CHEM 237-Davis
Organic Chemistry
Examination 3
April 15, 2009

YOUR NAME
(Last, First)

Initial of Last Name

Instructions

• Fill in your name in the space above and on the next page
• Print the initial of your last name in the box above
• Please sign the Honor Code acknowledgment on the following page

• DO NOT OPEN THIS EXAM UNTIL INSTRUCTED TO DO SO
• Answer questions in the spaces provided
CHEM 237-Davis, Examination 3

YOUR NAME ____________________________  
(Last, First)

University Honor Code Acknowledgment
I have neither given nor received assistance in taking this examination.

__________________________  Signature

Notes
• This exam is worth 125 points
• There are 6 Sections on pages 3-11. Make sure your exam has all the pages.
• Nothing written on page 12 will be graded-this is for scratch work

Points
Problem 1 ______ (10)
Problem 2 ______ (10)
Problem 3 ______ (45)
Problem 4 ______ (20)
Problem 5 ______ (20)
Problem 6 ______ (20)

Total ______ (125)

EXAM BEGINS ON NEXT PAGE 3
1. **Absolute Configuration (10 pts)**

A) In the left-hand box, add the necessary substituents to give the structure for 1-(R)-iodo-3-(R)-fluoro-cyclohexane 1. (5 pts)

B) In the box on right draw the low-energy chair conformation for 1-(R)-iodo-3-(R)-fluoro-cyclohexane 1. It is not necessary to draw all the hydrogen atoms. But, you must draw the hydrogen atoms at the chiral centers bearing the substituents. Identify each substituent as axial or equatorial. (5 pts)

![Structure 1](image1)

![Structure 2](image2)

2. A) Show a mechanism for reaction of cis-2,3-methylbutene 1 with ozone to give 3. (5)

![Mechanism](image3)
B) Calculate ΔH° for the rearrangement of 3 to 4. Use the following values for bond dissociation energies: C-C σ bond=90 kcal/mol, C-O σ bond=85 kcal/mol, O-O σ bond=50 kcal/mol, C-H σ bond=95 kcal/mol. (5 pts)

\[ \Delta H^0 = \]

3. **Energy Diagrams. A)** Using comparative reaction coordinate/energy diagrams, and a minimum of words, explain why S_N2 reactions (say reaction of methyl iodide with chloride anion) proceed faster in an aprotic solvent rather than in a polar protic solvent. Label all starting materials, transition states, intermediates (if any) and products, 2) label all ΔG values. (10 points)
B) Using comparative reaction coordinate/energy diagrams, and a minimum of words, explain why SN1 reactions proceed faster for 3° alkyl halides than for 1° alkyl halides. Label all starting materials, transition states, intermediates (if any) and products, 2) label all ΔG values. (10 points)
4. Short Answer (45 pts).

A) Circle any chiral compound(s).

B) Label any chiral center(s) in the following molecules with an asterisk (*).

C) Are the following compounds enantiomers (E), diastereomers (D), meso isomers (M) or the same (S)? Write E, D, M, or S in the blank provided.
D) Circle the following statement(s) does not correctly describe unimolecular nucleophilic substitution (S\textsubscript{N}1) reactions of alkyl halides? (”>“ means "reacts faster than")

a) Carbocations are intermediates in unimolecular nucleophilic substitutions.
b) The order of decreasing reactivity as a function of leaving group is RI > RBr > RCl.
c) The order of alkyl bromide reactivity is R\textsubscript{3}CBr > R\textsubscript{2}CHBr > R\textsubscript{2}CHBr > CH\textsubscript{3}Br.
d) The rate of an S\textsubscript{N}1 reaction depends on the concentration of the nucleophile.

E)

Rank the following alkenes in order of decreasing heat of hydrogenation.

\[
\begin{array}{cccc}
\text{1} & \text{2} & \text{3} \\
\hline
\text{A)} & 1 > 3 > 2 \\
\text{B)} & 3 > 2 > 1 \\
\text{C)} & 2 > 3 > 1 \\
\text{D)} & 1 > 2 > 3 \\
\end{array}
\]

F)

What is the product of the addition of Br\textsubscript{2} to cyclopentene?

\[
\begin{array}{cccc}
\text{A)} & \text{Br} & \text{Br} \\
\text{B)} & \text{Br} & \text{Br} \\
\text{C)} & \text{Br} & \text{Br} \\
\text{D)} & \text{Br} & \text{Br} \\
\end{array}
\]

Assume the reaction involves molecular Br\textsubscript{2} in CCl\textsubscript{4}
G)

How many chirality centers are in the molecule shown at the right?
A) 1
B) 2
C) 3
D) 4

H)

Which reagent reacts with an alkene to produce an epoxide?
A) \[
\begin{array}{c}
\text{CH}_3\text{COH} \\
\text{O} \\
\end{array}
\]
B) \[
\begin{array}{c}
\text{CH}_3\text{OCOH} \\
\text{O} \\
\end{array}
\]
C) \[
\begin{array}{c}
\text{CH}_3\text{COOH} \\
\text{O} \\
\end{array}
\]
D) \[
\begin{array}{c}
\text{CH}_3\text{OCH} \\
\text{O} \\
\end{array}
\]
5. Hydrobromination of indene 1 occurs at the double bond in the 5-membered ring to give 2. The reaction is regiospecific, as no compound 3 is formed. Note that the double bonds in the 6-membered ring of 1 are unreactive.

\[
\begin{align*}
\text{1} & \quad + \quad \text{HBr} & \rightarrow & \quad \text{2} \\
& & & + \quad \text{3}
\end{align*}
\]

\(100\%\) Yield \hspace{1cm} 0\%\) Yield

a) Draw a stepwise mechanism for the formation of compound 2 from indene 1 and HBr. Use arrows to indicate electron flow and show intermediates. (10 pts).

b) Briefly explain and illustrate why this reaction is regiospecific, giving only 2 and no 3. (5 pts)

c) Based on the above information draw the structure of the major product formed upon hydroboration/oxidation of indene 1. (5 pts).
6. **Mechanism.** Answer the following 2 questions. **(20 pts).**

**A)** The following substitution reaction proceeds with complete retention of configuration. Propose a mechanism for product formation that is consistent with the stereochemistry. Show all intermediates and indicate electron flow. Clearly indicate stereochemistry of all intermediates and products.

\[
\begin{align*}
&\text{H}_3\text{C}\text{(S)}\text{S}\text{CH}_3 + \text{NaBr} \xrightarrow{\text{H}_2\text{O}} \text{H}_3\text{C}\text{(S)}\text{S}\text{CH}_3 + \text{NaI} \\
\end{align*}
\]

**B)** Propose a mechanism for this transformation. Show all intermediates and electron flow.

\[
\begin{align*}
&\text{H}_3\text{C}\text{CH}_3 \xrightarrow{\text{H}_2\text{SO}_4} \text{H}_3\text{C}\text{CH}_3 + \text{H}_2\text{O} \\
\end{align*}
\]
Blank page for scratch work