Chemistry 3A - Spring 1998
Midterm Exam # 2

Professor Jean Fréchet
April 7, 1998

Your full signature __________________________
Print your full name __________________________
(Last name, First name, Middle)

Your SID ________________________________

Please check the section number and name of your GSI/TA.

111 DeForest, Sarah 311 DeForest, Sarah
121 Berseth, Polly 321 Keet, Corinne
131 Richards, Steven 331 Ponte, Maya
141 Yamamoto, Kana 341 Seymour, Sean
151 Brennan, Paul 351 Werkema, Evan
211 Esker, Todd 411 Esker, Todd
221 Kriesel, Josh 421 Peters, Eric
231 Zylstra, Eric 431 Freeman, Adam
361 Liang, Scott 511 Liang, Scott
371 Paisner, Sara 521 Magliery, Thomas
381 Kim, Esther 531 Kwon, David
391 Bise, Ryan 541 Winans, Katherine

If you are making up an I-grade, indicate the semester you took 3A ______ and the Professor ____________.

This exam has 9 pages; make sure that you have them all. We will only grade answers that are in the designated spaces. Please do your scratch work on the backs of the exam pages. Write only one answer to each problem; multiple answers will receive no credit, even if one of them is correct.

Note: This examination runs for a total of 80 minutes. No questions will be answered by proctors after the exam begins. Please write legibly; ambiguous or messy answers will receive no credit.

Do Not Write in this Box.

1. ______ (12)
2. ______ (10)
3. ______ (14)
4. ______ (10)
5. ______ (12)
6. ______ (15)
7. ______ (12)
8. ______ (15)

Total ______ (100)
Chem. 3A

Midterm Exam #2

1. (12 points)

(a) Draw a Fisher projection of

(2S,3R)-2-chloro-3-methylhexane

(b) Name the following compound:
(Use IUPAC nomenclature and do not forget stereochemistry)

\[
\begin{align*}
\text{CH}_2\text{CH}_3 \\
\text{H} \quad \text{Cl} \quad \text{CH}_2\text{CH}_2\text{Cl}
\end{align*}
\]

Answer:

(c) An old bottle of 2-iodobutane has a label marked "2-iodobutane mixture of enantiomers". The optical rotation \(\alpha\) of a solution of 0.08 g of this mixture in 2 mL of solvent measured in a 5 cm tube is found to be +0.192°. Given that the specific rotation of pure (R)-2-iodobutane is \([\alpha]_D = -16°\), What is the optical purity of the sample? Calculate the percentages of (S) and (R) enantiomers in the old bottle. Show the equation used for the calculation of \([\alpha]_D\) as well as the details of your calculation.

Answers: Optical Purity = % (S) = % (R) =
2. (10 points)

(a) Circle any molecule below that has an (R) configuration according to the Cahn-Ingold-Prelog convention

\[
\begin{align*}
\text{H} & \quad \text{H} \\
\text{CH}_3 & \quad \text{CH}_3 \\
\text{CH}_2\text{Cl} & \quad \text{CH}_2\text{Cl} \\
\text{CH}_2\text{Br} & \quad \text{CH}_2\text{Br}
\end{align*}
\]

(b) What is the observed reaction rate for the S_N2 reaction below given the following concentrations:

\[
[\text{CH}_3\text{Cl}] = 0.5 \text{ mol L}^{-1}, \quad [\text{OH}^-] = 0.03 \text{ mol L}^{-1}\]

and the rate constant \(k = 0.003 \text{ mol}^{-1} \text{ L s}^{-1}\). Your answer should show an equation for the rate law as well as all calculations.

\[
\begin{array}{c}
\text{CH}_3\text{Cl} + \text{OH}^- \rightarrow \text{CH}_3\text{OH} + \text{Cl}^-
\end{array}
\]

ANSWER

\[
\text{Rate} =
\]

(c) Circle any compound below that is optically active

\[
\begin{align*}
\text{Cl} & \quad \text{H} \\
\text{Cl} & \quad \text{Cl} \\
\text{Cl} & \quad \text{Cl} \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\end{align*}
\]
3. (14 points) (a) Explain why treatment of (S)-2-iodooctane with NaI causes the optical activity of the starting material to disappear. Your answer must name and describe in one sentence the type of reaction mechanism involved and its stereochemical consequences and show a complete equation with all materials (starting and final) and their stereochemistry. (2-iodooctane is CH₃CHI(CH₂)₅CH₃)

(b) Propose a step-by-step synthesis of CH₃CH=CHCH₃ from ethanol as the only source of C atoms. Show all reagents required for each step but no mechanisms or curved arrows are needed.
4. (10 points)

(a) Show the most favorable conformation (as a SAWHORSE projection) of the starting material for the E2 elimination below.

\[
\begin{array}{c}
\text{CH}_2\text{CH}_3 \\
\text{H} \\
\text{H}_3\text{C} \\
\text{CH}_2\text{CH}_3 \\
\text{H} \\
\text{Br} \\
\text{E2} \\
\rightarrow \\
\text{H}_3\text{C} - \text{C} = \text{CH} - \text{CH}_2\text{CH}_3 \\
\text{CH}_2\text{CH}_3
\end{array}
\]

(b) Show a clear stereochemical representation of the alkene produced in this reaction.

(c) Write clear structures for the products containing no oxygen atom that are formed when 2-bromo-2-methylbutane is allowed to react with excess warm potassium t-butoxide.

\[
\begin{array}{c}
\text{H} \\
\text{C} - \text{C} - \text{C} = \text{CH} - \text{CH}_2\text{CH}_3 \\
\text{Br} \\
\text{CH}_3 \\
\text{K}^\oplus \text{t-BuO}^\ominus \\
\Delta \\
\rightarrow
\end{array}
\]
5. (12 points)

(a) How many stereoisomers are possible in principle for the compound shown below (circle one number)

\[
\begin{array}{cccc}
2 & 4 & 6 & 8 \\
3 & 9 & 16 & 27 \\
18 & 20 & 24 & 32 \\
36 & 48 & 64 & 81 \\
\end{array}
\]

(b) Rank the following nucleophiles in order of reactivity for an S_N2 reaction

\[
H_2O \quad HS^- \quad C_2H_5O^- \quad Cl^-
\]

ANSWER: \underline{_______} > \underline{_______} > \underline{_______} > \underline{_______}

Most reactive \hspace{1cm} Least reactive

(c) Explain why the free-radical monobromination of
affords a racemic mixture. Show the structure of both products and the intermediate leading to them.

\[
\text{Structure of intermediate}
\]

\[
\text{Structure of products}
\]

Brief Explanation: a racemic mixture is obtained because...
(a) Show clear structures for all of the products normally expected in the reaction below. Assume that no rearrangement occurs and do not show any mechanism.

(b) What is the order of the reaction?

ANSWER: Order of reaction =

(c) Show a complete step-by-step mechanism (show all curved arrows!) for the reaction below
7. (12 points) (a) Which of the two synthetic routes, A or B, shown below would be best to obtain a high yield of the desired product? Explain your answer discussing briefly the type of mechanism involved and comparing the species in each reaction. Also show a clear structure for the side-product that might be obtained by the less desirable route.

A \[ \text{CH}_3\text{O}^- + \text{C}_6\text{H}_5\text{I} \rightarrow \text{CH}_3\text{OCH}_3 + \text{I}^- \]

B \[ \text{C}_6\text{H}_5\text{O}^- + \text{CH}_3\text{I} \rightarrow \text{C}_6\text{H}_5\text{OH} + \text{I}^- \]

Answer:

Best route to product

Answer:

Structure of side-product for less desirable route

(b) Complete the reactions below showing a clear structure for each of the missing reagent(s).

\[ \text{CH}_3\text{CH}_2\text{CH}_2\text{OH} \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{Cl} \]

\[ \text{CH}_3\text{CH}_2\text{CH}_2\text{OH} \rightarrow \text{CH}_3\text{CH}_2\text{CO}_2\text{H} \]
8. (15 points) Show the structure of the major product(s) obtained in each of the following reactions. Your answer must show clear stereochemistry where applicable, write NR if no reaction occurs. Do not show any mechanisms!

1. \[ \text{H} \quad \text{CH}_3S^- \quad \text{Acetone} \]

2. \[ \text{Cl} \quad \text{CH}_3 \quad \text{CH} \quad \text{CH}_3 \quad \text{KOH} \quad \Delta \]

3. \[ \text{Br} \quad \text{in CH}_3\text{COOH} \]

4. \[ \text{OH} \quad \text{TsO}^- \quad \text{pyridine} \]

5. \[ \text{Li} \quad 1) \text{O} \quad 2) \text{H}^+ / \text{H}_2\text{O} \]