

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

Chemistry 310N  
Dr. Brent Iverson  
1st Midterm  
Feb. 21, 2008

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 IS 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		(16)
2		(19)
3		(15)
4		(15)
5		(20)
6		(-)
7		(-)
8		(-)
9		(-)
10		(14)
11		(21)
12		(23)
13		(35)
14		(20)
15		(26)
16		(10)
17		(13)
18		(16)
19		(8)
Total		(271)
%		
T Score		
HW		
(HW score + Exam Grade) $\implies$	Total Grade	

## Honor Code

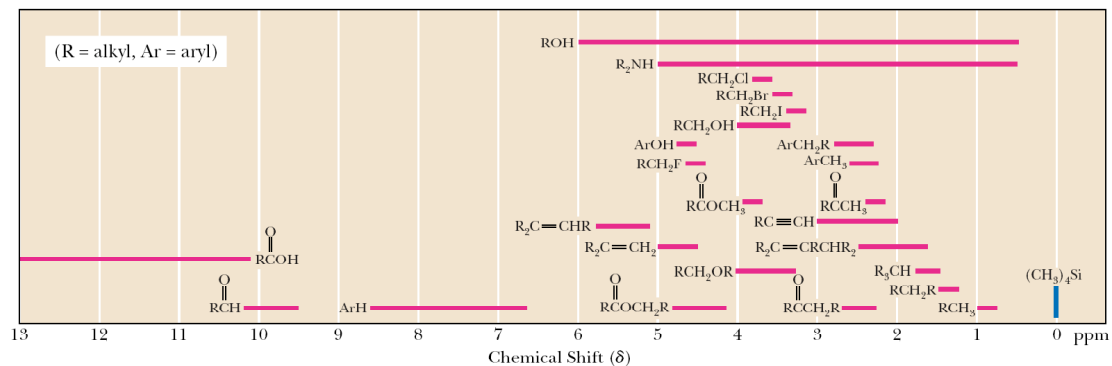
The core values of the University of Texas at Austin are learning, discovery, freedom, leadership, individual opportunity, and responsibility. Each member of the University is expected to uphold these values through integrity, honesty, trust, fairness, and respect toward peers and community.

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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.



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

For organic chemistry, NMR is primarily concerned with atoms having a spin quantum number of 1/2. The two most important isotopes for organic chemistry structure determination by NMR are  $^1\text{H}$  and  $^{13}\text{C}$ . Of these two,  $^1\text{H}$  is a common isotope and the predominant isotope found in molecules, while  $^{13}\text{C}$  is very rare.

Electron density is induced to move in a strong external magnetic field, and this movement induces a magnetic field that is opposed to the external magnetic field. This has the effect of shielding the underlying nuclei from the external magnetic field. The signal for an  $^1\text{H}$  atom with greater electron density around it will come at lower ppm in an NMR spectrum compared to a similar  $^1\text{H}$  atom with less electron density.

The spins of adjacent nuclei influence each other. If  $^1\text{H}$  atoms are no more than three bonds apart, the spin states couple.

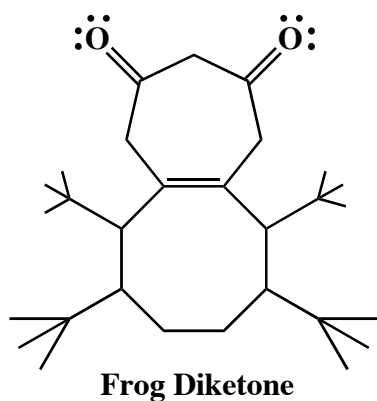
THEORY: When there are two sets of adjacent H atoms, the number of peaks multiply. For example, a  $\text{CH}_2$  group with a  $\text{CH}_2$  group and a  $\text{CH}_3$  group on either side shows a theoretical maximum of  $3 \times 4 = 12$  peaks in its signal!

PRACTICE: For alkyl groups that can rotate freely, complex splittings simplify because the coupling constant ("J") are all about the same. In practice, if there are n adjacent H atoms, equivalent or not, you will see  $n + 1$  peaks in a signal. This is an approximation, but almost always true on spectra taken with all but the most high resolution NMR spectrometers.

1. (cont.) (1 pt each)

In the FT NMR method, the FT stands for Fourier transform.

The basic idea is that a short pulse using a range of radio frequencies are used to flip the spins of all of the hydrogen nuclei at once. Then, the nuclear spins relax back to the +1/2 spin state and when they do, they emit electromagnetic radiation at the precise frequency at which they absorb.



**This is not part of a question.  
This little molecule creature is  
simply supposed to make you  
smile!**

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.

The popular medical diagnostic technique of **magnetic resonance imaging (MRI)** is based on the **same principles as NMR**, namely the **flipping (i.e. resonance) of nuclear spins of protons by radio frequency irradiation** when a patient is placed in a **strong magnetic field**. **Magnetic field gradients** are used to gain imaging information, and **rotation of the gradient around the center of the object** gives imaging in an entire plane (**i.e. slice inside patient**). In an MRI image, you are looking at **individual slices that when stacked make up the three-dimensional image of relative amounts of protons, especially the protons from water and fat, in the different tissues**.

3. (3 pts) The most important question in organic chemistry is:

**Where are the electrons?**

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4. (3 pts each) Write an acceptable IUPAC name or draw a structural formula for the following molecules:

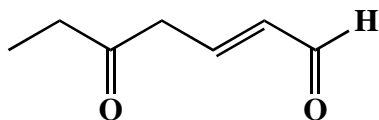
A.



**4-hydroxybutanal**

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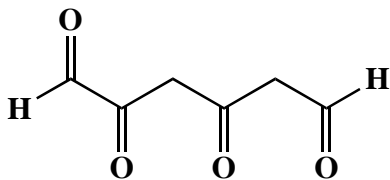
B.



**(E)-5-oxo-2-heptenal**

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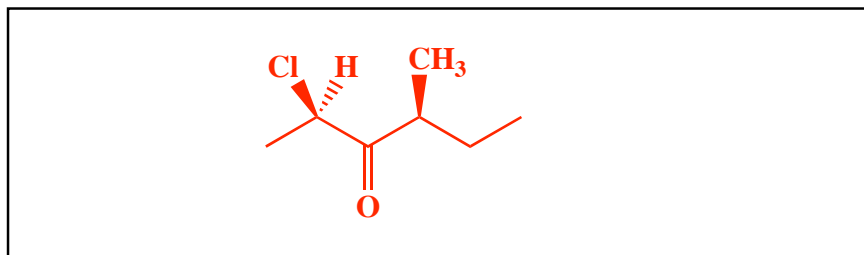
C.



**2,4-dioxohexanedial**

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D. **(2R,4S)-2-Chloro-4-methyl-3-hexanone**

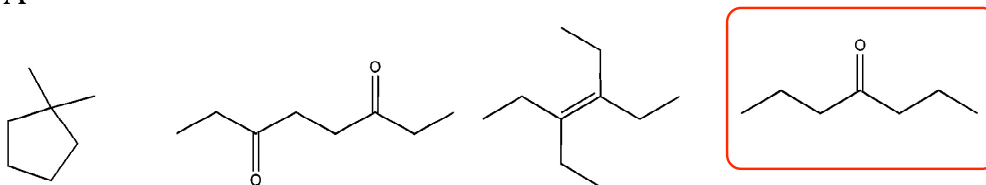


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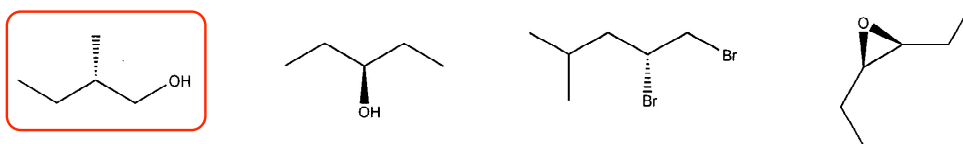
Pg 5 \_\_\_\_\_ (20)

5. (5 pts each) For A-D, circle a single structure from the four choices given. The structure you circle should be the one which matches the spectrum on the corresponding page.

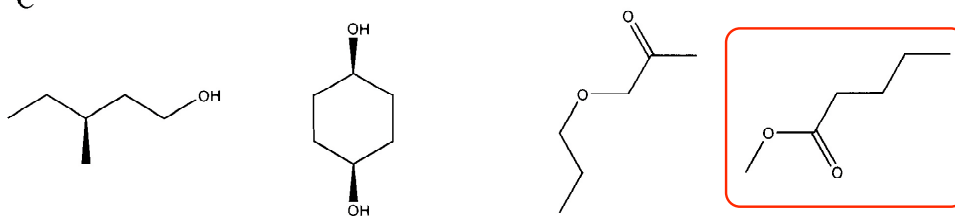
A



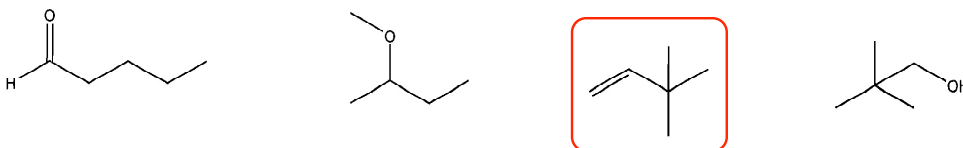
B



C



D



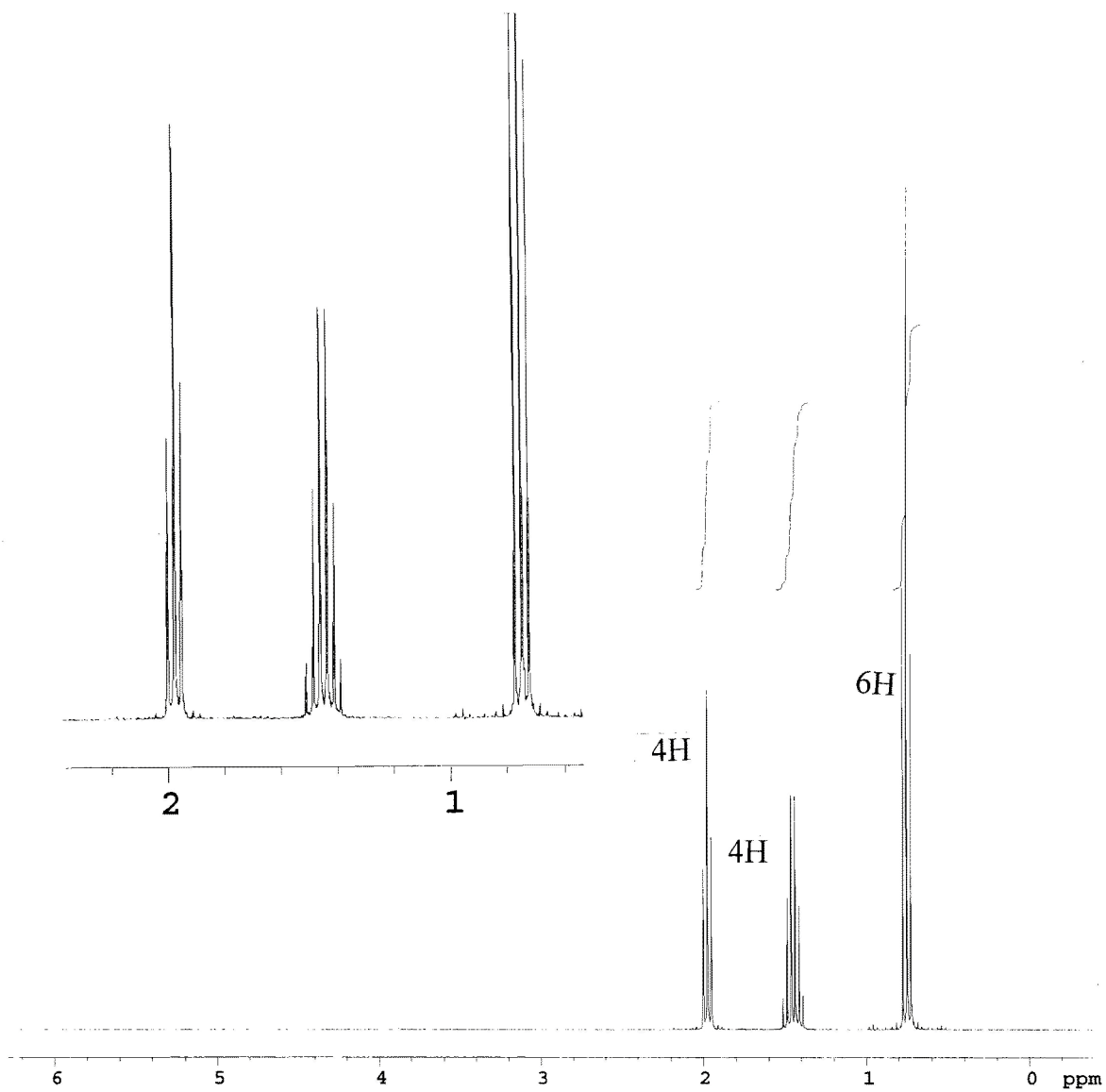


Signature \_\_\_\_\_

Pg 6 \_\_\_\_\_

5A. (5 pts each) Circle a single structure on page 4 from the four choices given. The structure you circle should be the one which matches the spectrum below.

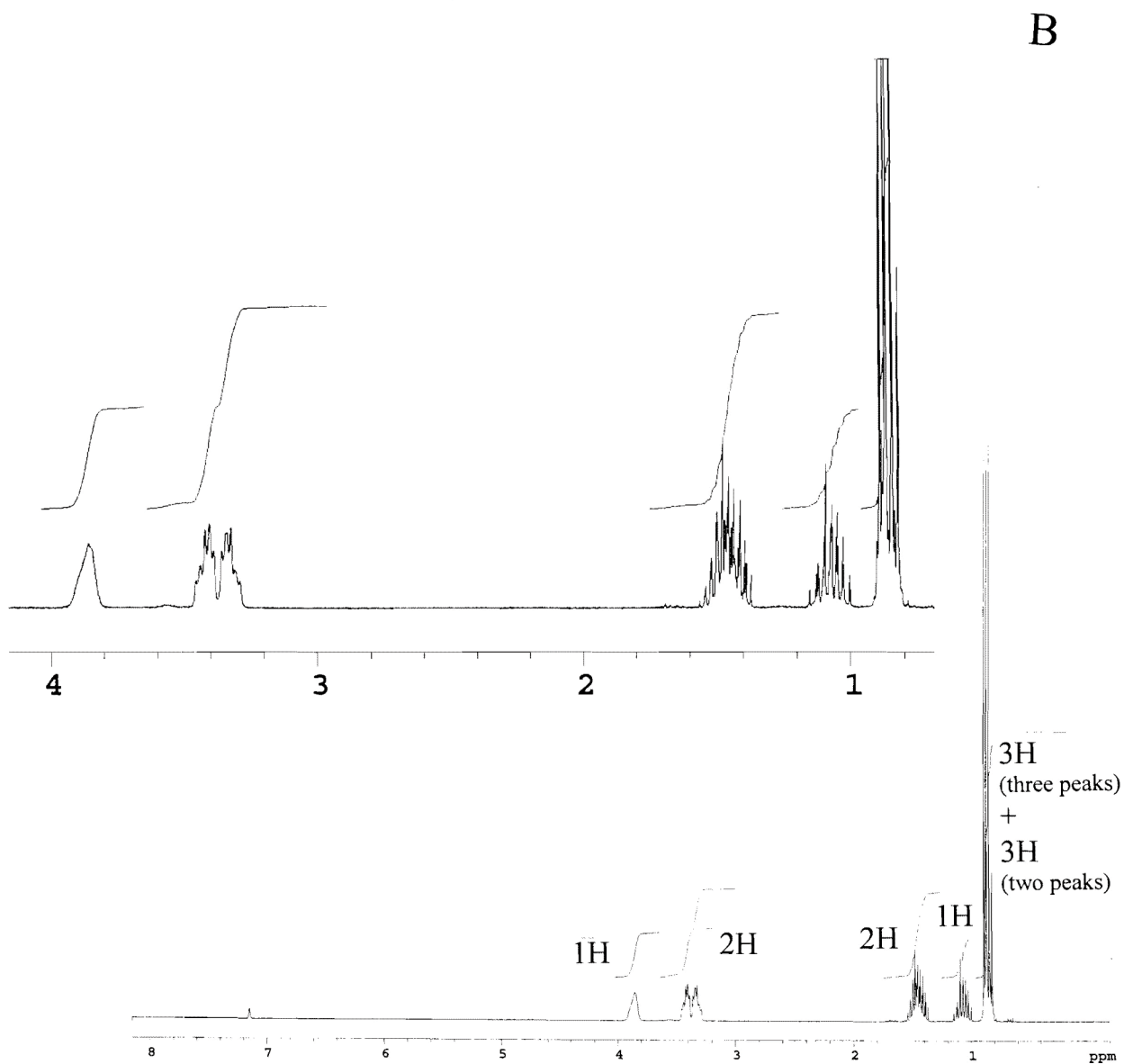
A



Signature \_\_\_\_\_

Pg 7 \_\_\_\_\_

5B. (5 pts each) Circle a single structure on page 4 from the four choices given. The structure you circle should be the one which matches the spectrum below.

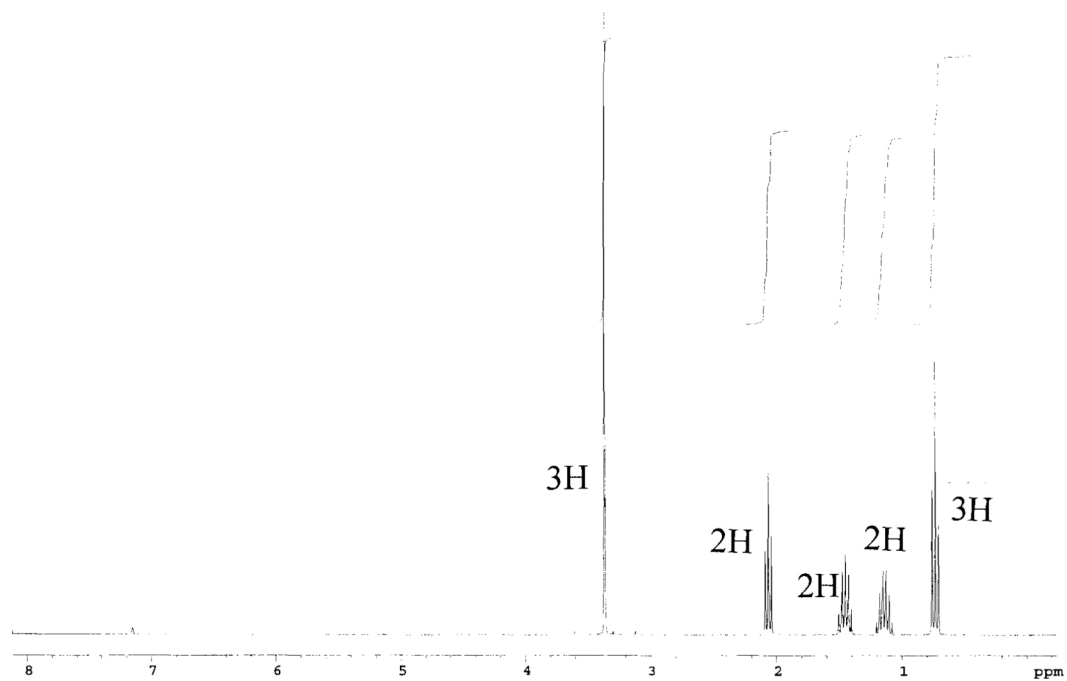
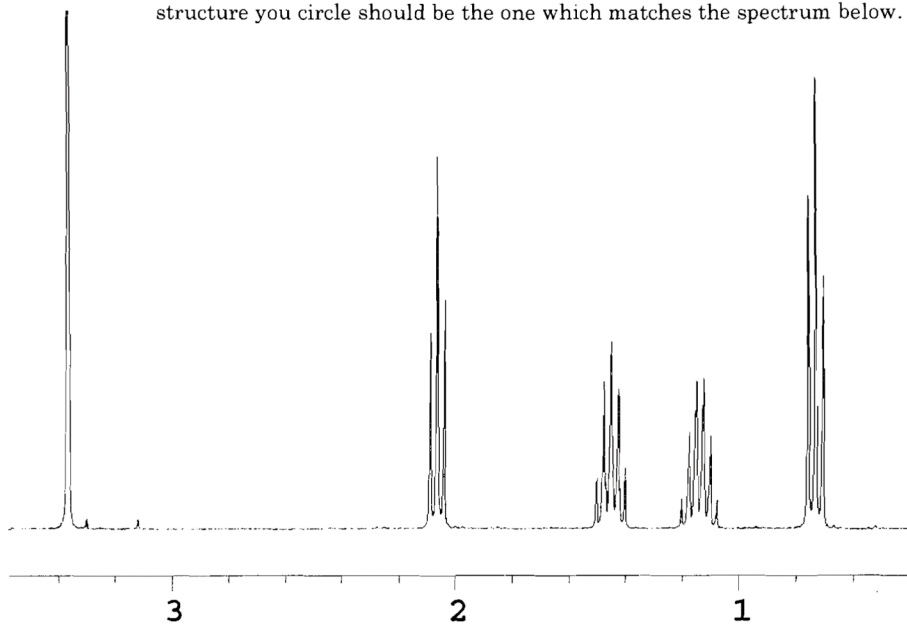


Signature \_\_\_\_\_

Pg 8 \_\_\_\_\_

5C. (5 pts each) Circle a single structure on page 4 from the four choices given. The structure you circle should be the one which matches the spectrum below.

C

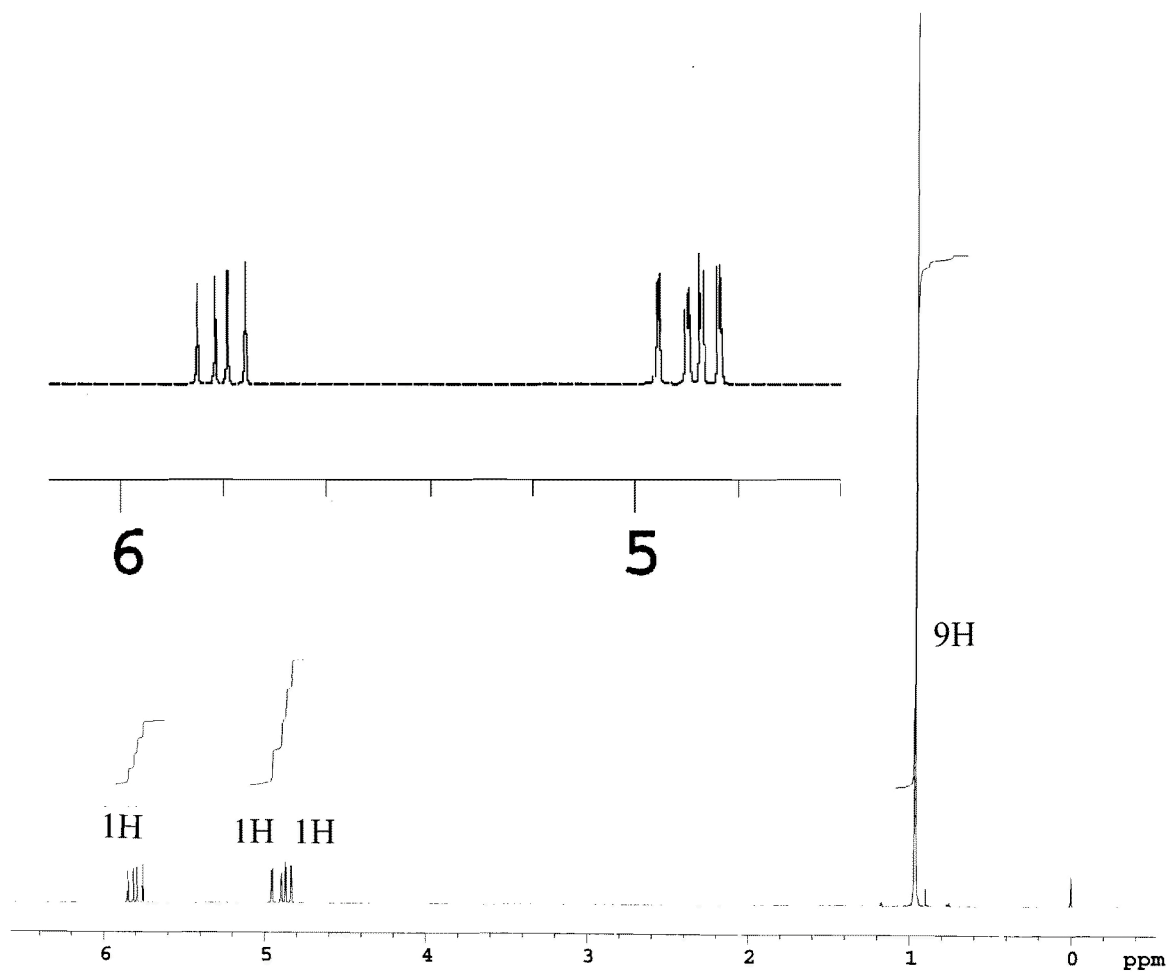


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Pg 9 \_\_\_\_\_

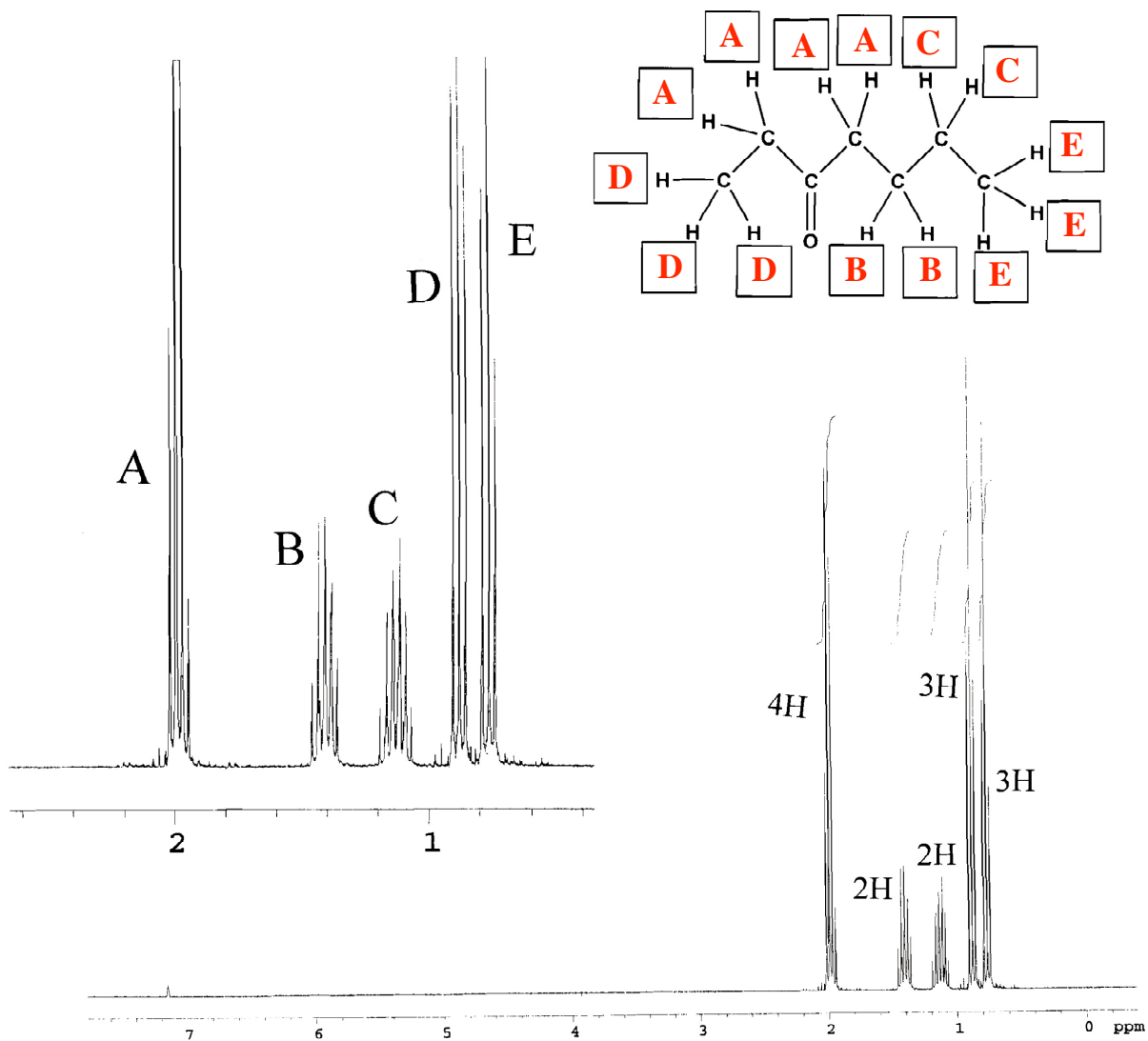
5D. (5 pts each) Circle a single structure on page 4 from the four choices given. The structure you circle should be the one which matches the spectrum below.

D

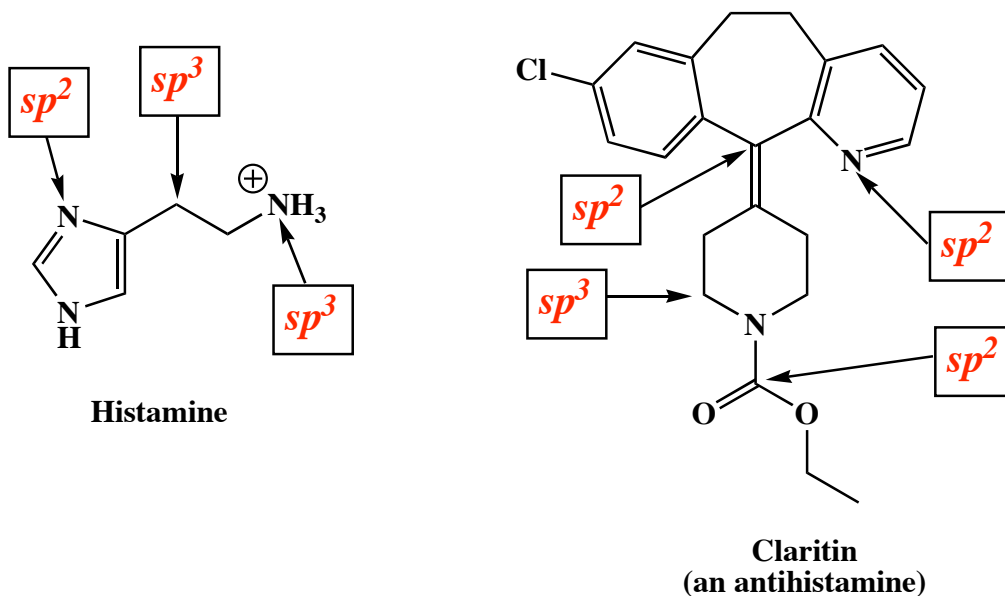


6. (14 pts) The following  $^1\text{H-NMR}$  spectrum of 3-heptanone has signals labeled with letters. In the boxes provided on the structure, place the letter of the signal that corresponds to the H atom in the adjacent box. Because of equivalence, more than one box can get the same letter!

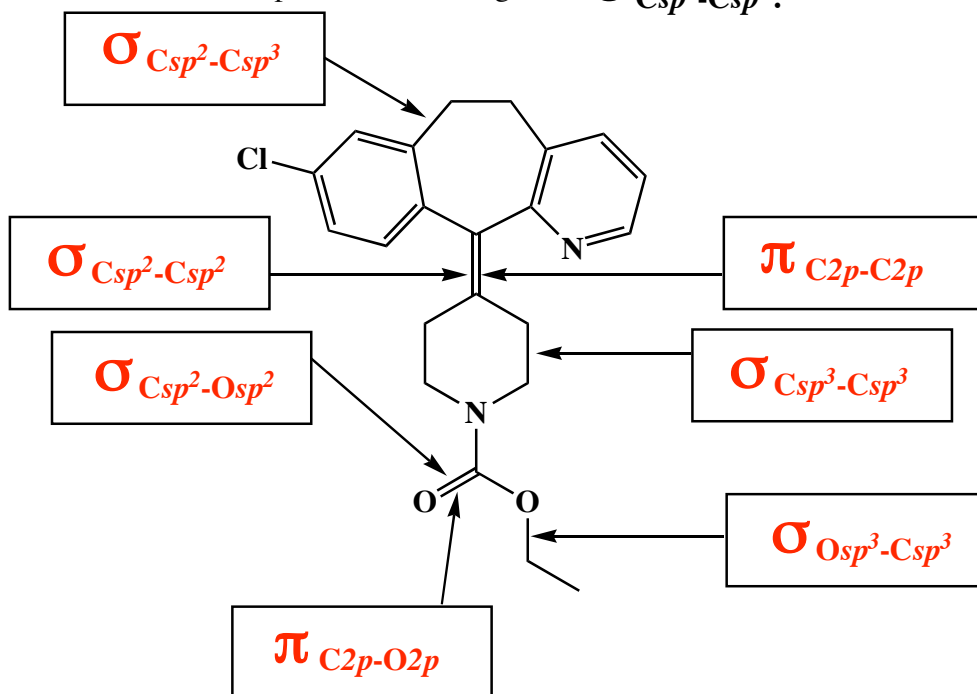
(No  $\text{D}_2\text{O}$  was added to the sample)



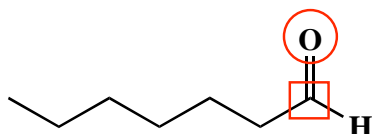
7. (1 pt each) I warned you about this. We need to make sure all of you understand hybridization. In the boxes provided, write the hybridization state of the atoms indicated by the arrows.



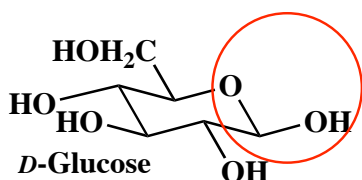
8. (2 pts each) I warned you about this also. Describe each bond indicated with an arrow as the overlap of orbitals. For example, an answer might be  $\sigma_{Csp^3-Csp^3}$ .



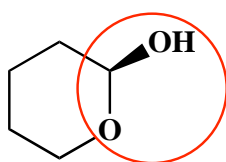
9. (4 pts) An important part of chemical understanding is being able to recognize the chemical reactivity of different functional groups. On the carbonyl group below, DRAW A BOX around the atom that will be attacked by nucleophiles and DRAW A CIRCLE around the atom that will be protonated in acid.



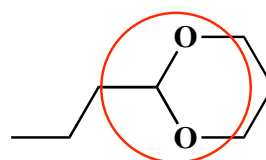
10. (3 pts each) Some functional groups are hard to recognize. For the following two molecules, DRAW A CIRCLE around either the acetal, cyclic hemiacetal, or cyclic acetal. Under each molecule, write the appropriate term (acetal, cyclic hemiacetal, or cyclic acetal).



Cyclic hemiacetal

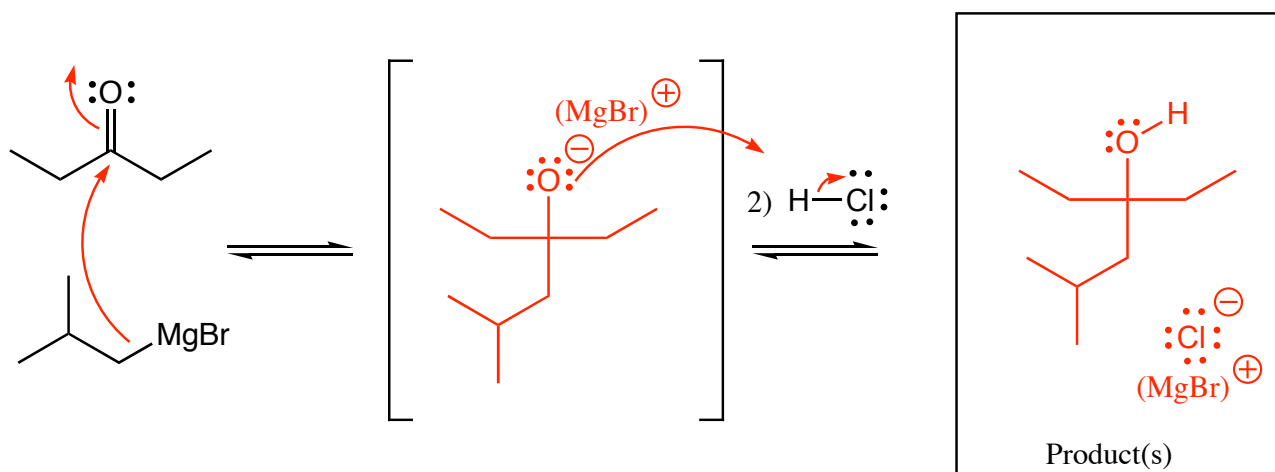


Cyclic hemiacetal

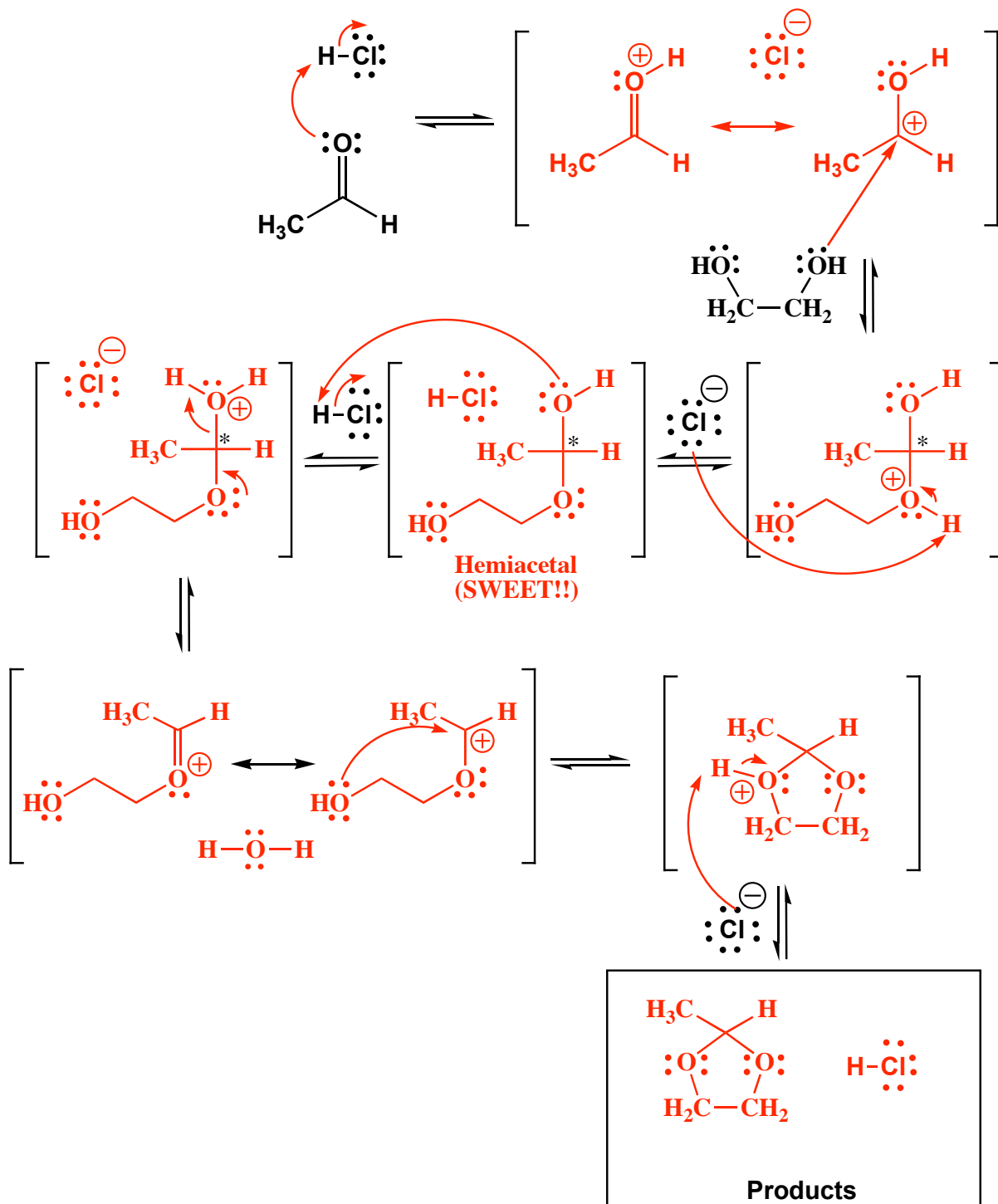


Cyclic acetal

11. (10 pts.) Complete the mechanism for the following Grignard 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. **IF A NEW CHIRAL CENTER IS CREATED IN AN INTERMEDIATE, MARK IT WITH AN ASTERISK.** **IF A CHIRAL CENTER IS CREATED IN THE PRODUCTS YOU NEED TO DRAW BOTH ENANTIOMERS, AND LABEL THE PRODUCT MIXTURE AS RACEMIC IF RELEVANT.** I realize these directions are complex, so please read them again to make sure you know what we want.

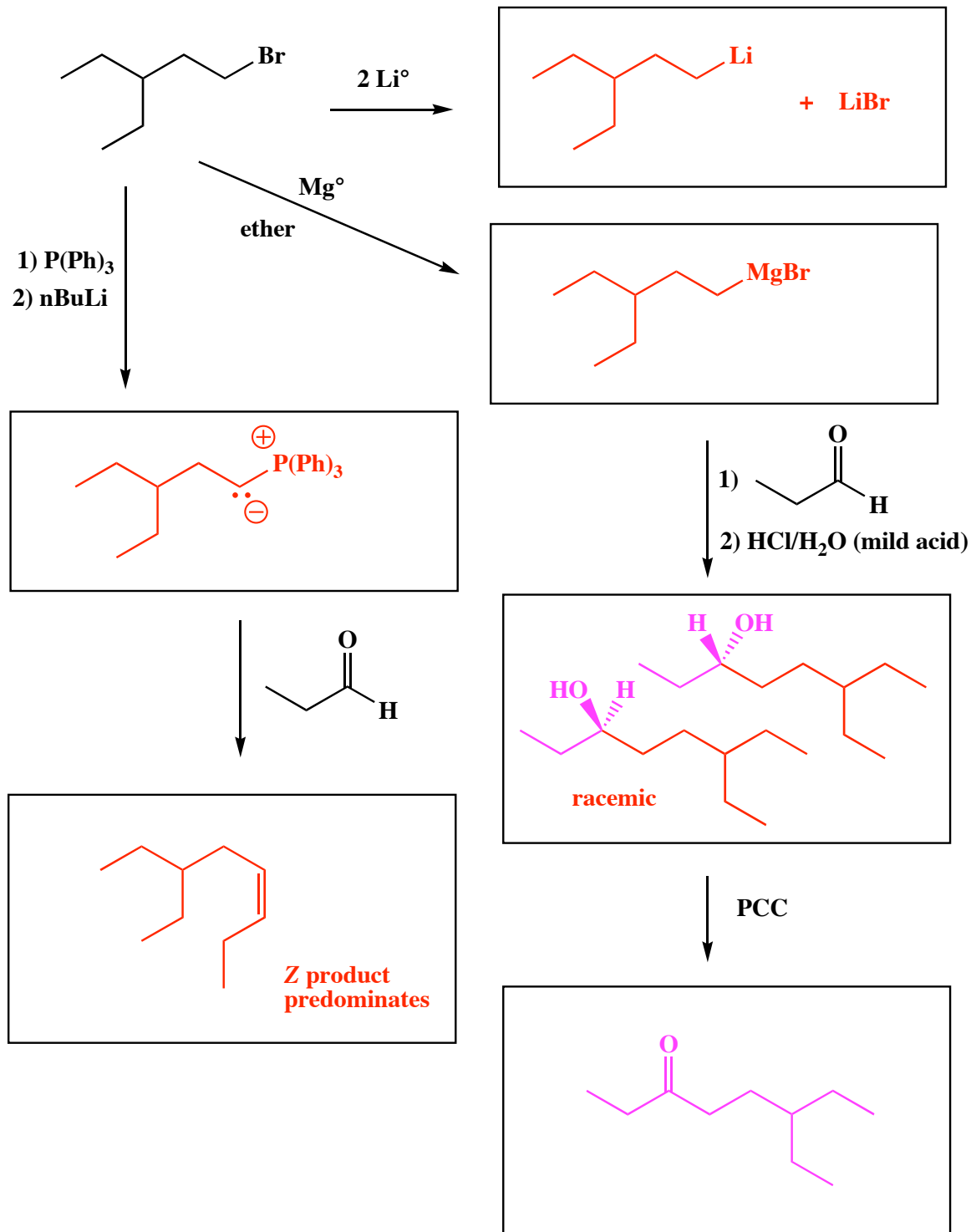


11. (cont.) (35 pts.) Complete the mechanism for the following acetal formation reaction. **Be sure to show arrows to indicate movement of all electrons, write all lone pairs, all formal charges, and all the products for each step.** Remember, I said all the products for each step. **IF A NEW CHIRAL CENTER IS CREATED IN AN INTERMEDIATE, MARK IT WITH AN ASTERISK. IF A CHIRAL CENTER IS CREATED IN THE PRODUCTS YOU NEED TO DRAW BOTH ENANTIOMERS, AND LABEL THE PRODUCT MIXTURE AS RACEMIC IF RELEVANT.** I realize these directions are complex, so please read them again to make sure you know what we want.

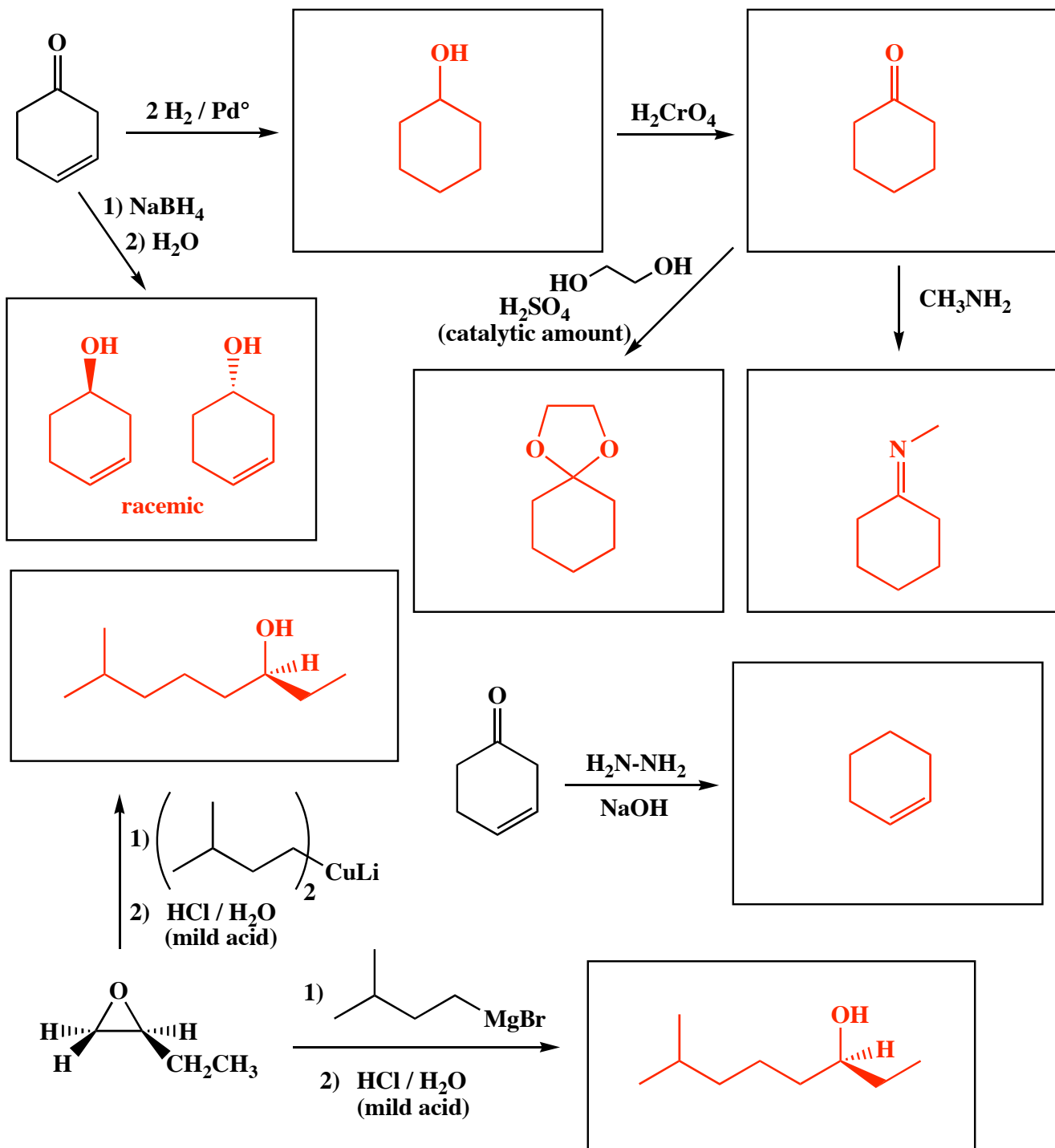




12. (3 or 5 pts.) Write the predominant product or products that will occur for each transformation. If a new chiral center is created and a racemic mixture is formed, you must draw both enantiomers and write "racemic" under the structure. Use wedges (  $\blacktriangleleft$  ) and dashes (  $\dashv$  ) to indicate stereochemistry. To get full credit, you only need to write the the major organic product for these. You do not have to worry about the other products.

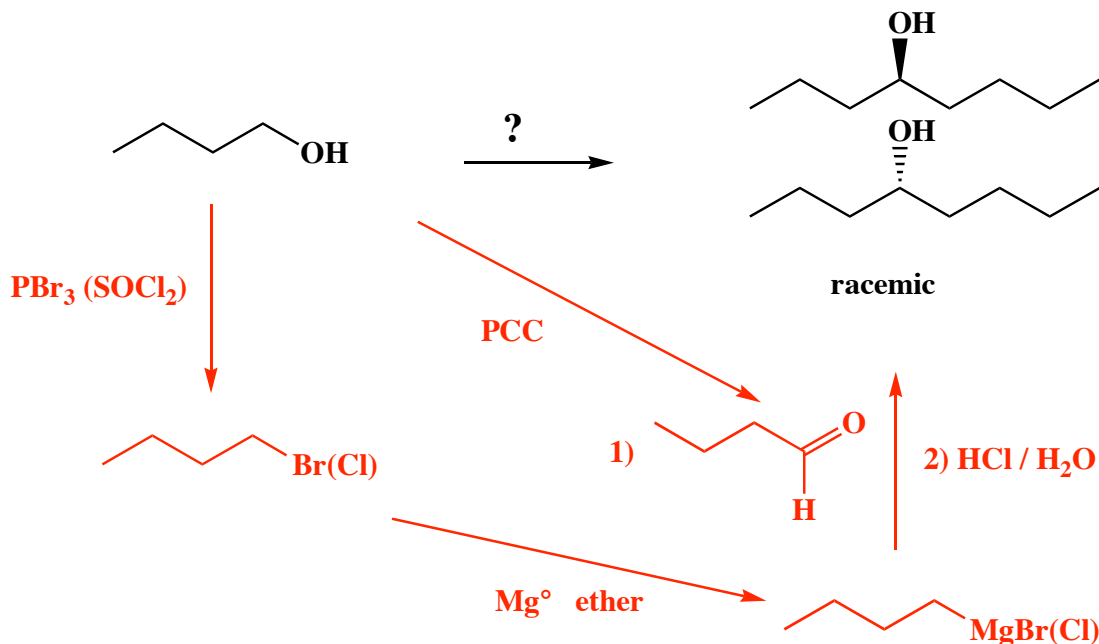


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13. These are synthesis questions. You need to show how the starting material can be converted into the product(s) shown. You may use any reactions we have learned. Show all the reagents you need. Show each molecule synthesized along the way and be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

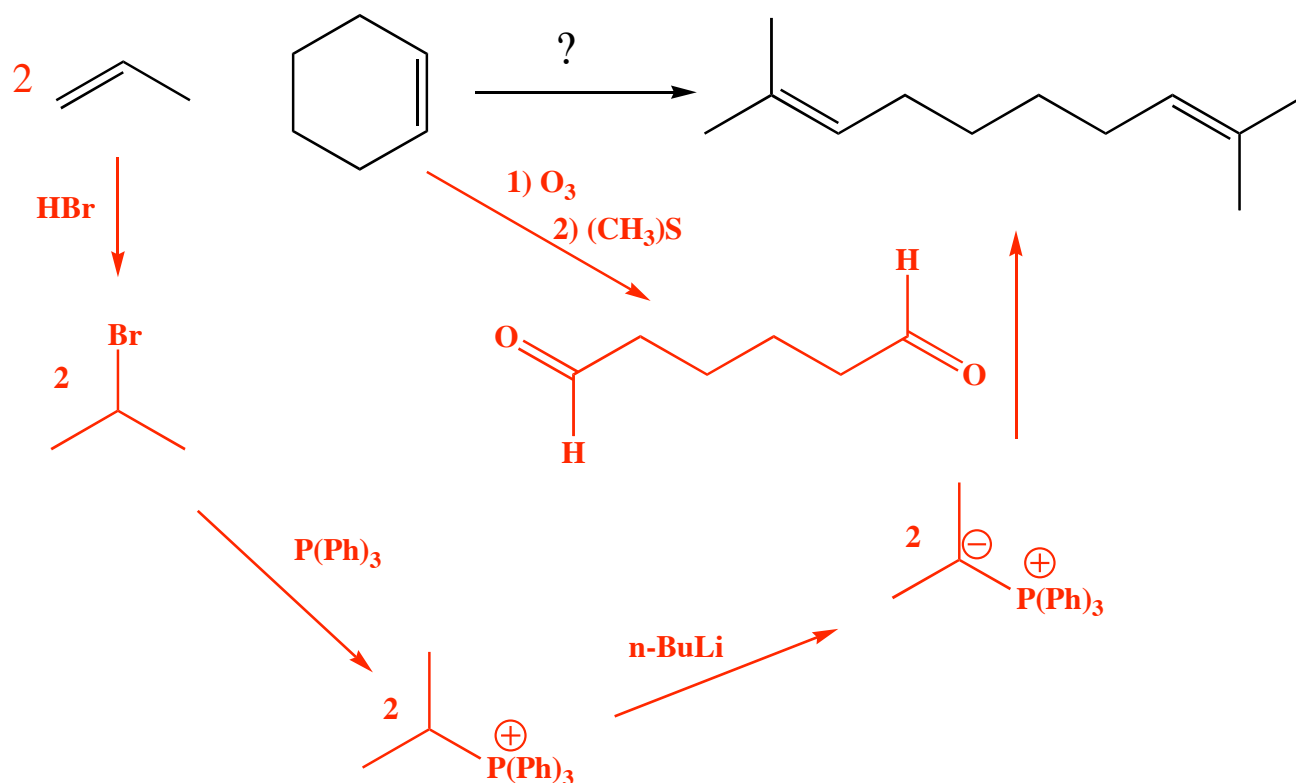
(10 pts) **All of the carbon atoms of the products must come from the starting materials for this one!**



**Recognize** that the product has eight carbons, exactly twice that of the starting alcohol, so assume to molecules of starting material must be connected. **Recognize** also that the product is an alcohol with an OH group adjacent to the new C-C bond, the Key Recognition Element of a Grignard reaction. In this case, the reaction must be between butyraldehyde and the Grignard made from the 1-bromobutane. These, in turn, are made from a PCC reaction of the starting alcohol (to give the aldehyde) and the sequence of  $\text{PBr}_3$  then Mg in ether, respectively. Note that it is perfectly acceptable to use  $\text{SOCl}_2$  in place of  $\text{PBr}_3$ , since chloro-Grignard reagents are suitable replacements for bromo-Grignards.

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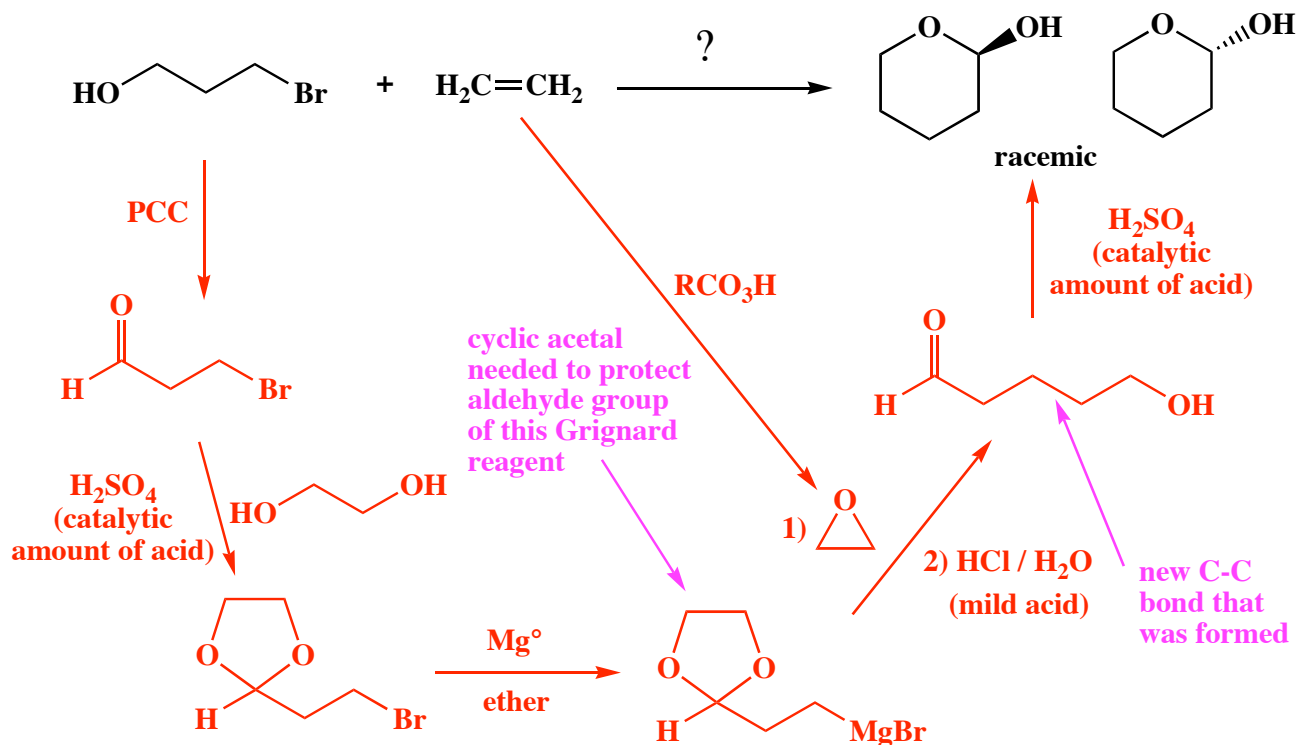
(13 pts) **All of the carbon atoms of the products must come from the starting materials for this one!**



Count carbons in the product (12) and realize that two molecules of the 3-carbon unit need to be added to one of the 6-carbon unit. **Recognize** that the last step makes alkenes in the locations required for carbon-carbon bond formation, indicating a Wittig reaction as the last step. **Recognize** that the ring can be opened to give the required dialdehyde by an ozonolysis. **Recognize** that the required Wittig ylide can be derived from the starting alkene via reaction with HBr (Markovnikov addition) followed by the unusual steps of adding  $\text{P(Ph)}_3$  followed by strong base (n-BuLi).

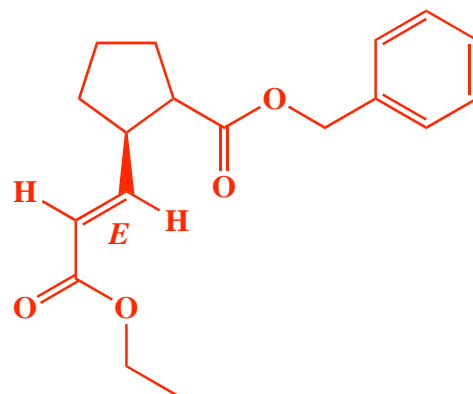
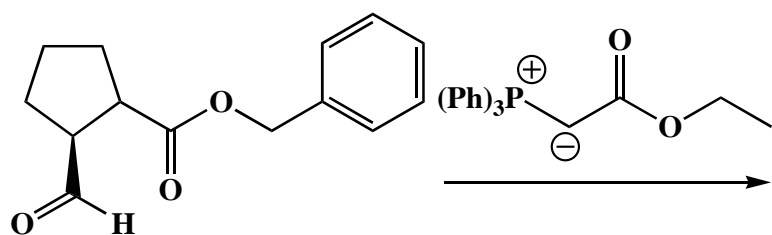
13. These are synthesis questions. You need to show how the starting material can be converted into the product(s) shown. You may use any reactions we have learned. Show all the reagents you need. Show each molecule synthesized along the way and be sure to pay attention to the regiochemistry and stereochemistry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

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



**Recognize** that the final product is a cyclic hemiacetal of 5-hydroxypropanal. Counting carbons tells you that one molecule from each starting material (3 + 2) is used. The first hard part of this synthesis is realizing that an epoxide (ethylene oxide) was used since the alcohol group is on the end even though the new carbon-carbon bond is formed between carbons 3 and 4 of the 5-hydroxypropanal. Given that insight, you need to recognize that a cyclic acetal protecting group was needed to protect the aldehyde group on the required Grignard reagent as discussed in class. This approach required that the starting 3-bromopropanol is oxidized with PCC to give the corresponding 3-bromopropanal in the first step.

14. (8 pts.) The key paradigm of organic chemistry is that functional groups behave the same in complex molecules as they do in the simpler ones we generally see in this course. The Wittig reaction is used often in complex molecule synthesis. Draw the predominant product of the following Wittig reactions.



Note the *E* stereochemistry of both alkene products

