Organic Chemistry I (CHE 230-001)
Final Examination
December 16, 2004
Key

Name (PRINT LEGIBLY): ________________________________

Please provide clear and concise answers to all of the following questions.
Please answer questions in the area provided, the back of an exam page or on the clearly labeled spare page.

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<td>2. (a-k)</td>
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PLEASE OBSERVE THE FOLLOWING.

1) Write LARGE and LEGIBLY. If I can’t read what you write, I can’t give you full or partial credit.

2) Read each question carefully before answering. If you don’t answer the question I posed, you will not receive credit.

3) Explanations must be clear, coherent, and unambiguous to receive credit.
1. (2 pts each, 18 pts. total). Use no more than one or two short sentences where an explanation is required.

i. What type of SN reaction will always result in inversion of configuration at the carbon involved in the reaction? 
\[ \text{SN}_2 \]

ii. What is the rate-determining step in the reaction of \( t \)-butyl chloride with water to produce \( t \)-butyl alcohol?

The loss of a chloride ion to form the \( t \)-butyl (3°) carbocation.

iii. The product of the addition of HCl to trans-2-butene is a racemate

iv. List two factors that would favor an elimination reaction.

Strong bases, heat, and hindered alkyl centers
- any two of the above answers is acceptable

v. What type of solvent would be best for an SN2 reaction?

A polar aprotic solvent

vi. The pKa of alcohols is about 16-18

vii. What is the order of importance of the three kinds of carbocation stabilization: hyperconjugation, lone pair resonance, and \( \pi \) bond resonance?

Lone pair resonance > \( \pi \) bond resonance > hyperconjugation.

viii. The anti-Markovnikov addition of H\(_2\)O to 1-cyclohexylethene could be accomplished by (name reactants or reaction type) hydroboration/oxidation (BH\(_3\) followed by H\(_2\)O\(_2\), NaOH, H\(_2\)O)

ix. In order for a strong base to extract a \( \beta \)-hydrogen in an E2 reaction, the hydrogen must be positioned _antiperiplanar_ to the leaving group.
2. (5 pts. each, 80 pts. total) Draw the major product of each of the following reactions. If no reaction is expected to occur, write “No reaction.” Be sure to indicate the stereochemistry of the product, where appropriate.

(a) 

\[ \text{Me} - \text{C} = \text{C} - \text{Et} \xrightarrow{\text{H}_2, \text{Pd/CaCO}_3/\text{Pb}} \text{Me} - \text{C} = \text{C} - \text{Et} \]

(b) 

\[ \text{H}_3\text{C} - \text{CH}_2 - \text{CH} = \text{CH}_3 \xrightarrow{\text{NaOEt, heat}} \text{H}_3\text{C} - \text{CH} = \text{CH} - \text{CH}_3 \]

(c) 

\[ \text{Me} \xrightarrow{\text{BH}_3} \text{Me} \]

(d) 

\[ \text{Me} \xrightarrow{\text{CH}_2\text{I}_2} \text{Me} \]
(e) Draw and clearly label products 1-4.

(f) Draw and clearly label products 5-7.
(g) 

\[ \text{Me} \quad \text{Et} \quad \text{Ph} \]

\[ \text{Me} \quad \text{Et} \quad \text{Ph} \quad (\text{m-CPBA}) \]

(h) Draw and clearly label products 8 and 9.
3. (12 pts.)
(a, 6 pts.) Draw the energy profile of an exergonic reaction ($K_{eq} > 1$) in which starting material $A$ produces a carbocation $B$ that rearranges once to a more stable carbocation $C$ and then produces product $D$. **Label** the intermediates ($B$ and $C$) and the transition states ($E$-$G$) on your diagram.
**Hint:** What will be the relative energies of the transition states involved?

![Energy profile diagram](image)

(2 pts. each)

(b) The energy difference between $A$ and $E$ might determine the rate of the reaction.

c. The energy difference between $A$ and $D$ might determine the ratio of product to starting material of the reaction.

d. The Hammond postulate states that the transition state between $B$ and $C$ is most similar in structure to $B$.
4. (10 pts. total) Describe the relationship of each pair of structures as specifically as possible and in no more than two words.

(a, 3pts)

4A NH₂

4B

Conformational enantiomers

(b, 3pts)

4C NH₂

4D

Configurational enantiomers

(c, 4pts) Briefly explain why 4A and 4B are expected to have identical biological properties whereas 4C and 4D are expected to have different biological properties.

Conformational enantiomers can interconvert rapidly, so they are expected to have the same biological properties. Configurational enantiomers cannot interconvert, so they have different biological properties.
5. (10 pts. each, 40 pts. total). Draw reasonable mechanisms for each of the following reactions. Use the curved arrow convention to show the movement of electrons.

(a) Reaction of methylcyclohexene with bromine in methanol yields only 1-bromo-2-methoxy-2-methylcyclohexane (I). Briefly explain why none of 1-bromo-2-methoxy-1-methylcyclohexane (II) is formed.

None of II is formed because C1 bears more positive charge than C2 since tertiary alkyl centers are better able to stabilize positive charge than secondary alkyl centers (3° carbocations are more stable than 2° carbocations).
(b)

\[ \begin{align*}
\text{O} & \text{Cl} \\
\text{OCl} & \text{OCl} \\
\text{Cl} & \text{Cl} \\
\text{O} & \text{O} \\
\text{80}^\circ & \text{C} \\
\text{CCl}_4 & \text{CCl}_4
\end{align*} \]

only product observed

**Hint:** Use O-Cl homolysis as an initiation step and provide a free radical chain mechanism for the reaction

**Mechanism:**

\[ \begin{align*}
\text{O} & \text{Cl} \\
\text{O•} & \text{O•} \\
\text{O•H} & \text{O•H} \\
\text{Cl•} & \text{Cl•} \\
\text{Cl} & \text{Cl} \\
\text{O} & \text{O}
\end{align*} \]
Mechanism:
6. (10 pts) Explain the following observation in no more than two or three short, easily understood sentences. When \( i\text{-PrO}^- \) is allowed to react with chlorocyclohexane, the major product is an alkene, but when \( \text{PhO}^- \) is allowed to react with chlorocyclohexane, the major product is an ether.

When a good base/good nucleophile reacts with a secondary alkyl halide, both E2 and \( \text{S}_{\text{N}}2 \) reactions can occur. Usually the E2 reaction predominates, but as the basicity of the nucleophile decreases, more and more \( \text{S}_{\text{N}}2 \) product is obtained. \( \text{PhO}^- \) is less basic than \( i\text{-PrO}^- \) because of resonance stabilization of the negative charge in the former, so more \( \text{S}_{\text{N}}2 \) product is obtained with this nucleophile.