Fall 2005 December 12, 2005

CHM 301 & 303
LAB WRITTEN EXAM

Name _____ Lab TA _____

You will be given two and a half hours for this exam. This is an open book exam, but you may only use materials that you have authored, such as your lab notebook, lab reports (including grading comments by your TA), and personal handwritten or typed notes. You may not use lab manuals, textbooks, photocopied material (except for the "spectral" handouts noted in the LWE Announcement), or guidelines created by your TA.

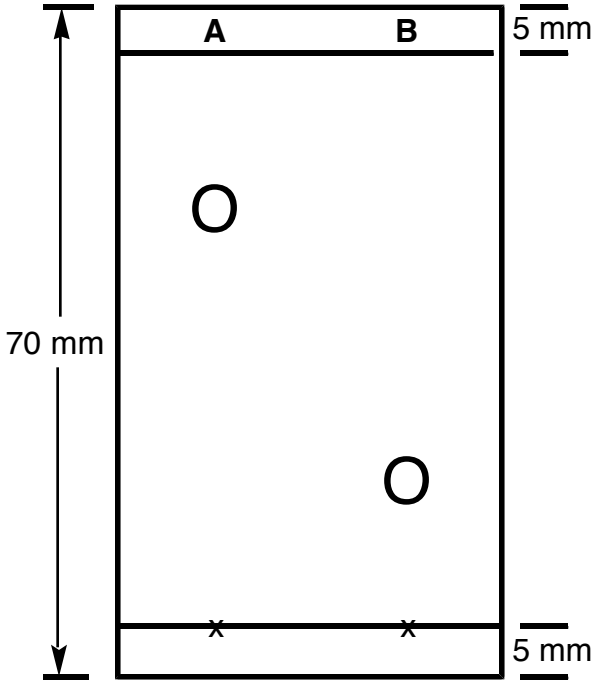
Question	Score
I. (8 pts)	_____
II. (14 pts)	_____
III. (33 pts)	_____
IV. (20 pts)	_____
V. (28 pts)	_____
VI. (33 pts)	_____

Total (136 pts)	_____

Pledge: I pledge my honor that I have not violated the Honor Code during this exam.

Signature _____

I. The R_f values for compounds **A** and **B** are 0.75 and 0.25, respectively. Calculate the distances (in mm) "travelled" by compounds **A** and **B** on the TLC plate represented below. (Don't try to measure these distances from the TLC plate, which is not necessarily drawn to scale.) [8 points]

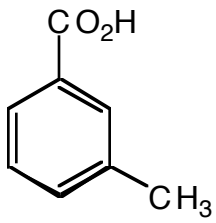


II. A) You would like to recover a valuable compound **C** from an aqueous suspension. A quick check of the literature reveals the following solubility properties for **C** at room temperature:

acetone, 0.40 g/10mL
ethanol, 0.75 g/10 mL
hexanes, 0.07 g/10 mL
methylene chloride, 0.15 g/10 mL
toluene, 0.24 g/10 mL

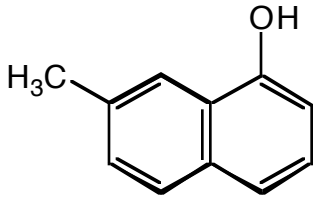
Based on these data, which solvent would be best for the extraction of compound **C** from the aqueous suspension? Why? [6 points]

II. B) Given an unknown sample that was thought to be either **D** or **E**, answer the following questions. (You may assume that authentic samples of **D** and **E** are available.)



D

mp 111 °C



E

mp 110-111 °C

1) How could you identify the unknown sample by melting point techniques alone? [4 points]

2) How could you identify the unknown by solubilty properties alone? [4 points]

III. A) Joe L. Sapphire, the noted orgo lab student, isolated *two* samples of aspirin and *no* acetaminophen, while performing the Method **B** separation in the Analgesic Experiment. That is, his recrystallized "acetaminophen" was shown to be aspirin, as demonstrated by both melting point and TLC analyses. What <u>single</u> step in the overall separation of the components of the analgesic powder, if performed poorly, would most likely be responsible for Joe L.'s problem? Explain. Where is Joe L.'s acetaminophen? (<u>Hint</u>: When asked how much water he used for his "acetaminophen" recrystallization, Joe L. replied, "I can't remember exactly, but I think I used between 5 and 10 mL of water for my recrystallization.") [10 points]

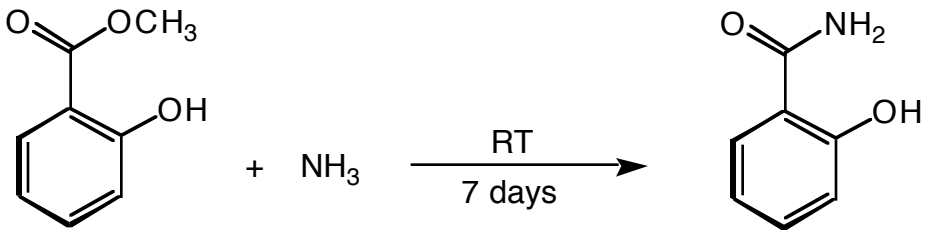
B) An orgo student dissolved the crude reaction mixture from the Oxidation-Reduction Experiment in water. Inadvertently, the student *next* added concentrated HCl and *then* extracted with methylene chloride. Upon concentration of the acidic aqueous layer (i.e., most of the water was boiled off), a colorless solid, which failed to melt below 400 °C, was isolated.

1) What was the solid and how did it form? [5 points]

2) Where is the student's carboxylic acid? Can the reaction mixture still be salvaged at this point? If so, how? If not, why? [10 points]

III. C) There are potentially <u>four</u> products from the reaction of 1-chloro-2-butene and ethanolic silver nitrate, as performed in orgo lab this semester. (Three of the products have a molecular formula of $C_6H_{12}O$, and the fourth product has a molecular formula of C_4H_6.) Please draw boxes around the four structures that you want graded. (<u>Notes</u>: Mechanisms are <u>not</u> required; however, a mechanistic analyses should help you arrive at the correct structures. Please pay attention to stereochemistry, when appropriate.) [8 points]

IV. Salicylamide (**2**), used in conjuction with aspirin and caffeine in BC® Analgesic Powders, was prepared from 0.500 mL of methyl salicylate (oil of wintergreen) (**1**) [density = 1.174 g/mL] and 5 mL of aqueous ammonia [density = 0.90 g/mL; 29% by weight ammonia], as shown below.



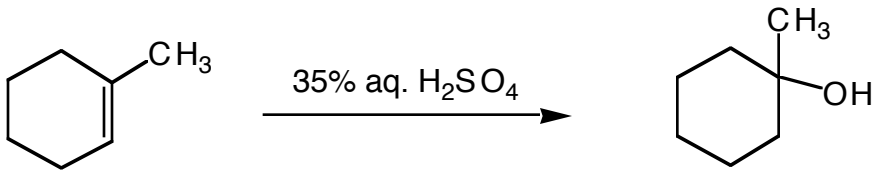
1 **2**

A) What is the limiting reagent in this reaction? (Show your calculations and indicate your reasoning!) [10 points]

B) If 413 mg of salicylamide (**2**) was obtained from this reaction, what is the % yield of salicylamide (**2**)? (Show your calculations!) [8 points]

C) What is the by-product in the reaction shown above? [2 points]

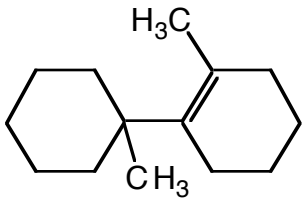
V. The acid-catalyzed hydration of 1-methylcyclohexene (**3**) affords 1-methylcyclohexanol (**4**).



3 **4**

V. A) Write an arrow formalism for the acid-catalyzed hydration of 1-methylcyclohexene (**3**) to give 1-methylcyclohexanol (**4**). Please show all intermediates and every proton transfer in exquisite detail. Please account for the regiospecifity of this hydration reaction. [5 points]

Interestingly, when the acid-catalyzed hydration of **3** is attempted in 70% aqueous sulfuric acid (i.e., more concentrated acid), very little **4** is produced. Instead, the major product of this reaction is a "dimer" of 1-methylcyclohexene ($C_{14}H_{24}$). Although this reaction was first reported in 1918, it was not until 1953 that structure **F** was assigned to this dimer.



F

This structural assignment was based on i) elemental analysis data, ii) catalytic hydrogenation of the "dimer" to a saturated hydrocarbon ($C_{14}H_{26}$), and iii) "the absence of olefinic units detectable by IR spectroscopic examination" (implying a tetra-substituted alkene).

B) Write an arrow formalism for the formation of dimer **F** from **3** in the presence of an acid catalyst. Please account for the regiospecifity of this reaction. Also explain why the dimer is favored over 1-methylcyclohexanol (**4**) in 70% aqueous sulfuric acid. [6 points]

In fact, the dimer ($C_{14}H_{24}$) does not exhibit a C=C stretch in its IR spectrum; however, it does display a weak peak at 3065 cm^{-1}. The proton NMR spectrum of the dimer is partially characterized by the following signals:

δ 0.65 (d, J = 6.8 Hz, 3H)
0.92 (s, 3H)
5.50 (t of d, J = 3.6 Hz, J = 1.8 Hz, 1H)

C) Are the spectral data for the dimer compatible with the proposed structure **F**? Briefly explain why or why not. If not, propose an alternate structure for the dimer, which is compatible with the spectral data. Again briefly explain how your alternate structure for the dimer is compatible with the spectral data. And, account for the formation of your proposed dimer (i.e., write an arrow formalism). [17 points]

VI. Steam distillation of the dried, ripe fruit of *Pimpinella anisisum* L. affords an oil, which consists of about 90% of compound **5**. Compound **5** gives 81.04% C and 8.16 % H upon elemental analysis. Upon mild catalytic hydrogenation, **5** yields compound **6**. Spectral data for compounds **5** and **6** are summarized below.

Compound **5**

mass spectrum: m/z = 148 (P, 100%), 147 (46%), 133 (34%)

ir (neat): 1660 (w), 1608 (s), 1511 (s), 1441 (m), 1247 (s), 1175 (s), 1036 (s), 965 (s), and 840 (s) cm^{-1}

^1H NMR ($CDCl_3$): δ 1.83 (d, J = 6.6 Hz, 3H)
3.76 (s, 3H)
6.06 (d of q, J = 15.8 Hz, J = 6.6 Hz, 1H)
6.33 (d, J = 15.8 Hz, 1H)
6.80 (d, J = 9 Hz, 2H)
7.23 (d, J = 9 Hz, 2H)

^{13}C NMR ($CDCl_3$): δ 18.4, 55.2, 113.9, 123.3, 126.8, 130.4, 130.8, 158.6

Compound **6**

mass spectrum: m/z = 150 (P, 17%), 121 (100%)

ir (vapor): 1611 (m), 1517 (s), 1467 (m), 1293 (m), 1250 (s), 1178 (m), 1049 (m), and 820 (m) cm^{-1}

A) What is the molecular formula of compound **5**? (Please show your calculations!) [3 points]

B) How many degrees of unsaturation are present in the molecular formula for compound **5**? [2 points]

C) Assign the peaks at 1660, 965, and 840 cm^{-1} in the IR spectrum of compound **5**. (Hint: It may be useful to compare the IR spectra of compounds **5** and **6**.) [3 points]

D) Deduce the structure of compound **5**. Indicate your reasoning. Please draw the structure of compound **5**, and label each different proton. Under this structure, please indicate your chemical shift assignments for all of the proton resonances. Also, carefully explain the splitting patterns and make coupling constant assignments. (Hint: Please pay attention to stereochemistry.) [20 points]

E) Are the ^{13}C NMR spectral data for compound **5** consistent with your proposed structure? Briefly explain. (Hint: Peak assignments are not required.) [3 points]

F) Deduce the structure of compound **6**. Briefly indicate your reasoning. [2 points]