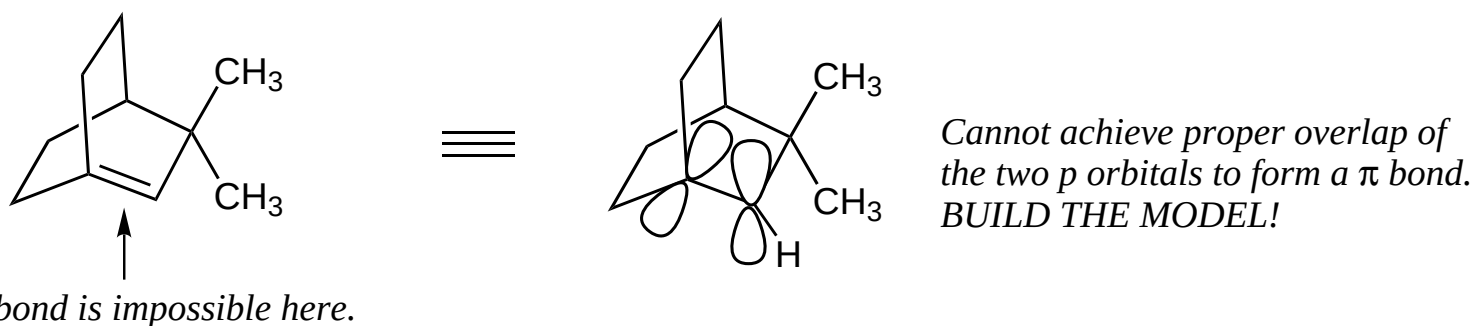
a. Draw the product(s) that you would expect from this reaction:



b. Can you prove your theory rigorously with this diene?

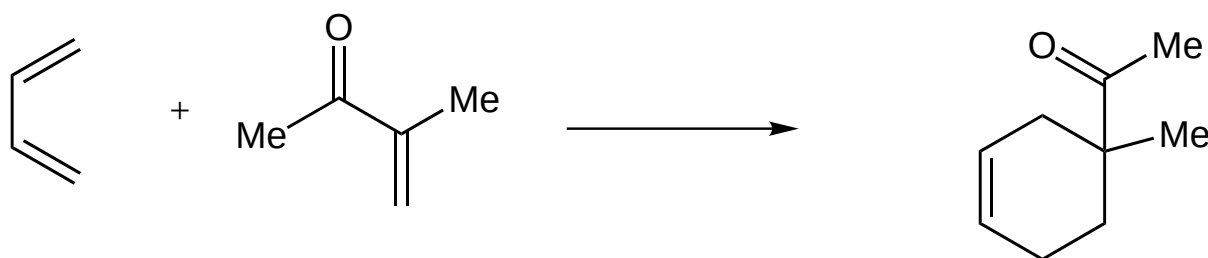
No. With 1,3-butadiene, a product is observed that is inconsistent with viewing 1,3-butadiene as two connected but non-interacting double bonds. However, with 1,3-cyclohexadiene, there is only one product observed, and its formation could be consistent with either theory.

5. When treated with base, the bicyclic alkyl bromide shown below does *not* undergo E2 elimination. Why not? (Models will be helpful here....)

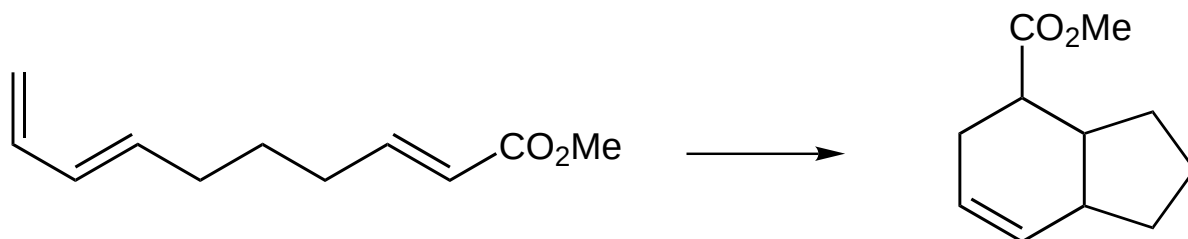


6. Predict the major product of the following Diels-Alder reactions:

a.



b.



c.

