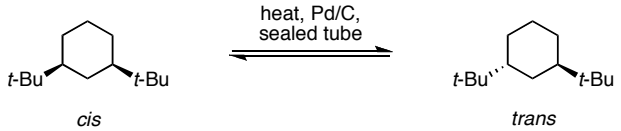
CHEM 633: Advanced Organic Chem: Physical
Problem Set 3
Due on 9/22/09

1. The temperature-dependent ratio of isomers of 1,3-di-*tert*-butylcyclohexane has been examined at equilibrium (*J. Am. Chem. Soc.* **1960**, *82*, 2393).

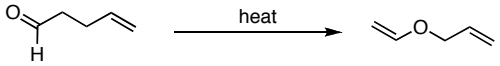


cis *trans*

Temperature (K)	% *trans*
492.6	2.69
522.0	3.61
555.0	5.09
580.0	6.42
613.0	8.23

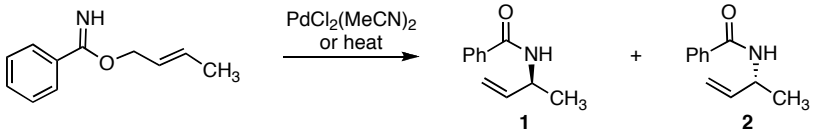
(a) Are the *cis* and *trans* conformations enantiomers or diastereomers?
(b) Determine $\Delta H°$ and $\Delta S°$ for this process in kcal/mol and eu, respectively.
(c) Compare the measured value of $\Delta S°$ with those determined for other alkyl substituents by NMR spectroscopy (Me = –0.03 eu, Et = 0.64, *i*-Pr = 2.31), and provide an explanation for the sign and magnitude of the observed value in the *t*-Bu case.

2. (a) Use Benson group increments to predict $\Delta H°$ for the following reaction.



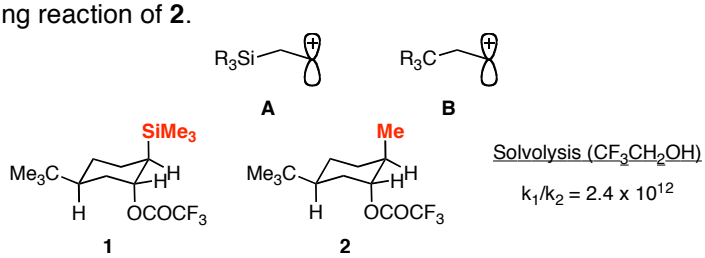
(b) Draw a reaction coordinate diagram, with $\Delta H°$ as the y-axis, for this reaction. Do you anticipate that this reaction will proceed?
(c) Propose an arrow-pushing mechanism for this reaction.

3. (a) Use Benson group increments to predict $\Delta H°$ for the following reaction.



(b) Draw a reaction coordinate diagram, with $\Delta H°$ as the y-axis, that includes both products **1** and **2**.
(c) What is the relationship between products **1** and **2**?
(d) Propose an arrow-pushing mechanism for the thermal variant of this reaction.

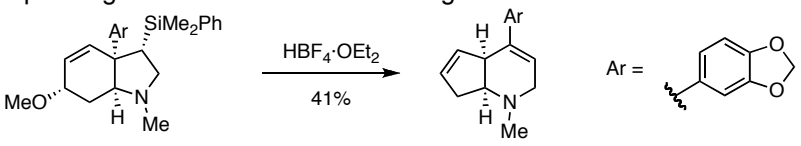
4. Carbonium ion **A** has been calculated to be 38 kcal/mol more stable than carbonium ion **B** (Jorgensen *J. Am. Chem. Soc.* **1985**, *107*, 1496). The prodound stabilization of carbonium ions by silicon in this fashion is referred to as the "β-silicon effect." For example, S_N1 solvolysis reaction of **1** is 10^{12} times as fast as the corresponding reaction of **2**.



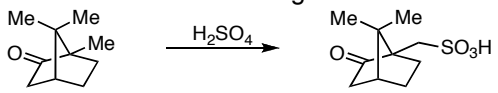
(a) Identify the HOMO-LUMO interactions in the S_N1 reactions of **1** and **2**.

(b) Use an orbital energy argument to explain why **A** is more stable than **B**. Draw energy diagrams to illustrate your answer.

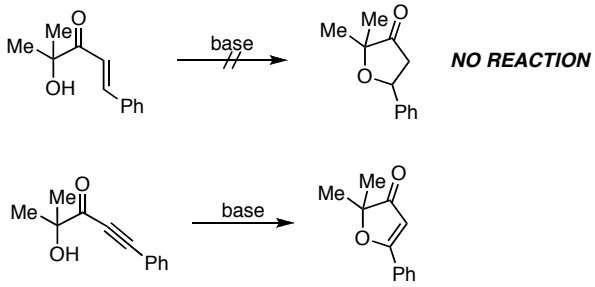
5. Propose an arrow-pushing mechanism for the following transformation.



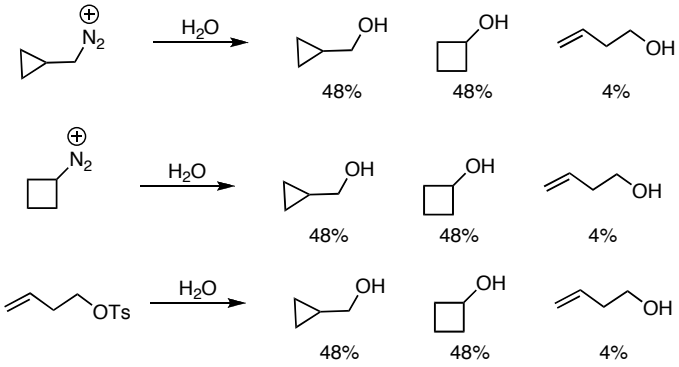
6. Propose an arrow-pushing mechanism for the following transformation.



7. Please use FMO analysis to show why 5-endo-trig cyclizations are disfavored, but 5-endo-dig cyclizations are favorable.



8. The solvolysis of the three starting materials shown below gives the same products in the same ratio, suggesting that the reactions proceed through a common intermediate (A&D, p. 664).
(a) Please propose arrow-pushing mechanisms for these reactions, identifying the common intermediate.



(b) Please use FMO theory to illustrate why this common intermediate has unusually good stability.