Chemistry 216 - Second Examination
April 21, 2009

(100 minutes; 120 points)
Professor Masato Koreeda

Please print
Name________ KEY _______

Please CHECK OFF your lab section.
Tuesday, AM
110 GSI: Ming Fang
111 Daniel Ehrmann
112 Ivy Tran
113 Bo Wang
114 Kaysia Ludford
115 Jessica Lee
116 Kira Landenberger
117 Chase Schuler
118 Miri Yoon
119 Lindsay Saunders

Tuesday, PM
120 Aireal Haley
121 Xin Liu
122 Eric Chen
123 Rebecca Chang
124 Jonathon Mahlow
125 Yingda Ye
126 Shana Santos
127 Eric Majchrzak
128 Karoline Chiou
129 Ravi Nanga

Wednesday, PM
130 Debasis Das
131 Kristy Bojazi
132 Megan Beems

Thursday, AM
310 Ming Fang
311 Brett Ehrmann
312 Ivy Tran
313 Bo Wang
314 Kaysia Ludford
315 Jessica Lee
316 Kira Landenberger
317 Aireen Romu
318 Li Wang
319 Lindsay Saunders

Thursday, PM
320 Larissa Kipa
321 Xin Liu
322 Natalie Vandeven
323 Jason Wu
324 Anthony Grillo
325 Yingda Ye
326 Shana Santos
327 Eric Majchrzak
328 Karoline Chiou
329 Ravi Nanga

Friday, AM
410 Larissa Kipa
411 Joseph Jankolovits
412 Aireen Romu
419 Li Wang
414 Miri Yoon

Friday, PM
420 Aireal Haley
421 Debasis Das
422 Tara Boinpally
423 Christie Young
424 Jonathon Mahlow

High : 120/120 (1 st); Median: 85/120 (71%)

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This exam has 12 pages including this cover page. The last 4 pages include a periodic table, tables of characteristic IR absorption frequencies of common chemical bonds, representative $^1$H and $^{13}$C NMR chemical shifts, and $^1$H/$^1$H coupling constants, and $pK_a$ values for representative acids.
I. (10 points) Draw the structures for the organic products containing a phenyl group \((\text{C}_6\text{H}_5)\) which are expected upon treatment of each of the following chemicals with \(\text{C}_6\text{H}_5\text{MgBr}\), followed by acidic work-up. Note that acetone is \((\text{CH}_3)_2\text{C}=\text{O}\).

(1) Dry ice \((\text{CO}_2)\)

(2) acetone

(3) \(\text{O} \xrightarrow{\text{H}} \) 

(4) \(\text{C}_6\text{H}_5\text{C}(=\text{O})\text{OH}\) (benzoic acid)

II. (6 points). The reaction of 5-bromo-1-pentanol (1) with magnesium in anhydrous diethyl ether does not give the expected Grignard reagent, 2. Provide in the box below an explanation for the failure of this reaction on the basis of the reaction mechanism using the curved arrow convention.

III. (9 points). In a number of experiments you performed in the lab, the product mixtures were extracted with diethyl ether or dichloromethane a few times. The combined organic layers were first washed with water and then with brine. The resulting organic solution then was dried over a drying agent such as anhydrous calcium chloride, sodium sulfate, and magnesium sulfate. Answer in the box provided the following questions.

(1) (3 points) What is brine? 

**saturated aqueous NaCl**

(2) (3 points) What is the purpose of this washing with brine?

**To reduce the amounts of water dissolved in an organic solvent**

(3) (3 points) What is the chemical basis for the use of an anhydrous agent? Explain using MgSO\(_4\) as the example. Be specific if any chemical process is involved.

**MgSO\(_4\) + 7H\(_2\)O \rightarrow MgSO\(_4\)\cdot7H\(_2\)O**

**or MgSO\(_4\) + xH\(_2\)O \rightarrow MgSO\(_4\)\cdotxH\(_2\)O**
IV. (20 points). For each of the reactions given below, draw in the box provided the structure of the expected major reaction product and propose a reasonable step-by-step mechanism for its formation using the curved-arrow convention.

(1)

\[
\begin{align*}
\text{Mechanism:} \\
\text{1. NaOH (excess)} \\
\quad \text{H}_2\text{O, } \Delta \\
\quad \text{2. H}_2\text{O}^+ (\text{pH} = 2) \\
\end{align*}
\]

These work-up steps not graded.

(2)

\[
\begin{align*}
\text{Mechanism:} \\
\text{Ph} = \text{C}_6\text{H}_5 (\text{phenyl}) \\
\end{align*}
\]
V. (5 points). The proton NMR peaks of a mixture of acetone [(CH\textsubscript{3})\textsubscript{2}C=O] (δ 2.17 ppm), p-dioxane (C\textsubscript{4}H\textsubscript{8}O\textsubscript{2}) (δ 3.50 ppm), and dichloromethane (CH\textsubscript{2}Cl\textsubscript{2}) (δ 5.20 ppm) are integrated. The integrated values are 12, 8, and 1 for acetone, p-dioxane, and dichloromethane peaks, respectively. In what mole ratio are these three substances present? Provide your answer in the box shown below. No explanation required. No partial credit will be given to this problem.

acetone : p-dioxane : dichloromethane = 4 : 2 : 1

\[ \frac{12}{6} : \frac{8}{8} : \frac{1}{2} = 2 : 1 : \frac{1}{2} = 4 : 2 : 1 \]

VI. (15 points). For each of the Diels-Alder reactions given below, draw in the box the structure of the expected organic major product. Make sure to indicate the stereochemistry of the product whenever applicable.

(1)

\[ \text{ + enantiomer} \]

correct connectivity: 3 pts; stereochem: 3 pts

(2)

\[ \text{ + enantiomer} \]

correct connectivity: 3 pts; stereochem: 3 pts

(3)

\[ \text{ + enantiomer} \]

correct connectivity: 3 pts; stereochem: 3 pts
VII. (12 points) The following three sets of $^1$H (at 300 MHz in CDCl$_3$) and $^{13}$C NMR spectra (at 25 MHz in CDCl$_3$) are of isomeric alcohols with formula C$_5$H$_{12}$O (i.e., no unit of unsaturation!). Draw in the boxes provided the structures of the compounds. No explanation needed. No partial credit will be given to this problem.

(1)

$^{13}$C NMR spectrum in CDCl$_3$
(TMS, CDCl$_3$ peaks not shown)

(2)

$^{13}$C NMR spectrum in CDCl$_3$
(TMS, CDCl$_3$ peaks not shown)
VII. (continued)

VIII. (10 points) On the basis of the spectroscopic information given, assign the structure to compound X, C$_5$H$_8$O.

Compound X – IR (liquid film): 3030 (weak), 2953 (weak), 2923 (weak), 2855 (weak), 2722 (weak), 1693 (strong), and 1630 (medium) cm$^{-1}$; no peaks in the 4000-3200cm$^{-1}$ region.

$^1$H-NMR (CDCl$_3$) $\delta$ 1.99 (3H, singlet), 2.18 (3H, singlet), 5.88 (doublet, $J = 8.1$ Hz), and 9.96 (1H, doublet, $J = 8.1$ Hz).

$^{13}$C NMR (CDCl$_3$) $\delta$ 18.91 (q), 27.23 (q), 128.14 (d), 160.67 (s), and 191.03 (d) ppm [note: q, d, and s denote the splitting patterns of each $^{13}$C peak when run under a proton-coupled mode).

(1) (1 point) What is (are) the unit(s) of unsaturation of this compound? 2

(2) (2 points) What does the IR and $^{13}$C NMR spectral information tell you in terms of the presence of an O-containing functional group in this compound? Aldehyde*

(3) (2 points) How many alkenic carbon peaks are there in the $^{13}$C spectrum? 2

(4) (5 points) Draw the structure of this compound in the box below.

*"Ketone" was also accepted.
IX. (19 points) On the basis of its spectroscopic information provided below, answer the questions given on page 8, and propose the structure of the compound \( \text{C}_{10}\text{H}_{12}\text{O}_2 \). Draw the proposed structure in the box below and give in the box on page 8 a brief explanation by assigning all \(^1\text{H}\) and \(^{13}\text{C}\) NMR peaks.

IR spectrum (liquid film):

\[
\begin{array}{c}
\text{1H NMR spectrum in CDCl}_3 \\
(\text{TMS peak not shown})
\end{array}
\]

\[
\begin{array}{c}
\text{13C NMR spectrum in CDCl}_3 \\
(\text{TMS, CDCl}_3 \text{ peaks not shown})
\end{array}
\]
IX. (continued)

(1) (1 point) What is (are) units(s) of unsaturation of this compound?  _______5_______

(2) (2 points) What do these sp^3^1^H peaks in the 1 – 3.2 ppm region tell you in terms of the presence of an alkyl group in this molecule?

__CH_3-CH_2-_____

(3) (2 points) What does the 3H singlet peak at 3.83 ppm in the ^1^H NMR peak tell you in terms of the presence of an O-containing functional group in this molecule?

__ROCH_3 or R-C(=O)OCH_3__

(4) (2 points) What does a pair of doublets in the 6.8 – 8.1 ppm region tell you in terms of a substitution pattern of the benzene ring?

__Para (or 1,4)-disubstituted_benzene__

(5) (2 points) What does the ^1^3^C NMR peak at 199 ppm tell you in terms of the O-containing functional group in this molecule?

__Ketone or aldehyde____

(6) (2 points) What is the structure of this compound. Draw the structure in the box below.

(7) (8 points) Assign all ^1^H and sp^3^ ^1^3^C chemical shifts to the structure in the box below.

X. (14 points). Show how many peaks you would expect to observe in the proton-decoupled ^1^3^C NMR spectra of the following compounds. Indicate your answers in the box provided. Do not count the ^1^3^C NMR peaks of the solvent and TMS.

(1)

(2)

(3)

(4)

(5)

(6)

(7) room temperature