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.

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

(a) \[
\text{H}_3\text{C} \]

(b) \[
\text{OH}
\]

(c) \[
\text{O} \quad \text{Cl}
\]

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

\[
\begin{array}{ccc}
\text{Me} & \text{H} & \text{Me} \\
\text{N=N} & \text{N=N} \\
\text{cis} & \text{trans} \\
\nu(\text{N–H}) = 2188 \text{ cm}^{-1} & \nu(\text{N–H}) = 2317 \text{ cm}^{-1} \\
\text{weaker N–H bond} & \text{stronger N–H bond}
\end{array}
\]
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.; Katritzky, A.; Snarey, M. J. Chem. Soc. B 1970, 135).

\[
\text{Me}_3\text{C} - \text{N} - \text{N} - \text{CMe}_3 \quad \quad \quad \text{Me}_3\text{C} - \text{N} - \text{N} - \text{CMe}_3
\]

\[\Delta G^\circ = -0.35 \text{kcal/mol}\]

(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 methacrylate results exclusively in the formation of product 3. Please explain the selectivity for product 3 over 4.

\[
\text{Me} \quad \text{CO}_2\text{Me} \quad \overset{\text{H}_2\text{N} \text{Ph}}{\text{Ph}} \quad \text{Me} \quad \text{CO}_2\text{Me} \quad + \quad \text{Me} \quad \text{CO}_2\text{Me} \quad \text{N} \quad \text{Me}
\]

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.

\[
\text{MeO}_2\text{C} \quad \text{NH}_2 \quad \text{CO}_2\text{Me} \quad \overset{\text{MeO}_2\text{C}}{\text{HN}} \quad \text{CO}_2\text{Me} \quad + \quad \text{MeO}_2\text{C} \quad \text{HN} \quad \text{N} \quad \text{Me}
\]

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 \(\Delta H^\circ\) for this equilibrium?

(b) What is \(\Delta S^\circ\) for this equilibrium?

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

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

$$\text{MeO}_2\text{C} \xrightarrow{\text{NaH}} \xrightarrow{\text{CO}_2\text{Me}} \xrightarrow{\text{MeO}_2\text{C} \to \text{CO}_2\text{Me}}$$