

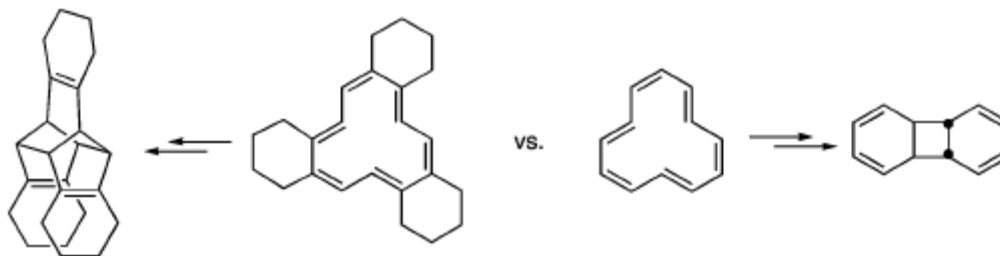
## Ground Rules

You may refer to your lecture notes, papers that we have read, any handouts that I have provided, and previous homeworks. Do not consult anything or anyone else. You will need access to the computer lab for problem #3. You may start on the exam when you receive it, and you may work on it as often and as much as you like. Please label your answers clearly so that I can connect them directly to my questions.

**Due: Monday, April 27, 4 pm, my office or mailbox**

## Problems

The abstract of a 2008 paper contrasted two different products obtained from [12]annulenes as follows:



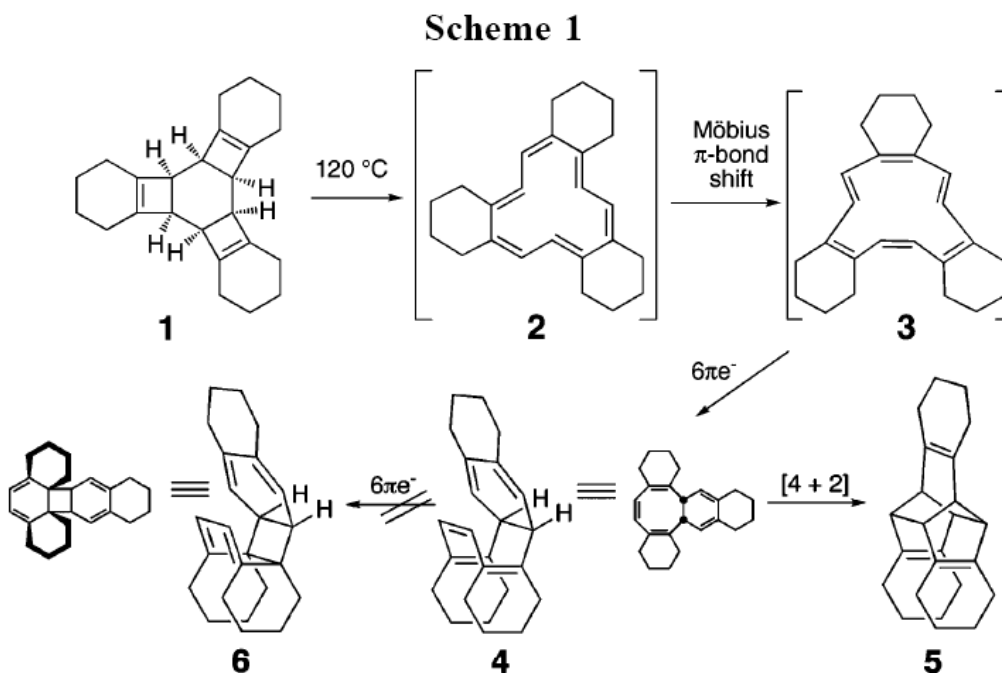
It is believed that each transformation involves a multi-step mechanism that features several pericyclic steps. Of special interest to these authors was the possibility of something that we have *not* studied, a so-called Möbius  $\pi$ -bond shift.<sup>1</sup>

I have duplicated each of the proposed mechanisms on the following page. Your task is to identify all of the pericyclic steps in each mechanism (ignore the Möbius  $\pi$ -bond shift) and describe these steps as completely as you can. “Describe,” of course, includes all of the things that we have been practicing:

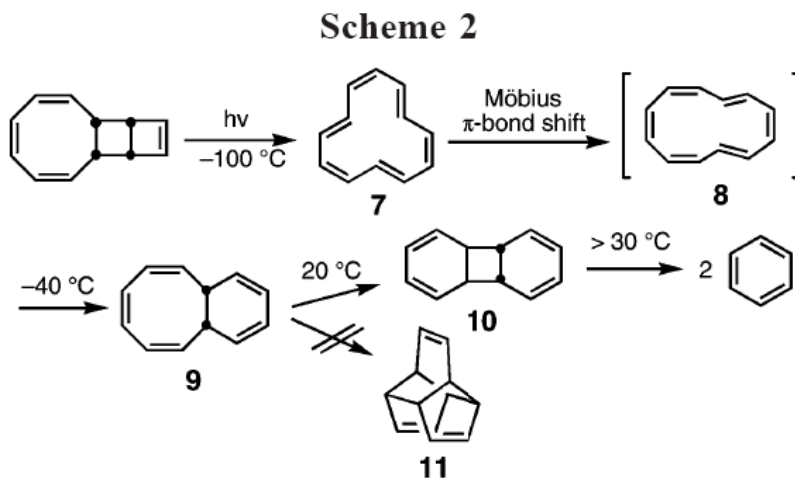
- Curved arrow drawing
- Type of pericyclic (cycloaddition, sigmatropic rearrangement, electrocyclization)
- Appropriate labels
- Analysis of transition state orbital array (include a drawing of orbital array)
- Allow or forbidden under the reaction conditions

<sup>1</sup> For more information on Möbius  $\pi$ -bond shifts in annulenes, see J. F. Moll *et al.*, *JACS*, **2007**, *129* (2), 274-275, DOI: 10.1021/ja0678469

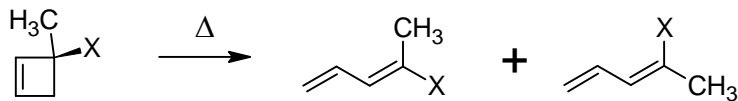
1. Analyze **Scheme 1** according to the instructions provided on the first page. Note: **1**  $\rightarrow$  **2** might occur in a single step as shown, or it might involve a three-step sequence. Analyze both possibilities.



2. Analyze **Scheme 2** according to the instructions provided on the first page. To avoid unnecessary duplication of effort, if any step in Scheme 2 can be described in exactly the same way as a step in Scheme 1, just identify the corresponding step in Scheme 1. Note: **7**  $\rightarrow$  **10** v. **11** is what concerns the authors, but you should also consider the reaction that forms **7**.



3. Build and use HF/3-21G models to evaluate the effect of fluorine on torquoselectivity for the following reaction. In order to save time, do not bother making ZPE or other energy corrections.



- What is the kinetic product when  $\text{X} = \text{F}$ ? What is  $\Delta(\Delta E^\ddagger)$ ?
- What effect does F have on the energy barrier, i.e., compare  $\Delta E^\ddagger$  for  $\text{X} = \text{H}$  and  $\text{X} = \text{F}$ .
- Which group should experience greater steric repulsion when it rotates inward,  $\text{CH}_3$  or F? Describe the basis for your conclusion.

d. **Email all models to me.**