Problem Set #3

Molecular Orbital Theory and Pericyclic Reactions

DUE DATE: Thursday, October 16, 2003 at 12 noon


3. Using retrosynthetic analysis, propose a synthesis of each of the molecules below using a Diels-Alder reaction in each case. Starting with the Diels-Alder reaction you decide to use, write your synthesis in the “forward” direction, showing all steps and reagents necessary.

4. Base-promoted elimination of 7-bromo-2,4-cycloheptadien-1-one provides cycloheptatrienone as expected, but in the five-membered ring series, only a “dimeric” product is obtained. Explain.

5. Compound A undergoes a ring-opening reaction when heated at 100 °C, but no reaction occurs when C is subjected to the same conditions. Suggest a mechanism for the conversion of A to B, identify the type of reaction involved, and explain why C does not undergo a similar transformation.
6. Name the type of pericyclic reaction involved in each of the following reactions. Classify each according to the Woodward-Hoffmann rules. That is, indicate how many electrons are involved in each case and comment on the stereochemical course of the reaction where relevant.

(a) \[ \text{Reaction} \rightarrow \text{Product} \]

(b) \[ \text{Reaction} \rightarrow \text{Product} \]

(c) \[ \text{Reaction} \rightarrow \text{Product} \]

(d) \[ \text{Reaction} \rightarrow \text{Product} \]

(e) \[ \text{Reaction} \rightarrow \text{Product} \]

(f) \[ \text{Reaction} \rightarrow \text{Product} \]

7. Propose a synthesis of D from 2,6-dimethylphenol, iodomethane, and trans-1-bromo-2-butene. Use any inorganic reagents (e.g. acids, bases, Lewis acids, etc.) necessary, but no other carbon-containing compounds. Write your synthesis in the forward direction, and show arrow-pushing mechanisms for each step.