Initials: _____

Name: _____

Chem 633: Advanced Organic Chemistry
Midterm 1

Please answer the following questions *clearly and concisely*.

Write your answers in the space provided.

Write your initials on each page you want graded.

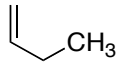
There are 8 total pages to this exam. Please be sure your copy has 8 pages before you begin.

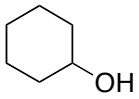
Molecular models are allowed.

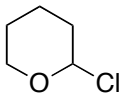
Calculators are unnecessary and prohibited.

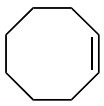
Problem	Points
1	_____/20
2	_____/10
3	_____/15
4	_____/15
5	_____/10
6	_____/20
7	_____/10
TOTAL	_____**/100**

1. (20 points) Please clearly draw the lowest energy conformations of the following molecules. No explanation is necessary.

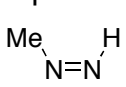
(a) 

(b) 

(c) 

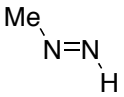
(d) 

2. (10 points) The N–H stretching frequency of *cis*-methyl diazine is 200 cm^{-1} lower than the trans isomer (Craig, N. C.; Kliewer, M. A.; Shih, N. C. *J. Am. Chem. Soc.* **1979**, *101*, 2480). Please provide an explanation for this result.



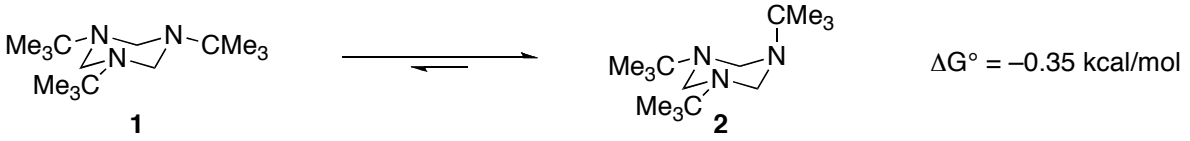
cis
ν(N–H) = 2188 cm^{-1}
weaker N–H bond

vs.



trans
ν(N–H) = 2317 cm^{-1}
stronger N–H bond

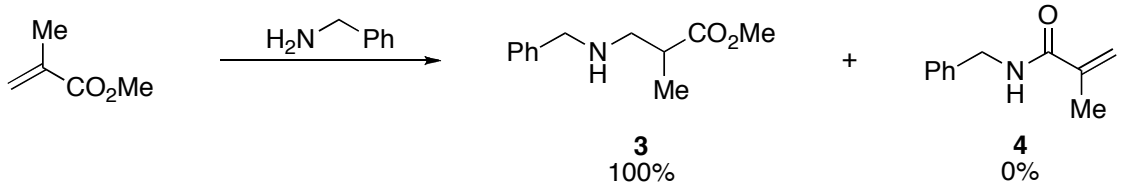
3. (15 points) Somewhat surprisingly, one of the *t*-butyl (CMe_3) groups adopts an axial position in the preferred conformation of 1,3,5-tri(*t*-butyl)hexahydro-1,3,5-triazine (Jones, R.; Katrizky, A.; Snarey, M. *J. Chem. Soc. B* **1970**, 135).



(a) Please draw a reaction coordinate diagram for this reaction.

(b) Please rationalize the preference for conformation **2**. In your answer, please address (1) why conformation **2** is more stable than conformation **1** and (2) why the conformation with an axial *t*-butyl group is accessible for hexahydro-1,3,5-triazine, but *not* accessible for *t*-butylcyclohexane.

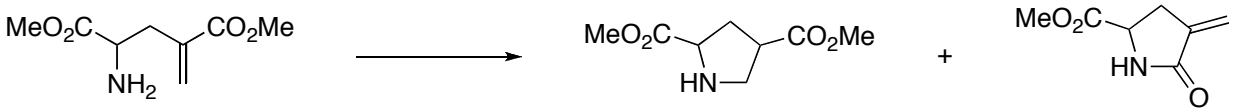
4. (15 points) (a) The reaction of benzylamine and methyl methylacrylate results exclusively in the formation of product **3**. Please explain the selectively for product **3** over **4**.



3
100%

4
0%

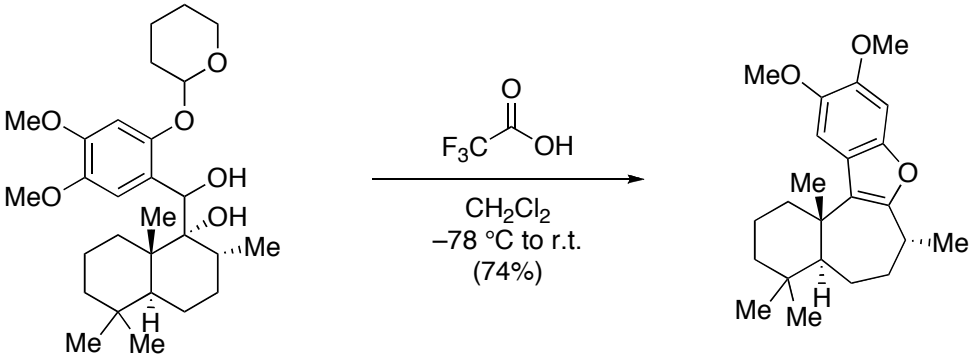
(b) In contrast, product **6** is the exclusive product in the intramolecular addition of an amine to a similar electrophile (Baldwin, J.; Cutting, J.; Dupont, W.; Kruse, L.; Silberman, L.; Thomas, R. *J. Chem. Soc., Chem. Commun.* **1976**, 736). Please explain the selectivity for product **6** over **5**.



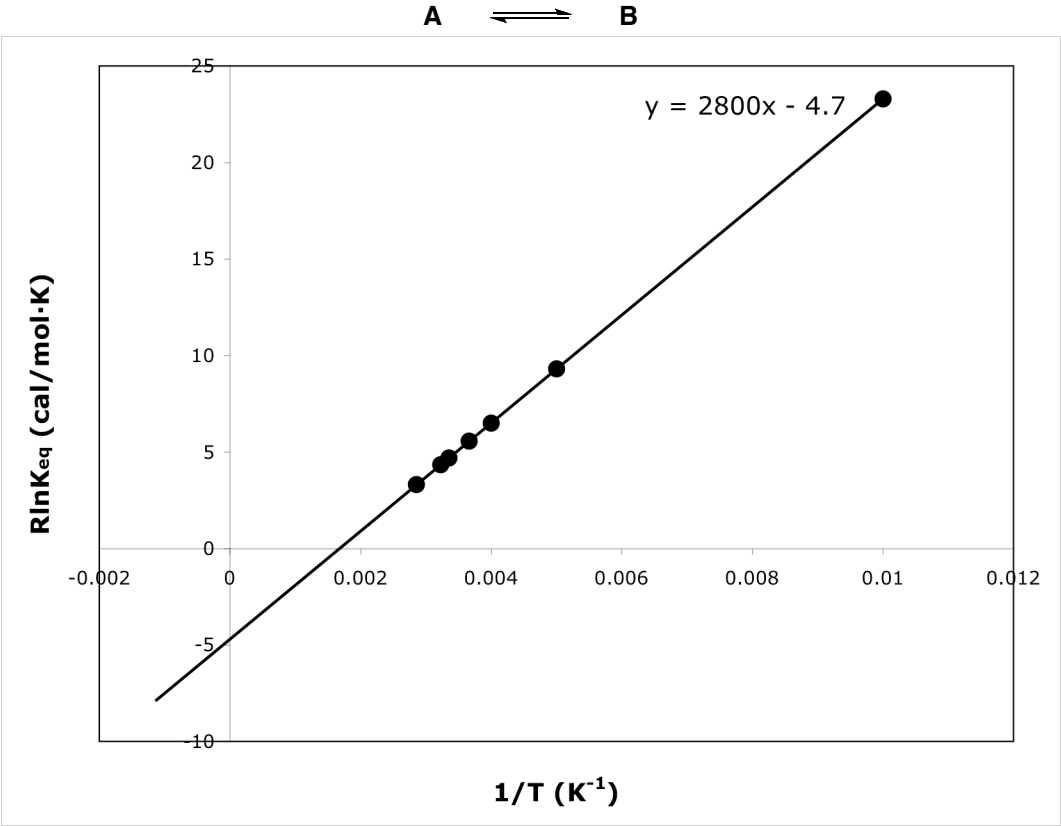
5
0%

6
100%

5. (10 points) George and coworkers reported the following acid-catalyzed rearrangement in their recent synthesis of liphagal (George, J. H.; Baldwin, J. E.; Adlington, R. M. *Org. Lett*. **2010**, *12*, 2394). Please propose a reasonable arrow-pushing mechanism for this transformation.



6. (20 points) The equilibrium constant (K_{eq}) of the equilibrium between **A** and **B** was measured at various temperatures, giving the plot shown below.



(a) What is $\Delta H°$ for this equilibrium?

(b) What is $\Delta S°$ for this equilibrium?

(c) What is $\Delta G°$ for this equilibrium at 25 °C?

(d) At 25 °C, what is the ratio of **A** : **B**?

7. (10 points) Please propose a reasonable arrow-pushing mechanism for the following transformation (Grossman, *The Art of Writing Reasonable Organic Reaction Mechanisms*, p. 101).