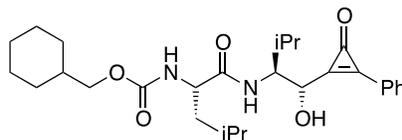


1. (15 points) Provide the correct value for each of the statements below.

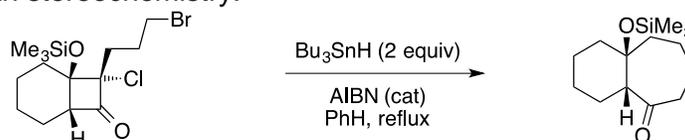
- _____ Strength of a C–H bond in CH₄ (kcal•mol⁻¹)
- _____ Rate constant for fastest unimolecular reaction (s⁻¹)
- _____ $\Delta\Delta G^\ddagger$ limit for d.r. $\geq 10:1$ (kcal•mol⁻¹)
- _____ ΔG^\ddagger for ethane rotation (kcal•mol⁻¹)
- _____ HOMO of formaldehyde (σ , π , n, π^* or σ^*)
- _____ ΔG° for $K_{eq} = 0.01$ (kcal•mol⁻¹)
- _____ Strength of a π -C–C bond (kcal•mol⁻¹)
- _____ Sign (+ or –) of ρ -value for an electrophilic reactive intermediate
- _____ Rate constant for fastest bimolecular reaction (s⁻¹)
- _____ Strength of a σ -C–C bond (kcal•mol⁻¹)
- _____ Methyl-Methyl gauche interaction (kcal•mol⁻¹)
- _____ ΔH° for a 6π -electron-electrocyclization (kcal•mol⁻¹)
- _____ ΔG^\ddagger for overnight reaction ($\tau_{1/2} = 1.5$ h, 100 °C, in kcal•mol⁻¹)
- _____ HOMO of methane (σ , π , n, π^* or σ^*)
- _____ Rotation rate constant (s⁻¹)

2. (15 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.



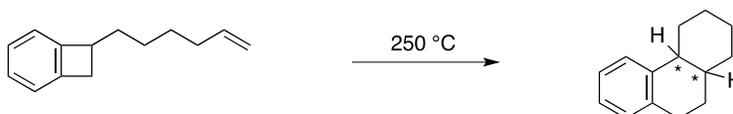
Ando, R.; Morinaka, Y.; Tokuyama, H.; Isaka, M.; Nakamura, E. *J. Am. Chem. Soc.* **1993**, *115*, 1174.

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



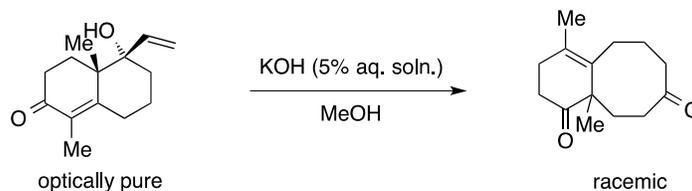
Zhang, W.; Dowd, P. *Tetrahedron Lett.* **1996**, *37*, 957.

4. (10 points) Provide a mechanism for the following transformation. Indicate the expected stereochemistry at the *-ed carbons.



Gowland, B. D.; Durst, T. *Can. J. Chem.* **1979**, *57*, 1462.

5. (10 points) Your mechanism must be consistent with observed stereochemistry.



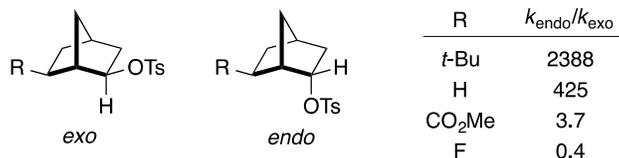
Uma, R.; Swaminathan, S.; Rajagopalan, K. *Tetrahedron Lett.* **1984**, *25*, 5825.

6. (10 points)

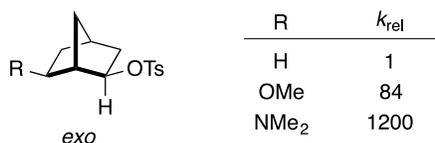


Jun, J.-G.; Ha, T. H. *J. Heterocycl. Chem.* **1997**, *34*, 325.

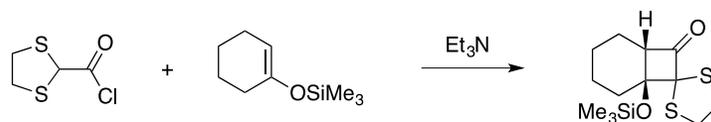
7. a. (5 points) The relative rates of solvolysis (H_2O , 70°C) of *exo* versus *endo* norbornyl systems are dependent upon other substituents on the ring. Explain the following trend by considering the mechanism for solvolysis.



- b. (5 points) The relative rates of solvolysis (H_2O , 70°C) of the following *exo* tosylates have been measured. Explain the trend.

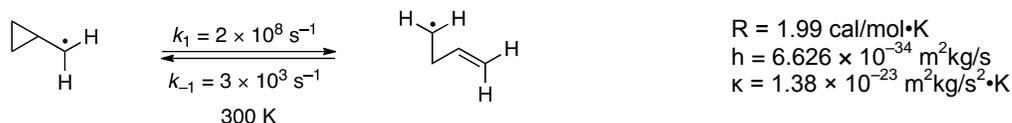


8. (20 points). The reaction below involves a ketene intermediate.



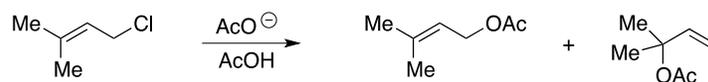
Pak, C. S.; Kim, S. K. *Bull Kor. Chem. Soc.* **1994**, *15*, 337.

- a. Provide a mechanism for the reaction.
- b. Assign the relevant HOMO and LUMO frontier molecular orbitals to the ketene and olefin. Based on the regioselectivity of the reaction, estimate the relevant coefficients by use of big and small circles of the reacting species. Be sure to include the phase of each orbital.
9. (20 points) Consider the reaction below.



- a. For this radical isomerization reaction, estimate ΔG^\ddagger for the forward and reverse directions at 300 K.
- b. Sketch a reaction coordinate diagram.
- c. Estimate the ΔG° for this reaction.
- d. Estimate the equilibrium constant.

10. (30 points). Consider the reaction below.



Young, W. G.; Winstein, S.; Goering, H. L. *J. Am. Chem. Soc.* **1951**, 73, 1958.

- Provide a mechanism to account for product formation.
- Draw a frontier molecular orbital diagram (only of the π -orbitals) for the reactive intermediate and the shape of each of the orbitals.
- Using the steady state approximation, derive the rate expression to describe product formation.
- The authors also observed no interconversion of the starting allylic chloride under the reaction conditions, irrespective of which isomer was used:



On the basis of their observation, simplify your derived rate expression, and fill in the following graphs for the expected relationship between the rate of the reaction and the concentration of the species.

