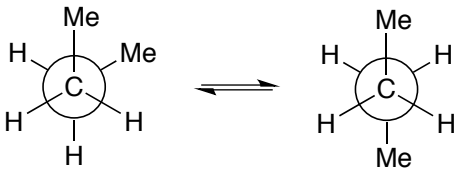
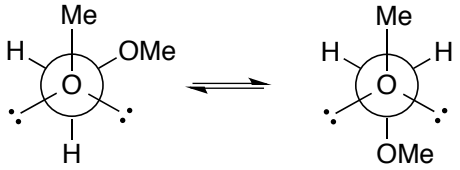
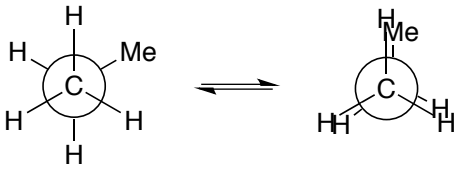
1. (10 points) Provide relative energies for the following equilibria. (The easiest way to do this is to assign "0" to the lower energy confomer, and indicate how much higher the other one(s) is/are (make sure your signs are right). Answers within about 30% of correct will be accepted.

(a) 

E_{rel} (kcal/mol) _____ _____

(b) 

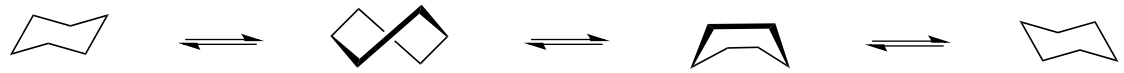
E_{rel} (kcal/mol) _____ _____

(c) 

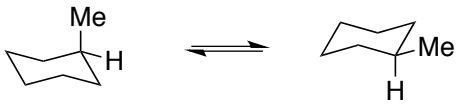
E_{rel} (kcal/mol) _____ _____

(d) 

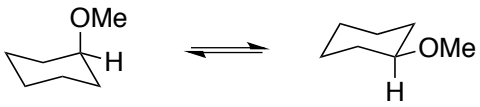
E_{rel} (kcal/mol) _____ _____

(e) 

E_{rel} (kcal/mol) _____ _____ _____ _____

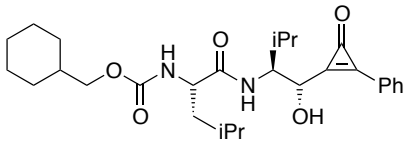
(f) 

E_{rel} (kcal/mol) _____ _____

(g) 

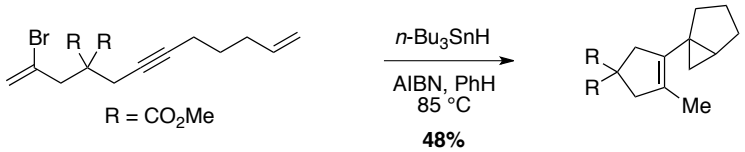
E_{rel} (kcal/mol) _____ _____

2. (10 points) The compound below was reported as an irreversible, electrophilic inhibitor of the enzyme papain. Please explain the source of its electrophilicity using an MO diagram.



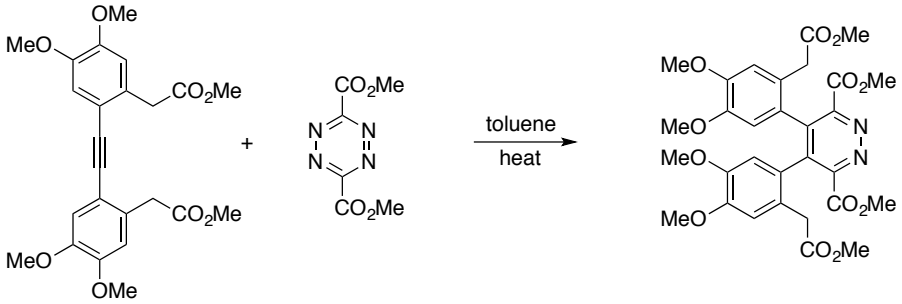
Ando, R.; Morinaka, Y.; Tokuyama, H.; Isaka, M.; Nakamura, E. *J. Am. Chem. Soc.* **1993**, *115*, 1174.

3. (10 points) Provide a mechanism for the following transformation. Show the initiation step(s) in detail! Do not concern yourself with stereochemistry.



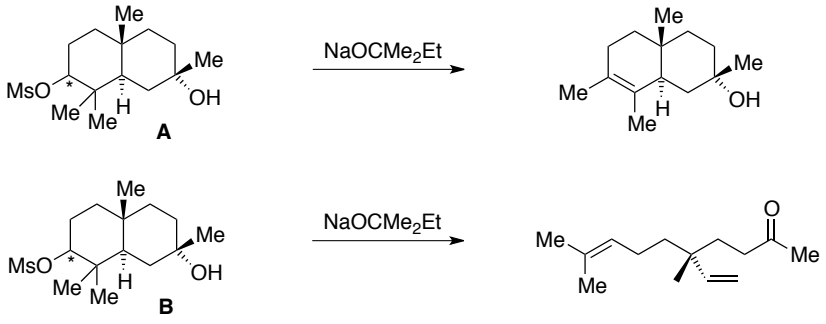
Journet, M.; Malacria, M. *J. Org. Chem.* **1994**, *59*, 718.

4. (10 points) Provide a mechanism for the following transformation.

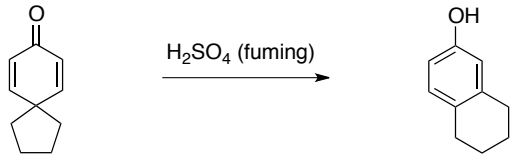


Hamasaki, A.; Zimpleman, J. M.; Hwang, I.; Boger, D. L. *J. Am. Chem. Soc.* **2005**, *127*, 10767.

5. (10 points) One diastereomer of the following mesylates (**A**) reacts with alkoxides to give cyclic products, but the other diastereomer (**B**) gives an acyclic product. Provide mechanisms for both of these transformations, and show the stereochemistry the molecules must possess at the asterisked carbon atom for each diastereomer.

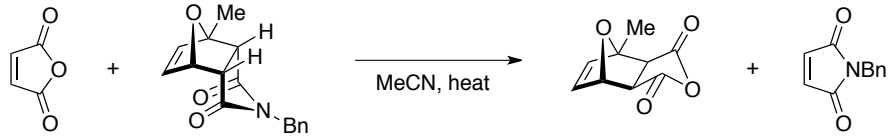


6. (10 points) Provide a mechanism for the following transformation.



Wilds, A. L.; Djerassi, C. *J. Am. Chem. Soc.* **1946**, *68*, 1715.

7. (30 points) Consider the reaction below.

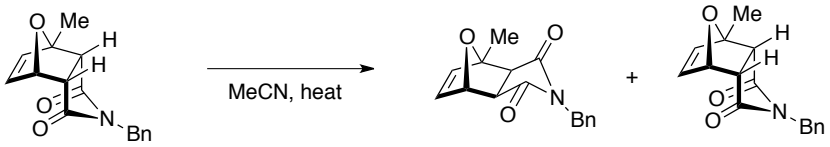


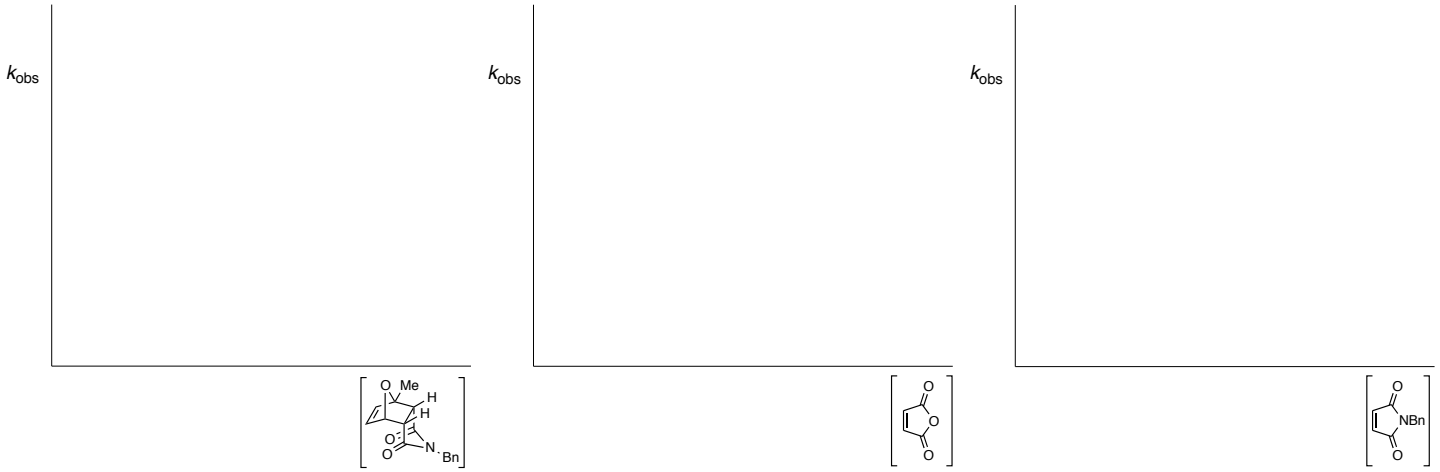
Dewar, M. J. S.; Pierini, A. B. *J. Am. Chem. Soc.* **1984**, *106*, 203.

a. Provide a two-step mechanism to account for product formation.

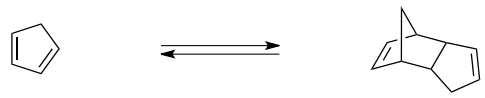
b. Using the steady state approximation, derive the rate expression to describe product formation.

c. Based on the observation below, fill in the following graphs for the expected relationship between the rate of the reaction and the concentration of the species.





8. (10 points) Consider the following cycloaddition dimerization reaction:



2 equiv

- The free energy change for this reaction was determined to be $\Delta G° = -11$ kcal/mol
- The activation free energy for the dimerization was determined to be $\Delta G^{‡} = +20$ kcal/mol

Calculate the free energy of activation for the reverse reaction. Show the reactants, products and transition state on a reaction coordinate diagram.