Chemistry 3A - Spring 2000
Final

Professor Jean Fréchet
May 15, 2000

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.

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If you are making up an L-grade, indicate the semester you took 3A_______ and the Professor___________.

This exam has 14 pages; make sure that you have them all.

Please be sure to use the very useful data given on page 14.

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 180 minutes. No questions will be answered by proctors after the exam begins. Please write legibly; ambiguous or messy answers will receive no credit.

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1. [16 Points] (a) propose a structure for an alcohol $\text{C}_4\text{H}_{10}\text{O}$ that has the following $^{13}\text{C}$ NMR data:
"normal" (proton decoupled) spectrum: peaks at $\delta = 19.0$, 31.6, and 69.5 ppm;
DEPT-90: $\delta = 31.6$ ppm; DEPT-135: positive peaks at $\delta = 19.0$ and 31.6; negative peak at $\delta = 69.5$ ppm.

Your answer should show a clear structure.

(b) A hydrocarbon has the formula $\text{C}_7\text{H}_{12}$, it exhibits the following spectroscopic properties: IR: peaks at 3072, 2900-3000, 1649 and 888 cm$^{-1}$; $^1\text{H}$ NMR spectrum $\delta = 1.3$ (m, 2H); 1.7 (m, 4H); 2.2 (m, 4H) and 4.8 ppm (quintet, 2H); $^{13}\text{C}$ NMR: $\delta = 26.8; 28.7; 35.7; 106.9$ and 149.7 ppm; hydrogenation affords a product with the formula $\text{C}_7\text{H}_{14}$. (Note: m means "multiplet")

(i) What is what is its degree of unsaturation of the hydrocarbon $\text{C}_7\text{H}_{12}$?

Answer: 2

(ii) What characteristic functional group is responsible for the IR band at 1649 cm$^{-1}$?

alkene

(iii) What is the structure of the hydrocarbon?

Answer:

(c) The characteristic IR stretching frequency for the carbon-carbon triple bonds of alkynes is:

(Circle one) 3310 cm$^{-1}$ 2120 cm$^{-1}$ 1950 cm$^{-1}$ 1640 cm$^{-1}$ 1430 cm$^{-1}$ 888 cm$^{-1}$
2. [19 Points] (a) Draw the $^1$H NMR spectrum for ClCH$_2$OCH$_2$CH$_3$ assuming perfect splitting of peaks. Make sure the location of the peaks is appropriate and label each peak. Also draw a realistic step integration.

(b) Show a fully labeled energy diagram for the following reaction

$$\text{CH}_2=\text{CHCH}_3 + \text{HCl} \rightarrow \text{CH}_3\text{CHCICICCH}_3$$
3. **[15 Points]** Name or draw as appropriate the following molecules. Show stereochemistry if relevant.

(a) Lithium diisopropylamide

(b) Z-2-fluoro-3-methoxy-2-pentene

(c) 7-chlorobicyclo[4.3.0]nonane

(d) 2,4-heptadiene

(e) 4-propyl-5-hexyn-1-ol
4. [16 Points]

(a) Show a step-by-step synthesis of \(\text{HO} - \text{H} - \text{OH}\) from cyclopentene \(\text{C}_5\text{H}_8\) (no mechanism)

(b) Show a step-by-step mechanism (including curved arrows) for the following reaction:

(c) The optical purity of a sample of (R)-2-bromobutane is 80%. What is its optical rotation given that pure (S)-2-bromobutane has a specific rotation of +25°. Also calculate the percentage of S-isomer in this sample.

Answers:

Optical rotation = \(-20^\circ\)

Percentage of S isomer in sample = 20%
5. [15 Points] Show the major product(s) obtained in the reactions below. Do not include minor products or by-products. Be sure to specify stereochemistry where appropriate.

\[
\begin{align*}
\text{HCl} \quad \text{HCl} \\
\text{1) O}_3 \\ 
\text{2) (CH}_3\text{)}_2\text{S} \\
\end{align*}
\]

\[
\begin{align*}
\text{1) OsO}_4, \text{THF} \\
\text{2) NaHSO}_3 \\
\end{align*}
\]

\[
\begin{align*}
\text{CH}_2\text{OH} \\
\text{1) MCPBA in CH}_2\text{Cl}_2 \\
\text{2) H}^+\text{/H}_2\text{O} \\
\end{align*}
\]

\[
\begin{align*}
\text{HBr} \\
\text{ROOR} \Delta \\
\end{align*}
\]
6. [17 Points]. Show the major product(s) obtained in the reactions below. Be sure to specify stereochemistry where appropriate.

\[
\text{CH}_3\text{C-CH}_3\text{Cl} + 3 \text{Na}^+ \text{NH}_2^- \xrightarrow{\text{in liquid NH}_3} \]

\[
\text{H}_3\text{C-CC}_3^=\text{C}^=\text{Li}^+ + \text{O} \text{ketone} \rightarrow \]

\[
\text{C}_7\text{H}_8 + \text{KMN}_4\text{conc.} \xrightarrow{\text{H}_2\text{O} \Delta} \]

\[
\text{C}_7\text{H}_8 + 1 \text{Cl} \text{benzoic acid} \rightarrow \]

\[
\text{C}_5\text{H}_8 \xrightarrow{1) \text{Hg(OAc)}_2 \text{in CH}_3\text{OH}} \rightarrow \]

\[
\text{C}_5\text{H}_8 \xrightarrow{2) \text{NaBH}_4 \text{in CH}_3\text{OH}} \rightarrow \]
7. **[19 Points]** (a) For each of the reaction sequences below show a clear structure for the missing intermediate and the reagents used for the second step.

(a) Reaction 1:

![Reaction 1 diagram]

(a) Reaction 2:

![Reaction 2 diagram]

(b) Write a step by step mechanism (with all curved arrows) for the following reaction:

![Mechanism diagram]
8. [17 Points]
(a) Consider the following reaction: $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}═\text{CH}_2 \rightarrow \text{CH}_2═\text{CH}_2 \; + \; \text{CH}_3\text{CH}=\text{CH}_2$

$\Delta H^\circ = +22.4 \text{ Kcal mole}^{-1} \quad \Delta S^\circ = +0.0333 \text{ Kcal deg}^{-1} \text{ mole}^{-1}$

(i) Is the reaction thermodynamically feasible at 100°C? Show your calculation and explain.

\[ \Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \]

\[ \Delta G^\circ = -22.4 - (373)(0.0333) \]

\[ \Delta G^\circ = -22.4 - (12.44) \]

\[ \Delta G^\circ = -34.84 \text{ Kcal/mol} \]

\[ \Delta G^\circ > 0 \]

Therefore, the reaction is not thermodynamically feasible at 100°C.

(b) Write the structures of the products of monochlorination of butane using chlorine and light, label them alphabetically (A, B, etc...) and calculate in what ratio (A : B : ...) the products will be formed.

Answer: Structures

Answer: Ratio

$A : B : C = 1 : 4 : 4$
9. [16 Points] (a) Show a step by step mechanism (with curved arrows) for the reaction:

\[
\begin{align*}
\text{H}_2\text{C}═\text{CH}−\text{CH}_3 & \quad 1) \text{Br}_2 / \text{H}_2\text{O} \\
\text{CH}_2−\text{CH}−\text{CH}_3 & \quad 2) \text{OH}⁻
\end{align*}
\]

(b) What is the structure of the compound \(\text{C}_4\text{H}_9\text{Cl}\) whose \(^1\text{H}\) NMR spectrum is shown below. Write a clear structure and provide a peak assignment using arrows to indicate which peak corresponds to each set of protons.
10. [16 Points]

(a) Draw the most and the least stable conformations of cis-1-tert-butyl-4-chlorocyclohexane (in chair form only) and calculate the equilibrium constant $K_{eq}$ for the least stable chair going to the most stable chair at 25°C.

\[
\Delta G^0 = \Delta G^0_{\text{prod}} - \Delta G^0_{\text{react}}
\]

\[
\Delta G^0 = -RT \ln K_{eq}
\]

\[
\Delta G^0 = -9.5 \text{ kJ/mol}
\]

\[
\Delta G^0 = -9.5 \times \frac{1000 \text{ J/mol}}{1 \text{ kJ/mol}} = -9500 \text{ J/mol}
\]

\[
K_{eq} = \exp \left( \frac{-\Delta G^0}{RT} \right)
\]

\[
K_{eq} = \exp \left( \frac{-9500 \text{ J/mol}}{8.314 \text{ J/(mol K)} \times 298 \text{ K}} \right)
\]

\[
K_{eq} = \exp \left( \frac{-9500}{25.31} \right)
\]

\[
K_{eq} = \exp (-377.17)
\]

\[
K_{eq} = 1901.4
\]

(b) Show the structure (with stereochemistry) of the product obtained in the reaction below:
11. [19 Points] (a) propose a synthesis of

from \( \text{H}_2\text{C}=\text{CH}-\text{CH}_3 \)

and \( \text{H}_3\text{C}=\text{C}=\text{O} \)

(b) Show the missing reagents required to effect the following transformations:

\[
\begin{align*}
\text{H}_3\text{C}-\text{C}=\text{C}-\text{CH}_3 & \quad \text{1) } \text{Na, NH}_3(\text{g}) \quad \text{2) } \text{H}_2\text{O} \\
\text{H}_3\text{C} & \quad \text{H} \\
\text{H} & \quad \text{CH}_3 \\
\end{align*}
\]
12. [15 Points]

Propose a step by step synthesis of \( \text{HC} = \text{C} - \text{CH}_2 - \text{CH} - \text{CH}_3 \) from ethyne and methane as the sole sources of C atoms. Show all steps and reagents.
**Typical \(^1\)H NMR chemical shifts**

| R-CH\(_3\) | 0.8-1.1 |
| R-CH\(_2\)-R' | 1.2-1.4 |
| R\(_3\)CH | 1.4-1.7 |
| R-CH\(_2\)-O-R' | 3.3-3.9 |
| R-CH\(_2\)Cl | 3.4-3.7 |
| R\(_2\)CHCl | 3.9-4.4 |
| RO-CH\(_2\)Cl | 5.2-5.6 |

Relative reactivity of CH bonds in radical chlorination
Tertiary : Secondary : Primary = 5 : 4 : 1

- Value of gas constant: \( R = 2.0 \text{ cal deg}^{-1} \text{ mol}^{-1} = 0.00197 \text{ kcal mol}^{-1} \)
- Value of e (base for natural logarithms) \( e = 2.718 \)
- Value of absolute zero (kelvin) = -273°C

Value of each 1,3-diaxial interaction for Cl - H = 0.25 Kcal mole\(^{-1}\)
Value of each 1,3-diaxial interaction for (CH\(_3\))\(_2\)C - H = 2.5 Kcal mole\(^{-1}\)
Value of each 1,3-diaxial interaction for CH\(_3\) - H = 1 Kcal mole\(^{-1}\)
Value of butane-gauche interaction = 1 Kcal mole\(^{-1}\)

**Glossary:** MCPBA is meta-chloroperoxybenzoic acid; ROOR is an organic peroxide; \( K_{eq} \) is the equilibrium constant.

**Partial periodic table of the elements**

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<th>II</th>
<th>IIIA</th>
<th>IVA</th>
<th>VA</th>
<th>VIA</th>
<th>VIIA</th>
<th>2 O</th>
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**Note:** There are no questions to be answered on this page. Not all of the data provided may be needed.