Laboratory Practice Final Exam
Chemistry 3B—Spring 2004
April 26, 2004

Student Name: ________________________________

Student ID #: __________________________________

Signature: ____________________________________

Please check the box by your lab section and GSI:

	111	Na Pi			**361**	Tanya Leavy
	112	Jeff McMahon			**362**	Derrick Siao
	161	Guangxin Liang			**363**	Scott Backer
	162	Hillary Peltier			**411**	Fiona Lin
	211	Takuya Kochi			**412**	Helen Hoyt
	212	Doug Mitchell			**511**	Lan Deng
	311	Alex Radosevich			**512**	Scoobie Mynar
	312	Amanda Crochet			**561**	Guangtao Li
	313	Chunqi Qian			**562**	Jared Lewis

Instructions:

- There are 12 pages total including this one—CHECK YOUR COPY.
- Please write your answers only in the spaces provided. Scratch work should be done on the blank sheets provided at the end of the exam and will not be graded.
- Show all calculations to receive credit.
- Write clearly. Illegible or ambiguous answers will be considered incorrect.
- You may use your lab notebook (not lab manual) and a calculator.
- You have **90** minutes to complete this exam.
- A sheet of potentially useful data appears on page 2.
- **Good luck!**

1. ________**(10)**
2. ________**(10)**
3. ________**(15)**
4. ________**(15)**
5. ________**(10)**

________**(60)**

Potentially useful data

TABLE 10-2 Typical Hydrogen Chemical Shifts in Organic Molecules

Type of hydrogen[a]	Chemical shift δ in ppm	
Primary alkyl, RCH_3	0.8–1.0	Alkane and alkane like hydrogens
Secondary alkyl, RCH_2R'	1.2–1.4	
Tertiary alkyl, R_3CH	1.4–1.7	
Allylic (next to a double bond), $R_2C{=}C(CH_3)R'$	1.6–1.9	Hydrogens adjacent to unsaturated functional groups
Benzylic (next to a benzene ring), $ArCH_2R$	2.2–2.5	
Ketone, $RC(=O)CH_3$	2.1–2.6	
Alkyne, $RC{\equiv}CH$	1.7–3.1	
Chloroalkane, RCH_2Cl	3.6–3.8	Hydrogens adjacent to electronegative atoms
Bromoalkane, RCH_2Br	3.4–3.6	
Iodoalkane, RCH_2I	3.1–3.3	
Ether, RCH_2OR'	3.3–3.9	
Alcohol, RCH_2OH	3.3–4.0	
Terminal alkene, $R_2C{=}CH_2$	4.6–5.0	Alkene hydrogens
Internal alkene, $R_2C{=}CHR'$	5.2–5.7	
Aromatic, ArH	6.0–9.5	
Aldehyde, $RC(=O)H$	9.5–9.9	
Alcoholic hydroxy, ROH	0.5–5.0	(variable)
Thiol, RSH	0.5–5.0	(variable)
Amine, RNH_2	0.5–5.0	(variable)

[a] R, R′, alkyl groups; Ar, aromatic group (not argon).

TABLE 10-6 Typical ^{13}C NMR Chemical Shifts

Type of carbon	Chemical shift δ (ppm)
Primary alkyl, RCH_3	5–20
Secondary alkyl, RCH_2R'	20–30
Tertiary alkyl, R_3CH	30–50
Quaternary alkyl, R_4C	30–45
Allylic, $R_2C{=}C(R'')CH_2R'$	20–40
Chloroalkane, RCH_2Cl	25–50
Bromoalkane, RCH_2Br	20–40
Ether or alcohol, RCH_2OR' or RCH_2OH	50–90
Carboxylic acids, RCOOH	170–180
Aldehyde or ketone, $RC(=O)H$ or $RC(=O)R'$	190–210
Alkene, aromatic, $R_2C{=}CR_2$	100–160
Alkyne, $RC{\equiv}CR$	65–95

TABLE 11-4 Characteristic Infrared Stretching Wavenumber Ranges of Organic Molecules

Bond or functional group	$\tilde{\nu}$ (cm^{-1})	Bond or functional group	$\tilde{\nu}$ (cm^{-1})
RO—H (alcohols)	3200–3650	$RC{\equiv}N$ (nitriles)	2220–2260
$RC(=O)O$—H (carboxylic acids)	2500–3300	$RC(=O)H$, $RC(=O)R'$ (aldehydes, ketones)	1690–1750
R_2N—H (amines)	3250–3500	$RC(=O)OR'$ (esters)	1735–1750
$RC{\equiv}C$—H (alkynes)	3260–3330	$RC(=O)OH$ (carboxylic acids)	1710–1760
$>C{=}C<$—H (alkenes)	3050–3150	$>C{=}C<$ (alkenes)	1620–1680
—C—H (alkanes)	2840–3000	RC—OR′ (alcohols, ethers)	1000–1260
$RC{\equiv}CH$ (alkynes)	2100–2260		

1 H 1.00794							2 He 4.002602
3 Li 6.941	4 Be 9.012182	5 B 10.811	6 C 12.0107	7 N 14.00674	8 O 15.9994	9 F 18.9984032	10 Ne 20.1797
11 Na 22.989770	12 Mg 24.3050	13 Al 26.981538	14 Si 28.0855	15 P 30.973761	16 S 32.066	17 Cl 35.4527	18 Ar 39.948
19 K 39.0983	20 Ca 40.078	31 Ga 69.723	32 Ge 72.61	33 As 74.92160	34 Se 78.96	35 Br 79.904	36 Kr 83.80
37 Rb 85.4678	38 Sr 87.62	49 In 114.818	50 Sn 118.710	51 Sb 121.760	52 Te 127.60	53 I 126.90447	54 Xe 131.29
55 Cs 132.90545	56 Ba 137.327	81 Tl 204.3833	82 Pb 207.2	83 Bi 208.98038	84 Po (209)	85 At (210)	86 Rn (222)

Equations and constants:

Degree of unsaturation = $(H_{sat}-H_{actual})/2$
$\mathbf{H_{sat}} = 2n_C + 2 - n_X + n_N$

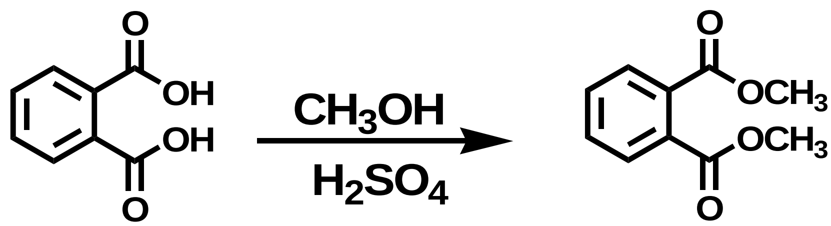
Avogadro's number: 6.022×10^{23} molecules/mol

***c* (speed of light)** = 3.0×10^{8} m/s

***h* (Planck's constant)** = 6.626×10^{-34} J·s

$E=h\nu$ $c=\nu\lambda$

Question 1 (10 points): Consider the reaction, data and experimental procedure listed below.



isophthalic acid **dimethylisophthalate**

Table of reagents

Compound:	*Isophthalic acid*	*Methanol*	*Sulfuric Acid*	*Ethyl acetate*	*Dimethylisophthalate*
MW:	166	32	98	88	194
Density (g/mL):	---	0.791	1.84	0.902	---

Experimental procedure: Isophthalic acid (5.0g) was placed in a 50-mL round-bottom flask. Methanol (20mL) was then added, followed by slow addition of 1mL of 6M sulfuric acid. An air condenser was attached, and the solution was heated to a gentle reflux until the reaction was complete (by TLC).

The reaction mixture was then cooled to room temperature and poured into 10mL of ice water. The aqueous solution was then extracted twice with 2mL portions of ethyl acetate. The ethyl acetate layers were combined and then evapored until all of the ethyl acetate was removed, leaving a white solid mixed in with a liquid. The solid was recrystallized from 95% ethanol to give 4.0g of dimethylisophthalate.

(a). How many mmol of isophthalic acid were used?

(b). How many mmol of methanol were used?

(c). How many mmol of sulfuric acid were used?

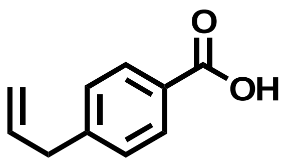
(d). What is the limiting reagent in this reaction?

(e). Calculate the percent yield.

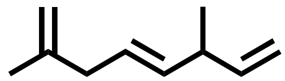
(f). What is the liquid mixed in with the white solid after evaporation of all of the ethyl acetate? What should have been done to avoid the presence of this liquid?

Question 2 (10 points):

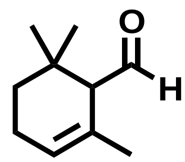
You have been assigned the task of carrying out a TLC analysis of a mixture of compounds **A** through **D** (below) in a 90% ethyl acetate:10% hexane solvent system.



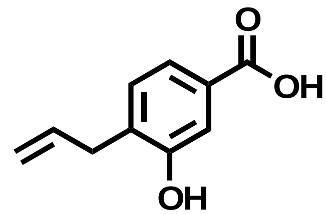
A



B



C



D

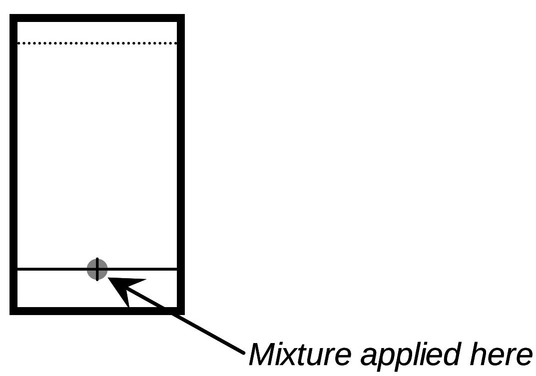
(a). What does the acronym TLC stand for?

(b). Define the term R_f. How is it calculated and what are its units?

(c). Rank compounds **A**-**D** from *largest to smallest* R_f below:

_____ **>** _____ **>** _____ **>** _____

(d). On the "plate" below, draw your predicted TLC results (exact locations and intensities are not expected nor required) for the spotted mixture.



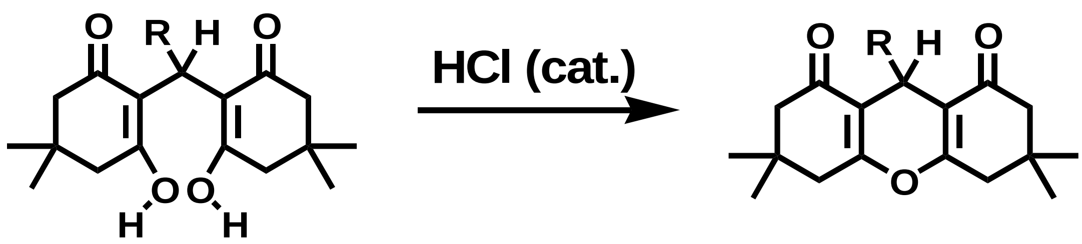
(e). Which of the compounds would show up under a UV lamp (assuming the TLC plate had been coated with a fluorescent indicator)?

(f). Which of the compounds would show up after the plate was dipped in a solution of dinitrophenylhydrazine (DNPH)?

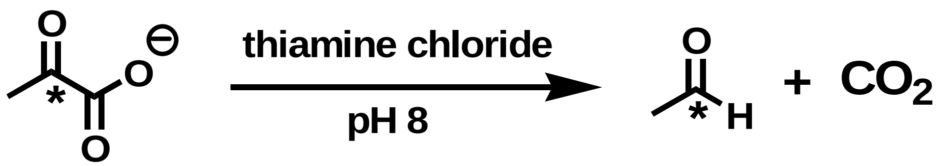
Question 3 (15 points):

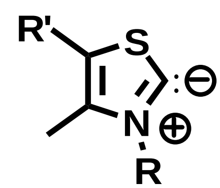
Provide detailed mechanisms for the following transformations:

(a). Under acidic conditions, a dimethone forms a cyclic anhydride (Lab #5).



(b). As was the case with the benzoin reaction carried out in lab #7, thiamine chloride can be used to catalyze the following biological reaction in the absence of enzyme. Propose a mechanism for this reaction **in H_2O** (hint: the carbon indicated in the starting material is the same as the one indicated in the product).





(thiamine chloride)

Question 4 (15 points):

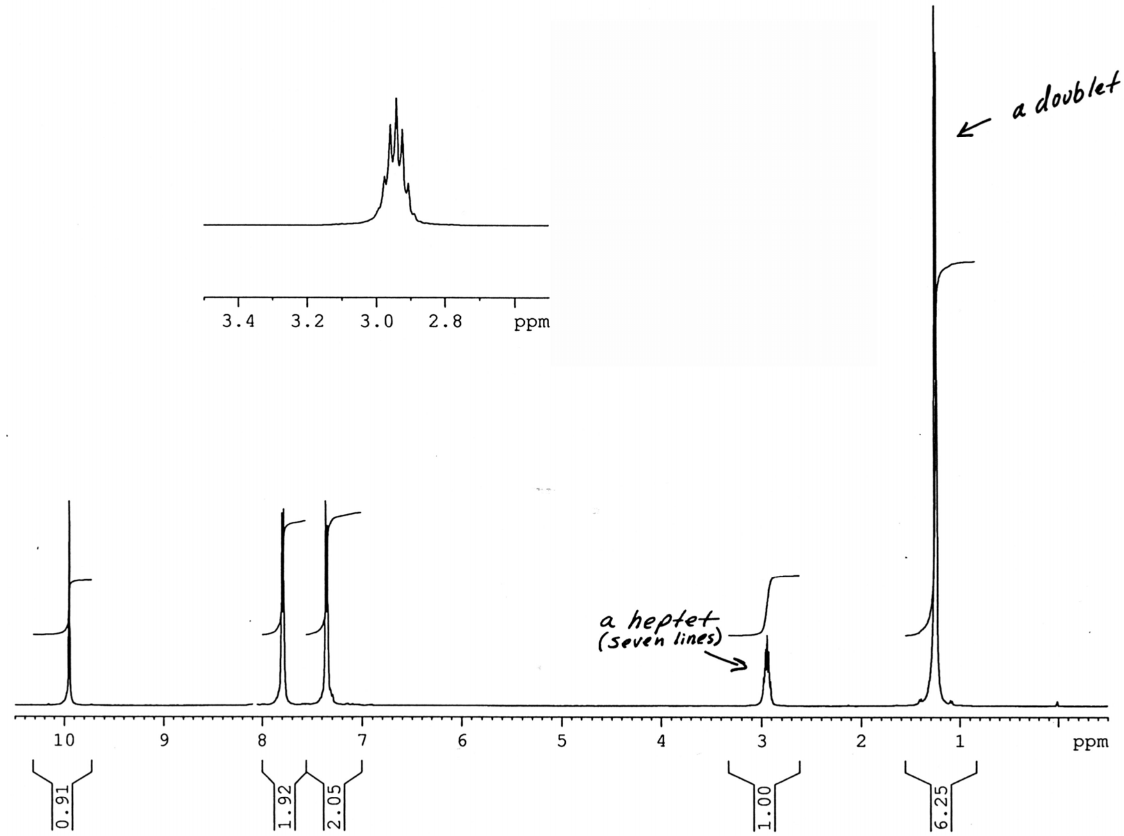
You've just finished running a reaction in lab but your melting point is far from the literature value for your expected product. You hypothesize that an impurity might have been present in your reaction mixture and decide to isolate the compound and analyze it. The data provided below are what you obtained from your analysis. Your task is to identify the structure of your obtained product.

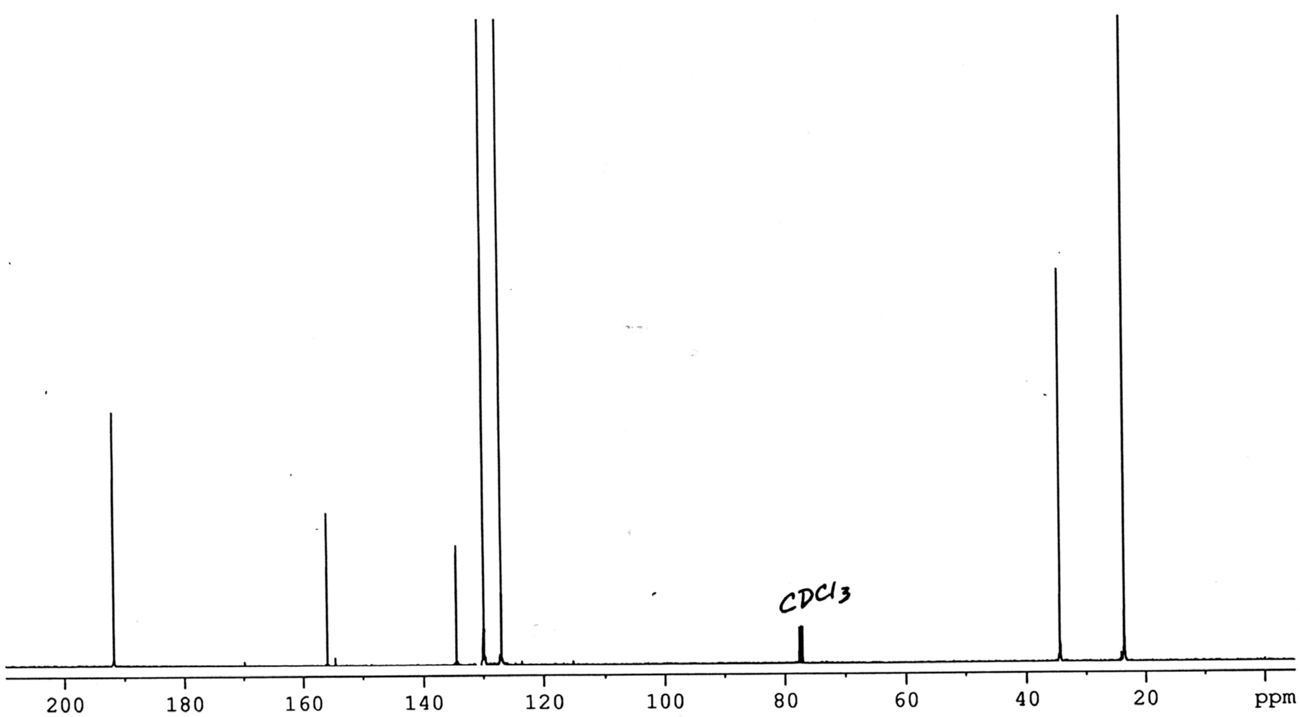
(a). On the next page is the ^{1}H and ^{13}C NMR spectra of your obtained product. In addition to this, you obtained IR data which show a strong absorption at 1763 cm^{-1} and significant absorption both right above and below 3000 cm^{-1}. Elemental analysis has yielded the following chemical formula for your product: **$C_{10}H_{12}O$**.

Draw the structure of your obtained product:

structure of obtained product

(b). Label all unique hydrogens in the structure above AND assign them to the various ^{1}H resonances with which they are associated **on the spectrum provided**.


a doublet
a heptet
(seven lines)
3.4
3.2
3.0
2.8
ppm
10
9
8
7
6
5
4
3
2
1
ppm
0.91
1.92
2.05
1.00
6.25


CDCl3
200
180
160
140
120
100
80
60
40
20
ppm

Question 5 (10 points):

Below is a table of the temperature dependence of the solubility of two solids, **X** and **Y**, in four common solvents:

Solubility of X (g/mL)

	3°C	25°C	60°C
acetone	0.1	0.5	1.5
ethanol	0.2	0.5	20
water	1.1	2.1	3
hexanes	5	12	40

Solubility of Y (g/mL)

	3°C	25°C	60°C
acetone	0.1	0.5	1
ethanol	1	3	5
water	5	15	25
hexanes	0.01	1	7

(a). Which would be the best solvent for recrystallizing a crude sample of compound **X**? Explain (3 sentences max.).

(b). Which would be the best solvent for recrystallizing a crude sample of compound **Y**? Explain (3 sentences max.).

(c). Suppose you had a crude sample of **X** where **Y** was the impurity. Which solvent would be best for obtaining pure **X** via recrystallization? Assume your crude sample contains 18g of **X** and 2g of **Y**. Explain (3 sentences max.)

(d). Describe a detailed procedure for how you would accomplish the recrystallization / separation described in part (c) above.

SCRATCH PAPER

SCRATCH PAPER

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