


Massachusetts Institute of Technology  
Organic Chemistry 5.13

Friday, March 22, 2002

Prof. Timothy F. Jamison

Hour Exam #2

Name

 SOLUTIONS  
\_\_\_\_\_  
(please both print and sign your name)

Recitation Instructor \_\_\_\_\_

**Directions:** Closed book exam, no books, notebooks, notes, etc. allowed. However, calculators and molecular model sets are permitted.

Please read through the entire exam before beginning, in order to make sure that you have all the pages and in order to gauge the relative difficulty of each question. Budget your time accordingly.

**Show all of your work if you wish to receive partial credit.**

You should have 9 pages total: 7 exam pages including this page and 2 blank pages for scratchwork.

**Question:**

1. \_\_\_\_\_/ 24 points

2. \_\_\_\_\_/ 20 points

3. \_\_\_\_\_/ 30 points

4. \_\_\_\_\_/ 26 points

**Grader:**

\_\_\_\_\_

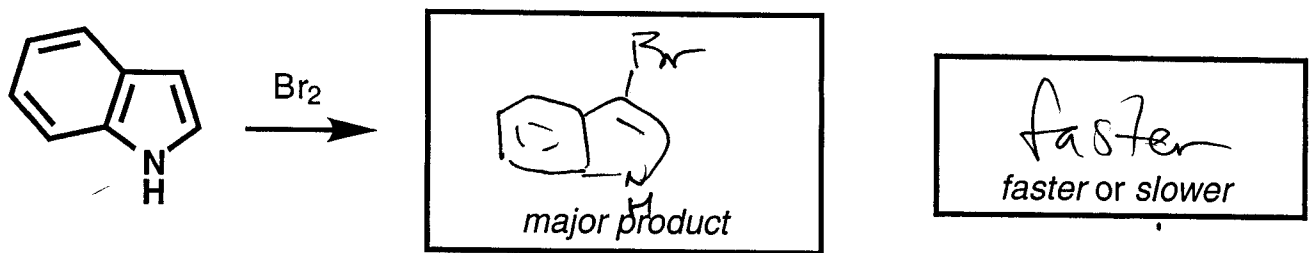
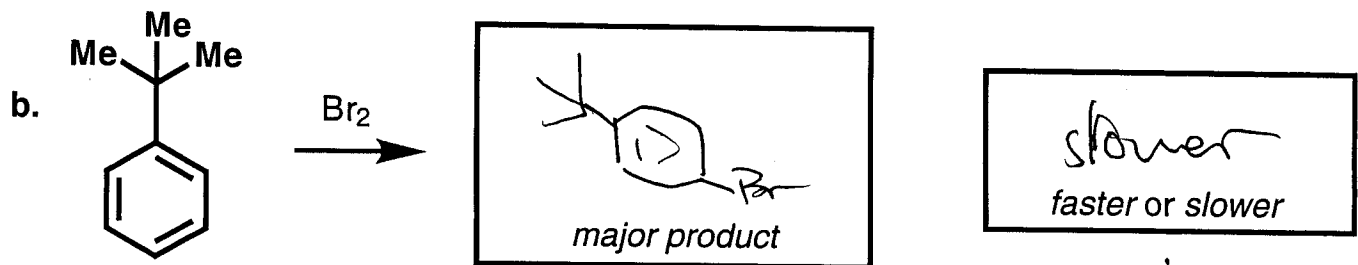
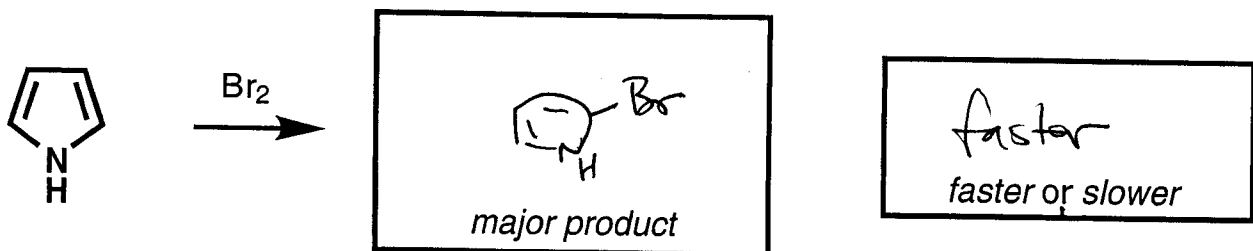
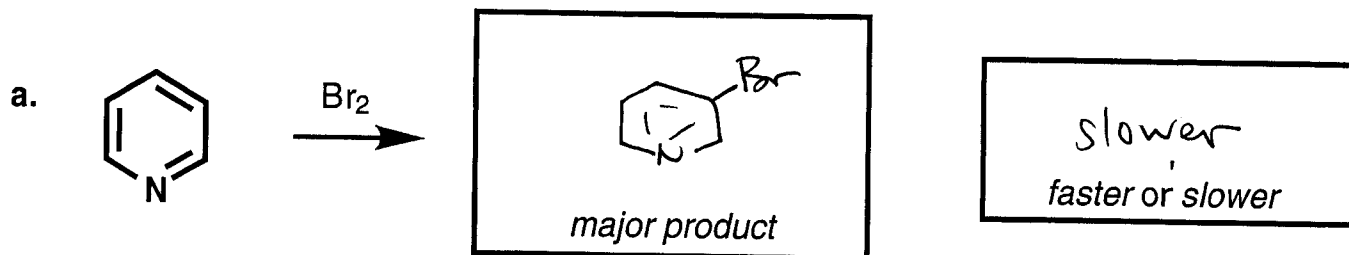
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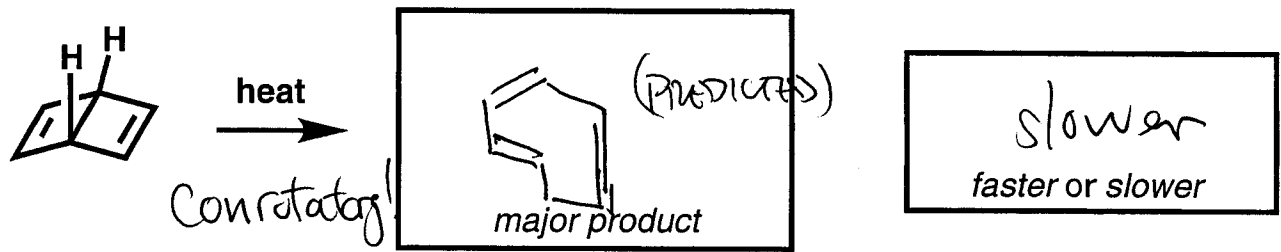
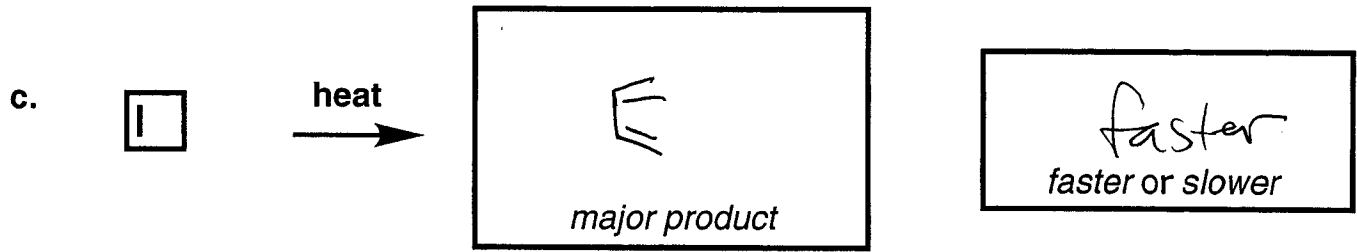
**Total:** \_\_\_\_\_/ 100 points

1. (24 points total) For all 8 reactions below, draw the structure of the **predicted major product**. Obey the Woodward-Hoffmann rules where applicable! Clearly indicate **stereochemistry** where relevant. For each pair of reactions, indicate which you would expect to be the faster one and the slower one by writing "faster" or "slower" in the boxes provided.

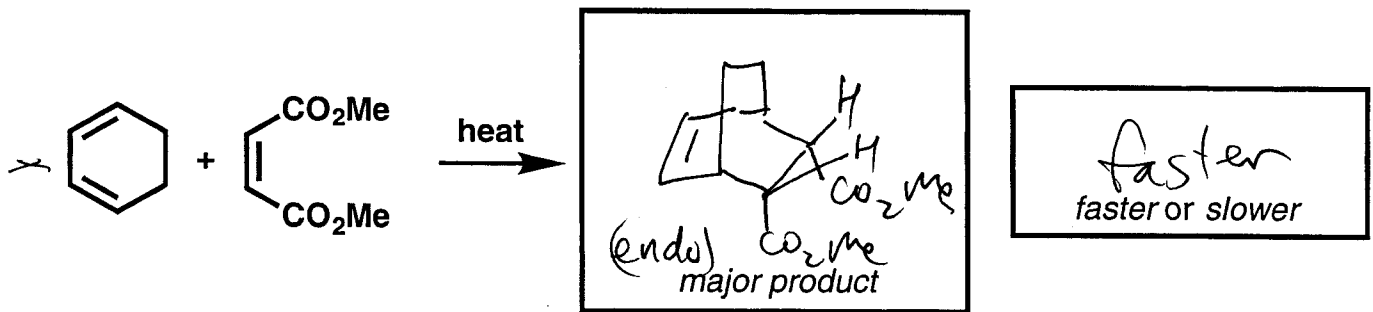
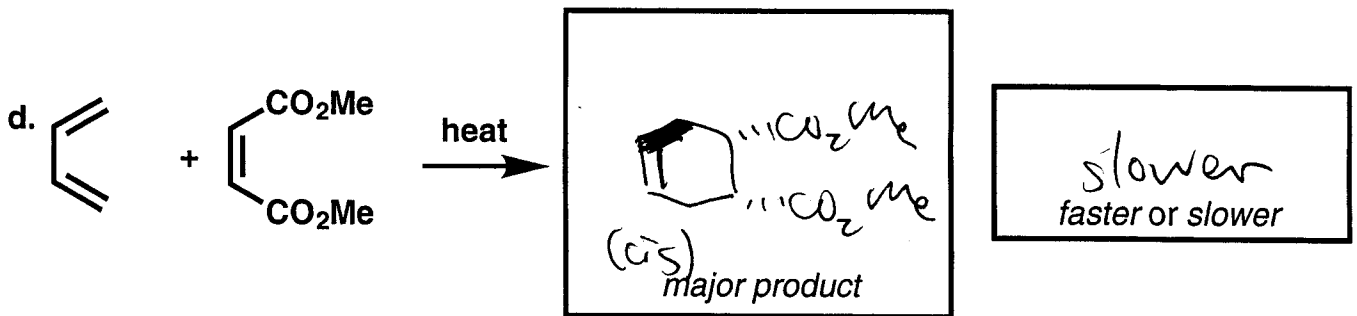


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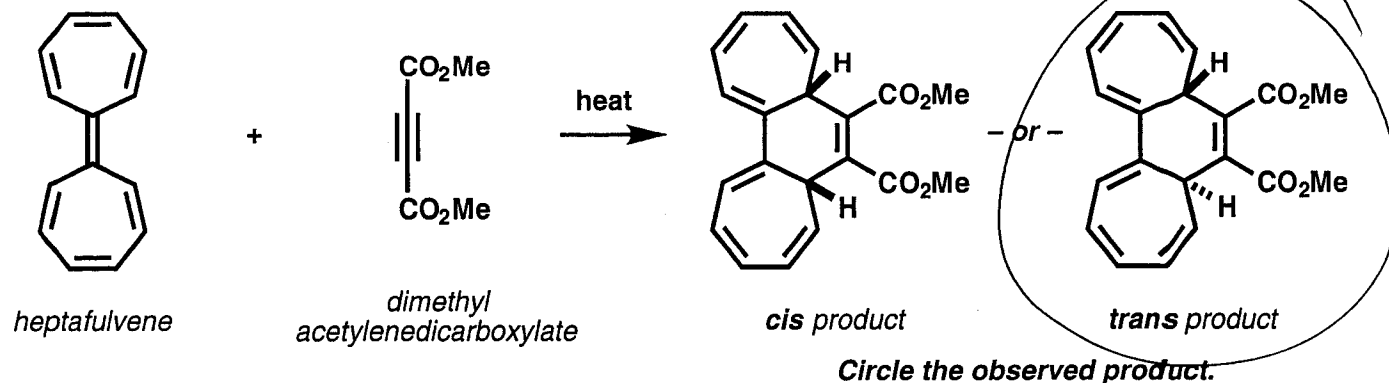
1. (Continued - see instructions on previous page)



(GIVES  BY DIFFERENT MECHANISM)



2. (20 points total) Like all cycloaddition reactions, the transformation below obeys the Woodward-Hoffmann rules.



a. (8 points) Classify the reaction above according to the Woodward-Hoffmann rules by filling in the 4 blanks below.



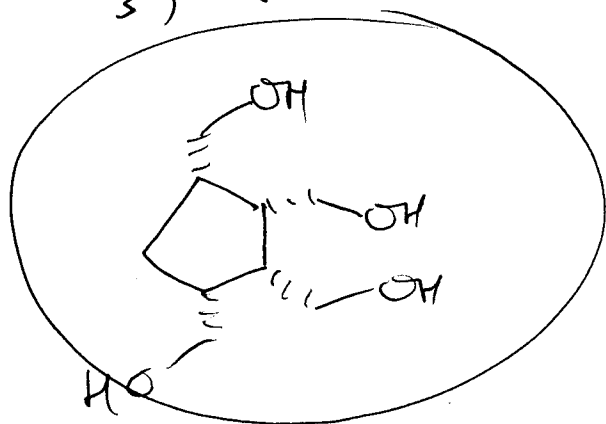
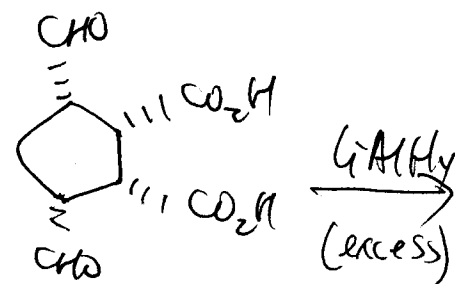
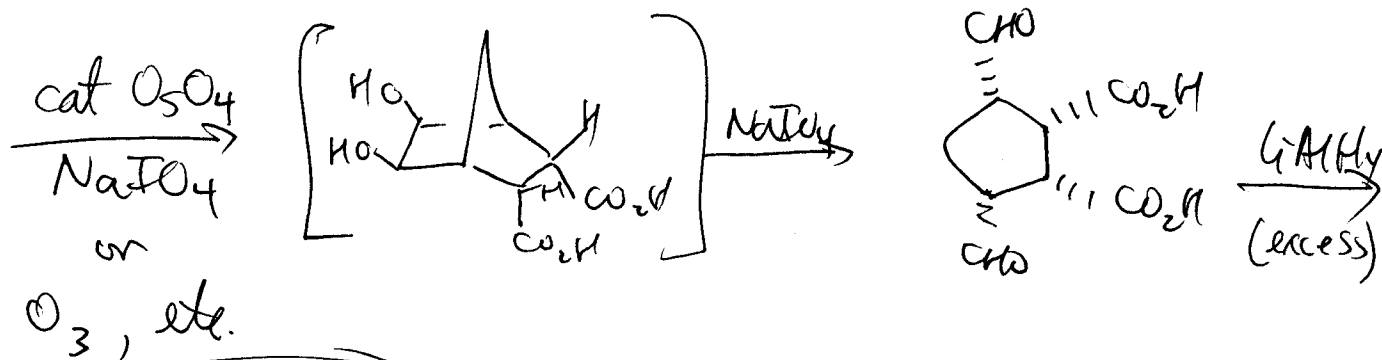
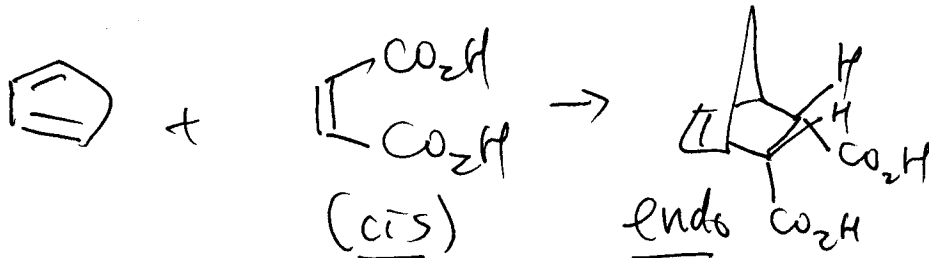
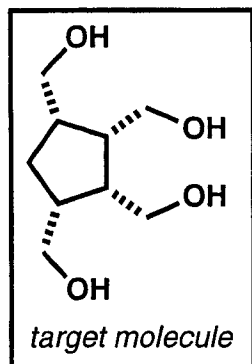
b. (8 points) Circle the observed product above and briefly explain your choice in the space below.

antarafacial w.r.t. heptafulvene

c. (4 points) Is the product observed in the reaction above chiral or achiral? Explain briefly.

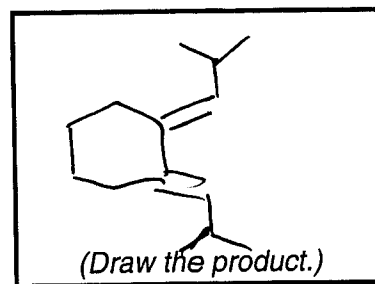
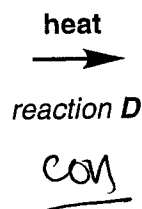
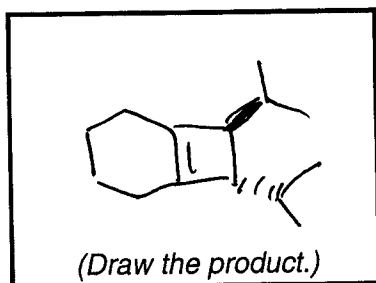
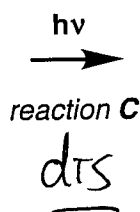
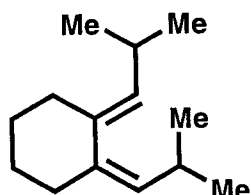
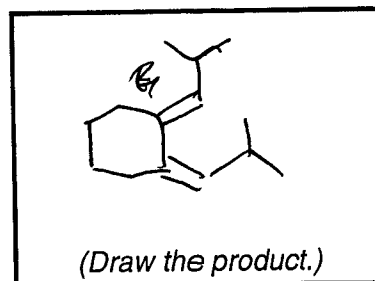
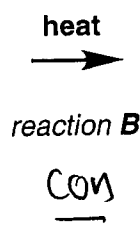
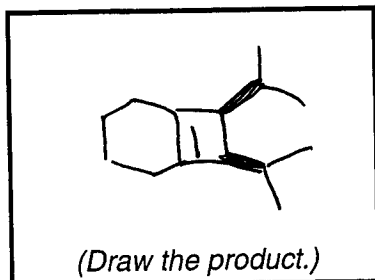
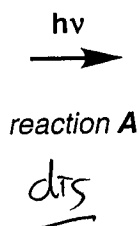
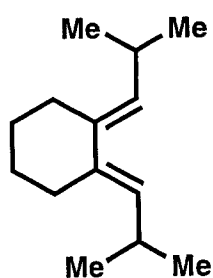
chiral ( $C_2$  AXIS OF SYMMETRY)

3. (30 points) In the space provided, propose an efficient synthetic route to the target molecule shown in the box from **cyclopentadiene** and a **dicarboxylic acid**. Assume that your "stockroom" of available reagents includes **any inorganic compounds**. Your synthesis should provide a way to control the **relative stereochemistry** of the target molecule. Write your synthesis in the **forward direction**, showing all necessary reagents and relevant reaction conditions for each step.



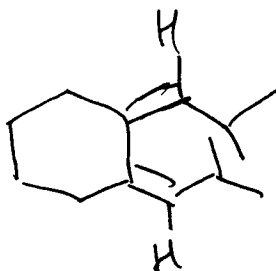
4. (26 points total)

a. (16 points) Draw the products of all reactions **A-D** shown below in the boxes provided. **Clearly** indicate **relative stereochemistry**, where applicable. (If the product of a given reaction is chiral, you need draw only one of the two possible enantiomers.)



b. (10 points) In one of the 4 reactions above, **2 products** that are **not enantiomeric to one another** are allowed by the Woodward-Hoffmann rules. Which reaction is it (i.e. **A**, **B**, **C**, or **D**)? Draw the structure of the product **not** formed and briefly explain why it is not observed, even though the Woodward-Hoffmann rules do not exclude the possibility of its formation.

(D)



NOT OBSERVED

DUE TO SEVERE STERIC  
 INTERACTION IN T.S.

LEADING TO THIS COMPOUND.