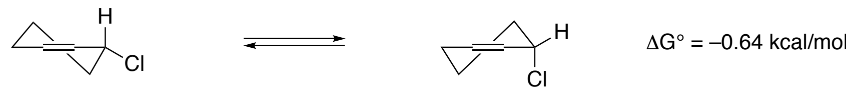
1. (10 points) Using a combination of Raman and IR spectroscopy, the energy difference for the half-chair flip of 3-chlorocyclohexene was estimated:

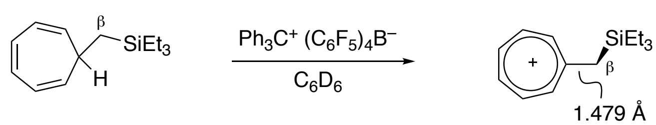


(a) Explain this observation using Frontier Molecular Orbital theory.

(b) In contrast, the A-value of chlorocyclohexane was found to be 0.4 kcal/mol.

With this data, what is the energetic stabilization (kcal/mol) of the FMO interaction of axial Cl in cyclohexene?

2. (10 points)

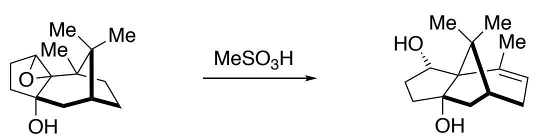


Hassall, K. S.; White, J. M. *Org. Lett.* **2004**, *6*, 1737.

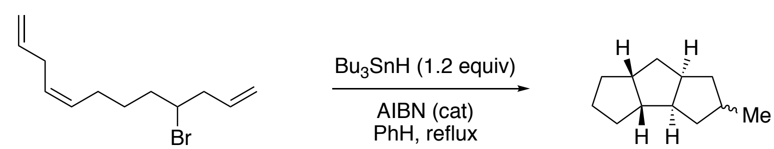
a. Draw a molecular orbital diagram that explains its unusual stability of the product cation.

b. Use FMO theory to explain why the β-$SiEt_3$ group is orthogonal to the tropylium ion.

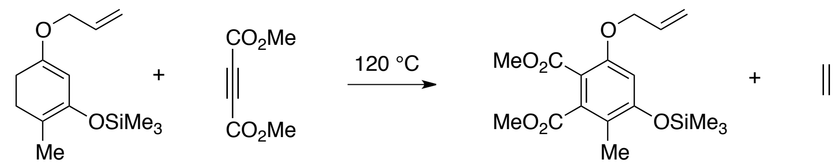
3. (10 points).



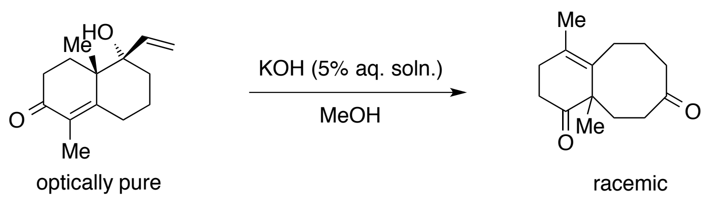
4. (10 points). Provide a mechanism for the following transformation. <u>Show the initiation step(s) in detail!</u> Do not concern yourself with stereochemistry.



5. (10 points)

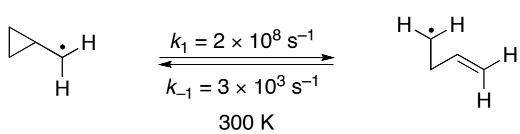


6. (10 points). Provide a mechanism for the following transformation. Make sure that your answer provides an explanation for the lack of stereochemistry observed in the product.



7. (10 points). Ozone, O_3, reacts with alkenes in a [3+2] cycloaddition reaction.
(a) Draw the Lewis structure for ozone.
(b) Draw an orbital representation of this molecule and show explicitly the number and location of the π electrons for cycloaddition.

8. (15 points). Consider the reaction below.



$R = 1.99$ cal/mol•K
$h = 6.626 \times 10^{-34}$ m²kg/s
$\kappa = 1.38 \times 10^{-23}$ m²kg/s²•K

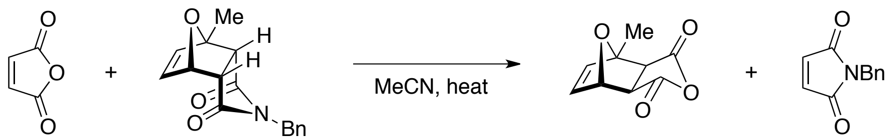
a. For this radical isomerization reaction, estimate $\Delta G^{\ddagger}$ for the forward and reverse directions at 300 K.

b. Sketch a reaction coordinate diagram.

c. Estimate the $\Delta G°$ for this reaction.

d. Estimate the equilibrium constant.

9. (15 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.