NAME (Print):	Chemistry 310N
	Dr. Brent Iverson
SIGNATURE:	1st Midterm Feb. 21, 2008

first three letters of your last name in the three boxes
--

**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		
	нw		
+ Exam Grade) $\Longrightarrow$	Total Grade		

(HW score

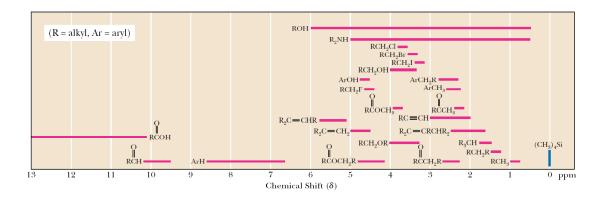
## **Honor Code**

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.

(Your signature)

Type of Hydrogen (R = alkyl, Ar = aryl)	Chemical Shift (δ)*	Type of Hydrogen (R = alkyl, Ar = aryl)	Chemical Shift (δ)*
		RCH <sub>2</sub> OH	3.4-4.0
R <sub>2</sub> NH	0.5-5.0	RCH <sub>2</sub> Br	3.4-3.6
ROH	0.5-6.0	RC <b>H</b> <sub>2</sub> Cl	3.6-3.8
RCH <sub>3</sub>	0.8-1.0	°,	
RCH <sub>2</sub> R	1.2-1.4	R <sup>L</sup> OCH <sub>3</sub>	3.7-3.9
R₃C <b>H</b>	1.4-1.7	<b>O</b>	
$R_2 C = CRCHR_2$	1.6-2.6	RCOCH <sub>2</sub> R	4.1-4.7
RC≡CH	2.0-3.0	RCH <sub>2</sub> F	4.4-4.5
O II		ArOH	4.5-4.7
RCCH3	2.1-2.3	$R_2C=CH_2$	4.6-5.0
O II		R₂C=C <b>H</b> R	5.0-5.7
RCCH <sub>2</sub> R	2.2-2.6	ō	
ArCH <sub>3</sub>	2.2-2.5	H <sub>2</sub> G-CH <sub>2</sub>	3.3-4.0
$RCH_2NR_2$	2.3-2.8		0.5.10.1
RCH <sub>2</sub> I	3.1-3.3	RĊH	9.5-10.1
RCH <sub>2</sub> OR	3.3-4.0	RCOH	10-13

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



Signature

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 \_\_\_\_\_\_. The two most important isotopes for organic chemistry structure determination by NMR are \_\_\_\_\_\_ and \_\_\_\_\_. Of these two, \_\_\_\_\_\_ is a common isotope and the predominant isotope found in molecules, while \_\_\_\_\_\_ is very rare.

Electron density is induced to move in a strong external magnetic field, and this movement induces a \_\_\_\_\_\_ field that is \_\_\_\_\_\_ to the external magnetic field. This has the effect of \_\_\_\_\_\_ the underlying nuclei from the external magnetic field. The signal for an <sup>1</sup>H atom with greater electron density around it will come at \_\_\_\_\_\_ ppm in an NMR spectrum compared to a similar <sup>1</sup>H atom with less electron density.

The \_\_\_\_\_\_ of adjacent nuclei influence each other. If <sup>1</sup>H atoms are no more than \_\_\_\_\_\_ bonds apart, the spin states couple.

THEORY: When there are two sets of adjacent H atoms, the number of peaks \_\_\_\_\_\_\_. For example, a  $CH_2$  group with a  $CH_2$  group and a  $CH_3$  group on either side shows a theoretical maxium of \_\_\_\_\_\_\_ peaks in its signal!

PRACTICE: For alkyl groups that can rotate freely, complex splittings simplify because the \_\_\_\_\_\_ ("J") are all about the same. In practice, if there are n adjacent H atoms, equivalent or not, you will see \_\_\_\_\_\_ 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)

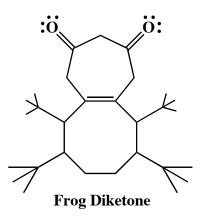
Signature\_\_\_\_\_

In the FT NMR method, the FT stands for \_\_\_\_\_\_\_. 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 \_\_\_\_\_\_\_ at once. Then, the nuclear spins

\_ back to the +1/2 spin state and when they do, they

\_\_\_\_\_ 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 minumum of 7 key points here.

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

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

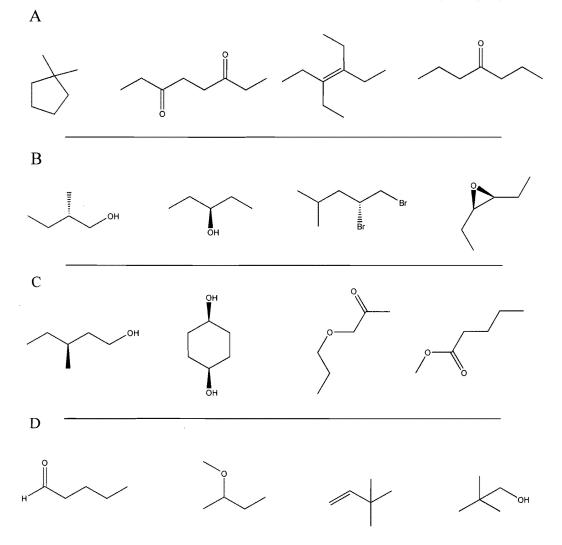
A.  $OH O \\
CH_2CH_2CH_2CH$ B.  $(-+)CH_2CH_2CH$   $(-+)CH_2CH_2CH$   $(-+)CH_2CH_2CH$   $(-+)CH_2CH_2CH$   $(-+)CH_2CH_2CH$   $(-+)CH_2CH_2CH$ 

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



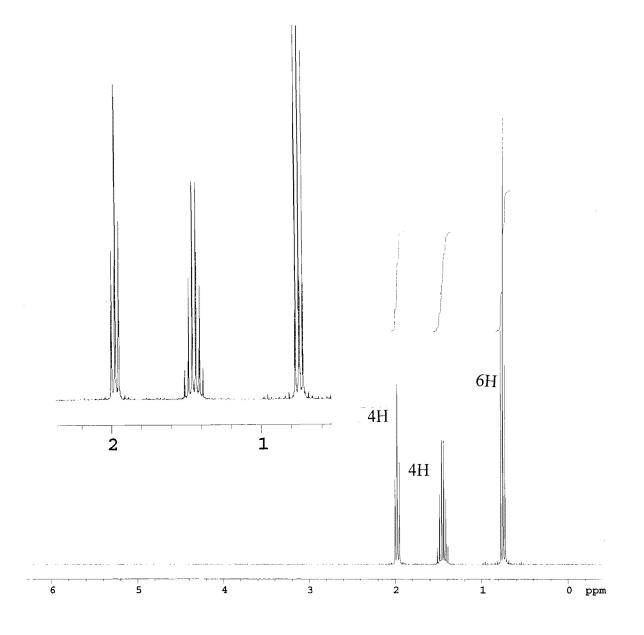
Signature\_

**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.



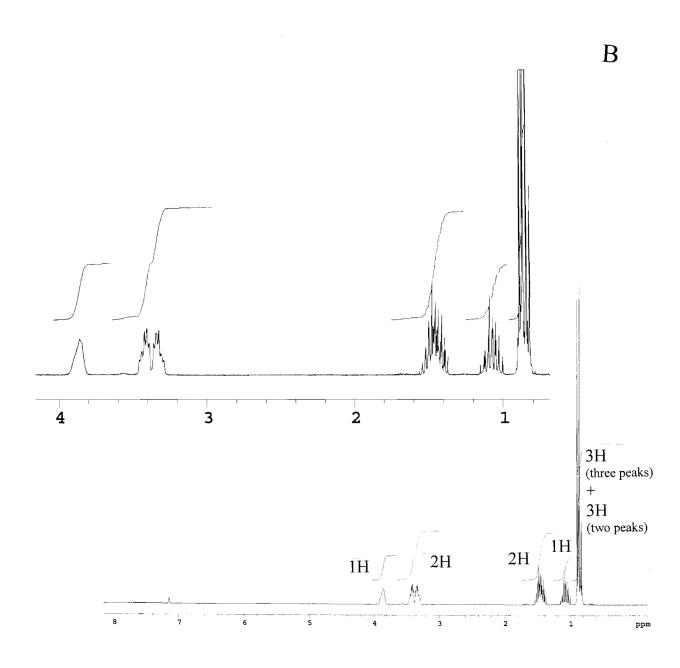
A

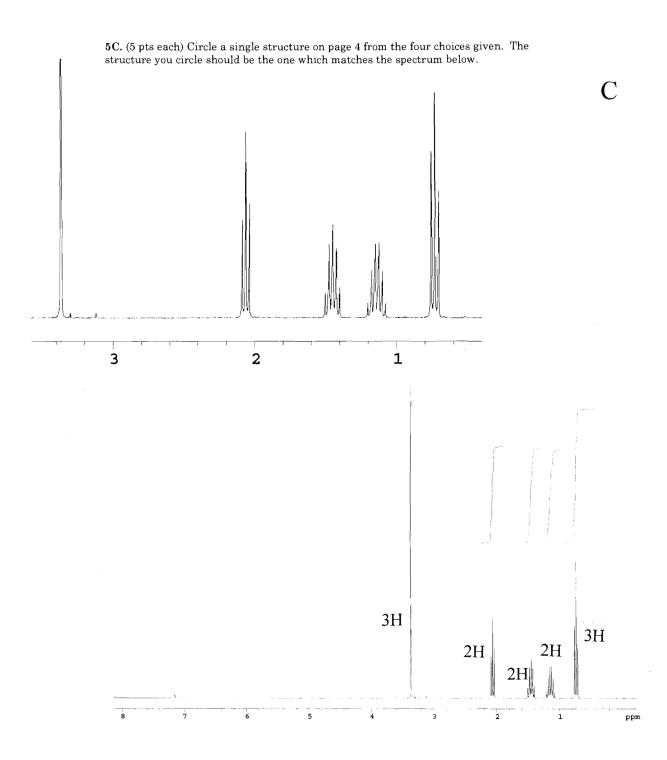
5A. (5 pts each) Circle a single structure on page 4 from the four choices given. The structure you circle should be the one which matches the spectrum below.



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

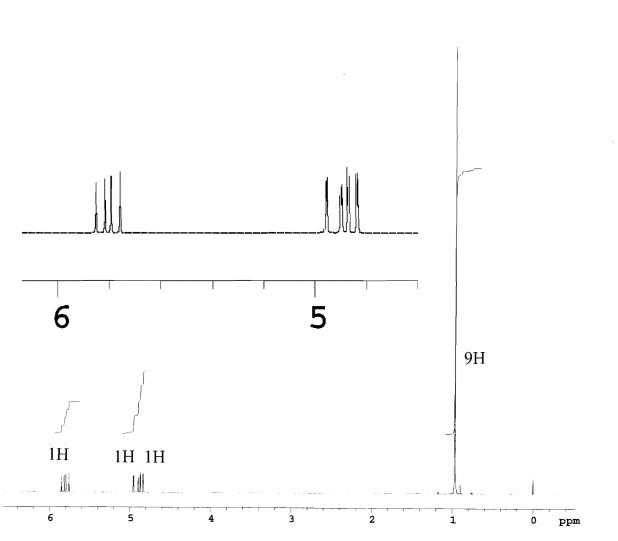
 ${\bf 5B.}$  (5 pts each) Circle a single structure on page 4 from the four choices given. The structure you circle should be the one which matches the spectrum below.





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

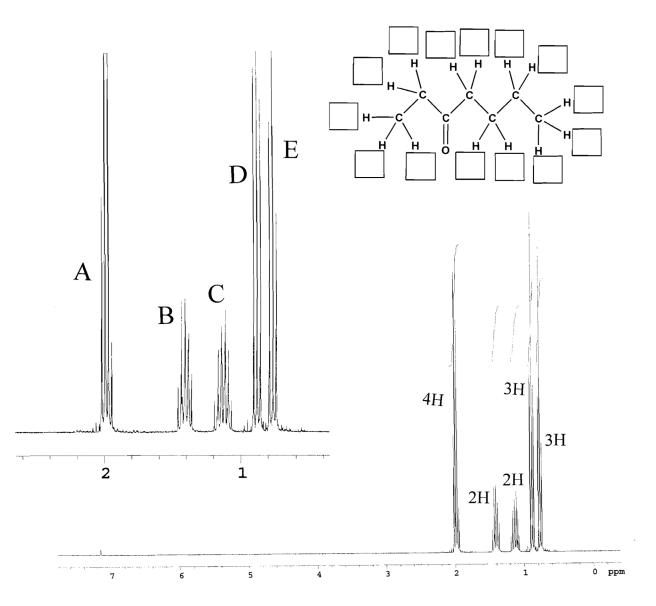
 $5D.~(5~{\rm pts}~{\rm each})$  Circle a single structure on page 4 from the four choices given. The structure you circle should be the one which matches the spectrum below.



D

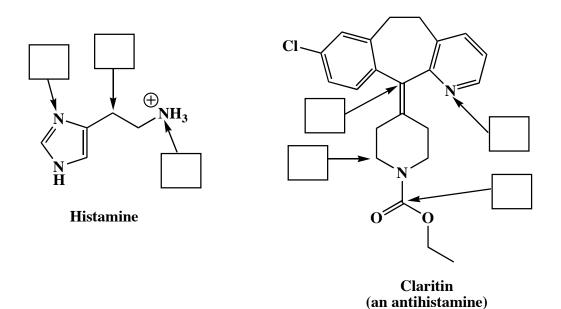
**6.** (14 pts) The following <sup>1</sup>H-NMR spectrum of 3-heptanone has signals labeled with letters. In the boxes provided on the structure, place the letter of the signal that corresponds to the H atom in the adjacent box. Because of equivalence, more than one box can get the same letter!

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

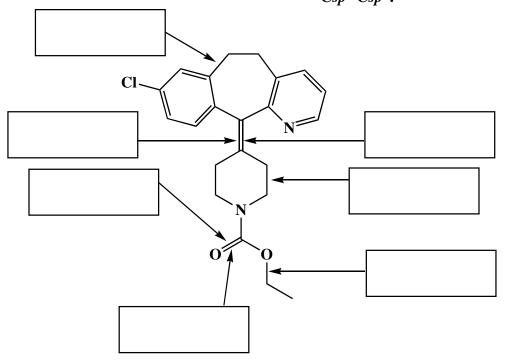


Signature\_

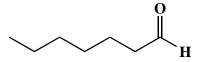
**7.** (1 pt each) I warned you about this. We need to make sure all of you understand hybridization. In the boxes provided, write the hybridization state of the atoms indicated by the arrows.



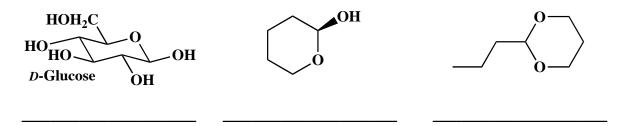
8. (2 pts each) I warned you about this also. Describe each bond indicated with an arrow as the overlap of orbitals. For example, an answer might be  $\mathcal{O}_{Csp^3-Csp^3}$ .



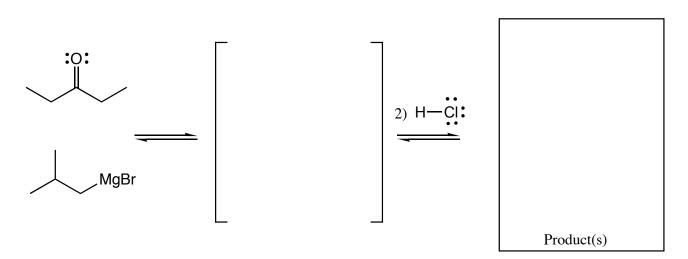
**9.** (4 pts) An important part of chemical understanding is being able to recognize the chemical reactivity of different functional groups. On the carbonyl group below, DRAW A BOX around the atom that will be attacked by nucleophiles and DRAW A CIRCLE around the atom that will be protonated in acid.



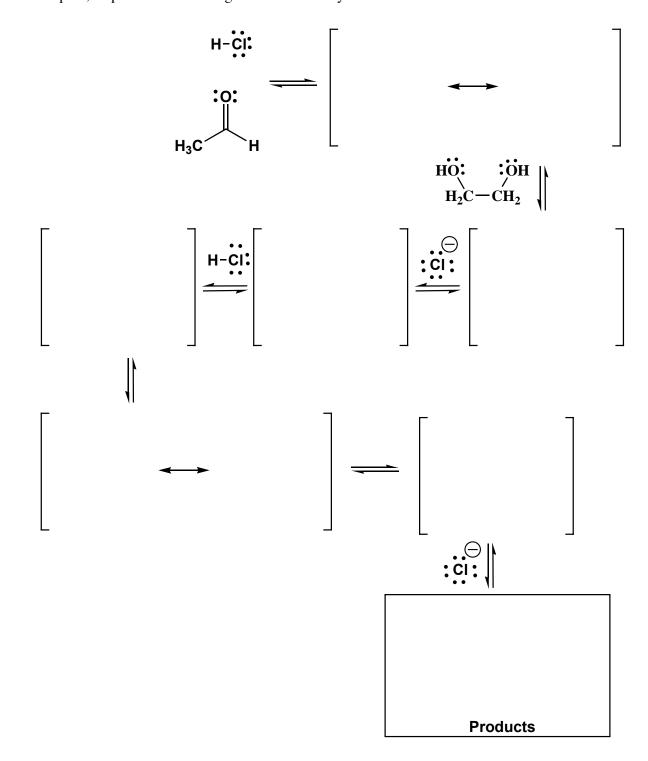
**10.** (3 pts each) Some functional groups are hard to recognize. For the following two molecules, DRAW A CIRCLE around either the acetal, cyclic hemiacetal, or cyclic acetal. Under each molecule, write the appropriate term ( acetal, cyclic hemiacetal, or cyclic acetal).

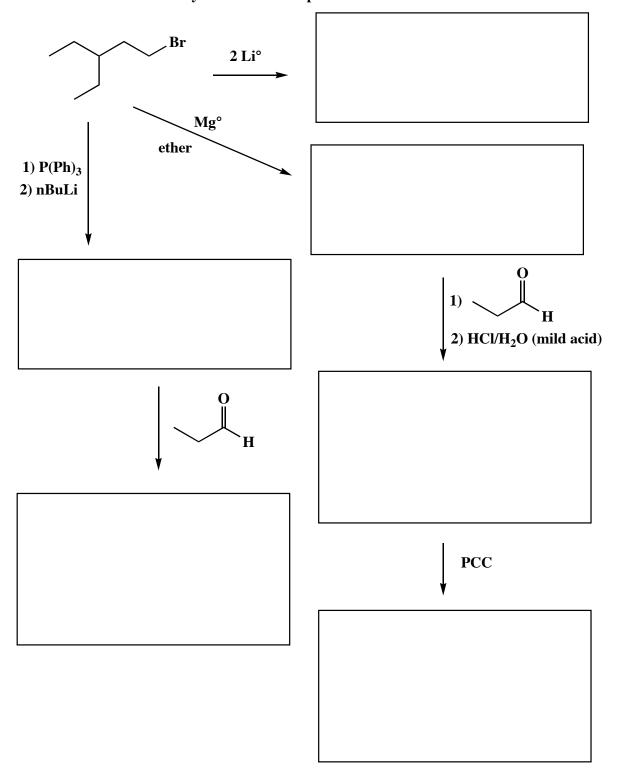


11. (10 pts.) Complete the mechanism for the following Grignard reaction. Be sure to show arrows to indicate movement of <u>all</u> electrons, write <u>all</u> lone pairs, <u>all</u> formal charges, and <u>all</u> the products for each step. Remember, I said <u>all</u> the products for each step. IF 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 ENANTIONMERS, 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.



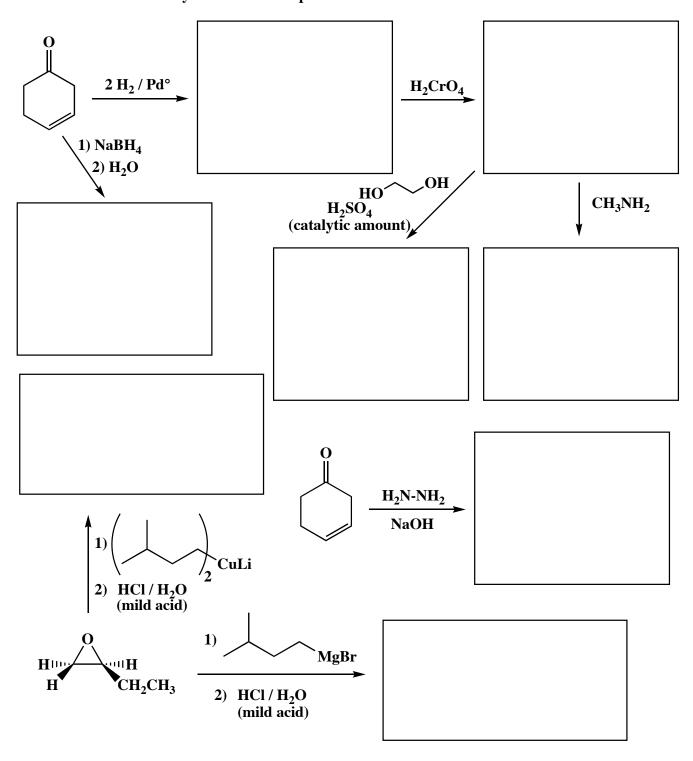
11. (cont.) (35 pts.) Complete the mechanism for the following acetal formation reaction. Be sure to show arrows to indicate movement of <u>all</u> electrons, write <u>all</u> lone pairs, <u>all</u> formal charges, and <u>all</u> the products for each step. Remember, I said <u>all</u> the products for 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 ENANTIONMERS, 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.





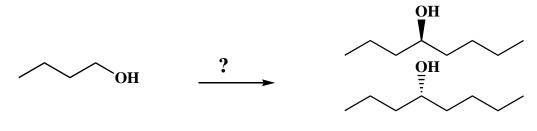
Signature\_

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 ( — ) and dashes ( — ) 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.



**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.

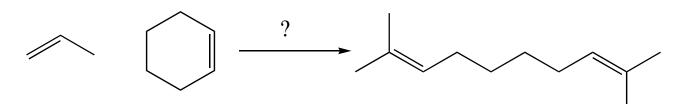
(10 pts) All of the carbon atoms of the products must come from the starting materials for this one!



racemic

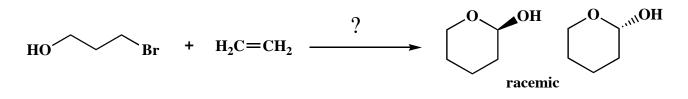
**13.** These are synthesis questions. You need to show how the starting material can be converted into the product(s) shown. You may use any reactions we have learned. Show all the reagents you need. Show each molecule synthesized along the way and be sure to pay attention to the regiochemistry and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

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



**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. *Note, this is pretty challenging so you might want to save it until last.* 

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



Signature\_

**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 followig Wittig reactions.

