Assignment

**Modeling reminder** – Whenever an assignment asks you to use a molecular model, use a model with an optimized geometry. If your molecule is a stable compound or reaction intermediate, calculate its **equilibrium geometry**. If your molecule is a transition state, calculate its **transition state geometry**.

1. Build HF/3-21G(*) models of the following molecules and obtain their frontier MO energies.

![Dienes and Dienophiles](image)

Within each set, use your frontier MO energies to predict the relative reactivity of these molecules in a:

a. *normal* Diels-Alder reaction
b. *inverse electron demand* Diels-Alder reaction

Are there any surprises? Explain.

2. Ethylene might react with allyl anion and cation to form cyclopentyl anion and cation, respectively (* = – and +):

![Reaction](image)

One of these reactions should be an allowed concerted cycloaddition. The other should be a forbidden **concerted** reaction, and should proceed by a **stepwise** mechanism instead.

The following questions ask you to address this problem using a) orbital symmetry conservation principles, and b) frontier MO theory.

a. What symmetry operation is conserved during a concerted addition? (Assume a least-motion, high symmetry reaction coordinate.)

b. Use this symmetry operation to draw an orbital symmetry correlation diagram for the cycloaddition reaction. Your diagram should include the following: *(over)*

   i. Drawings of the 5 reactant MO (3 from allyl, 2 from ethylene)
ii. Drawings of the 5 product MO ($4 \sigma/\sigma^*$ and 1 $p$-type orbital)

iii. Correct relative energies for the MO (note: one allyl orbital is nonbonding and an isolated $p$-type orbital is nonbonding)

iv. Symmetry labels for all of the orbitals

v. Correlation lines

c. Allyl anion will populate more orbitals with electrons than allyl cation. Use this fact to predict which reaction is allowed as a concerted reaction.

d. Draw the frontier MO of ethylene, allyl anion, and allyl cation (use HF/3-21G(*) models). Provide MO energies (in eV).

e. Identify the most important donor-acceptor MO interaction for ethylene + allyl anion, and for ethylene + allyl cation

f. Draw the interacting frontier MO at the transition state geometry. Use your drawings to predict the degree of MO overlap (large, small, zero) and then to predict whether the cycloaddition is an allowed concerted reaction.

g. Do both methods of analysis give the same prediction?

3.

Draw plausible mechanisms for the reactions shown below. As usual, draw the reactant(s) and product(s) of all elementary steps and draw curved arrows. *Hint:* Every mechanism involves a Diels-Alder cycloaddition.

Predict the stereochemistry of each product. *Hint:* Some conclusions can be reached by thinking about the stereospecific nature of concerted cycloadditions. Beyond this, try assuming the preferred product is the one that is least strained, and build a model of each possible product stereoisomer to evaluate its strain energy (minimize button).