

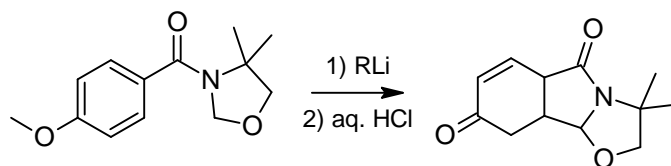
Ground Rules

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 #4. 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.

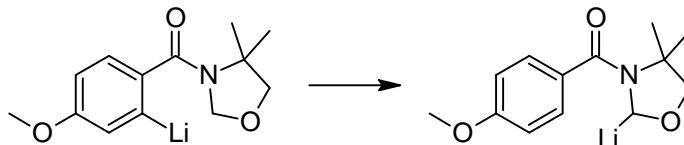
Due: Monday, April 28, 3 pm, my office or mailbox

Problems

1. A recent paper reported the following transformation.



The authors proposed a mechanism involving lithiation of the aromatic ring *ortho* to the carbonyl group followed by proton transfer between rings (below) and subsequent pericyclic formation of the 5-membered ring (not shown).

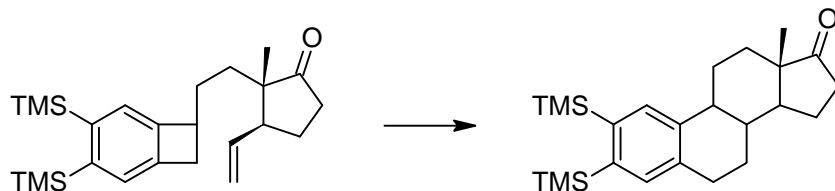


b. Draw the pericyclic reaction using curved arrows.

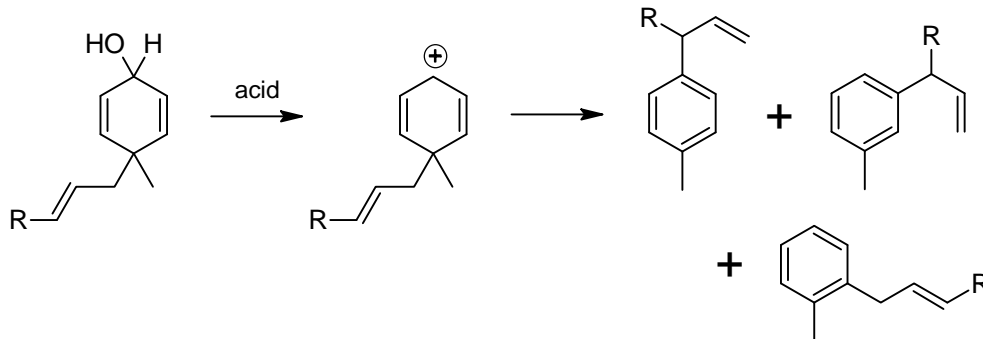
c. What must the product's stereochemistry be if the pericyclic reaction is allowed? Provide a full justification for your answer.

d. Draw a detailed mechanism for the acid-promoted steps following the pericyclic reaction.

2. Draw a mechanism for the following reaction. If pericyclic steps are involved, provide appropriate labeling.



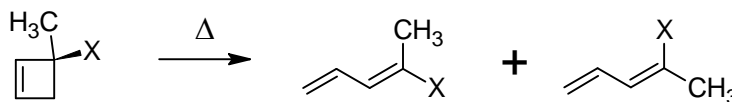
3. A textbook I like describes the following acid-catalyzed transformations:



a. Assuming each product results from a single carbocation rearrangement and deprotonation, draw all of the required two-step mechanisms.

b. Provide appropriate labeling for the carbocation rearrangements: order, geometry, and allowed/forbidden.

4. 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.



a. What is the kinetic product when X = F? What is $\Delta(\Delta E^\ddagger)$?

b. What effect does F have on the energy barrier, i.e., compare ΔE^\ddagger for X = H and X = F.

c. Which group should experience greater steric repulsion when it rotates inward, CH₃ or F? Describe the basis for your conclusion.

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