Massachusetts Institute of Technology

Organic Chemistry 5.13

October 8, 2003
Prof. Timothy F. Jamison

Problem Set #3

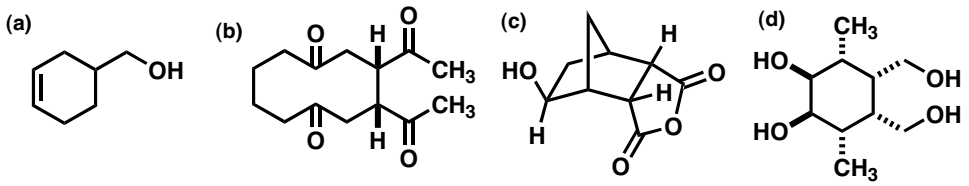
Molecular Orbital Theory and Pericyclic Reactions

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

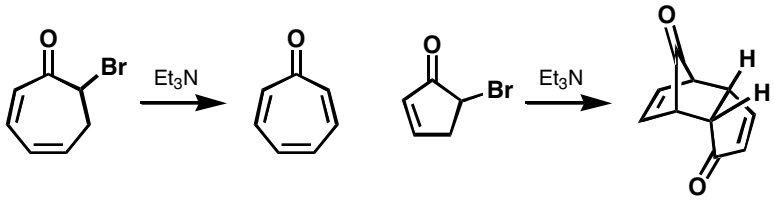
1. Problem 15-30, Wade, p. 676 (15-30, p. 687 in 4th edition)

2. Problem 15-33, Wade, p. 676 (15-33, p. 688 in 4th edition)

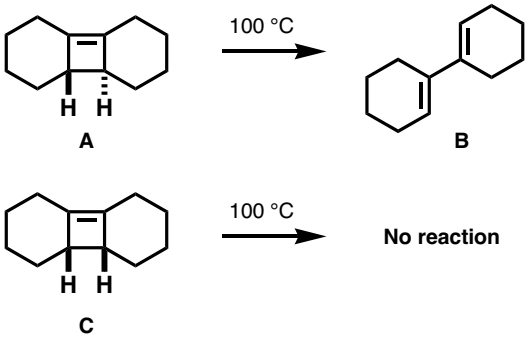
3. Using retrosynthetic analysis, propose a synthesis of each of the molecules below using a Diels-Alder reaction in each case. Starting with the Diels-Alder reaction you decide to use, write your synthesis in the "forward" direction, showing all steps and reagents necessary.



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.

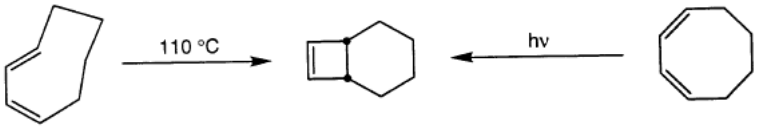


5. Compound **A** undergoes a ring-opening reaction when heated at 100 °C, but no reaction occurs when **C** is subjected to the same conditions. Suggest a mechanism for the conversion of **A** to **B**, identify the type of reaction involved, and explain why **C** does not undergo a similar transformation.

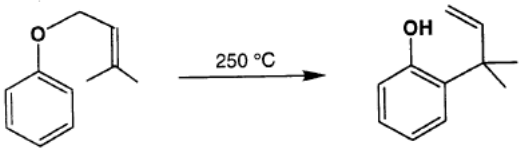


6. Name the type of pericyclic reaction involved in each of the following reactions. Classify each according to the Woodward-Hoffmann rules. That is, indicate how many electrons are involved in each case and comment on the stereochemical course of the reaction where relevant.

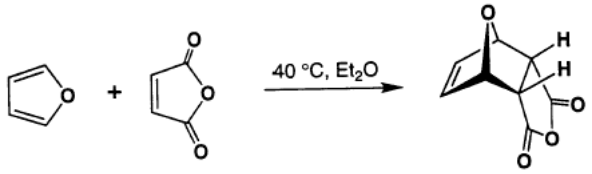
(a)



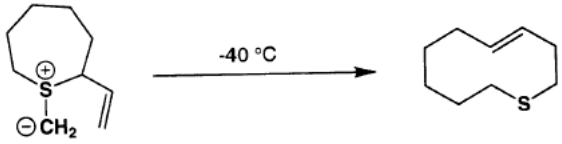
(b)



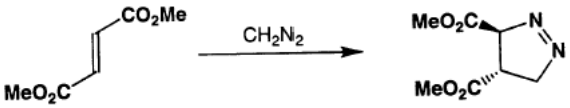
(c)



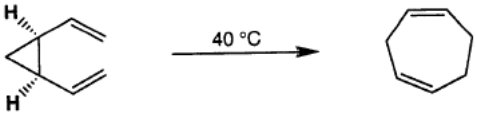
(d)



(e)



(f)



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.