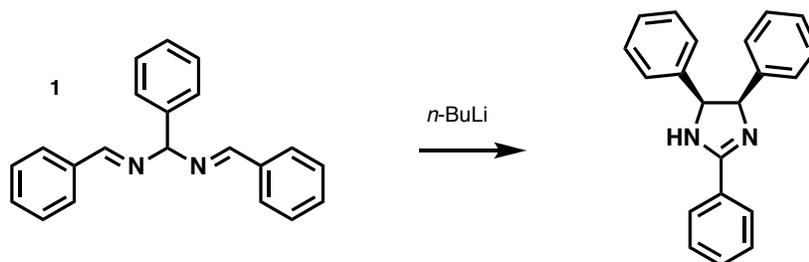


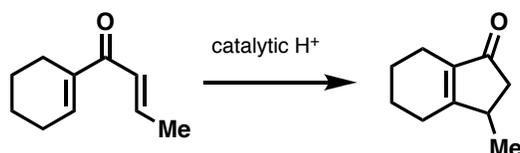
Problem Set #4

Due Friday, October 20, 12:05 p.m., in lecture (before lecture)

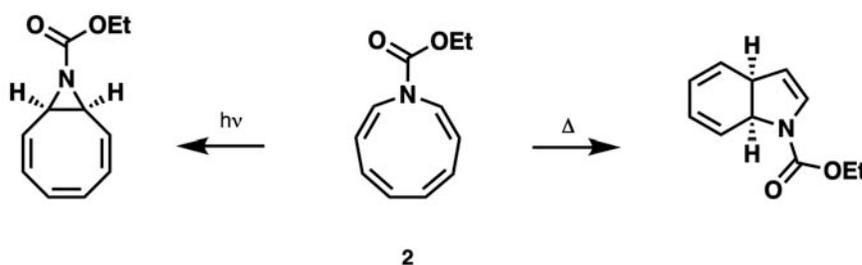
1. Treatment of compound **1** below with a strong base (e.g., *n*-BuLi) gives a heterocycle with a 5-membered ring treatment with a weak acid (work-up). Account for the relative stereochemistry observed in the product.



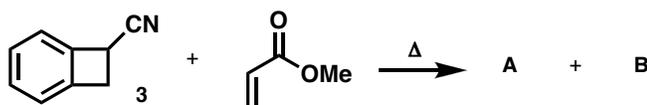
2. Propose a mechanism for the reaction below that involves a thermal 4π electrocyclic ring closure. Clearly indicate the relative stereochemistry in all intermediates.



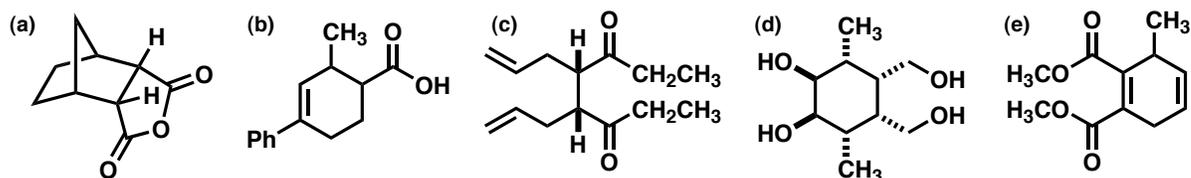
3. Based on the photochemical and thermal electrocyclic reactions of compound **2** below, comment on the nature of the π system in its 9-membered ring. Account for the relative stereochemistry observed in each of the two reactions.



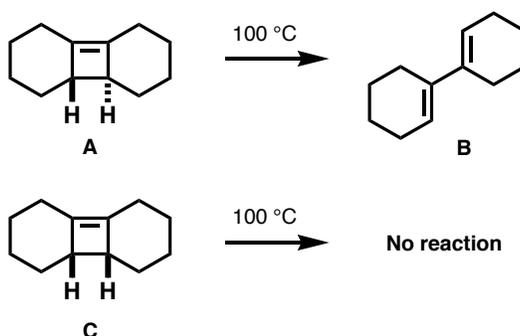
4. Heating compound **3** below at reflux in toluene in the presence of methyl acrylate affords two products, **A** and **B** in a 1:1 ratio of **diastereomers**. With a catalytic amount of base, **A** is converted to **B**. What are the structures of **A** and **B**? **Clearly** indicate the **relative stereochemistry** in each. Hint: A Diels-Alder reaction is involved in part of the mechanism.



5. Using retrosynthetic analysis, propose a synthesis of the five 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.



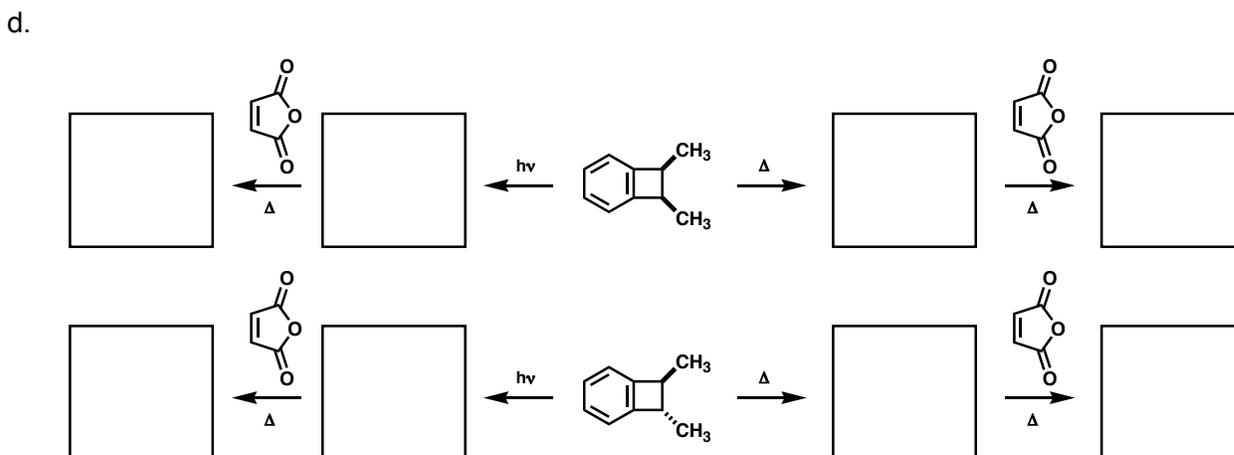
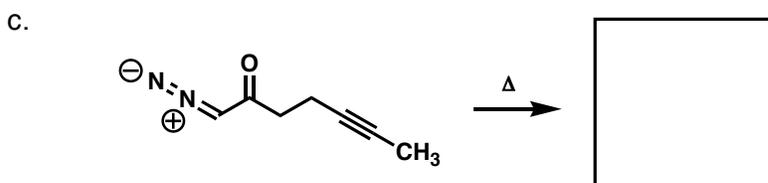
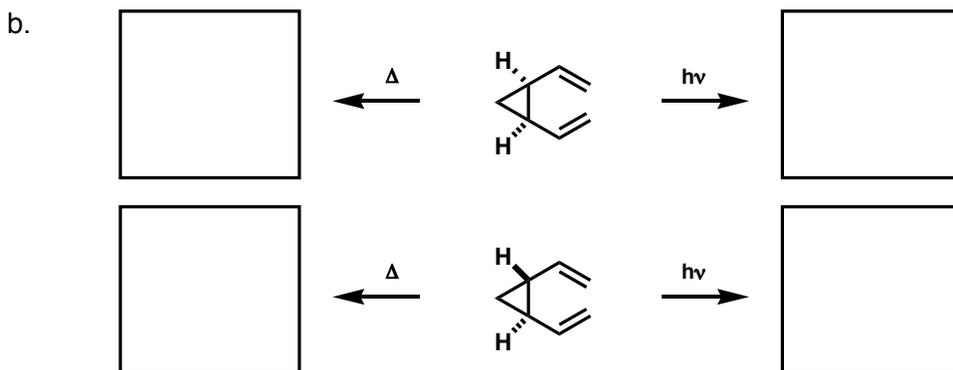
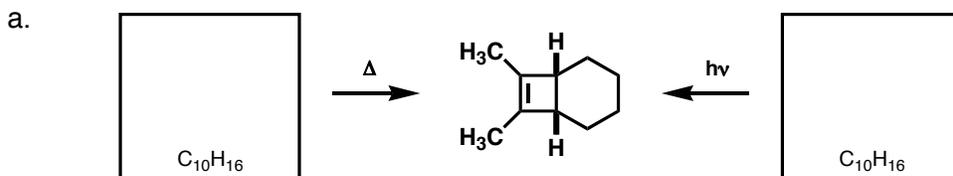
6. Compound **A** undergoes a ring-opening reaction when heated at 100 °C, but no reaction occurs when **C** is subjected to the same conditions. Suggest a mechanism for the conversion of **A** to **B**, identify the type of reaction involved, and explain why **C** does not undergo a similar transformation.

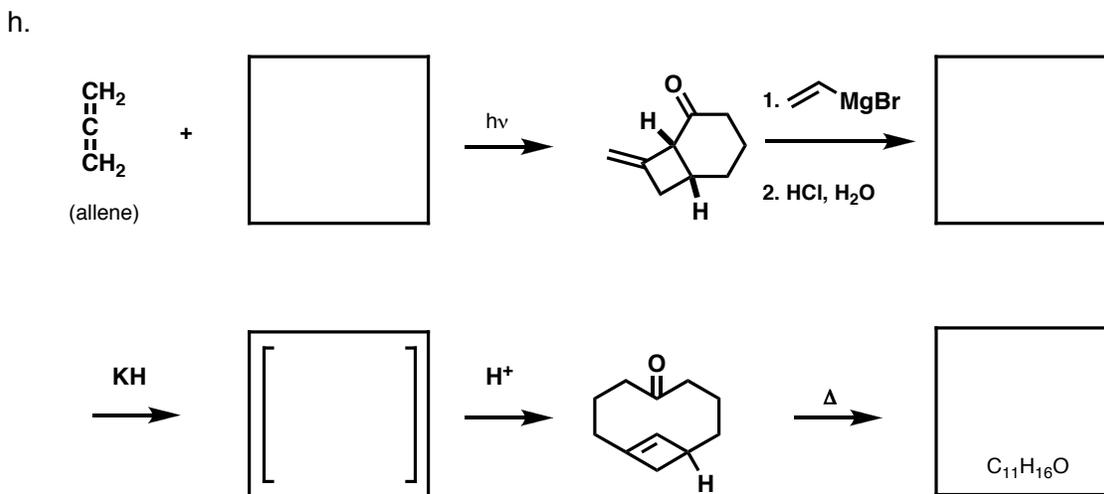
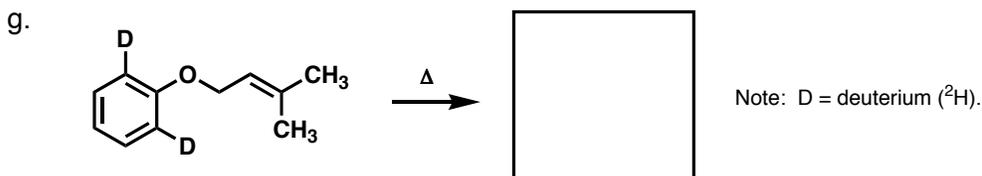
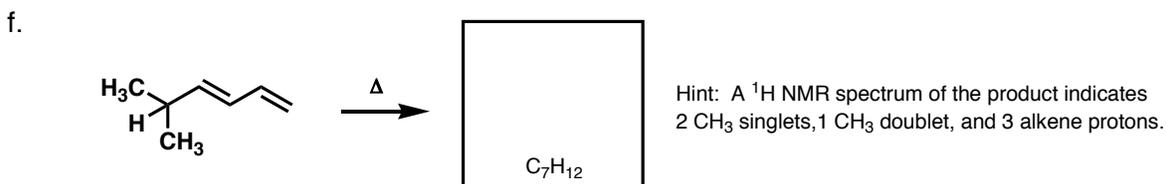
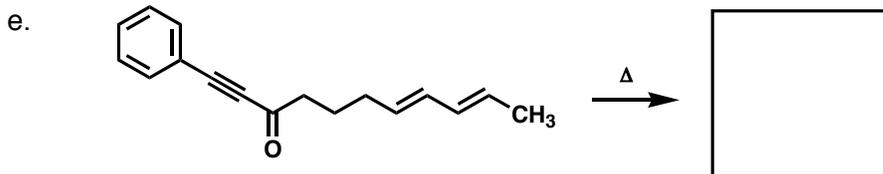


Practice Problems for Exam 2. (You do not need to turn these in with your problem set.) Some of the following problems cover material that we will not have covered by the time Problem Set 4 is due. Not all of the problems on the exam will be like this, but they are representative of some of the ones you might encounter.

For each of the following problems:

- Fill in the boxes with the predicted product or necessary starting material. Indicate relative stereochemistry and/or double bond geometry, where appropriate. If no reaction occurs, write "no reaction" and skip parts ii. and iii.
- Classify each pericyclic reaction according to the Woodward-Hoffmann rules ($[\pi 4s + \pi 2s]$ cycloaddition, e.g.).





Note: The brackets indicate that the product of the reaction with potassium hydride is not isolated, but rather rapidly converted to the next structure after treatment with acid.

Note: A ^{13}C NMR spectrum of this compound shows 11 signals: one at 208.2 ppm, 4 between 100 and 150 ppm, and 6 between 10 and 50 ppm.