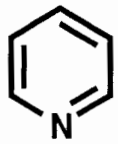
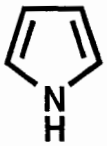
1. **(24 points total)** For all 8 reactions below, draw the structure of the **predicted major product**. Obey the Woodward-Hoffmann rules where applicable! Clearly indicate **stereochemistry** where relevant. For each pair of reactions, indicate which you would expect to be the faster one and the slower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

a.  Br_2 →

major product

slower

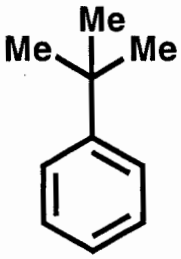
faster or slower

 Br_2 →

major product

faster

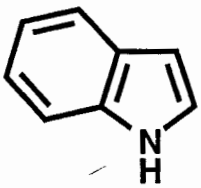
faster or slower

b.  Br_2 →

major product

slower

faster or slower

 Br_2 →

major product

faster

faster or slower

Continued on next page

1. (**Continued** - see instructions on previous page)

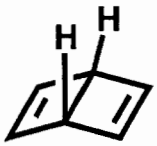
c.

heat →

major product

faster

faster or slower



heat →

Conrotatory

(PREDICTED)

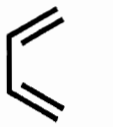
major product

slower

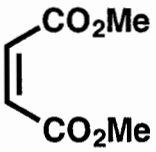
faster or slower

(GOES BY DIFFERENT MECHANISM)

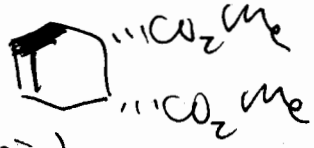
d.



+



heat →

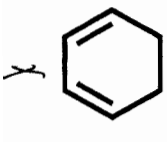


(cis)

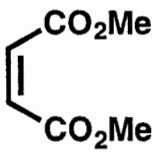
major product

slower

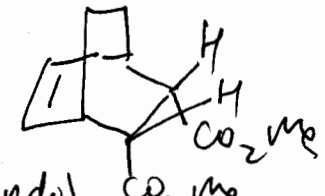
faster or slower



+



heat →



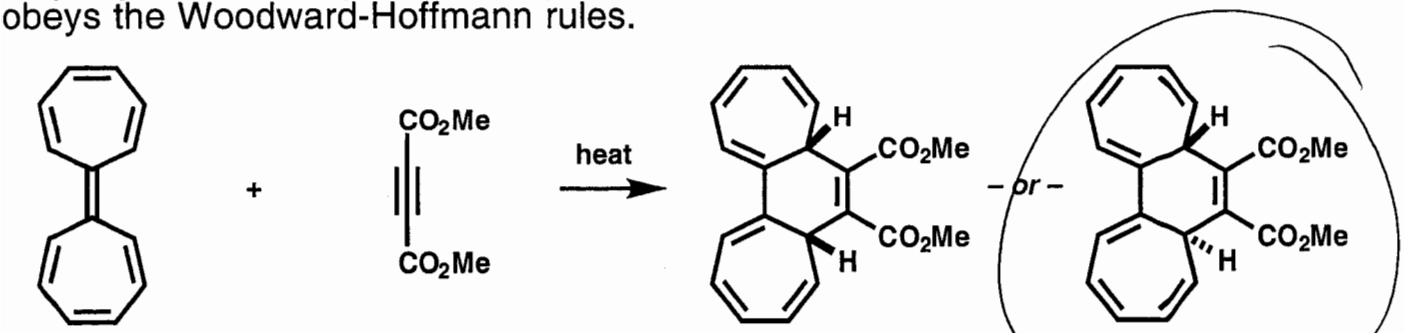
(endo)

major product

faster

faster or slower

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



heptafulvene + *dimethyl acetylenedicarboxylate* → ***cis*** *product* – *or* – ***trans*** *product*

Circle the observed product.

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

$$\left[\pi \ \underline{14} \ \underline{a} + \pi \ \underline{2} \ \underline{s}\right]$$

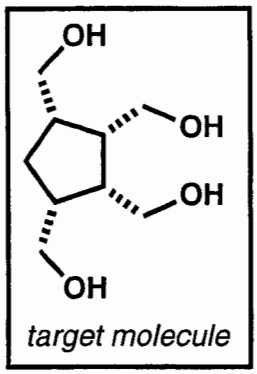
b. (8 points) Circle the observed product **above** and briefly **explain your choice** in the space **below**.

antarafacial w.r.t. heptafulvene

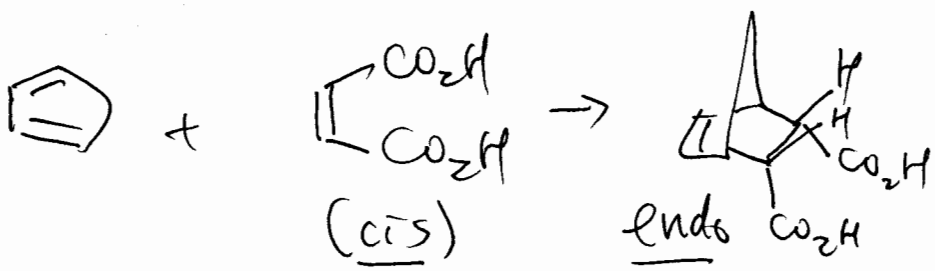
c. (4 points) Is the product observed in the reaction above **chiral** or **achiral**? Explain briefly.

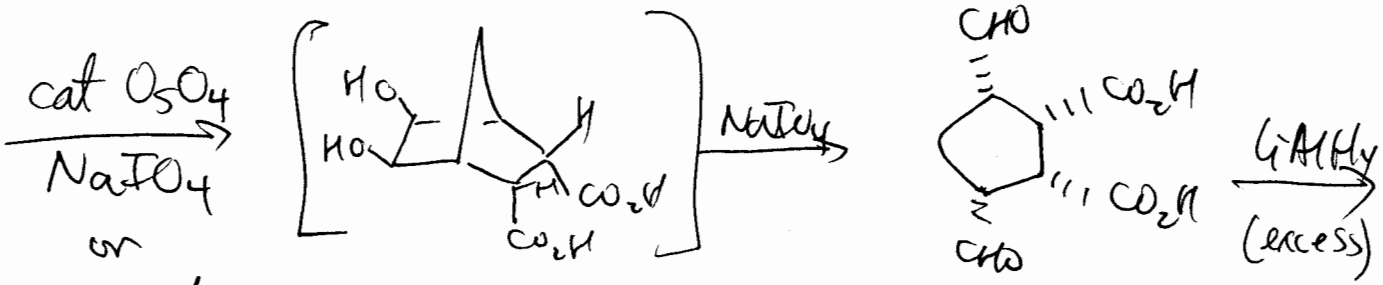
Chiral (C_2 AXIS OF SYMMETRY)

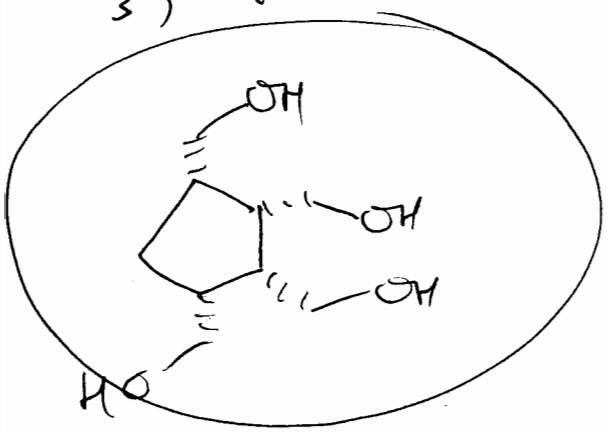
3. (30 points) In the space provided, propose an efficient synthetic route to the *target molecule* shown in the box from **cyclopentadiene** and a **dicarboxylic acid**. Assume that your "stockroom" of available reagents includes **any inorganic compounds**. Your synthesis should provide a way to control 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.



target molecule

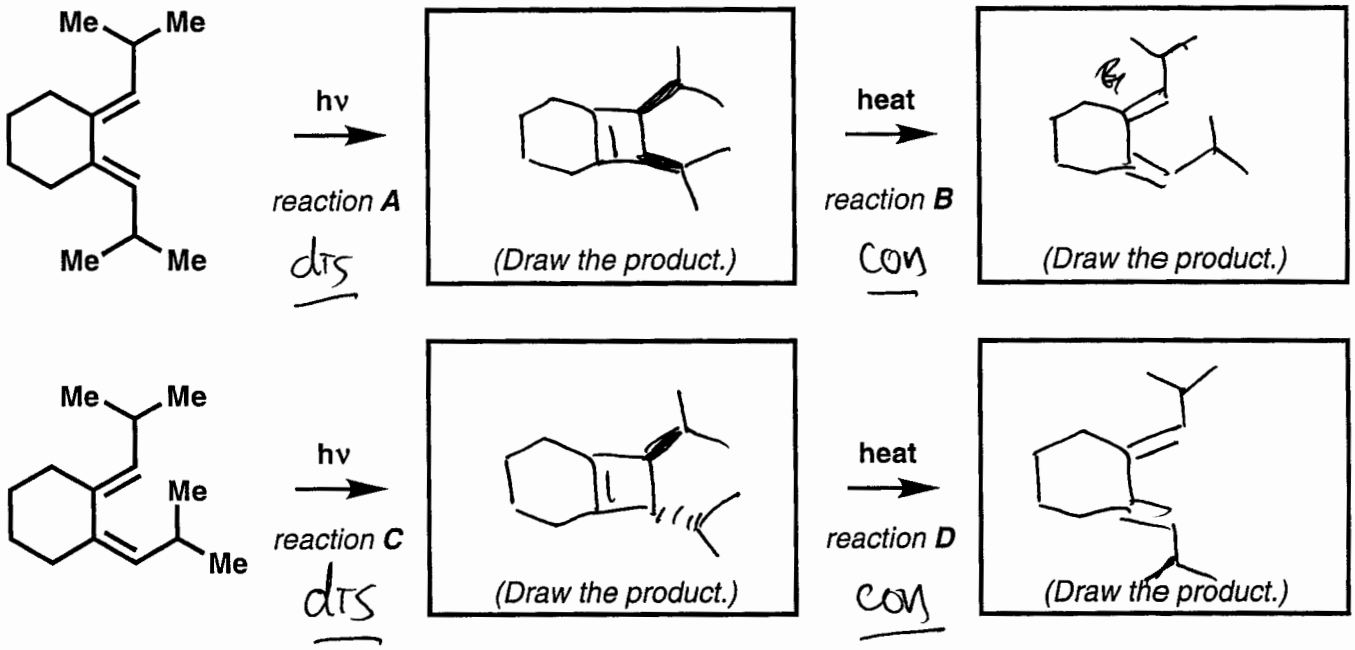






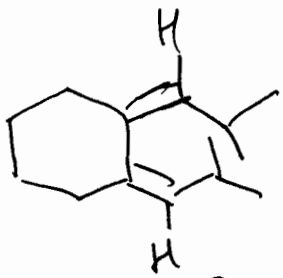
4. (26 points total)

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.