

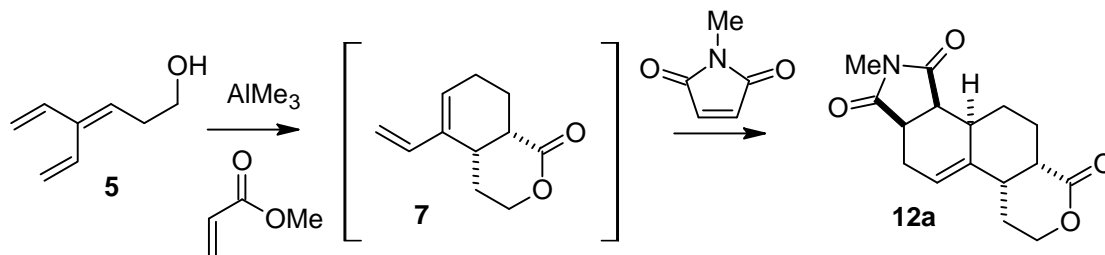
Ground Rules

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 #2, part c. 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: Saturday, March 8, 3 pm, my office or mailbox

Problems

1. The sequential double Diels-Alder reaction **5** \rightarrow **12a** occurs in 81% yield, $dr = 7:1$. The experiment is performed in the following way: **5** and methyl acrylate and AlMe_3 are combined to produce **7** (Diels-Alder precedes lactone formation), then *N*-methyl maleimide is added to the solution containing **7** to form **12a**.



a. AlMe_3 binds to one of the starting materials prior to the Diels-Alder. Draw this adduct and explain how binding changes the starting material's reactivity.

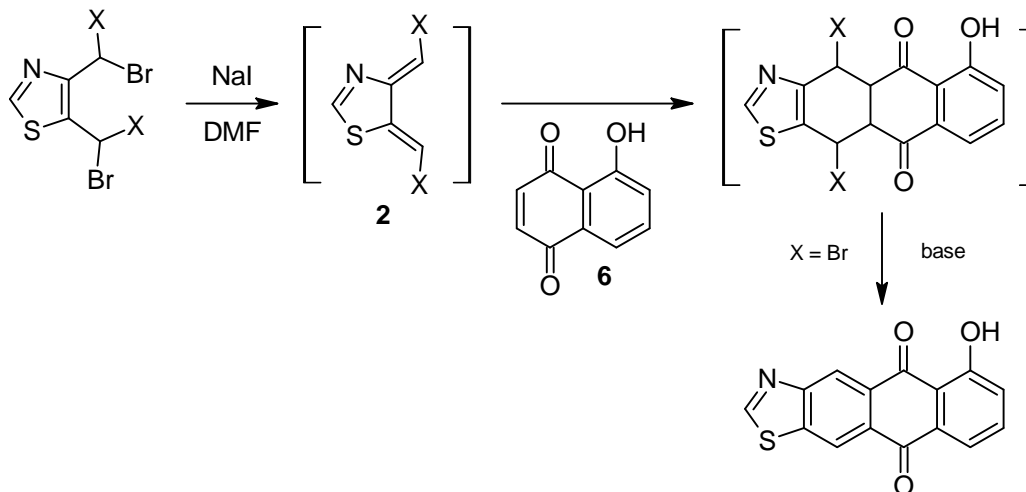
b. Assuming compound **7** is the only product from the first step, draw the two isomers that are being compared by *dr*.

c. Describe each addition as “*endo*-selective” or “*exo*-selective” and draw the minor stereoisomer in each case.

d. What other kinds of selectivity are demonstrated by these Diels-Alder additions, that is, other than *endo/exo* selectivity? Where possible, clarify your answer by drawing a minor product. (Hint: this question is a little tricky.)

e. Briefly, how do you account for each kind of selectivity listed in part d? (Note: you don't have to give me a complicated theory if a simple “rule” will do.)

2. Treatment of the starting material shown below with sodium iodide gives an unstable intermediate, compound **2**, which can be trapped by a Diels-Alder addition with a reactive dienophile, compound **6**. When X = Br, the adduct is unstable and two polycyclic aromatic compounds are isolated (only one is shown).



- Draw the second polycyclic aromatic that is obtained.
- Draw a detailed mechanism for the entire sequence for the case of X = Br. Include curved arrows and relevant symbols wherever they are needed.
- Perform a Frontier MO analysis of the cycloaddition for the case of X = H using HF/3-21G models. Describe your procedure, observations, and conclusions. Also, **email your models of compounds 2 & 6 to me**. I will be looking for an accurate procedure, a complete set of observations, and a comprehensible description of how you moved from observation to conclusion.