

Circle one: I wish to have my exam  
put in the rack.

I wish to pick up  
my exam.

Printed Name Answer Key  
(Please print clearly)

Signature \_\_\_\_\_

**CHEMISTRY 262**

Exam II  
100 Points

February 26, 2013  
6:30 – 8:30 PM

This exam has 8 problems on pages 2 through 9.

**RULES**

1. The use of a calculator and model kits are **not** permitted.
2. This exam is closed book and closed note. No aids other than writing implements are permitted.
3. Answer the questions in the spaces provided on this exam.
4. If you wish to ask a question about procedures or about a problem on the exam, raise your hand.

1. \_\_\_\_\_

6. \_\_\_\_\_

2. \_\_\_\_\_

7. \_\_\_\_\_

3. \_\_\_\_\_

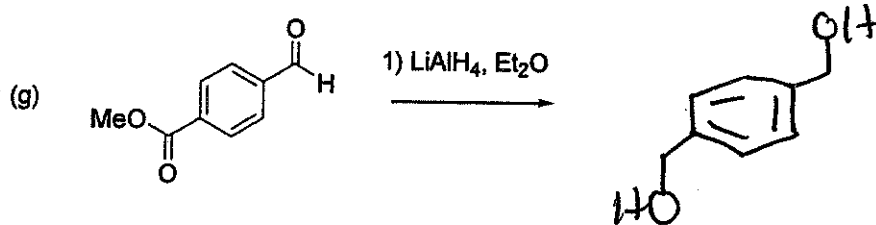
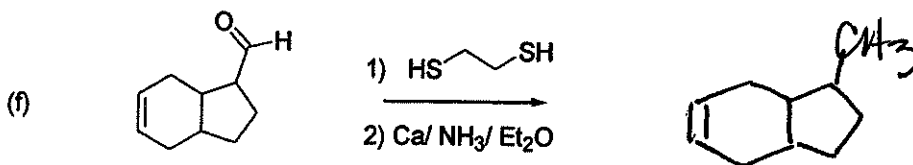
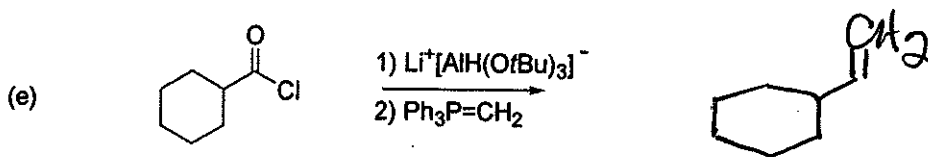
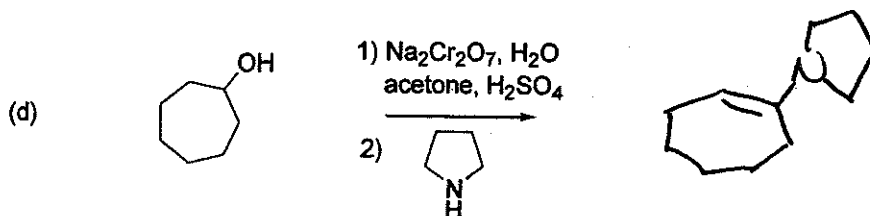
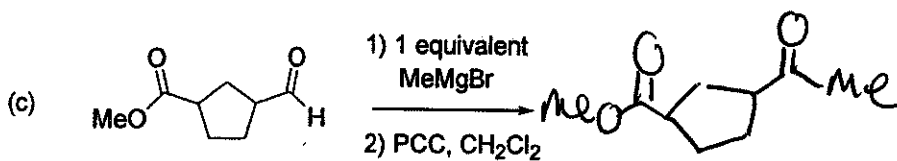
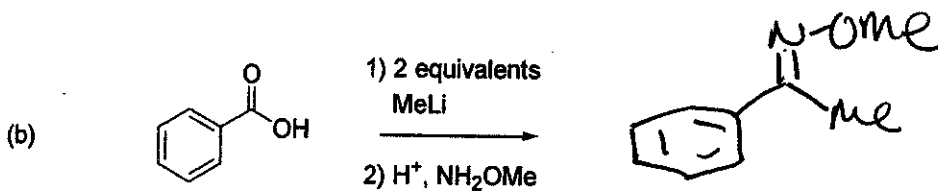
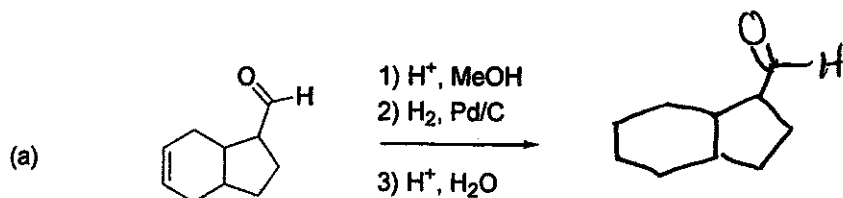
8. \_\_\_\_\_

4. \_\_\_\_\_

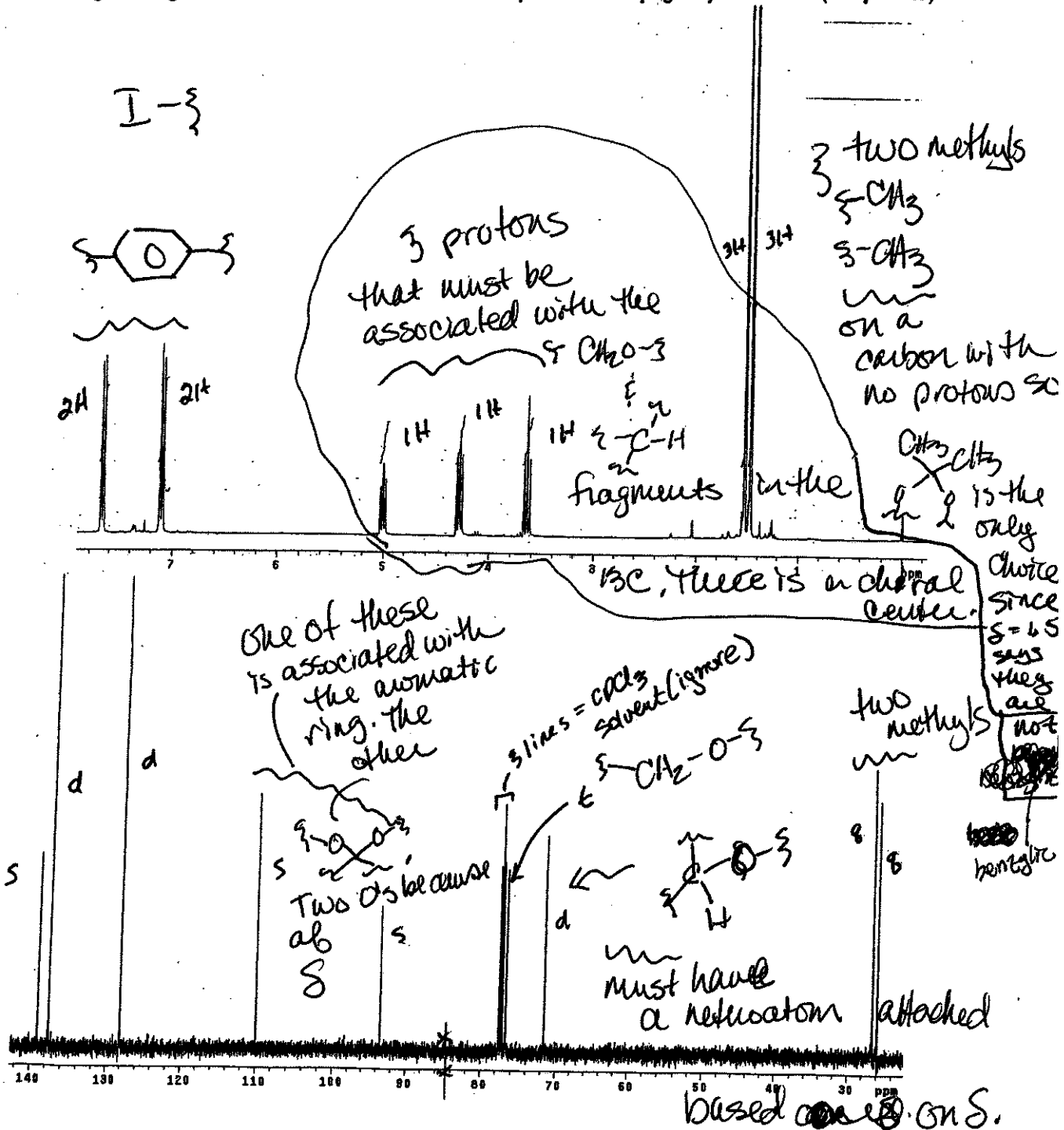
5. \_\_\_\_\_

TOTAL: /100

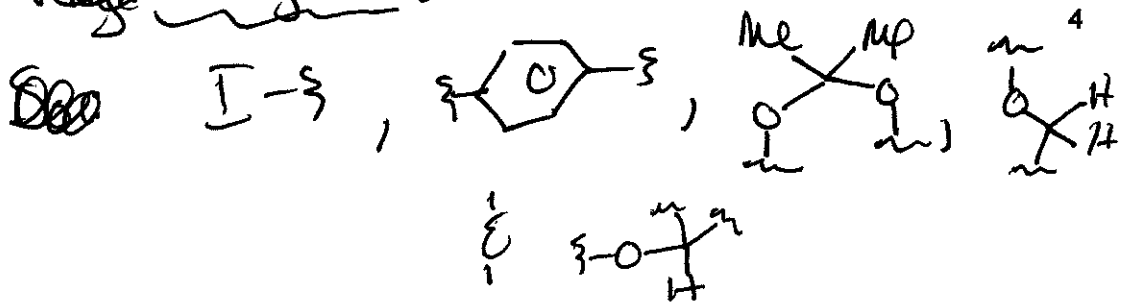
1. Predict the major product or products (be inclusive) that you would expect to be formed in five of the following seven reactions. If you feel that no reaction will occur, then answer no reaction. You may assume a workup step for each reaction. Be sure to answer only five problems. If you answer more than five, then *only your first five will be graded*. (15 points/ 3 pts. each)



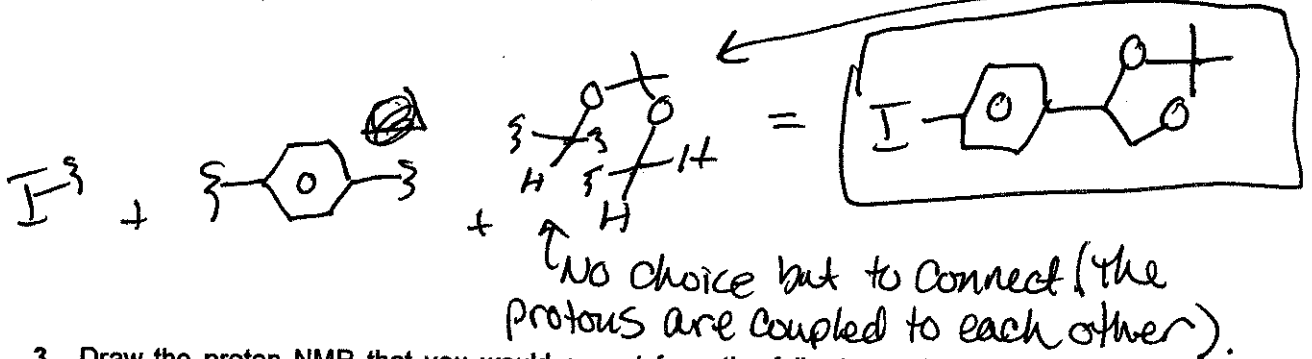
2. Assign the structure of the unknown compound that gives rise to the proton NMR and carbon NMR illustrated below. Please pay attention to the notes written on the spectra. All of the NMR signals for the molecule are shown and are "referenced" to tetramethylsilane. The multiplicities for the off resonance  $^{13}\text{C}$  NMR spectrum are given in parenthesis (s=singlet, d=doublet, t=triplet, q=quartet). The IR spectrum for the molecule shows no significant stretches (no carbonyl, OH, acid, etc.). By high resolution mass spectroscopy, the molecular formula for the compound was found to be  $\text{C}_{11}\text{H}_{13}\text{O}_2$ . Be sure that you clearly indicate what structure you want graded. Please note that we will give you partial credit for assigning fragments of the molecule correctly, but only for fragments that are incorporated into your final structure. If you can't determine a final structure then clearly indicate that you want your fragments graded. There is extra room at the top of the next page if you need it. (15 points)



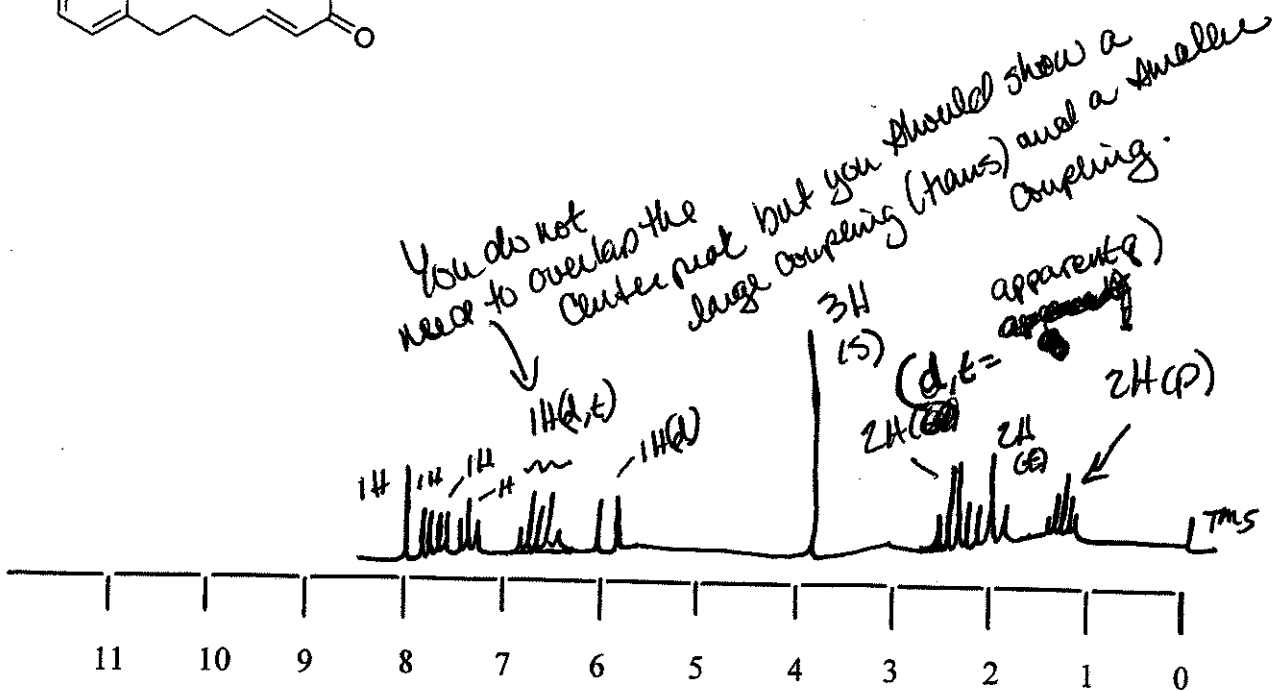
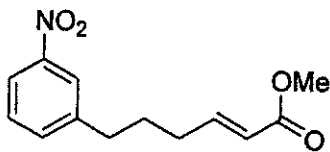
Fragment:



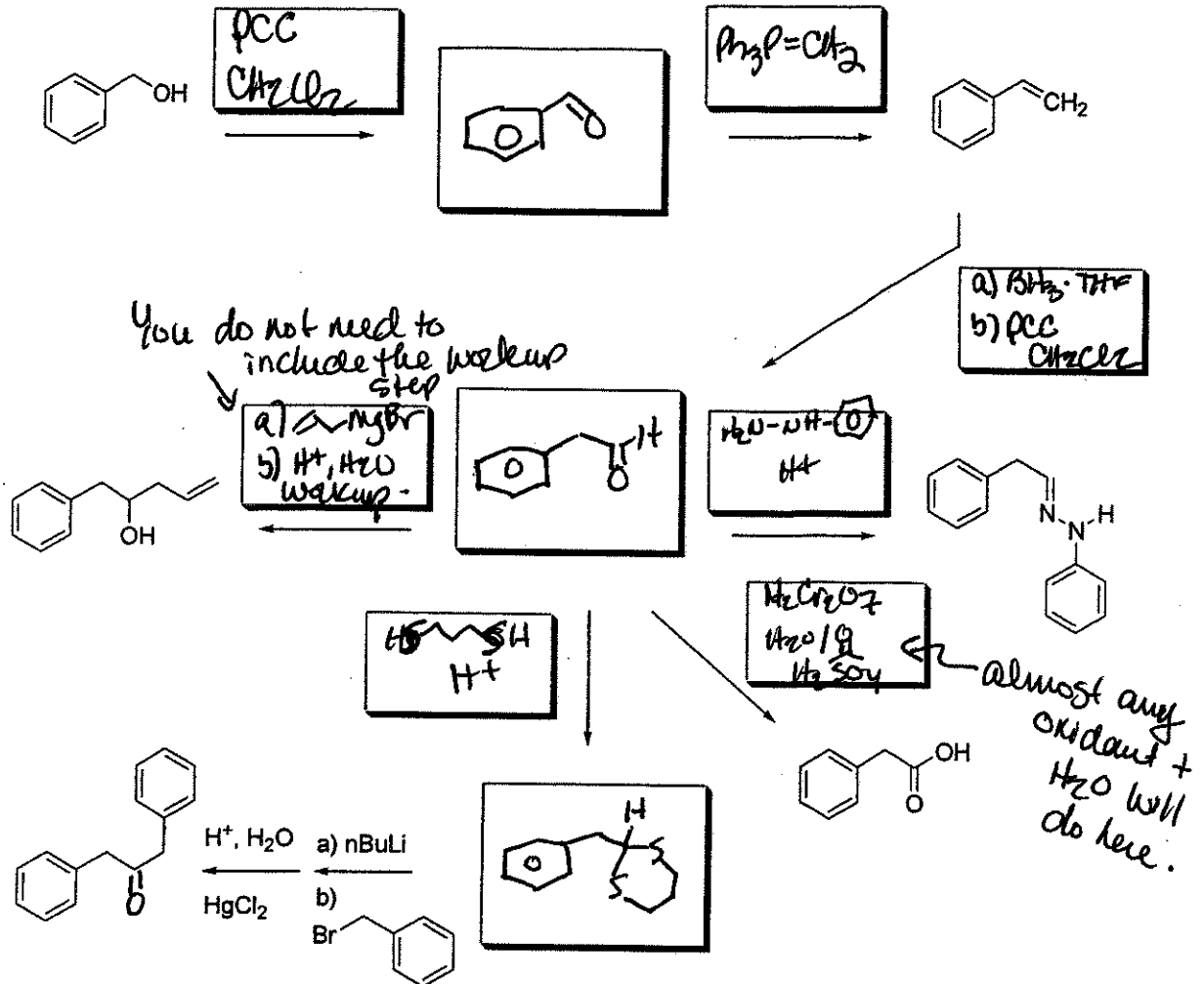
Only two oxygens <sup>in the molecule</sup> ~~leads to~~ so one must have



3. Draw the proton NMR that you would expect from the following molecule. Make sure that you include the expected chemical shifts, coupling patterns, and integration. (10 points)

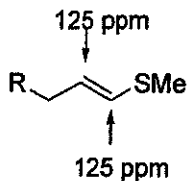


4. For each box below provide either the molecule or the reagents needed to complete the scheme. (10 points)



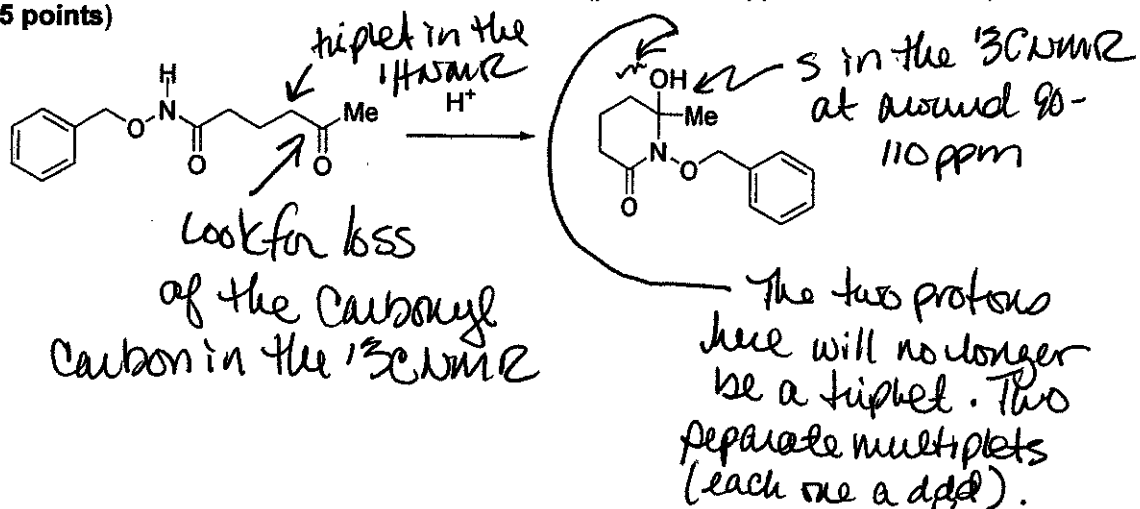
5. Consider the following spectroscopy questions.

- a. What does the following  $^{13}\text{C}$ -NMR data "tell us" about the ability of a sulfur to donate its lone-pair electrons to a carbon-carbon double bond? Remember that sulfur has the same electronegativity as carbon. (5 points)

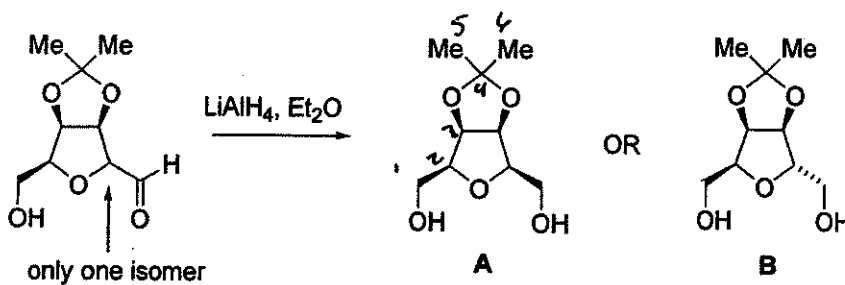


*It doesn't! The fact that the chemical shifts are the same suggests that there is no donation of the sulfur lone pair electrons to the double bond.*

- b. How could you use NMR-spectroscopy (either proton or carbon) to monitor the following reaction for both the formation of product and the loss of the starting material. Be specific in terms of what signals you would look for (provide an approximate location, etc.). (5 points)



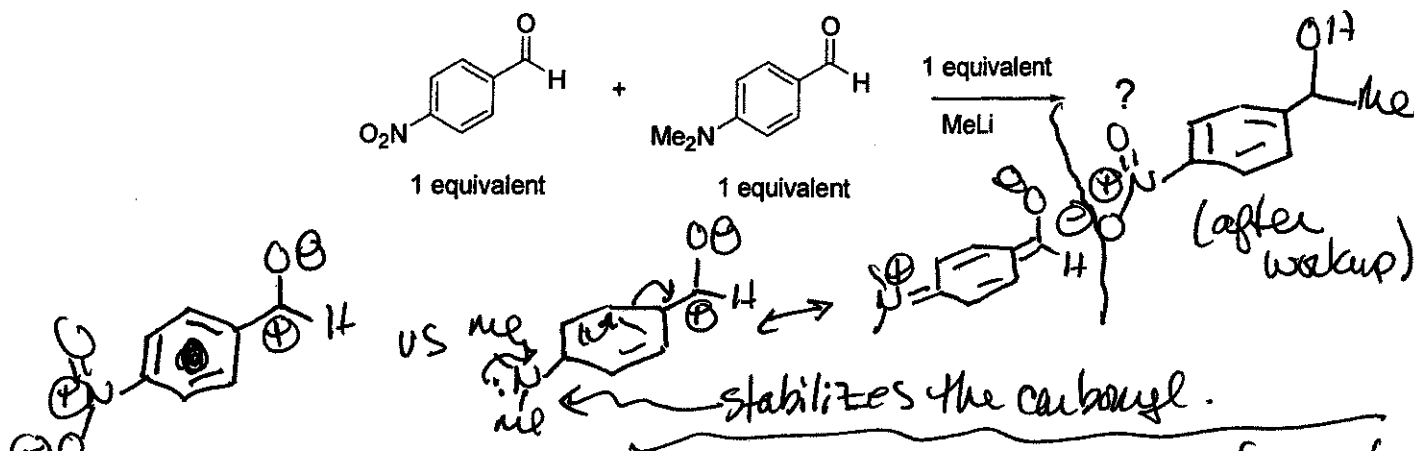
- c. Sugars can be very difficult to assign. For example, the aldehyde below was synthesized as a single isomer by a graduate student here at Washington University. Assigning which isomer he had was very difficult because the chemical shifts in the proton NMR were very close to each other. However, the graduate student was very clever. He reduced the aldehyde to an alcohol so that he could immediately tell if he had isomer A or isomer B. Why was it so easy for him to tell the difference between isomer A and isomer B? (5 points)



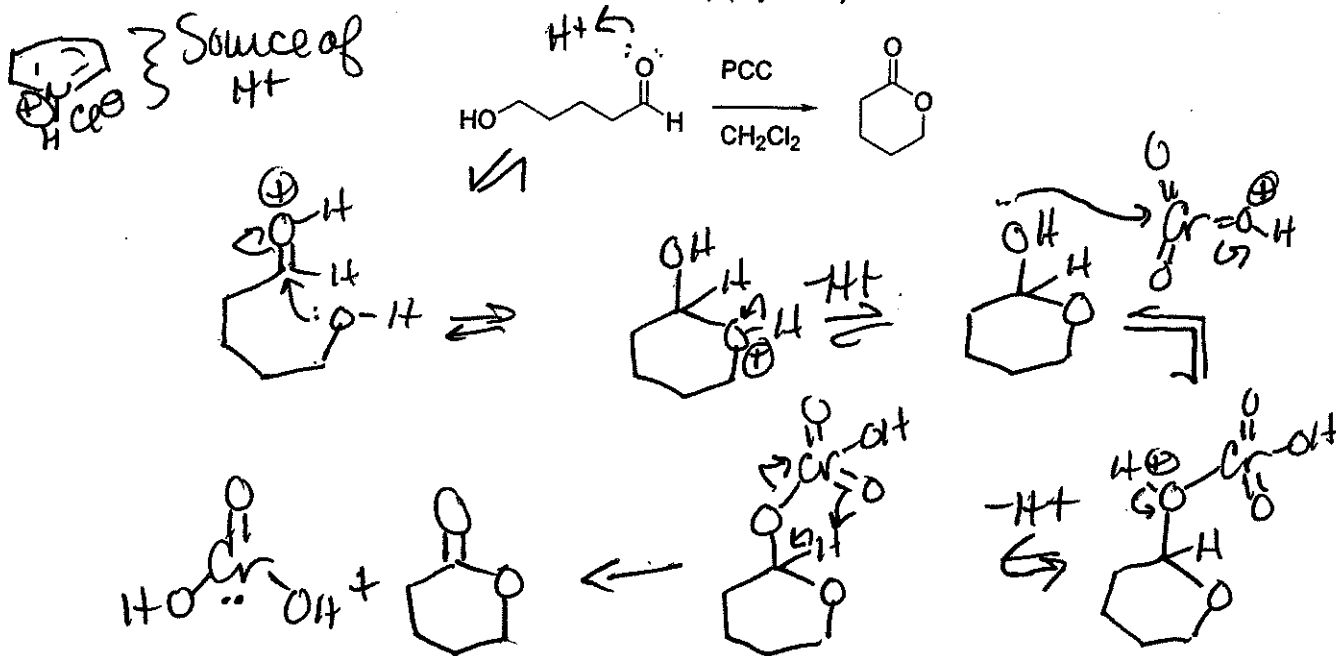
Isomer A has a plane of symmetry and will show only 6 carbons in a fully decoupled  $^{13}\text{C NMR}$ . Isomer B will show 9 lines.

6. Consider the following synthetic questions:

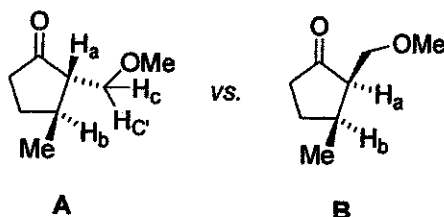
a. In the competition reaction illustrated below, one equivalent each of two aldehydes was treated with one equivalent of MeLi to form only one product. What was the product formed and why? (5 points)



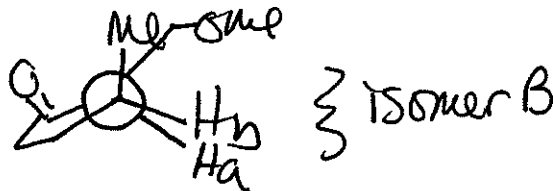
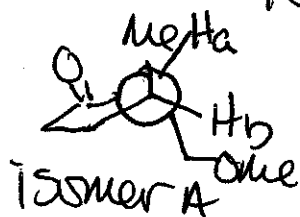
b. In the reaction below, the aldehyde is oxidized instead of the alcohol in spite of the fact that there is no water present. Draw a "curved-arrow" mechanism for formation of the product that illustrates why this happens. (Remember that PCC is pyridinium chlorochromate. It has both  $\text{CrO}_3$  and an acid) (5 points)



7. a. You can assign the stereochemistry for the following two products from the coupling constant  $J_{a,b}$ . Would you expect this coupling constant to be larger for isomer A or isomer B? Why? Remember that five-membered rings are mainly planar. (5 points)



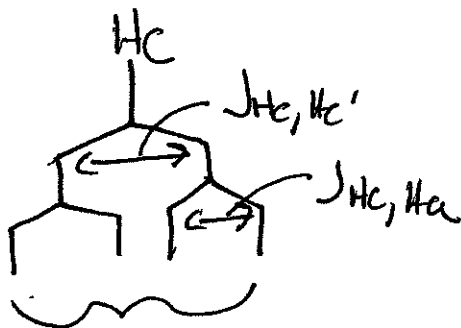
Isomer B:  $0 \sim 0^\circ$  for isomer B and  $\sim 120^\circ$  for isomer A



- b. Why are Hc and Hc' in isomer A not labeled the same? Please answer in no more than one sentence. (5 points)

They are not labeled the same because ~~they are~~ the molecule is chiral. Therefore, Hc & Hc' are diastereotopic.

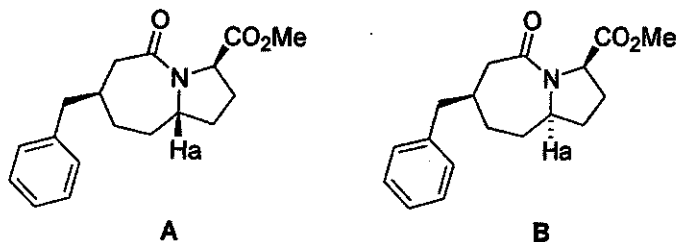
- c. Draw a splitting tree that indicates the coupling pattern that you would expect to see for Hc. (5 points)



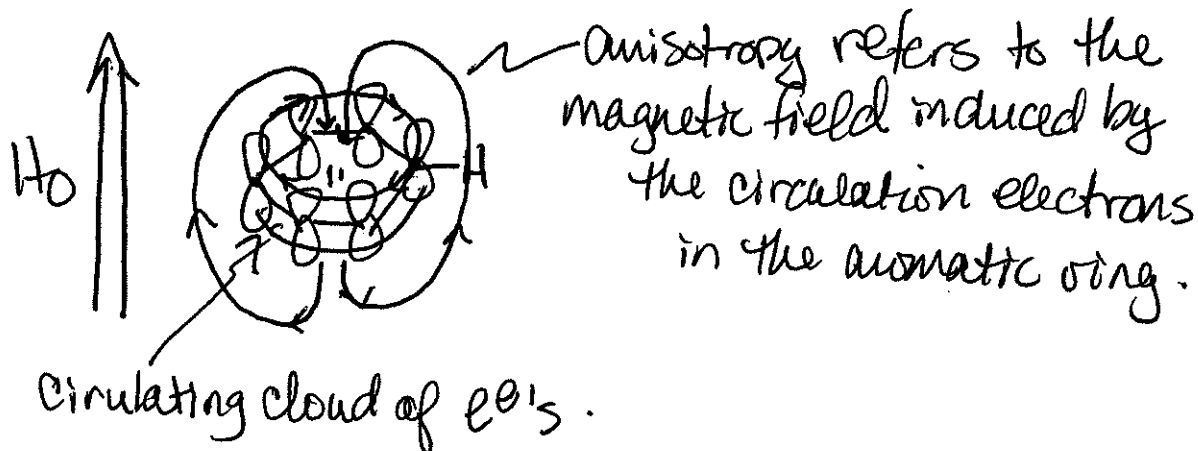
doublet of doublets.



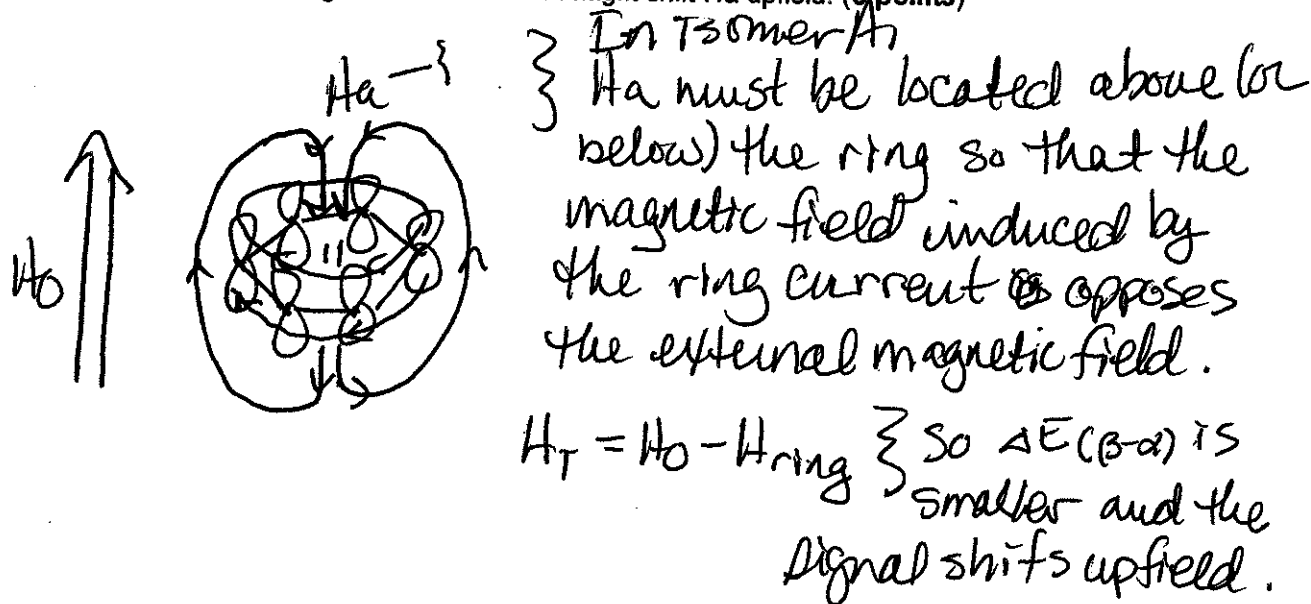
8. Phenyl rings can sometimes cause a number of upfield and downfield shifts in a molecule. For example, Ha in isomer A below is found at almost a part per million upfield from Ha in isomer B. The question is why?



- a. To start answering the question, use a phenyl ring to illustrate what is meant by anisotropy. (5 points)



- b. Use your answer to part a to provide an explanation for how a phenyl group on the same side of the ring as Ha in isomer A might shift Ha upfield. (5 points)



# Periodic Table of the Elements

1
11
1.008

3 Li 6.94	4 Be 9.01											5 B 10.81	6 C 12.011	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
11 Na 22.99	12 Mg 24.31											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.06	17 Cl 35.45	18 Ar 39.95
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.90	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.71	29 Cu 63.55	30 Zn 65.37	31 Ga 69.72	32 Ge 72.59	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc 98.91	44 Ru 101.07	45 Rh 102.91	46 Pd 106.4	47 Ag 107.87	48 Cd 112.40	49 In 114.82	50 Sn 118.69	51 Sb 121.75	52 Te 127.60	53 I 126.90	54 Xe 131.30
55 Cs 132.91	56 Ba 137.34	57 La 138.91	72 Hf 178.49	73 Ta 180.95	74 W 183.85	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.09	79 Au 196.97	80 Hg 200.59	81 Tl 204.37	82 Pb 207.19	83 Bi 208.98	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra (226.03)	89 Ac (227)	104 (Rf) (261)	105 (11a) (262)	106 (263)												

TABLE 11-4  
Isotopic composition of some common elements

Element	M + 0	M + 1	M + 2
hydrogen	<sup>1</sup> H 100.0%		
carbon	<sup>12</sup> C 98.9%	<sup>13</sup> C 1.1%	
nitrogen	<sup>14</sup> N 99.6%	<sup>15</sup> N 0.4%	
oxygen	<sup>16</sup> O 99.8%		<sup>17</sup> O 0.2%
sulfur	<sup>32</sup> S 95.0%	<sup>33</sup> S 0.8%	<sup>34</sup> S 4.2%
chlorine	<sup>35</sup> Cl 75.5%		<sup>37</sup> Cl 24.5%
bromine	<sup>79</sup> Br 50.5%		<sup>81</sup> Br 49.5%
iodine	<sup>127</sup> I 100.0%		

Lanthanides

Actinides

58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm (145)	62 Sm 150.35	63 Eu 151.96	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.04	71 Lu 174.97
90 Th 232.04	91 Pa (231)	92 U 238.03	93 Np (237)	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (249)	98 Cf (249)	99 Es (254)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (260)

Numbers in parentheses: available radioactive isotope of longest half-life.