Chem 6353 — Midterm I:
Additions, Eliminations, Aromatic Substitutions
Given in class period on 09/24/2008

Name:__________________________________________________________

UH Student ID#:________________________________________________

Question 1:_____/40
Question 2:_____/30
Question 3:_____/60
Question 4:_____/40
Question 5:_____/30
Total:__________/200

This exam should have seven (7) pages.
If it does not, ask Ognjen for a replacement immediately.
**Question 1—40 points**

Consider the kinetic isotope effect that would be observed in the reaction of semicarbazide with benzaldehyde:

\[
\begin{align*}
\text{H}^+ & \quad \text{O} \\
\text{H}^+ & \quad \text{N} \\
\text{N} & \quad \text{H}_2 \text{N} \quad \text{H}_2 \text{O} \\
\text{H}_2 \text{NN} & \quad \text{O} \\
\text{H} & \quad \text{N} \\
\text{N} & \quad \text{H}_2 \end{align*}
\]

Would you expect to find \( k_{\text{H}} / k_{\text{D}} \) to be normal or inverse? Would you expect \( k_{\text{H}} / k_{\text{D}} \) to be constant, or would it vary (and how) with pH?
Question 2—30 points (20 + 10)

Provide reasonable mechanisms for the following reactions, and account for the stereochemistry of the product in the first reaction:

\[
\begin{align*}
\text{HO} & \quad \text{OBs} \\
\text{Ph} & \quad \text{Ph} \\
\end{align*}
\]

\[
\begin{align*}
x & \quad \text{CO}_2\text{Me} \\
\text{Ph} & \\
\end{align*}
\]

1) Br₂
2) NaOMe

\[
\begin{align*}
\text{HO} & \quad \text{OBs} \\
\text{Ph} & \quad \text{Ph} \\
\end{align*}
\]

\[
\begin{align*}
\text{HO} \\
\text{Ph} & \quad \text{Ph} \\
\end{align*}
\]
Question 3—60 points

The Friedel-Crafts alkylation of anisole (shown below) is catalyzed by strong Lewis acids such as AlCl₃:

\[
\text{Ph} \quad \text{Me} \quad + \quad \text{Cl} \quad \xrightarrow{\text{AlCl}_3} \quad \text{Ph} \quad \text{Me} \quad \text{Cl}
\]

The following information has been obtained about the mechanism of this reaction:

i. At low concentrations of anisole, the reaction is first order in [anisole] and is inhibited by added AlCl₄⁻.

ii. At low concentrations of anisole, addition of AlCl₄⁻ enriched in the isotope \(^{37}\text{Cl}\) results in exchange of labeled chloride into the \(t\)-butyl chloride starting material.

iii. At high concentrations of anisole, the rate becomes independent of [anisole] and added AlCl₄⁻ has a negligible effect on the rate of formation of product.

Provide a mechanism for this Friedel-Crafts reaction and show that the rate law for your mechanism is consistent with each one of the above observations. State clearly all assumptions you make in your analysis.
Question 4—40 points

Sketch the qualitative dependence of the observed rates of hydrolysis ($k_{obs}$) for the two compounds as a function of pH. Provide arrow-pushing explanations for different trends that you depict. Cover the pH=1–13 range, and don’t worry about the absolute values of $k_{obs}$.

![Compound Structures]
Question 5—30 points (15+15)

Predict the stereochemistry of the addition of ethylmagnesium bromide onto the following compounds:

In which case would you expect the selectivity to be higher, and why?
If you need extra space, use this page. Clearly specify what problem are you solving here. No external pieces of paper will be graded.