Chem 30A Fall 2004

MIDTERM #2
(50 Min)

Mon November 22nd

INTERPRETATION OF THE QUESTIONS IS PART OF THE EXAM – DO NOT ASK FOR THE QUESTIONS TO BE EXPLAINED TO YOU

ONLY ANSWERS WRITTEN IN THE BOXES PROVIDED WILL BE GRADED

***DO NOT OPEN THIS EXAM UNTIL INSTRUCTED TO DO SO***

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Human beings, who are almost unique in having the ability to learn from the experience of others, are also remarkable for their apparent disinclination to do so.

- Douglas Adams
Q1. What is the mechanism of the reaction shown below? (15 points) (Show all intermediates, all appropriate lone pairs, formal charges, and curly arrows).
Q2. Each of the reactions drawn below produces ONE MAJOR PRODUCT. In each case, draw this product (including relative stereochemistry where appropriate) in the large box provided (3 points each). Note: for two-step reactions, just give the final product, DO NOT draw intermediates. If a reaction produces a racemic mixture (i.e., a pair of enantiomers), write an ‘E’ in the small box next to it – be sure of your answer, +1 point for each correct ‘E’ and –1 point for each incorrect ‘E’.

(a)

\[
\begin{align*}
\text{\hspace{1cm}} & \text{Cl}_2 \\
& \text{H}_2\text{O}
\end{align*}
\]

(b)

\[
\begin{align*}
\text{\hspace{1cm}} & \text{(i) BH}_3\cdot\text{THF} \\
& \text{(ii) NaOH / H}_2\text{O}_2
\end{align*}
\]

(c)

\[
\begin{align*}
\text{\hspace{1cm}} & \text{Br}_2 \\
& \text{CCl}_4
\end{align*}
\]

(d)

\[
\begin{align*}
\text{\hspace{1cm}} & \text{(i) Hg(OAc)}_2 / \text{H}_2\text{O} \\
& \text{(ii) NaBH}_4
\end{align*}
\]

(e)

\[
\begin{align*}
\text{\hspace{1cm}} & \text{(i) OsO}_4 \\
& \text{(ii) NaHSO}_3 / \text{H}_2\text{O}
\end{align*}
\]

Question 2 continues on the next page...
(f) \[ \text{Cyclohexene} \xrightarrow{(i) \text{O}_3} \text{O}_3 \xrightarrow{(ii) \text{Me}_2S} \text{Product} \]

(g) \[ \text{Cyclohexene} \xrightarrow{\text{H}_2, \text{Pt}} \text{Product} \]

(h) \[ \text{Cyclohexene} \xrightarrow{1/3 \text{equiv of BH}_3\cdot\text{THF}} \text{Product} \]

(i) \[ \text{Cyclohexene} \xrightarrow{\text{HI, ether}} \text{Product} \]

(j) \[ \text{Cyclohexene} \xrightarrow{\text{H}_2\text{O, H}_2\text{SO}_4\text{(cat)}} \text{Product} \]
Q3. Consider the two reactions shown below. At a temperature of 500 K, the reaction of Y to give Z is 100 times faster than the reaction of W to give X (i.e., \(k_2/k_1 = 100\)). Both of the reactions have a pre-exponential factor (A) of \(10^{12}\) s\(^{-1}\). The Arrhenius equation, linking the rate constant (k) of a reaction to the Gibbs free energy of activation (\(\Delta G^\ddagger\)), is shown below. You may find it useful to know that \(R = 2\) cal/K·mol, and that the natural logarithm of a number N (lnN) is equal to 2.3 \(\times\) log\(_{10}\)N.

\[
\begin{align*}
W & \xrightarrow{k_1} X \\
Y & \xrightarrow{k_2} Z
\end{align*}
\]

\[k = A \cdot e^q\text{ where } q = \left(\frac{-\Delta G^\ddagger}{RT}\right)\]

(a) Which reaction has the highest activation barrier (\(\Delta G^\ddagger\))? (3 points)

(b) What is the numerical difference (in kcal/mol) between the activation barriers (\(\Delta G^\ddagger\)) for these two reactions? (12 points)
Q4. (a) When 6-methyl-hept-5-en-2-ol (A) is reacted with mercury acetate in water, compound B is obtained, which is converted to compound C (molecular formula C₈H₁₆O) upon reaction with sodium borohydride. What are the structures of B and C? (4 points each)

(b) In the box below, draw the mechanism of the reaction that converts A into B. (12 points) (Show all intermediates, all appropriate lone pairs, formal charges, and curly arrows).
Q5. Each of the reactions drawn below produces ONE MAJOR PRODUCT. In each case, draw this product in the box provided, CAREFULLY INDICATING the position of any D atoms it may contain. (3 points each). Note: for two-step reactions, just give the final product, DO NOT draw intermediates, and... deuterium (D) is just a heavier isotope of hydrogen (H) – it reacts just as H would.

(a)  \[
\begin{align*}
\text{Me} & \quad \text{H} \\
\rightarrow & \\
\text{(i) (sia)}_{2}\text{BD} & \\
\text{(ii) CH}_{3}\text{CO}_{2}\text{D} \\
\end{align*}
\]

(b)  \[
\begin{align*}
\text{Me} & \quad \text{H} \\
\rightarrow & \\
\text{(i) (sia)}_{2}\text{BD} & \\
\text{(ii) CH}_{3}\text{CO}_{2}\text{H} \\
\end{align*}
\]

(c)  \[
\begin{align*}
\text{Me} & \quad \text{H} \\
\rightarrow & \\
\text{(i) (sia)}_{2}\text{BH} & \\
\text{(ii) CH}_{3}\text{CO}_{2}\text{D} \\
\end{align*}
\]

(d)  \[
\begin{align*}
\text{Me} & \quad \text{H} \\
\rightarrow & \\
\text{(i) (sia)}_{2}\text{BH} & \\
\text{(ii) NaOH / H}_{2}\text{O}_{2} \\
\end{align*}
\]

(e)  \[
\begin{align*}
\text{Me} & \quad \text{H} \\
\rightarrow & \\
\text{Hg(OAc)}_{2} & \\
\text{H}_{2}\text{SO}_{4} / \text{H}_{2}\text{O} \\
\end{align*}
\]
EXTRA CREDIT. The pKₐ values for 4-cyanophenol (I) and 4-nitrophenol (II) are approximately the same, i.e., the phenolic protons (bold) in each of these compounds are equally acidic. In contrast, however, the dimethyl-substituted compounds differ significantly in their acidity; the dimethyl-cyano compound (III) is much more acidic than the dimethyl-nitro compound (IV). Explain (using both words and drawings as you feel appropriate) this observation in the box below. (15 points) Hint: think resonance...

\[ \text{I} \quad \text{II} \quad \text{III} \quad \text{IV} \]