

NAME (Print): \_\_\_\_\_

Chemistry 310N  
Dr. Brent Iverson  
1st Midterm  
Feb. 22, 2007

SIGNATURE: \_\_\_\_\_

Please print the  
first three letters  
of your last name  
in the three boxes

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**Please Note:** This test may be a bit long, but there is a reason. I would like to give you a lot of little questions, so you can find ones you can answer and show me what you know, rather than just a few questions that may be testing the one thing you forgot. **I recommend you look the exam over and answer the questions you are sure of first**, then go back and try to figure out the rest. Also make sure to **look at the point totals** on the questions as a guide to help budget your time.

*For synthesis problems GO FOR PARTIAL CREDIT EVEN IF YOU DO NOT KNOW THE ENTIRE ANSWER!! WRITE DOWN WHAT YOU DO KNOW IN THE REACTION SEQUENCE SOMEWHERE. YOU WILL GET PARTIAL CREDIT IF IT IS CORRECT*

**Note: You must have your answers written in pen if you want a regrade!!!!**

Page	Points	
1		(15)
2		(20)
3		(26)
4		(5)
5		(5)
6		(5)
7		(5)
8		(12)
9		(21)
10		(32)
11		(19)
12		(15)
13		(30)
14		(---)
15		(13)
16		(23)
Total		(241)
HW		
T Score		

## Honor Code

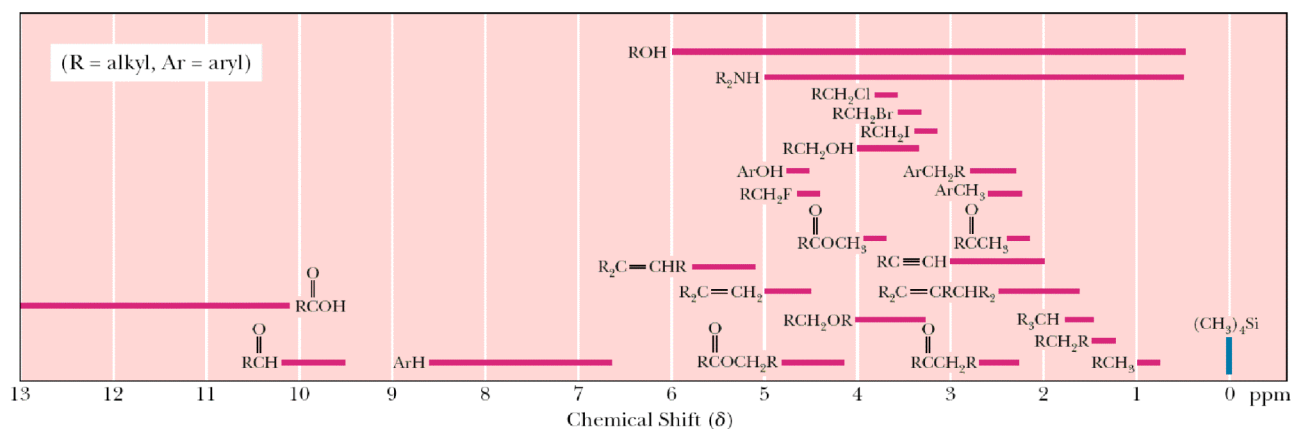
The core values of the University of Texas at Austin are learning, discovery, freedom, leadership, individual opportunity, and responsibility. Each member of the University is expected to uphold these values through integrity, honesty, trust, fairness, and respect toward peers and community.

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(Your signature)

Type of Hydrogen (R = alkyl, Ar = aryl)	Chemical Shift ( $\delta$ )*	Type of Hydrogen (R = alkyl, Ar = aryl)	Chemical Shift ( $\delta$ )*
$R_2NH$	0.5-5.0	$RCH_2OH$	3.4-4.0
$ROH$	0.5-6.0	$RCH_2Br$	3.4-3.6
$RCH_3$	0.8-1.0	$RCH_2Cl$	3.6-3.8
$RCH_2R$	1.2-1.4	$\begin{array}{c} O \\    \\ RCOCH_3 \end{array}$	3.7-3.9
$R_3CH$	1.4-1.7	$\begin{array}{c} O \\    \\ RCOCH_2R \end{array}$	4.1-4.7
$R_2C=CRCHR_2$	1.6-2.6	$RCH_2F$	4.4-4.5
$RC\equiv CH$	2.0-3.0	$ArOH$	4.5-4.7
$\begin{array}{c} O \\    \\ RCCH_3 \end{array}$	2.1-2.3	$R_2C=CH_2$	4.6-5.0
$\begin{array}{c} O \\    \\ RCCH_2R \end{array}$	2.2-2.6	$R_2C=CHR$	5.0-5.7
$ArCH_3$	2.2-2.5	$\begin{array}{c} O \\ / \backslash \\ H_2C-CH_2 \end{array}$	3.3-4.0
$RCH_2NR_2$	2.3-2.8	$\begin{array}{c} O \\    \\ RCH \end{array}$	9.5-10.1
$RCH_2I$	3.1-3.3	$\begin{array}{c} O \\    \\ RCOH \end{array}$	10-13
$RCH_2OR$	3.3-4.0		

\* Values are relative to tetramethylsilane. Other atoms within the molecule may cause the signal to appear outside these ranges.



Signature \_\_\_\_\_

Pg 1 \_\_\_\_\_(15)

1. (1 pt each) Fill in each blank with the word that best completes the following sentences about NMR.

We care about the nuclei \_\_\_\_\_ and \_\_\_\_\_ since these are commonly found in organic molecules and they have spin quantum numbers of 1/2. Nuclei with spin quantum number 1/2 are quantized in one of two orientations, " \_\_\_\_\_ " (lower energy) or " \_\_\_\_\_ " (higher energy) in the presence of an external magnetic field, that is, with and against the external field, respectively. The difference in energy between nuclear spin states is \_\_\_\_\_ to the strength of the magnetic field felt by the nucleus.

\_\_\_\_\_ density is induced to circulate in a strong external magnetic field, which, in turn produces a \_\_\_\_\_ field that opposes the external \_\_\_\_\_ field. This \_\_\_\_\_ nuclei from the external \_\_\_\_\_ field. The greater the electron density around a nucleus, the more \_\_\_\_\_ it is, and the lower the energy (frequency) of electromagnetic radiation required to \_\_\_\_\_ its nuclear spin state.

\_\_\_\_\_, \_\_\_\_\_, and \_\_\_\_\_ attached to an H atom influence shielding in predictable ways by removing differing amounts of electron density around adjacent nuclei.

1. (1 pt each) Fill in each blank with the word that best completes the following sentences about NMR.

\_\_\_\_\_ hydrogen atoms in a molecule give the same NMR signal.

\_\_\_\_\_ hydrogen atoms in a molecule have an

\_\_\_\_\_ relationship to all the other atoms in the molecule, and

are found on the same  $sp^3$  atom (bond rotation makes them \_\_\_\_\_)

or entire groups are equivalent due to \_\_\_\_\_ in the molecule.

Adjacent nuclei have \_\_\_\_\_ fields associated with their spins. The

spins of equivalent adjacent nuclei can be either \_\_\_\_\_ or \_\_\_\_\_, and at room

temperature they are found in about a \_\_\_\_\_ mixture at any given nucleus.

These can add to give \_\_\_\_\_ different spin combinations in the proportions

predicted by Pascal's triangle. Each different spin combination produces a different

\_\_\_\_\_ field, which leads to \_\_\_\_\_ splittings in the peaks

of the NMR spectra of the adjacent (no more than \_\_\_\_\_ bonds away)

nuclei. The distance between peaks split in this way is called the \_\_\_\_\_

\_\_\_\_\_ ("J").

**THEORY:** When there are two sets of adjacent H atoms, the number of peaks

\_\_\_\_\_.

**PRACTICE:** For alkyl groups with free bond \_\_\_\_\_ complex

splittings simplify because \_\_\_\_\_ ("J") are all

about the same. In practice, if there are n adjacent H atoms, equivalent or not, you will

see \_\_\_\_\_ peaks. This is an approximation, but almost always true on spectra

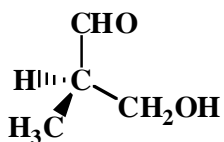
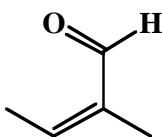
taken with all but the most sophisticated NMR spectrometers.

Signature \_\_\_\_\_

Pg 3 \_\_\_\_\_(26)

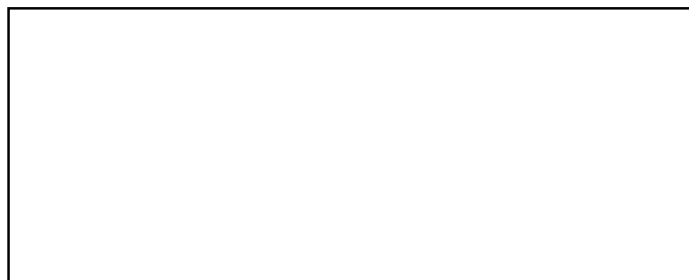
2. (14 points) Suppose a relative of yours is having an MRI. In no more than four sentences, explain to them what is happening when they have the MRI scan. We will be looking for a minimum of 7 key points here.

3. (4 pts each) In the space provided, write the IUPAC name (including stereochemistry where appropriate) for the following two molecules:



4. (4 pts) In the space provided, draw the following molecule:

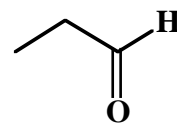
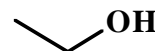
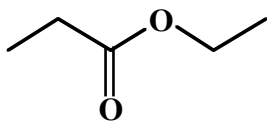
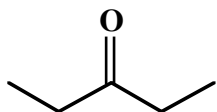
**4-Hydroxy-4-methyl-2-pentanone**



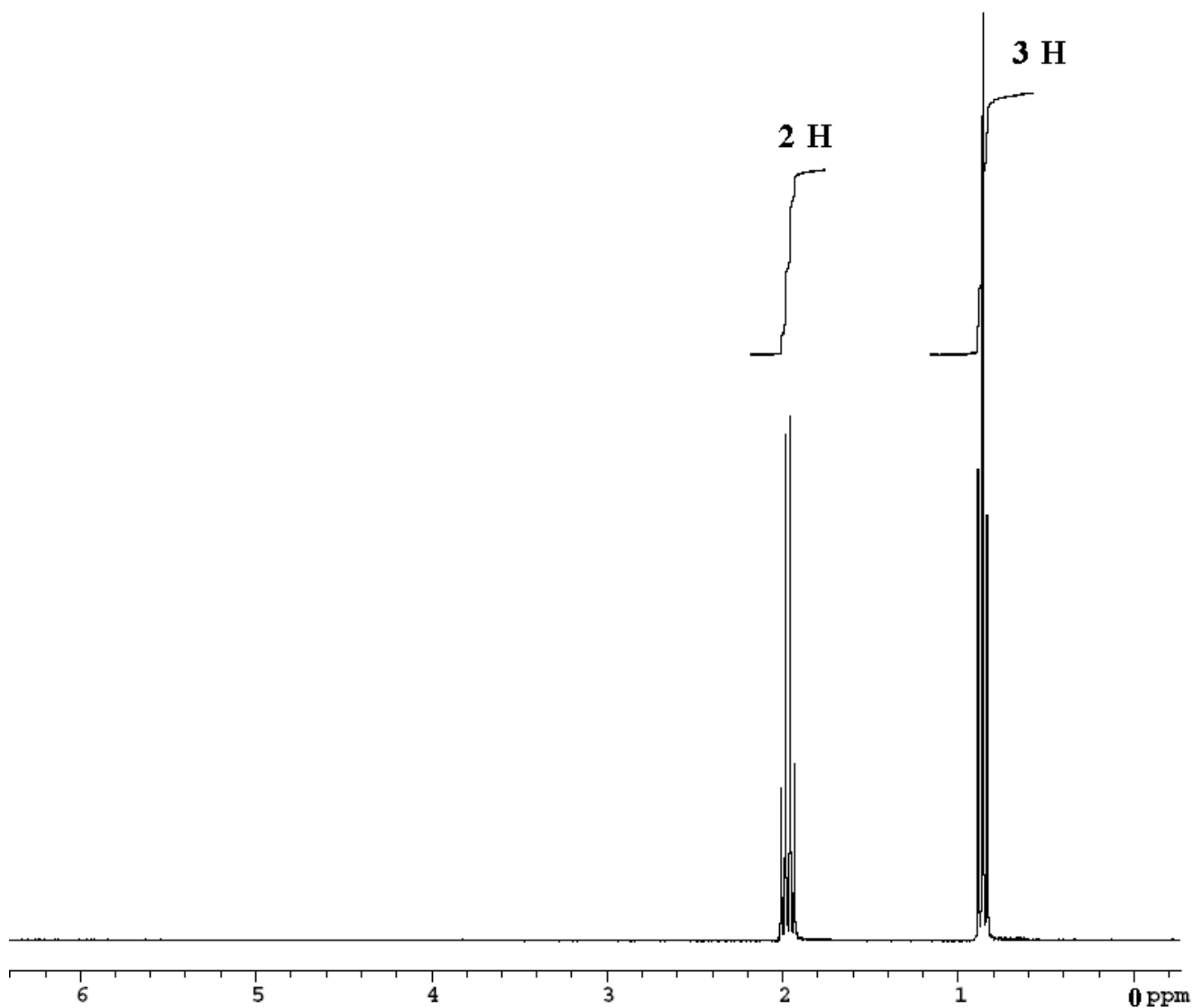
Signature \_\_\_\_\_

Pg 4 \_\_\_\_\_(5)

5. (5 pts) Circle the structure that corresponds to the following spectrum.



(No D<sub>2</sub>O was added to the sample)

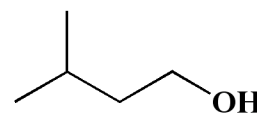
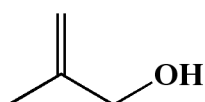
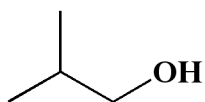
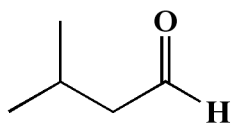




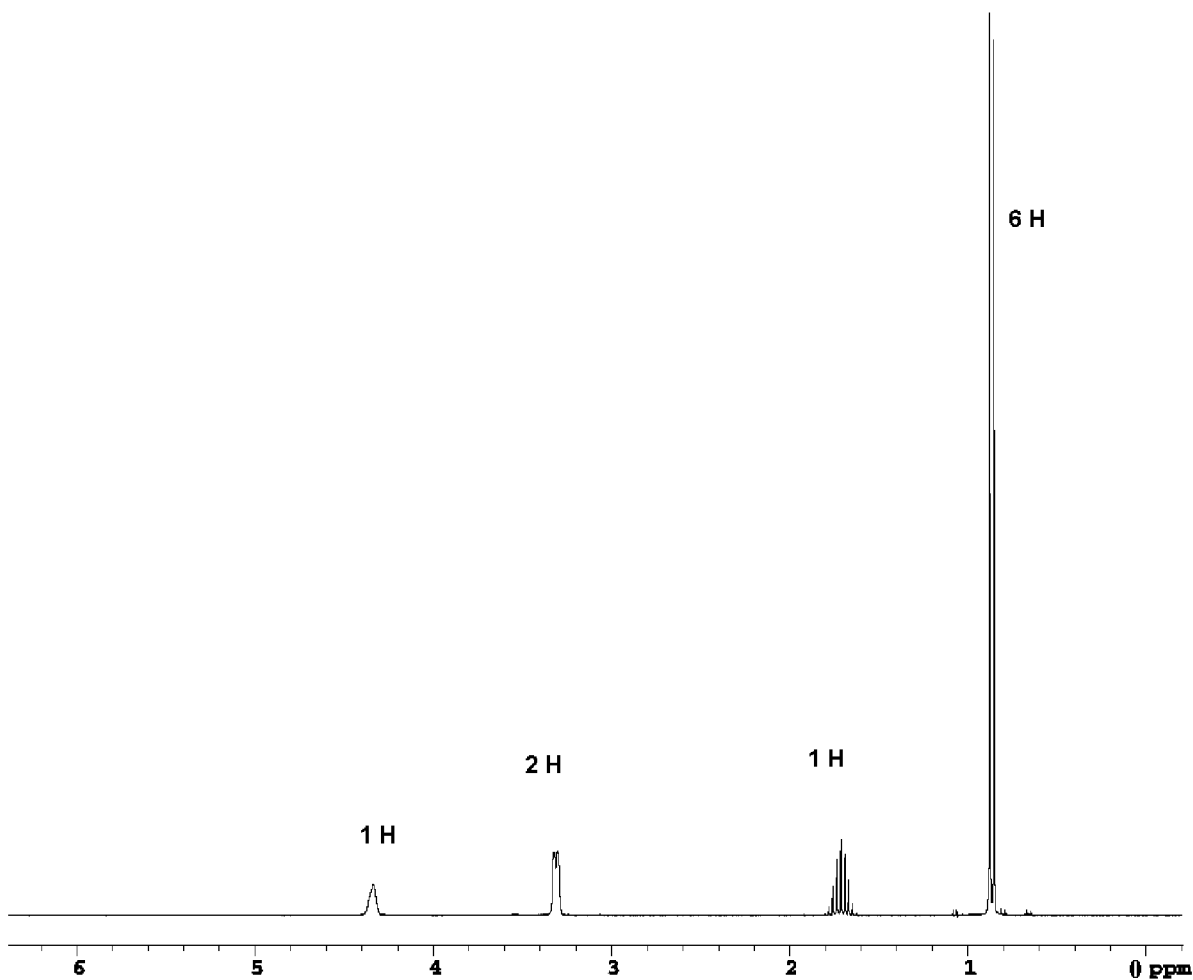
Signature \_\_\_\_\_

Pg 5 \_\_\_\_\_(5)

6. (5 pts) Circle the structure that corresponds to the following spectrum.



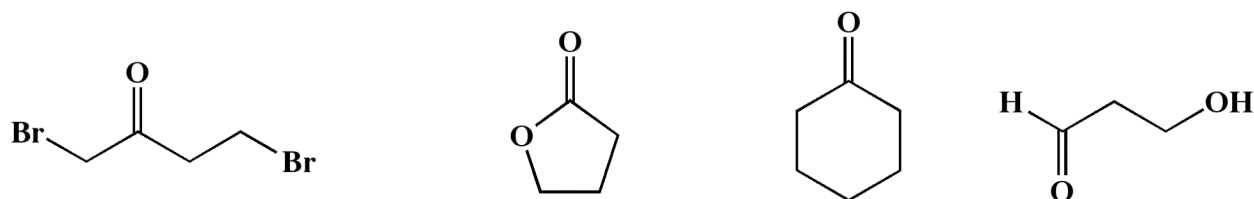
(No D<sub>2</sub>O was added to the sample)



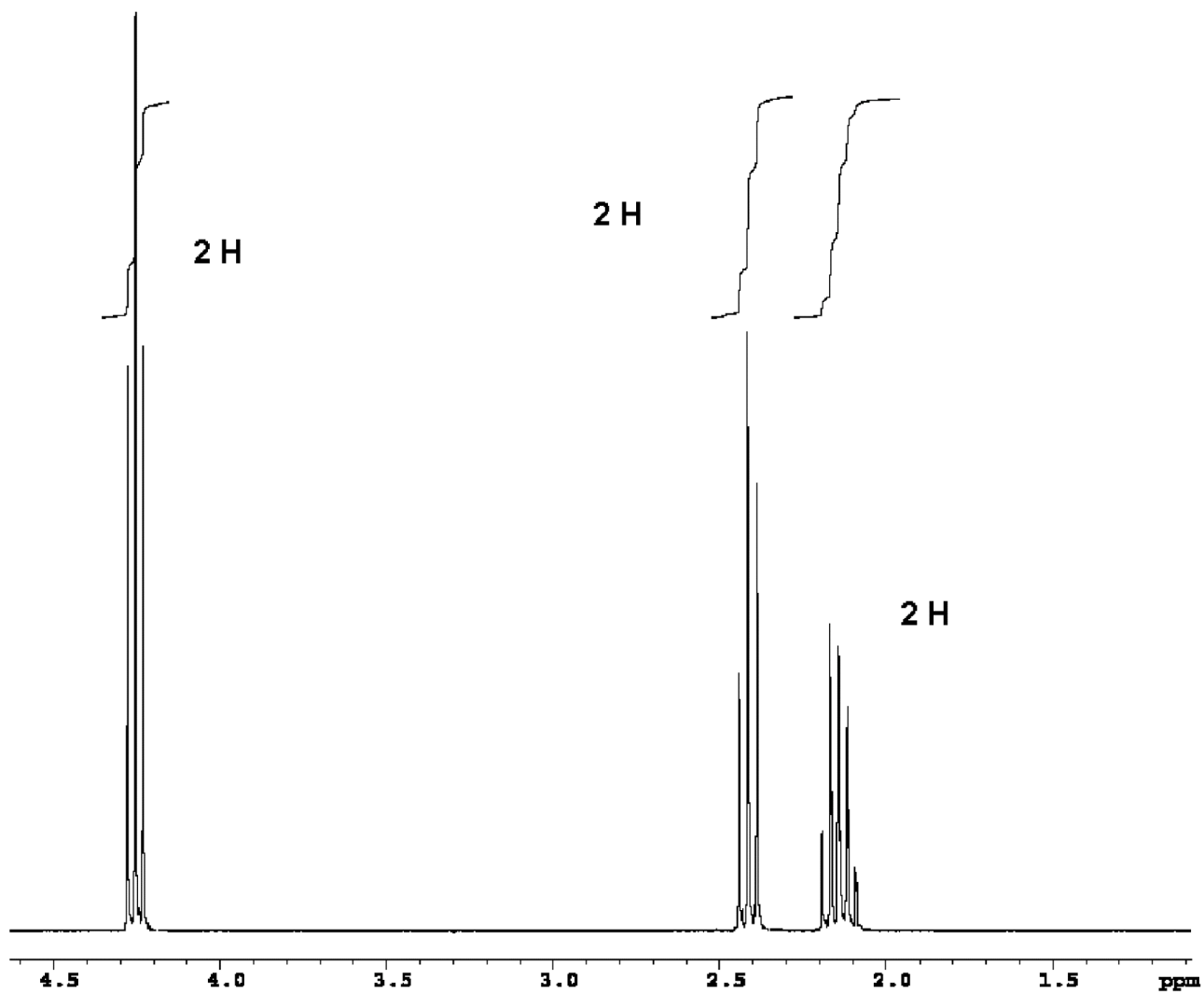
Signature \_\_\_\_\_

Pg 6 \_\_\_\_\_(5)

7. (5 pts) Circle the structure that corresponds to the following spectrum.



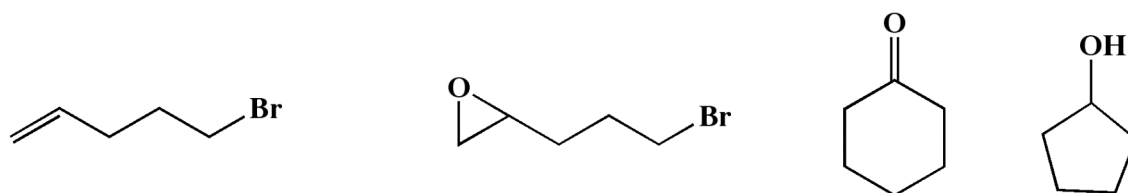
(No D<sub>2</sub>O was added to the sample)



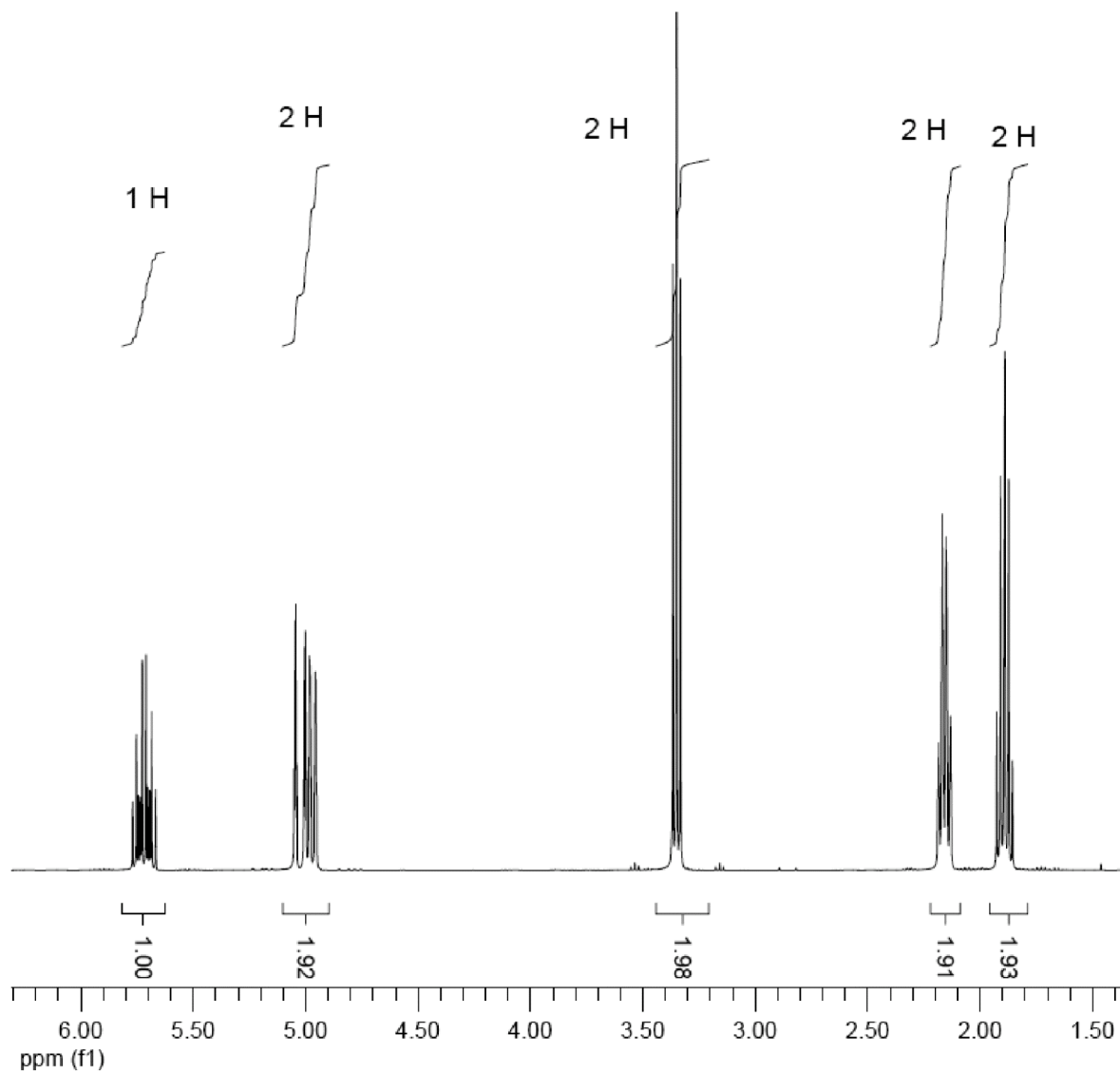
Signature \_\_\_\_\_

Pg 7 \_\_\_\_\_(5)

8. (5 pts) Circle the structure that corresponds to the following spectrum.

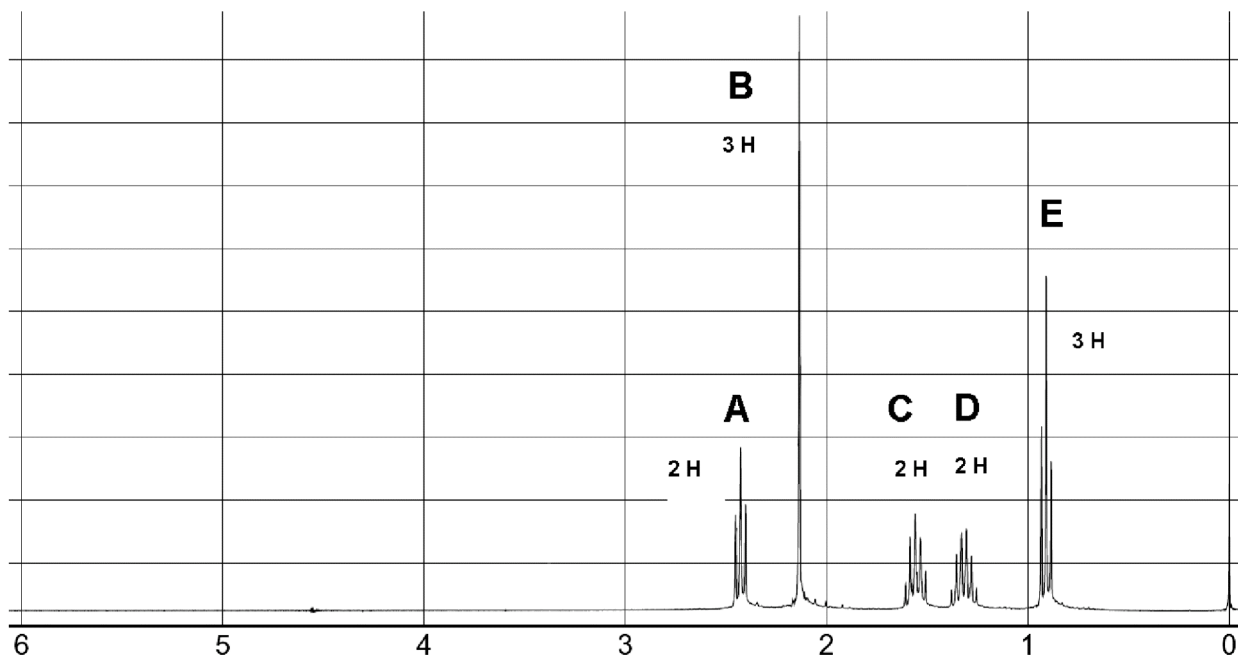
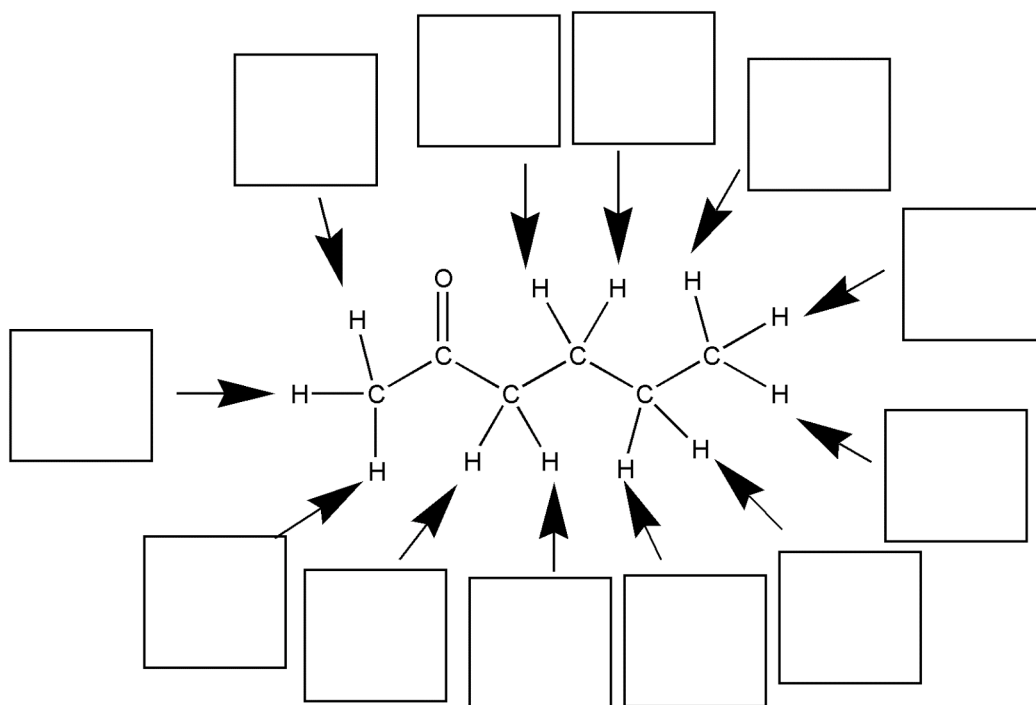


(No D<sub>2</sub>O was added to the sample)

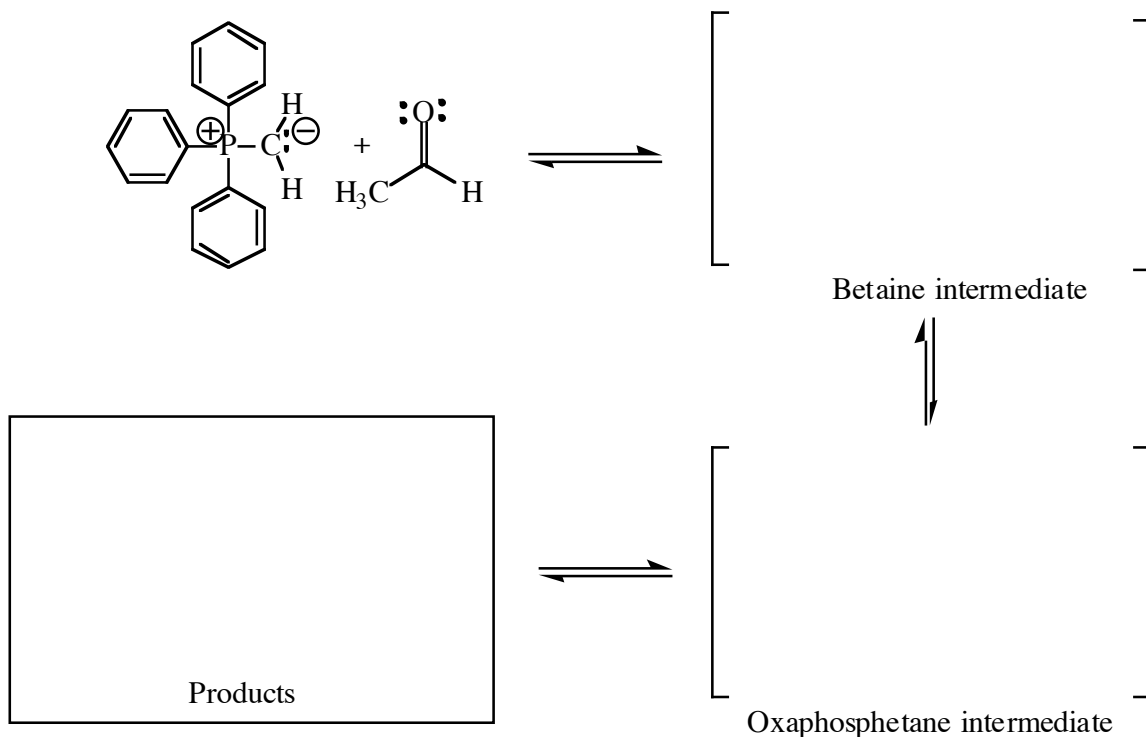


9. (12 pts) The following  $^1\text{H-NMR}$  spectrum of 2-hexanone has signals labeled with letters. In the boxes provided on the structure, place the letter of the signal that corresponds to the H atoms indicated by the arrows. Because of equivalence, more than one box can get the same letter!

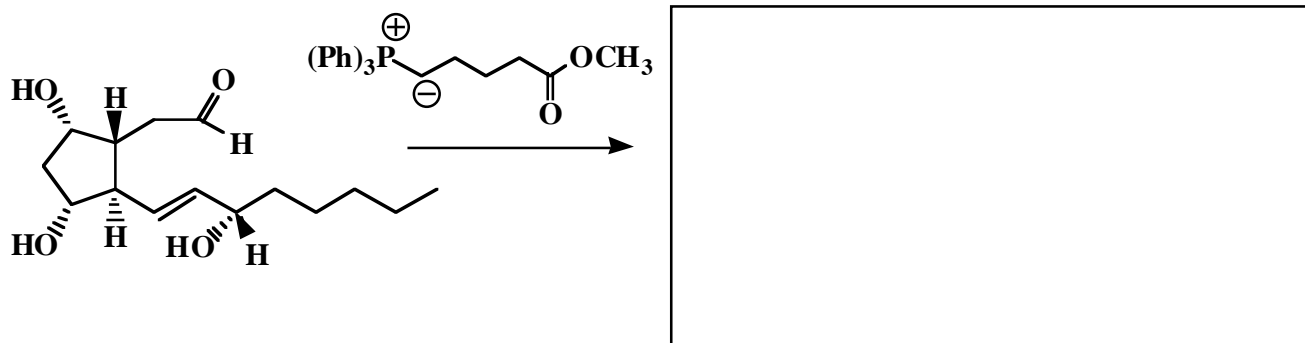
(No  $\text{D}_2\text{O}$  was added to the sample)



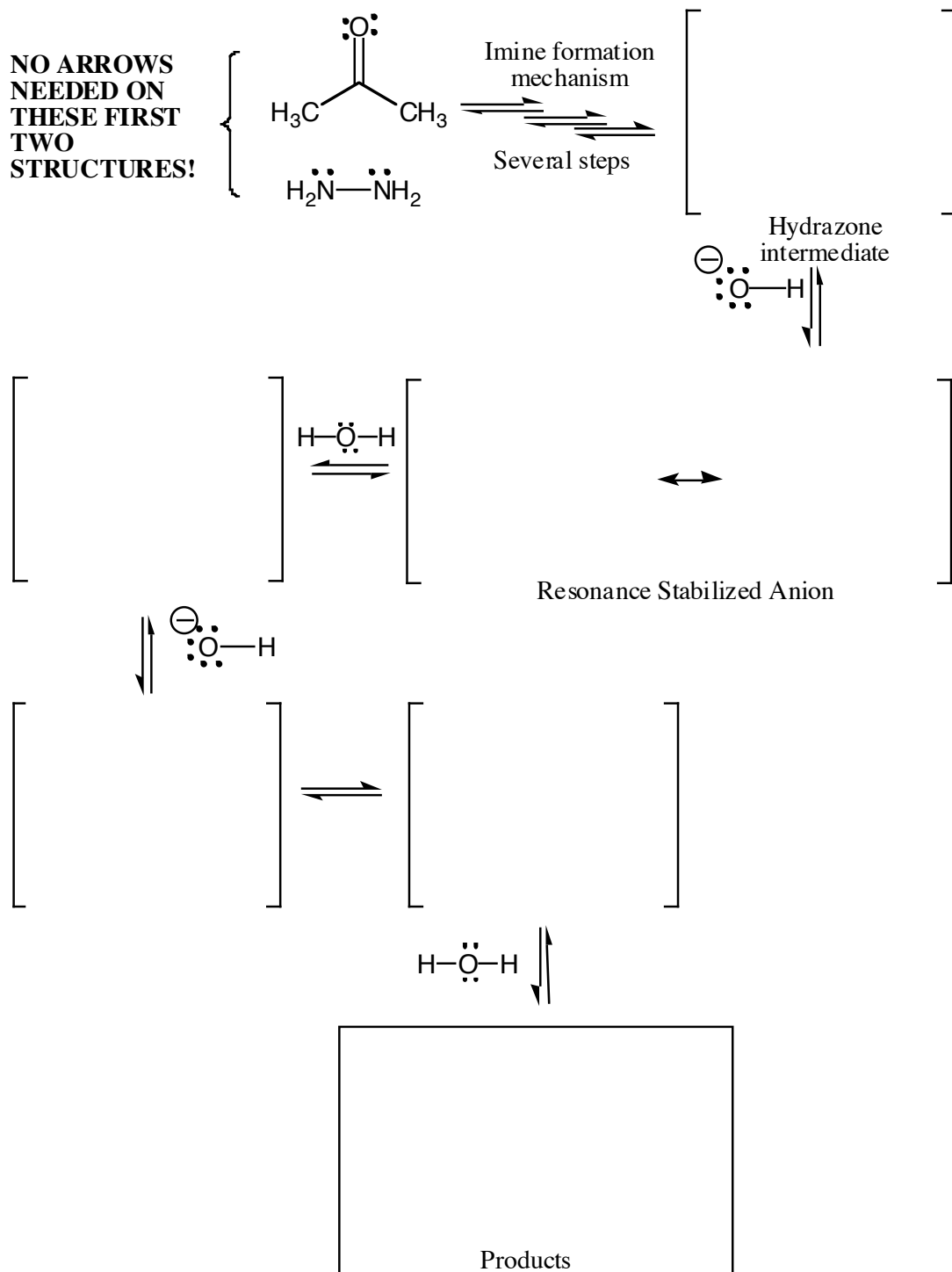
10. (16 pts.) Complete the mechanism for the following reaction. **Be sure to show arrows to indicate movement of all electrons, write all lone pairs, all formal charges, and all the products for each step.** Remember, I said all the products for each step.



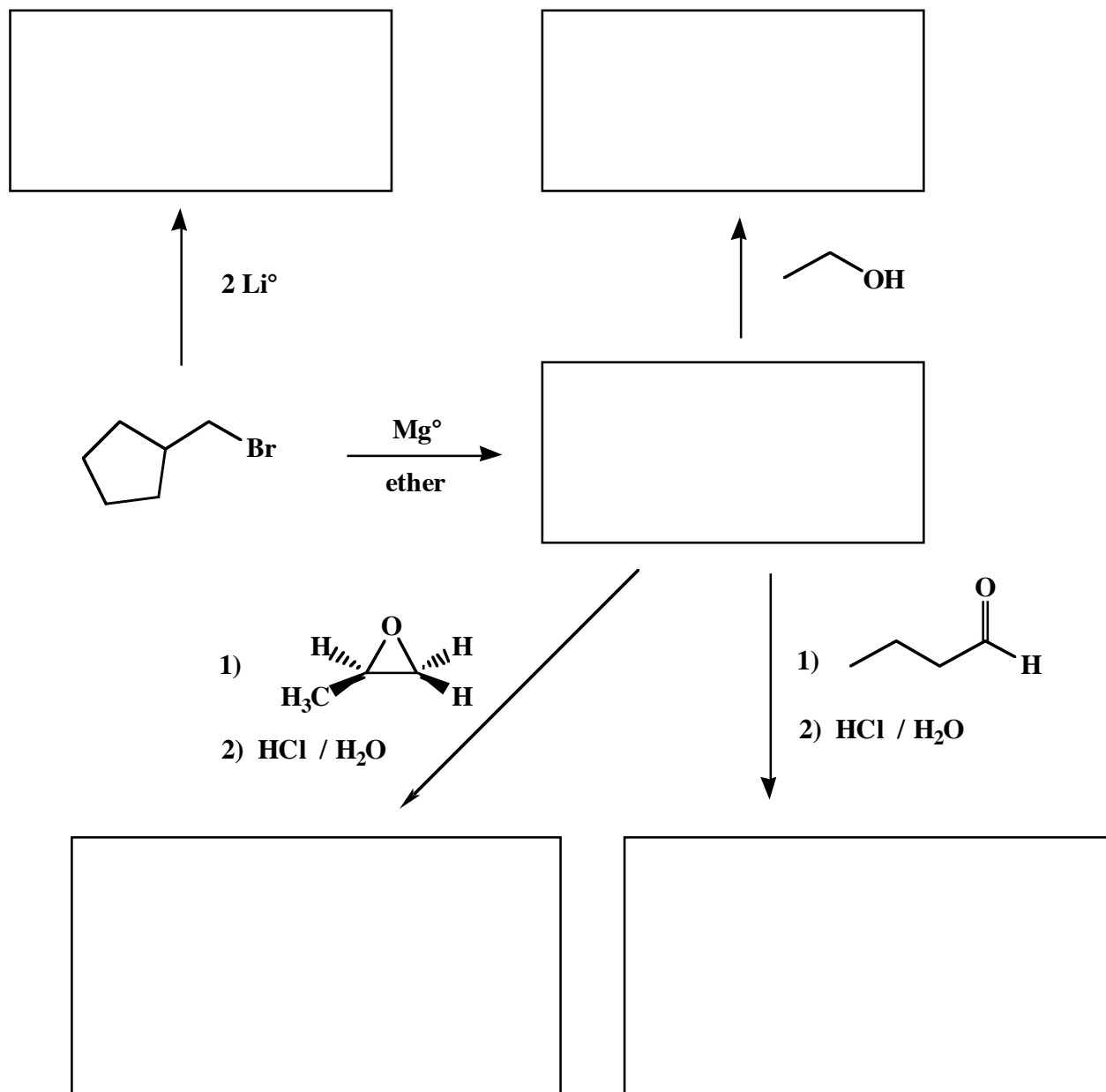
(5 pts) It is important that you are able to recognize reactive functional groups even in the context of complex molecules. You understand the chemistry important for the following reaction. In the space provided, draw the predominant product (including stereochemistry) of the following reaction (that was used in the actual synthesis of an important natural molecule, a prostaglandin).



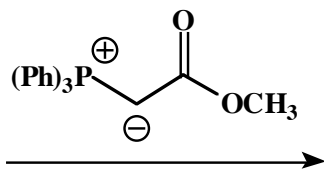
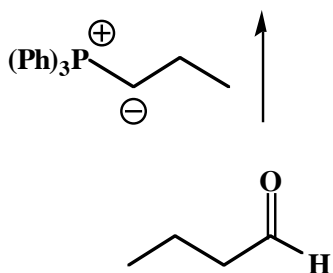
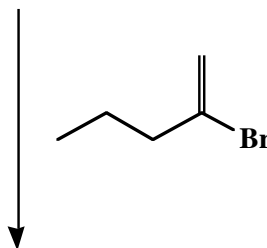
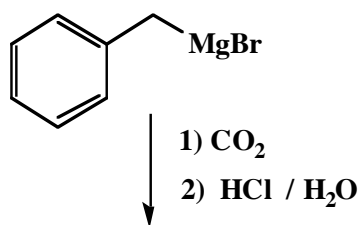
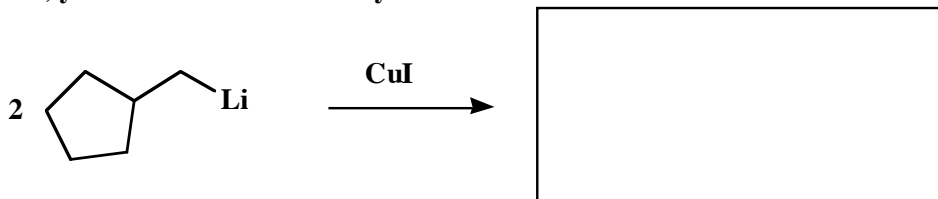
11. (32 pts.) Complete the mechanism for the following reaction. **Be sure to show arrows to indicate movement of all electrons, write all lone pairs, all formal charges, and all the products for each step.** Remember, I said all the products for each step. **In the box with the resonance arrow, you need to draw both resonance contributing structures.** You only need to indicate the flow of electrons on one structure (i.e. contributing structure) per intermediate.



12. (3-5 pts each) For the following reactions, write the predominant product or products in the box provided. Note that in some cases, the product of one step may be the starting material for another. If a racemic mixture is formed, mark the chiral center(s) with an asterisk "\*" and write "racemic" under the molecule. You do not have to draw both enantiomers.

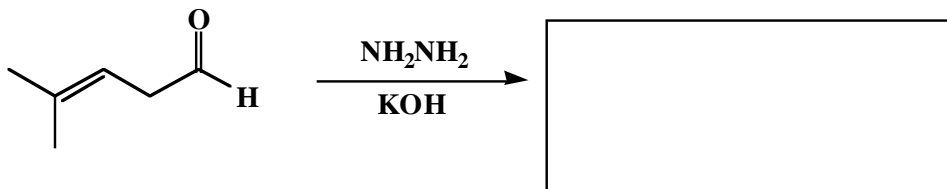
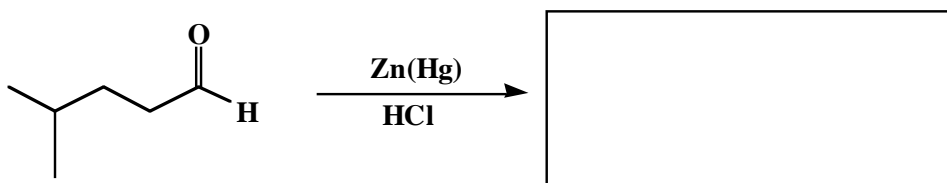
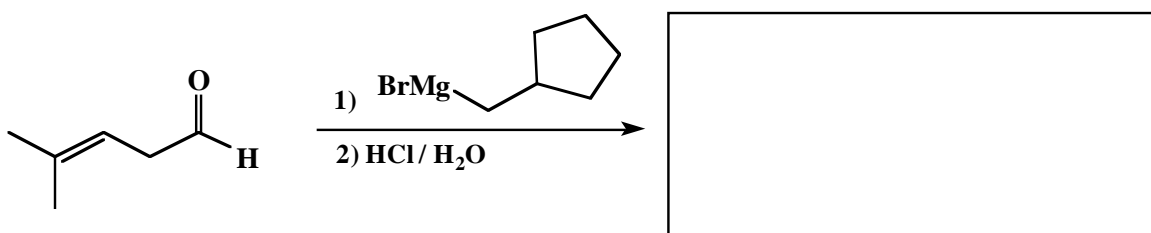
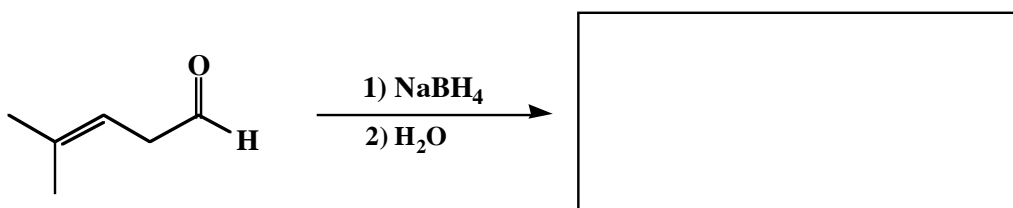
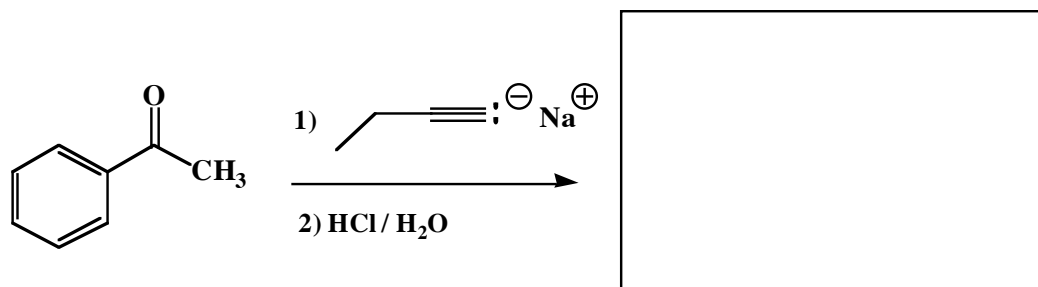
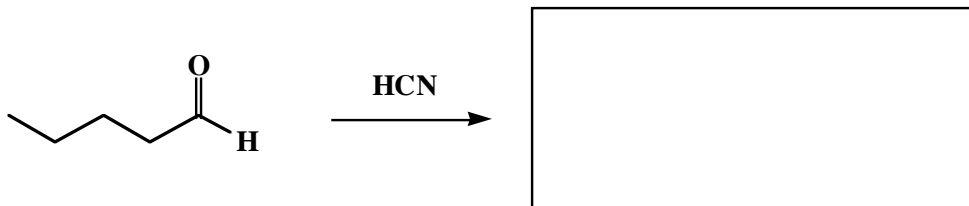


13. (3-5 pts each) For the following reactions, write the predominant product or products in the box provided. Note that in some cases, the product of one step may be the starting material for another. If a racemic mixture is formed, mark the chiral center(s) with an asterisk "\*" and write "racemic" under the molecule. You do not have to draw both enantiomers. **If an "E" or "Z" alkene is the predominant product, you must indicate that in your structure.**

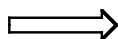




14. (3-5 pts each) For the following reactions, write the predominant product or products in the box provided. Note that in some cases, the product of one step may be the starting material for another. If a racemic mixture is formed, mark the chiral center(s) with an asterisk "\*" and write "racemic" under the molecule. You do not have to draw both enantiomers.

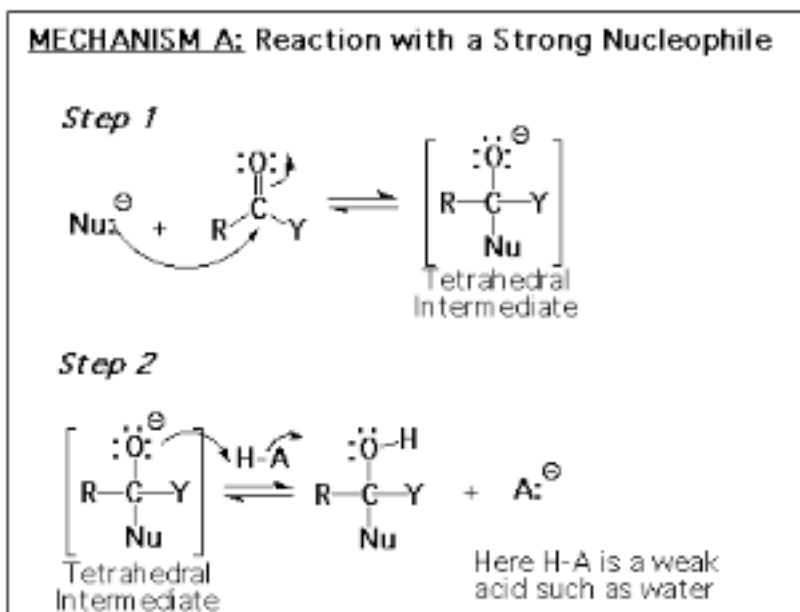


**NOTICE THIS!!!!**



(1 pt each) For the above reactions, circle the ones for which the mechanism is considered to be entirely by Mechanism A (Mechanism A is given on the next page for your reference.) (1 pt per reaction).

This is to be used as reference for the previous problem.

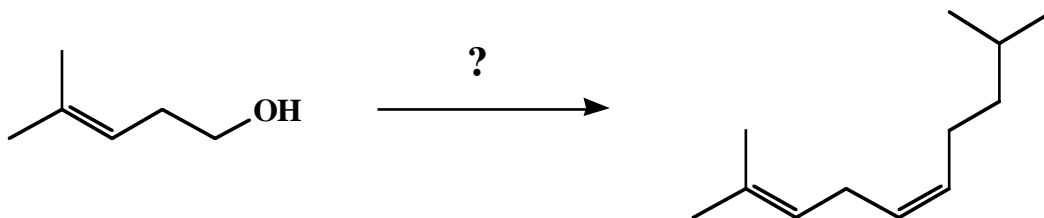


Signature \_\_\_\_\_

Pg 15 \_\_\_\_\_(13)

**15.** These are synthesis questions. You need to show how the starting material can be converted into the product(s) shown. You may use any reactions we have learned. Show all the reagents you need. Show each molecule synthesized along the way and be sure to pay attention to the regiochemistry and stereochemistry preferences for each reaction. You can only use a reaction if the predominant product is the one you need for your synthesis.

(13 pts) **All of the carbon atoms of the products must come from the starting materials for this one!**



Signature \_\_\_\_\_

Pg 16 \_\_\_\_\_(23)

**16.** These are synthesis questions. You need to show how the starting material can be converted into the product(s) shown. You may use any reactions we have learned. Show all the reagents you need. Show each molecule synthesized along the way and be sure to pay attention to the regiochemistry and stereochemistry preferences for each reaction. You can only use a reaction if the predominant product is the one you need for your synthesis.

(23 pts) **All of the carbon atoms of the products must come from the starting materials for this one!**

**This is a hard one, so save it until the end. Keep your wits about you, be systematic, and go for partial credit if you cannot get the whole thing!!**

