Name: _____

CHEM 322. Midterm 2

Spring 2011

Prof Donald Watson, Prof Mary Watson

Please write your answers clearly in the boxes provided. If your answer is illegible or outside the box, it will not be graded. You may use the back of test pages for scratch work.

You may use molecular models.

Use of calculators, cell phones, headphones, or any other electronic device during this exam is prohibited.

No notes or books may be used during this exam. Tables of spectral data and a periodic table are provided on page 14 of this exam.

You may raise your hand to ask a question if you are not sure what is being asked of you.

There are 16 pages in this exam. Please check that your test has 16 pages before you begin. The last 2 pages are blank and may be used as scratch paper.

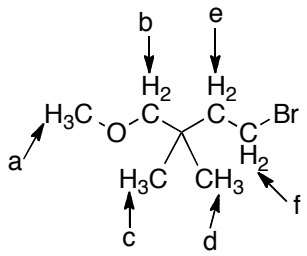
Please circle your lab section:

Mon 12:20–3:20 (Amber, 031)
Mon 3:35–6:35 (Tatsiana, 032)
Mon 7–10 (Craig, 033)
Tues 9:30–12:30 (Srimoyee, 020)
Tues 12:30–3:30 (Neo, 021)
Tues 3:30–6:30 (Peter, 022)
Tues 7–10 (Peter, 023)
Wed 12:20–3:20 (Tatsiana, 034)
Wed 7–10 (Tatsiana, 035)
Thurs 9:30–12:30 (Srimoyee, 024)
Thurs 12:30–3:30 (Neo, 026)
Thurs 3:35–6:35 (Srimoyee, 027)
Thurs 7–10 (Neo, 030)
Fri 9:05–12:05 (Amber, 036)
Fri 12:20–3:20 (Amber, 028)
Fri 3:35–6:35 (Jesse, 025)
Fri 7–10 (Jesse, 039)

Question	Points	
1	_____	/8
2	_____	/10
3	_____	/6
4	_____	/8
5	_____	/10
6	_____	/20
7	_____	/8
8	_____	/8
9	_____	/8
10	_____	/14
Total	_____	/100

Name: _____

1. (8 points) Consider the structure of 1-methoxy-2,2-dimethyl-4-bromobutane to answer the following questions.



(a) How many signals do you expect to see in the ^{1}H NMR spectrum?

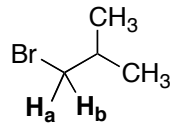
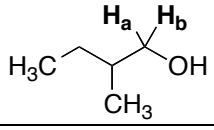
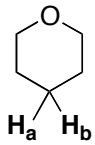
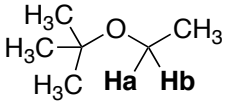
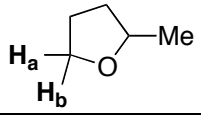
(b) Which of the indicated protons should appear the furthest upfield?

(c) What should be the splitting pattern of the protons labeled **e** (singlet, doublet, etc)?

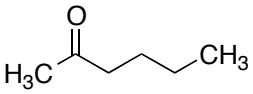
(d) What should be the splitting pattern of the protons labeled **a** (singlet, doublet, etc)?

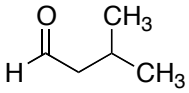
Name: _____

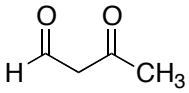
2. (10 points) Are H_a and H_b in the following molecules homotopic, enantiotopic or diastereotopic? Do you expect to see 1 or 2 signals corresponding to those protons in the ^1H NMR spectrum?

	Compound	Homotopic, enantiotopic or diastereotopic?	1 or 2 signals?
(a)			
(b)			
(c)			
(d)			
(e)			

3. (6 points) Please provide the IUPAC names for each of the following molecules.

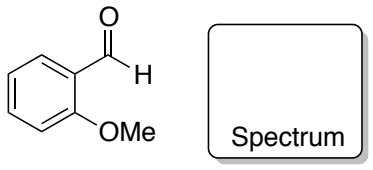
(a) 

(b) 

(c) 

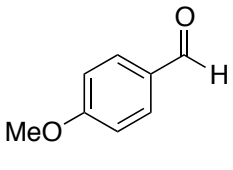
Name: _____

4. (8 points) (a) Match *o*-anisaldehyde and *p*-anisaldehyde to the ^{1}H NMR spectra below (A or B). Write the letter of the spectrum in the box next to the structure,



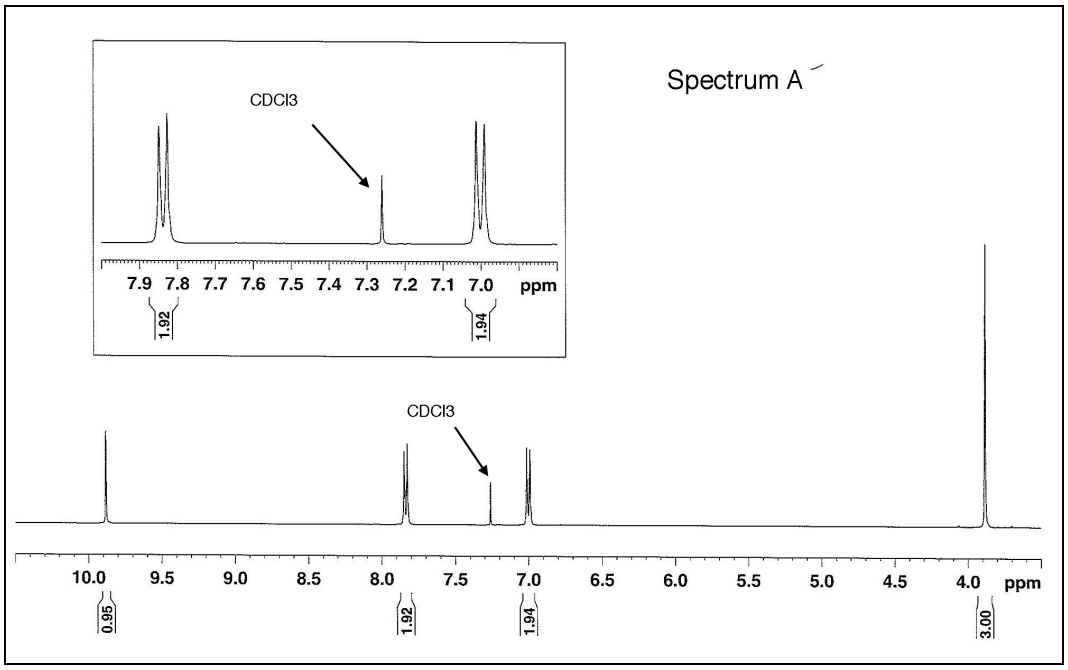
Spectrum

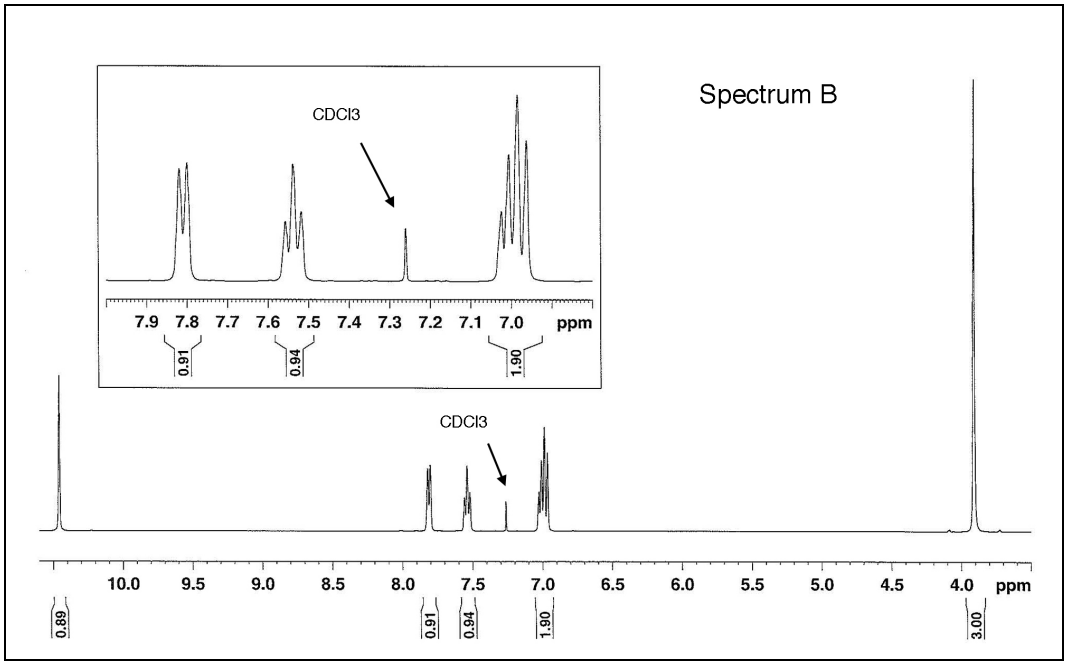
o-anisaldehyde



Spectrum

p-anisaldehyde





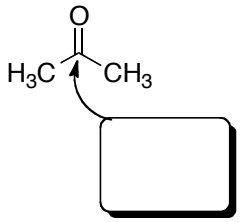
Name: _____

(b) Briefly (20 words or less), in the space below, explain how you determined which compound matched which spectrum.

Name: _____

5. (10 points)

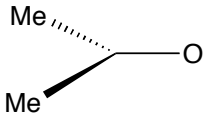
(a) In acetone, what is the hybridization of the carbonyl C?



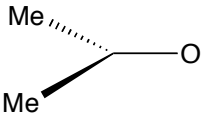
(b) Draw the major resonance structures of acetone.

(c) In a carbonyl fragment (C=O), which atom is electrophilic and which is nucleophilic?

(d) On the partial structures below, draw a 3-D picture of the C=O π and π^* molecular orbitals of acetone. Clearly indicate the geometry, phasing and relative sizes of the lobes.



π

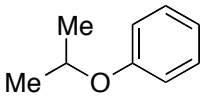


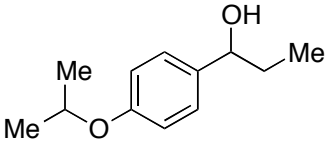
π*

Name: _____

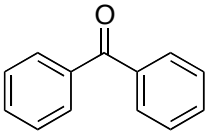
6. (20 points) Please provide the missing reagent(s) or expected major product in the empty boxes below. If no reaction is expected, write "No Reaction."

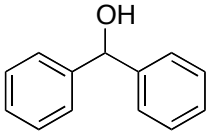
(a)



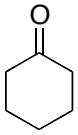


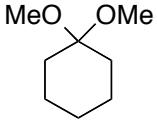
(b)



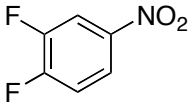


(c)





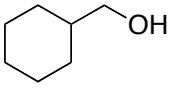
(d)



$NaOCH_3$

CH_3OH, Δ

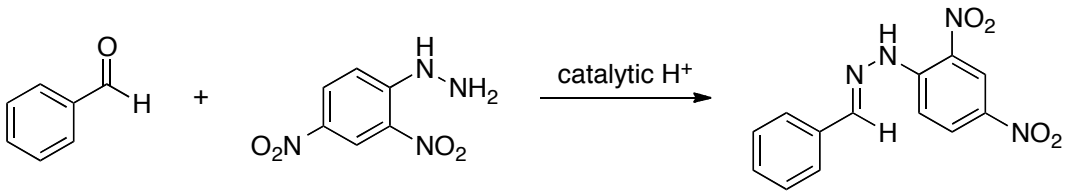
(e)



$Na_2Cr_2O_7$, H_2SO_4, H_2O

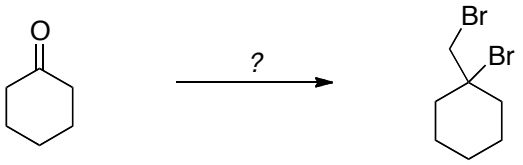
Name: _____

7. (8 points) Please draw a reasonable arrow-pushing mechanism for the following reaction.



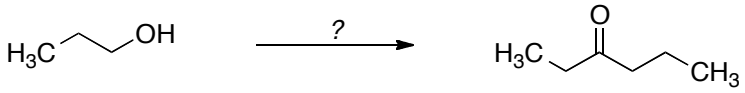
Name: _____

8. (8 points) Provide a synthesis of 1-bromo-1-bromomethylcyclohexane from cyclohexanone. You may use any other reagents you require.



Name: _____

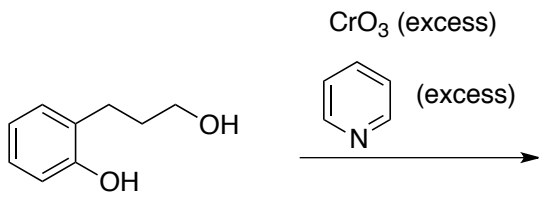
9. (8 points) Using 1-propanol as your only source of carbons, provide a synthesis of the 3-hexanone. You may use any inorganic reagents.



Name: _____

10. (14 points) When diol **1** is treated with CrO_3 and pyridine, the product is *not* the product normally expected for this reaction. The product has a molecular formula of $C_9H_8O_2$. The ^1H NMR, ^{13}C NMR and IR spectra of the product are shown on the next page.

(a) Based on this information, please draw the product of this reaction.

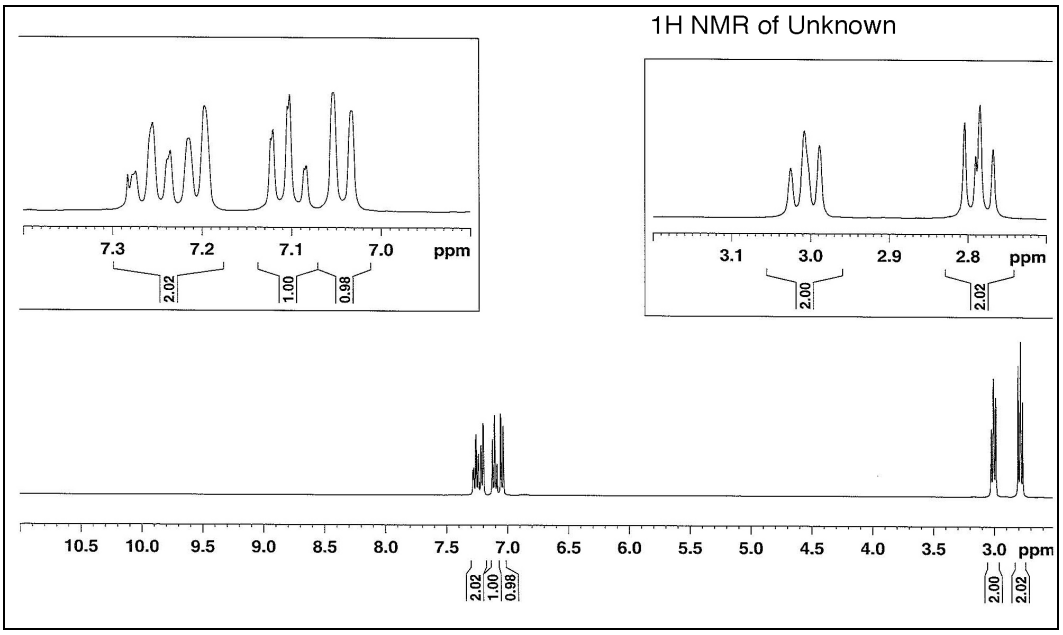


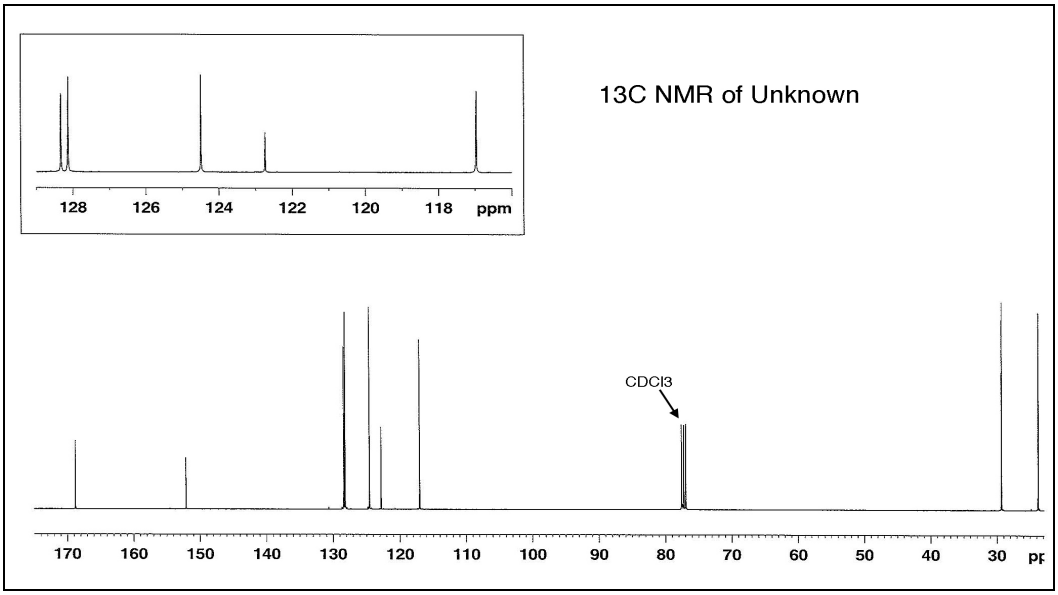
1
$C_9H_{12}O_2$

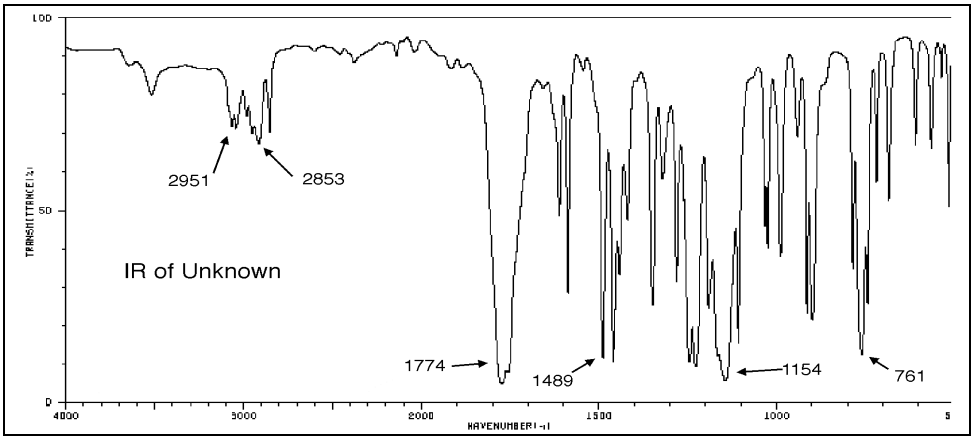
$C_9H_8O_2$

(b) In the space below, briefly (20 words or less) explain how your proposed structure is consistent with the data.

Name: _____


1H NMR of Unknown
7.3
7.2
7.1
7.0
ppm
2.02
1.00
0.98
3.1
3.0
2.9
2.8
ppm
2.00
2.02
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
ppm


13C NMR of Unknown
128
126
124
122
120
118
ppm
CDCl3
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30


2951
2853
IR of Unknown
1774
1489
1154
761

(c) Draw a reasonable arrow-pushing mechanism for the transformation of **1** to your proposed product.

Name: _____

Approximate IR Absorption Frequencies

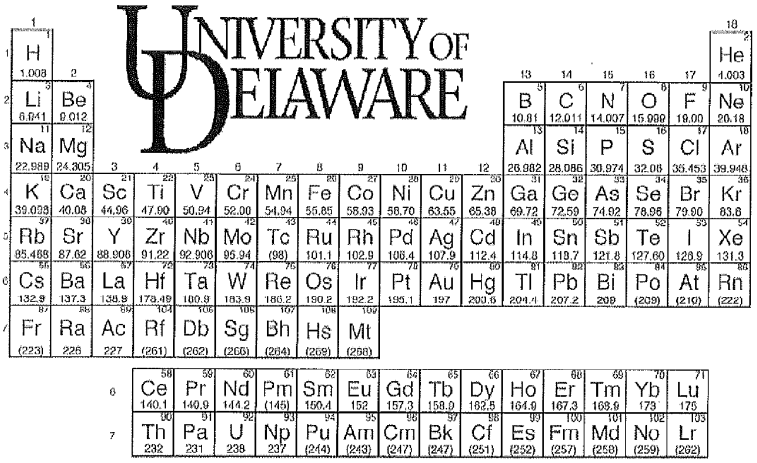
Bond	Frequency (cm^{-1})	Intensity
O–H (alcohol)	3650–3200	Strong, broad
O–H (carboxylic acid)	3300–2500	Strong, very broad
N–H	3500–3300	Medium, broad
C–H	3300–2700	Medium
C≡N	2260–2220	Medium
C≡C	2260–2100	Medium to weak
C=O	1780–1650	Strong
C–O	1250–1050	Strong

Approximate ^{1}H NMR Chemical Shifts

Hydrogen	δ (ppm)
CH_3	0.8–1.0
CH_2	1.2–1.5
CH	1.4–1.7
$C{=}C{-}CH_x$	1.7–2.3
$O{=}C{-}CH_x$	2.0–2.7
$Ph{-}CH_x$	2.3–3.0
$\equiv C{-}H$	2.5
$R_2N{-}CH_x$	2.0–2.7
$I{-}CH_x$	3.2
$Br{-}CH_x$	3.4
$Cl{-}CH_x$	3.5
$F{-}CH_x$	4.4
$O{-}CH_x$	3.2–3.8
C=CH	4.5–7.5
Ar–H	6.8–8.5
O=CH	9.0–10.0
ROH	1.0–5.5
ArOH	4.0–12.0
RNH_x	0.5–5.0
$CONH_x$	5.0–10.0
RCOOH	10–13

Approximate ^{13}C NMR Chemical Shifts

Carbon	δ (ppm)
Alkanes	
Methyl	0–30
Methylene	15–55
Methine	25–55
Quaternary	30–40
Alkenes	
C=C	80–145
Alkynes	
C≡C	70–90
Aromatics	110–170
Benzene	128.7
Alcohols, Ethers	
C–O	50–90
Amines	
C–N	40–60
Halogens	
C–F	70–80
C–Cl	25–50
C–Br	10–40
C–I	–20–10
Carbonyls, C=O	
$R_2C{=}O$	190–220
RXC=O (X = O or N)	150–180



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