Chem 125 Midterm Exam
100 points; 50 minutes
May 6, 2016

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**Academic Honesty Policy.** Academic honesty is strictly enforced on homework, exams, and other aspects of this course. Academic dishonesty will result in a failing grade in the class and a letter in the student's file. Activities constituting academic dishonesty include:

*Cheating*
- Copying from others during an examination.
- Communicating exam answers with other students during an examination.
- Offering another person's work as one's own.
- Taking an examination for another student or having someone take an examination for oneself.
- Tampering with an examination after it has been corrected, then returning it for more credit.
- Using unauthorized materials, prepared answers, written notes, or concealed information during an examination.

*Dishonest Conduct*
- Stealing or attempting to steal an examination or answer key from the instructor.
- Allowing another student to copy off of one's own work during a test.

*Collusion*
- Any student who knowingly or intentionally helps another student perform any of the above acts is subject to discipline for academic dishonesty.

I understand and will abide by this academic honesty policy: ___________________________ (signature)

Seat: _____
1. Draw the complete structures for the following compounds. (20 points)

NOTE: Tables 1.1-1.4 and 4.1 are provided as an appendix on the final pages of the exam.

a. 2,4-dimethylbenzo[g]quinoline (Problem 1.1)

b. (1R,6S,7S)-4-(t-butyldimethylsiloxy)-6-(trimethylsilyl)bicyclo[5.4.0]undec-4-en-2-one (Problem 1.9)
2. Chiral imines can be used in Michael additions, giving a high degree of stereoselectivity. In the reaction below, racemic 2-methylcyclohexanone give the octalone product in 44% overall yield and 96% ee. The reaction proceeds through Michael addition of the enamine intermediate with 3-buten-2-one to generate an imine adduct. (Problem 3.19, 20 points)

a. Sketch the structure of the enamine intermediate that acts as the nucleophile in the Michael addition.

b. Write a reasonable curved-arrow mechanism, showing how the enamine intermediate might generate the imine adduct.

c. Explain the stereoselectivity of the Michael addition.

The 3-buten-2-one prefers to add from the face of the enamine bearing the smaller methyl group rather than the larger phenyl group (steric hindrance). As drawn, this is the top face, rather than the bottom face.
3. The rates of reaction of substituted benzoyl chlorides with excess methanol at 0 °C were measured and found to give a good correlation with the Hammett equation. The pseudo-first-order rate constant for p-methylbenzoyl chloride is 0.0178 mol/l min and for p-nitrobenzoyl chloride is 0.413 mol/l min. (Problem 4.2, 20 points)

\[
\begin{align*}
\ce{+\text{CH}_2\text{OH}} & \quad \ce{\text{excess}} & \quad \ce{-\text{OCCH}_3}
\end{align*}
\]

NOTE: Tables 1.1-1.4 and 4.1 from the textbook are provided as an appendix on the final pages of the exam.

HINT: The use of the data above allows calculation of the pseudo-first-order rate constant for benzoyl chloride to be 0.0312 mol/l min.

\[
\begin{align*}
p &= 1.438 \\
\log \frac{k}{k_0} &= e \sigma \\
\log 0.0178 &= 0.78p \\
\log 0.0312 &= 0.78p \\
p &= 1.438
\end{align*}
\]

a. Calculate the value of the Hammett parameter \( \rho \) (rho) for the reaction.

\[
\begin{align*}
\log \frac{k}{k_0} &= e \sigma \\
\log 0.413 &= 0.78p \\
\log 0.0312 &= 0.78p \\
p &= 1.438
\end{align*}
\]

b. Calculate the pseudo-first-order rate constant for \( m \)-bromobenzoyl chloride.

rate constant for \( m \)-bromobenzoyl chloride = \[
\frac{0.113}{0.0312} \text{ mol/l min}
\]

Show your work below:

\[
\begin{align*}
\log k &= e \sigma \\
\log k - \log k_0 &= e \sigma \\
\log 0.113 &= (1.438)(0.39) \\
\log k &= (1.438)(0.39) + \log 0.0312 \\
\log k &= 0.945025 \\
k &= 10^{-0.945025} = 0.11344
\end{align*}
\]
4. Draw likely intermediates in the mechanism in the following reaction. (Problem 4.16, 20 points)

NOTE: The reaction sequence begins by way of a halogen-metal exchange reaction.

Use the space below to work through the mechanism and figure out the answers that you will write in the boxes above.
5. Write a mechanism for the following reaction, showing each step and the intermediates that are involved. (Problem 5.8, 20 points)

Use curved arrows to illustrate the mechanism of each step. Name the type pericyclic reaction that occurs in each step.