NAME (Print): _____

SIGNATURE: _____

Chemistry 310N
Dr. Brent Iverson
1st Midterm
Feb. 18, 2010

Please print the 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.

You must have your answers written in PERMANENT ink if you want a regrade!!!! This means no test written in pencil or ERASABLE INK will be regraded.

Please note: We routinely xerox a number of exams following initial grading to guard against receiving altered answers during the regrading process.

FINALLY, DUE TO SOME UNFORTUNATE RECENT INCIDENCTS YOU ARE NOT ALLOWED TO INTERACT WITH YOUR CELL PHONE IN ANY WAY. IF YOU TOUCH YOUR CELL PHONE DURING THE EXAM YOU WILL GET A "0" NO MATTER WHAT YOU ARE DOING WITH THE PHONE. PUT IT AWAY AND LEAVE IT THERE!!!

Page	Points	
1		(13)
2		(19)
3		(18)
4		(15)
5		(5)
6		(5)
7		(5)
8		(5)
9		(5)
10		(14)
11		(22)
12		(18)
13		(20)
14		(12)
15		(16)
16		(10)
17		(15)
18		(13)
19		(28)
Total		(258)
%		
T Score		
HW		
Total Grade		

(HW score + Exam Grade) ⟹

Honor Code

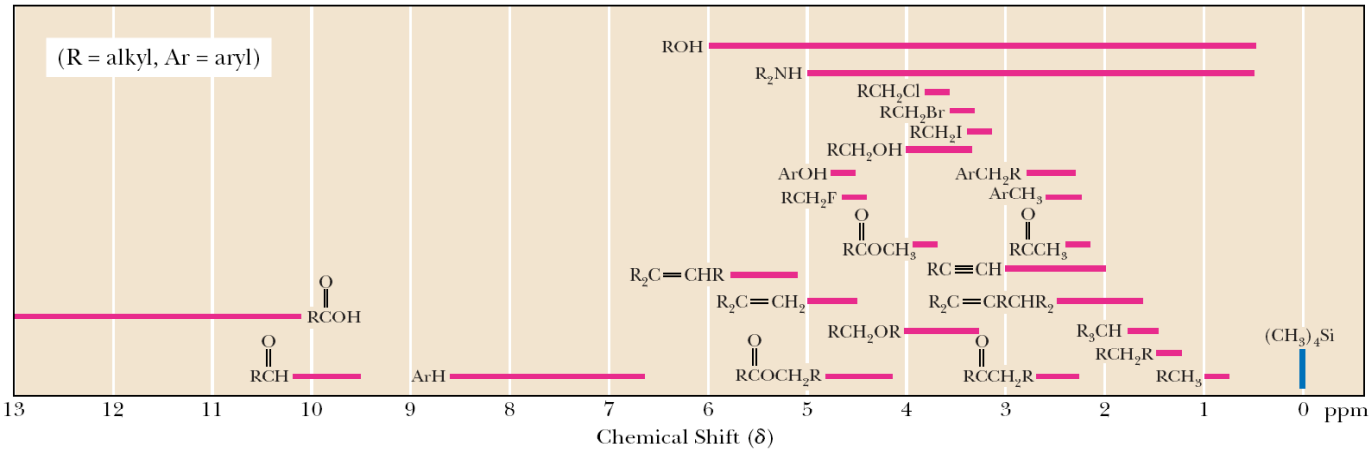
The core values of the University of Texas at Austin are learning, discovery, freedom, leadership, individual opportunity, and responsibility. Each member of the University is expected to uphold these values through integrity, honesty, trust, fairness, and respect toward peers and community.

_____

(Your signature)

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

The two most important isotopes for organic chemistry structure determination by NMR are _____^{1}H_____ and _____^{13}C_____. Of these two, _____^{1}H_____ is a common isotope and the predominant isotope found in molecules, while _____^{13}C_____ is relatively rare.

Nuclei with spin quantum number 1/2 are quantized in one of two orientations: _____+1/2_____ (lower energy) or _____-1/2_____ (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_____proportional_____ to the strength of the magnetic field experienced by the nucleus.

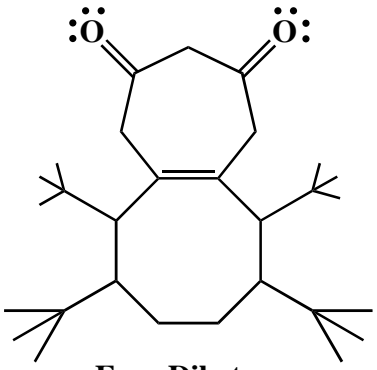
Electron density is induced to move in a strong external magnetic field, and this movement induces a _____magnetic_____ field that is _____opposed_____ to the external magnetic field. This has the effect of _____shielding_____ the underlying nuclei from the external magnetic field.

All other factors being the same, the signal for an ^{1}H atom with greater electron density around it will come at _____lower_____ ppm in an NMR spectrum compared to a similar ^{1}H atom with less electron density.

The _____spins_____ of adjacent nuclei influence each other. If ^{1}H atoms are no more than _____three_____ bonds apart, the spin states couple.

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 is 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.



Frog Diketone

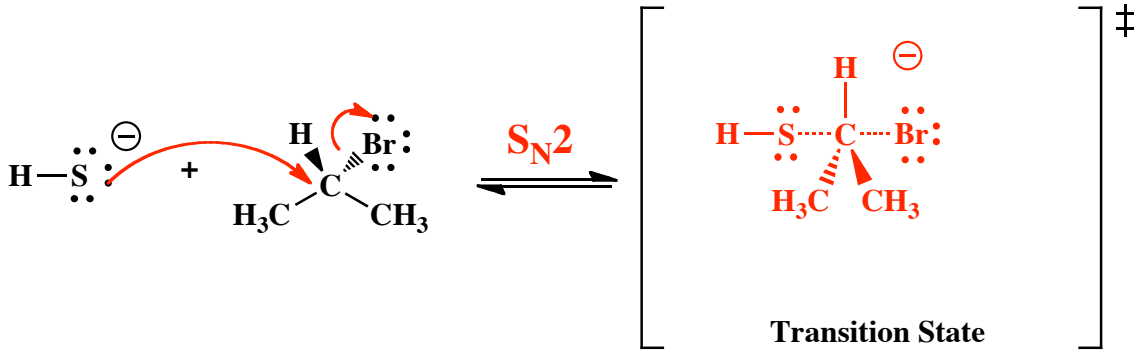
This is not part of a question. This little molecule creature is simply supposed to make you smile!

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 wil be looking for a minumum of 7 key points here.

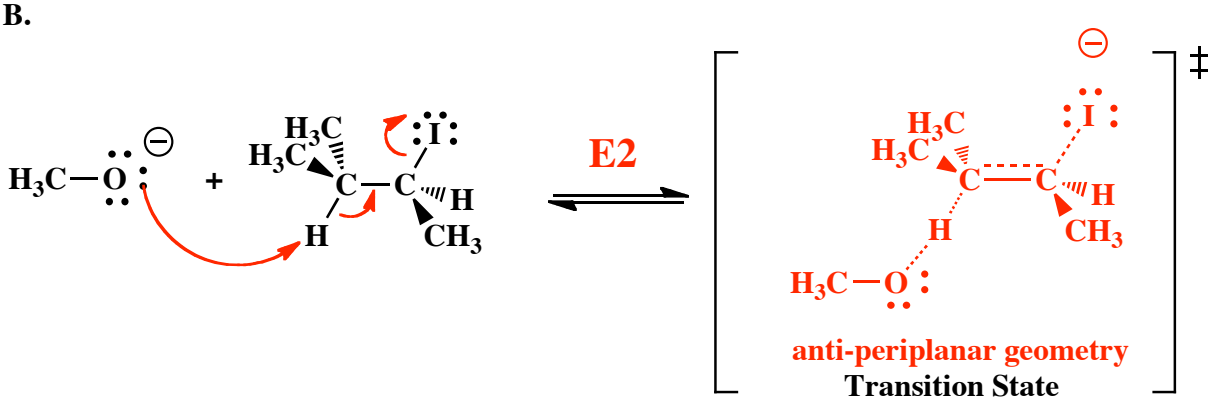
The popular medical diagnostic technique of **magnetic resonance imaging (MRI)** is based on the **same principles as NMR**, namely the **flipping (i.e. resonance) of nuclear spins of protons** by **radio frequency irradiation** when a patient is placed in a **strong magnetic field**. **Magnetic field 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.**

15. (13 pts total) I promised you this one!! For each set of reagents below, draw the **key transition state** that occurs during the reaction. **Use dotted lines to indicate bonds that are in the process of being broken or made. Write all lone pairs and any formal charges. On the starting structures, draw all appropriate arrows to indicate the flow of electrons.**

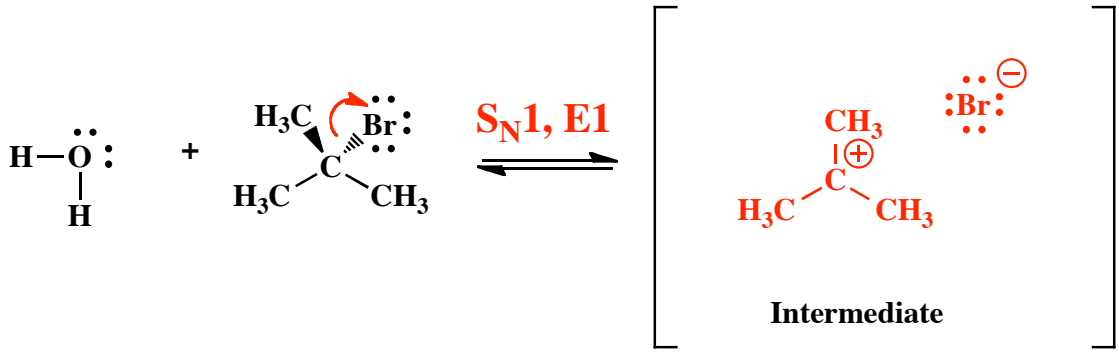
A.



B.



16. (5 pts total) For the set of reagents below, draw the **first key intermediate** that occurs during the indicated reaction. We do not want the entire mechanism or products, just the first key intermediate. **Write all lone pairs and formal charges. On the starting structures, draw all appropriate arrows to indicate the flow of electrons.**

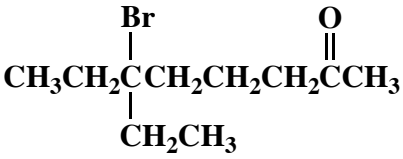


3. (3 pts) The most important question in organic chemistry is:

Where are the electrons?

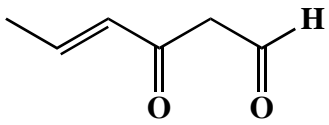
4. (3 pts each) Write an acceptable IUPAC name or draw a structural formula for the following molecules:

A.



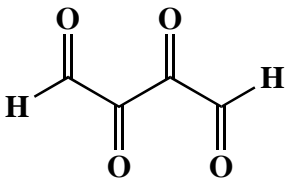
6-Bromo-6-ethyl-2-octanone

B.



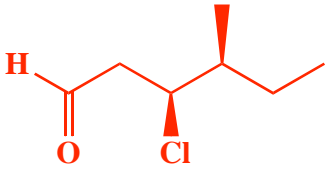
(*E*)-3-oxo-4-hexenal

C.

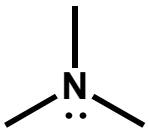


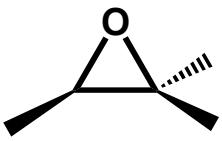
2,3-Dioxobutanedial (2,3-Dioxosuccinaldehyde)

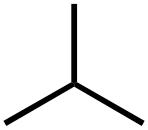
D. **(*3S*,*4S*)-3-Chloro-4-methylhexanal**

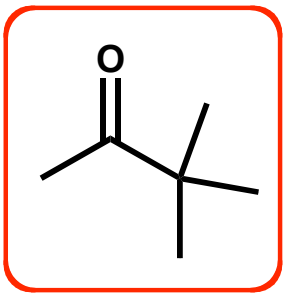


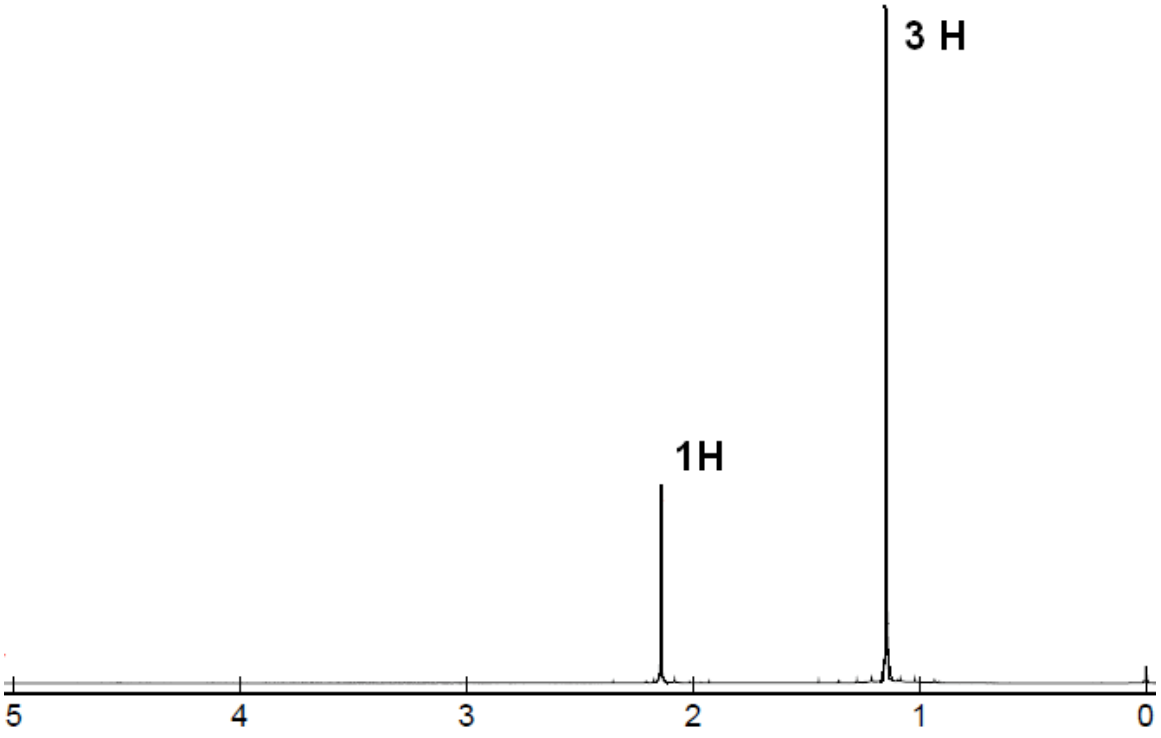
5. (5 pts) Circle the molecule that corresponds to the NMR spectrum shown below.











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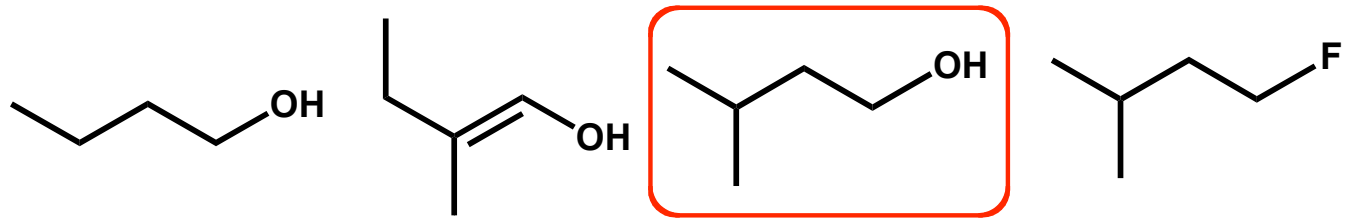

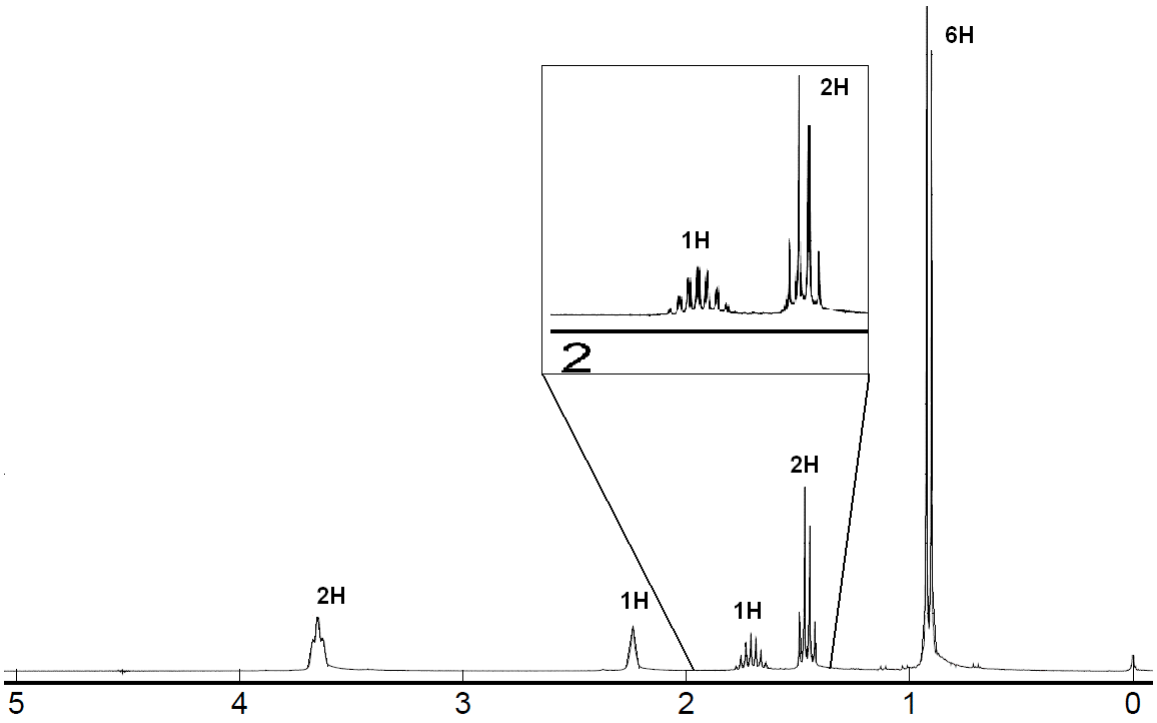

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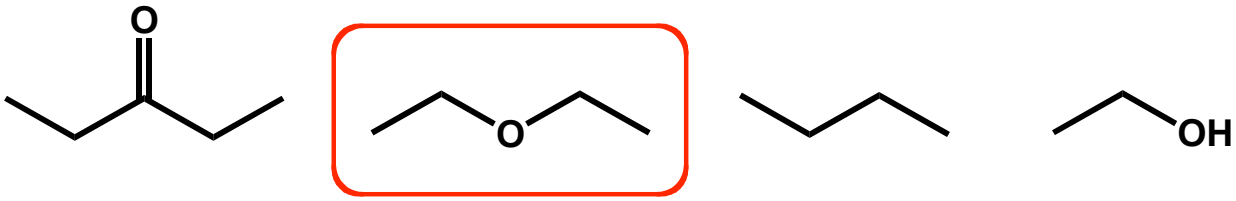

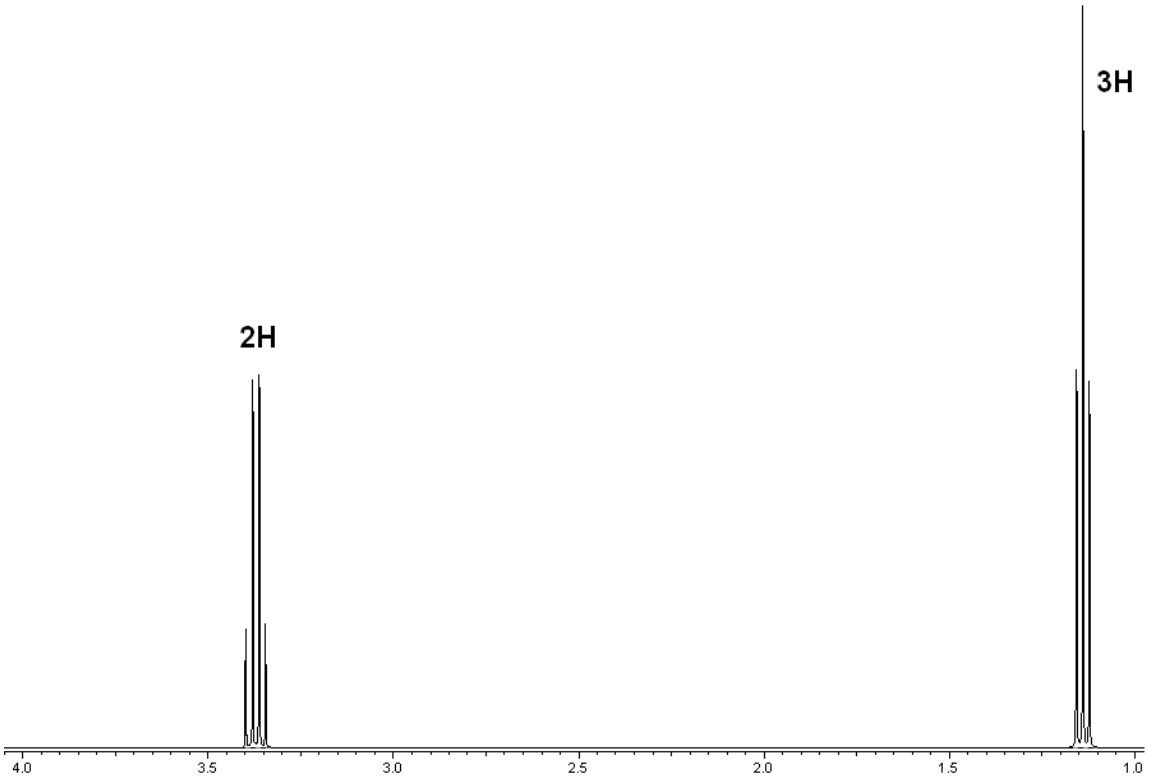

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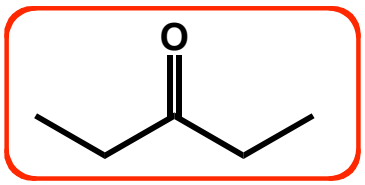

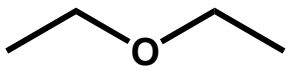

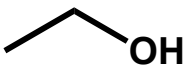

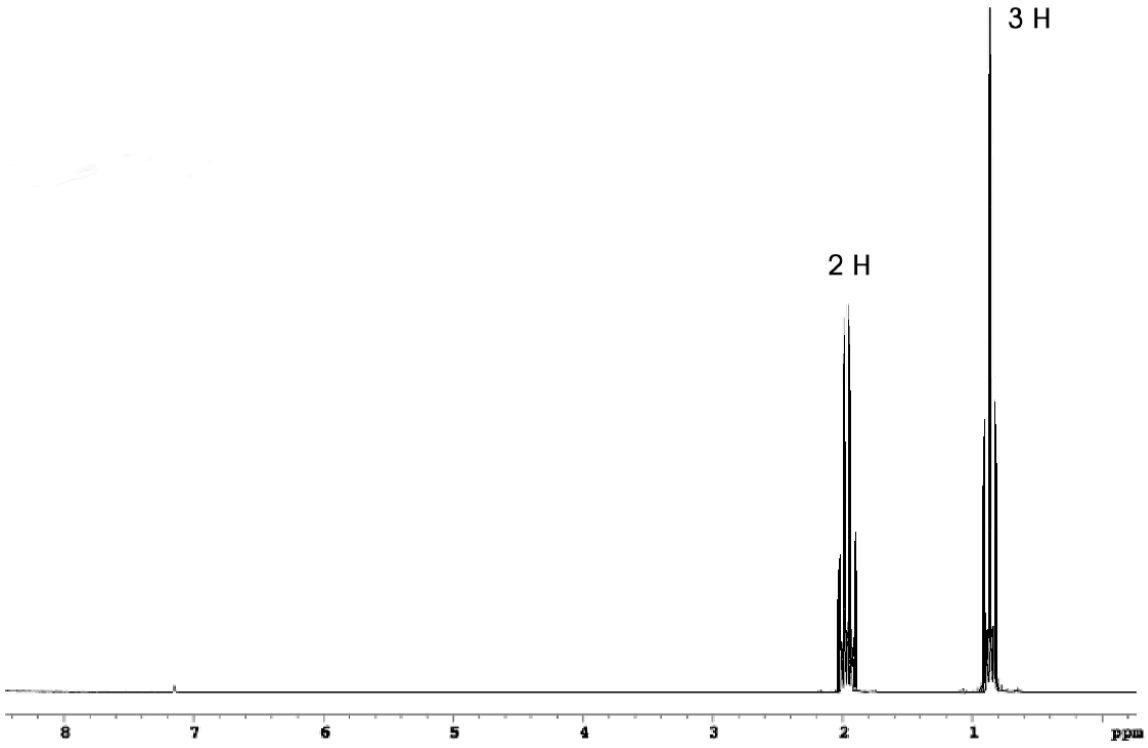

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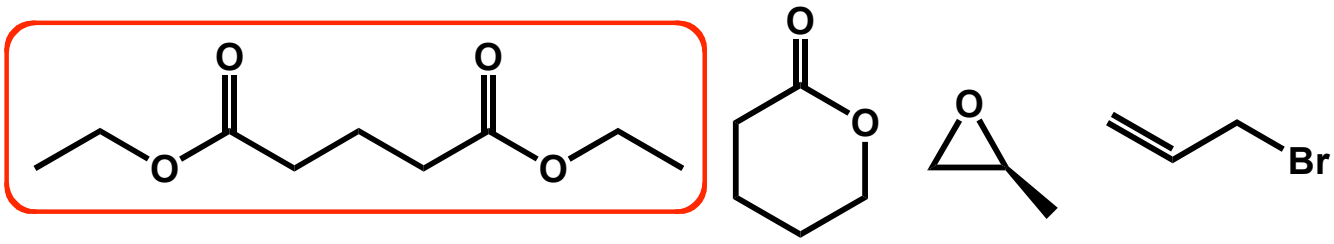
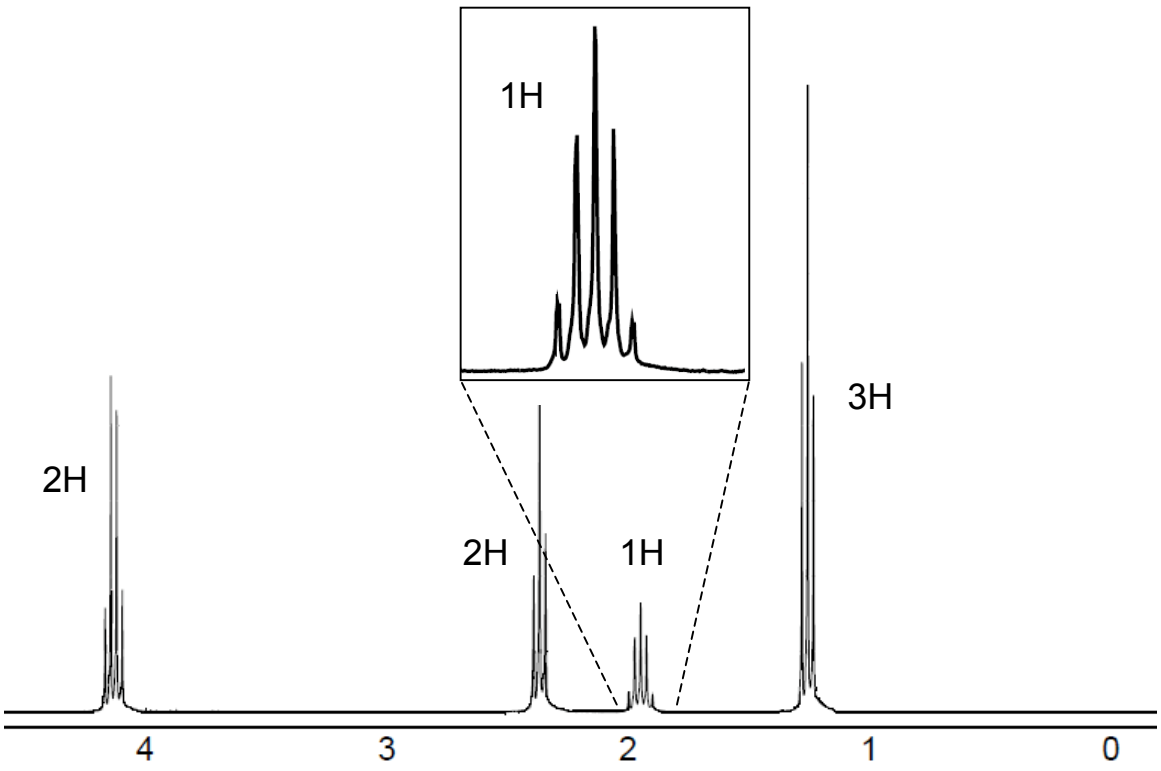
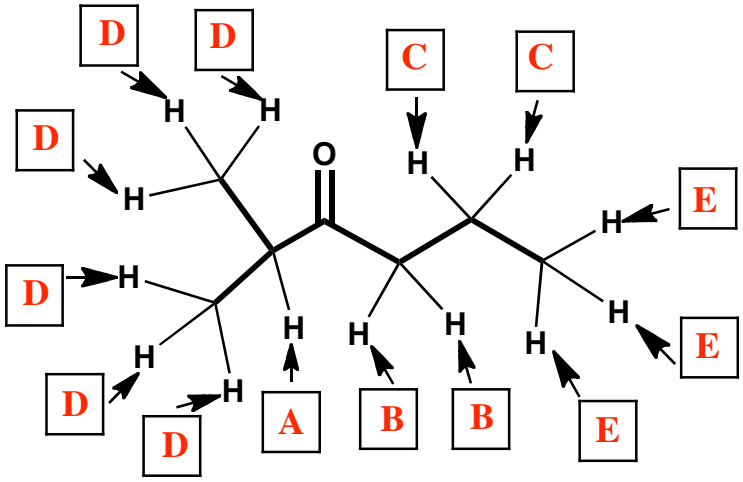
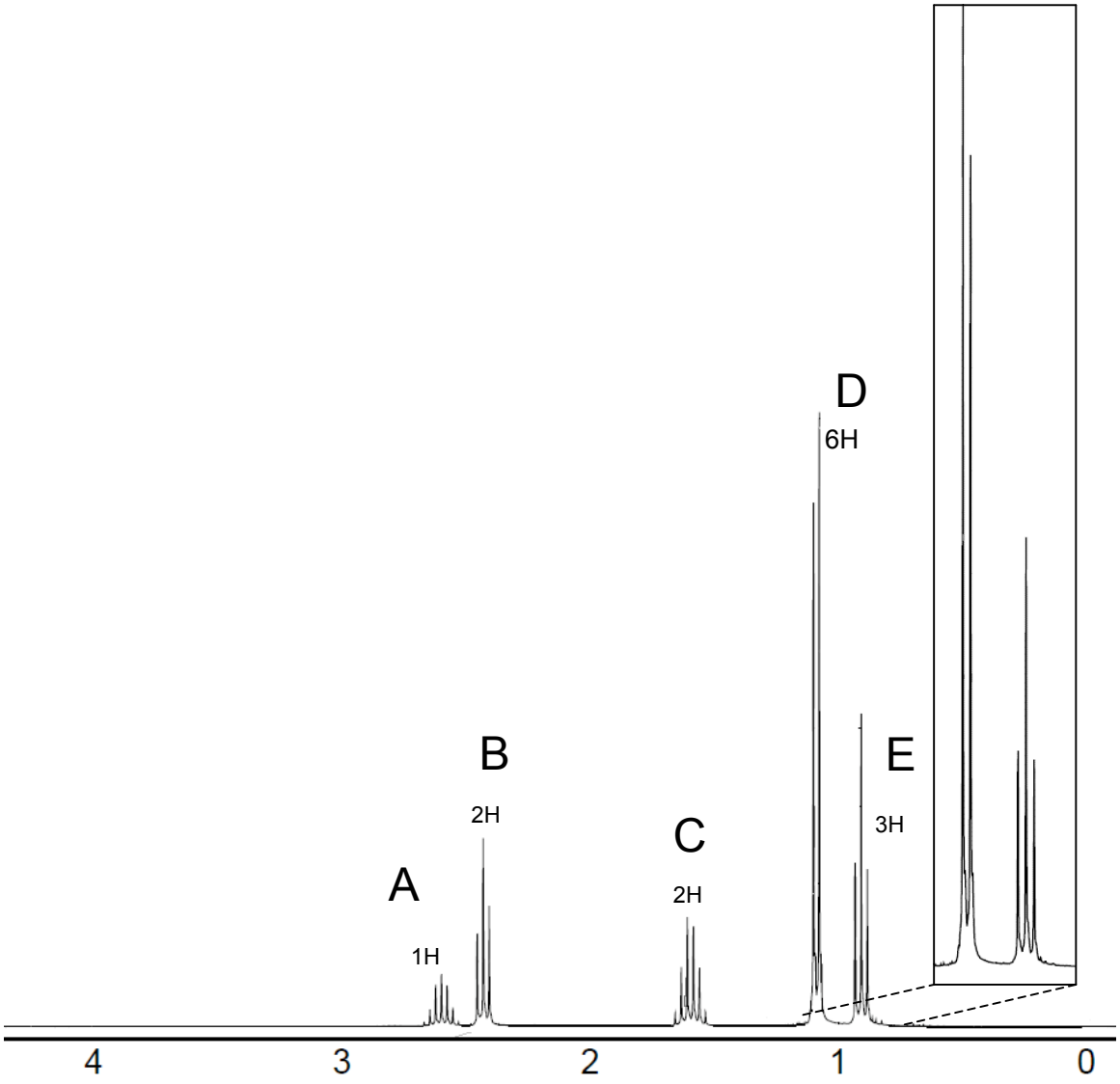


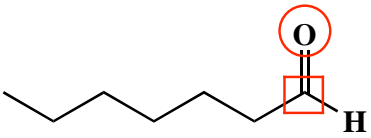


5. (14 pts) In the boxes provided, place that letter (A, B, C, etc.) that corresponds to the signals in the spectrum provided below.

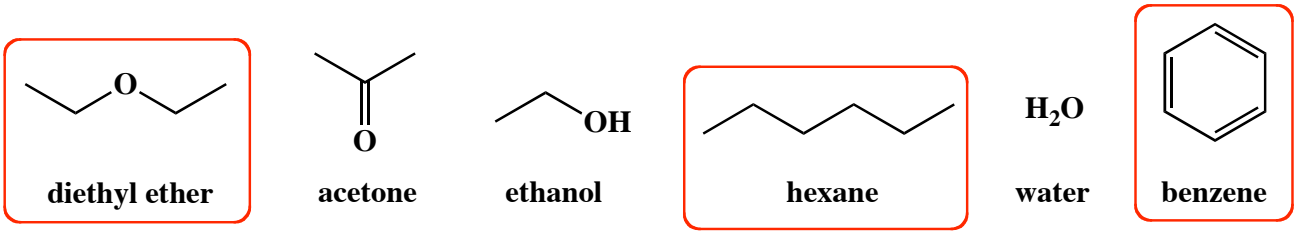




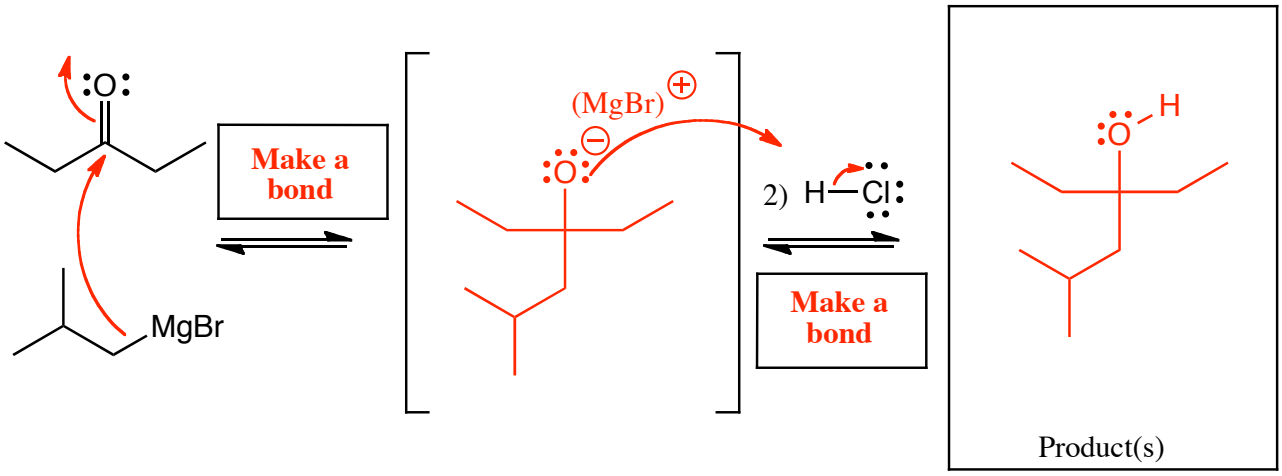
6. (4 pts) An important part of chemical understanding is being able to recognize the chemical reactivity of different functional groups. On the carbonyl group below, DRAW A BOX around the atom that will be attacked by nucleophiles and DRAW A CIRCLE around the atom that will be protonated in acid.



7. (6 pts) It is important to remember that organometallic reagents are bases as well as nucleophiles. These are important considerations when choosing a solvent. From the following list of common solvents, circle any that would be compatible with using an organolithium reagent.



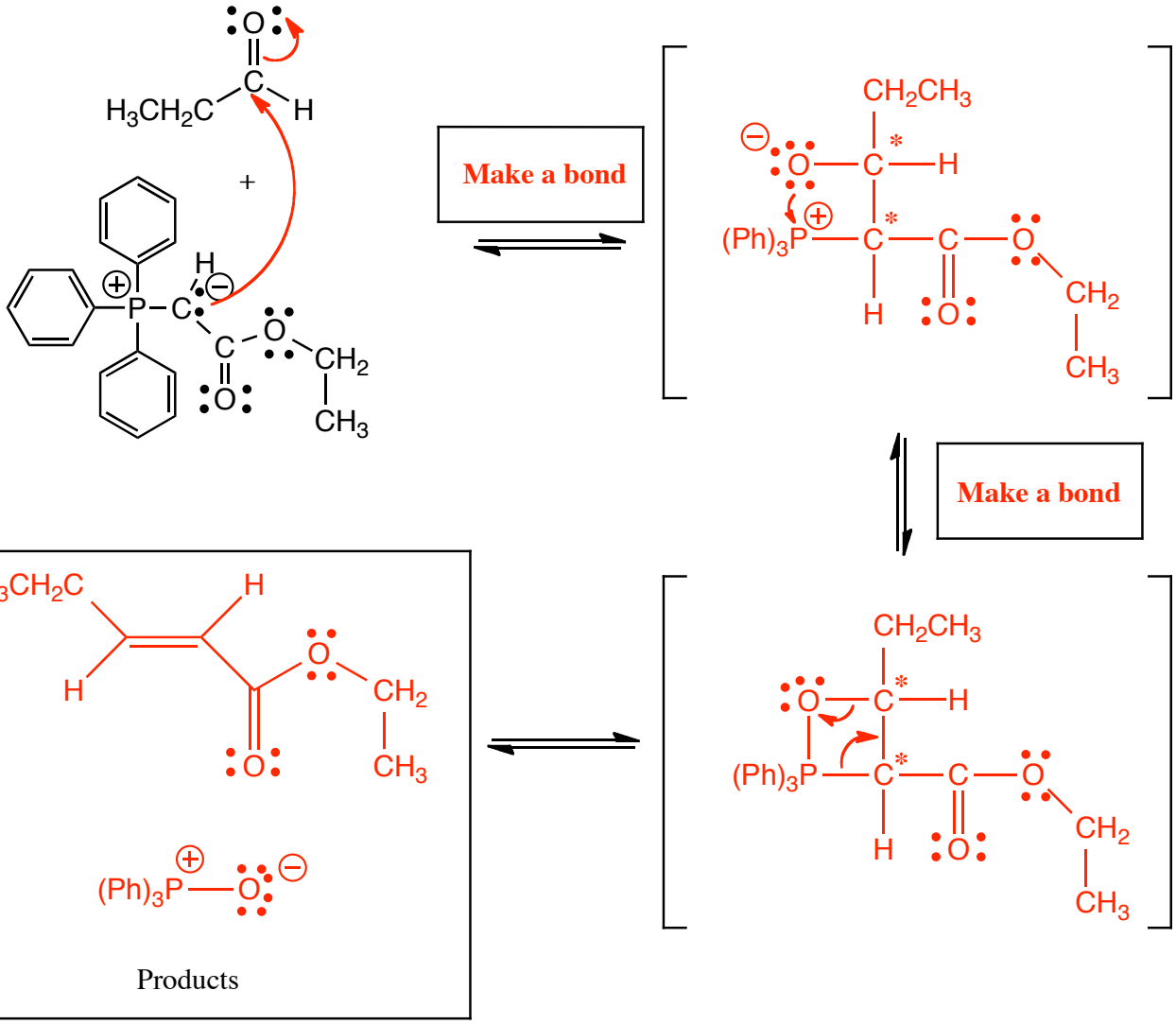
8. (12 pts. total) Complete the mechanism for the following Grignard reaction. **Be sure to show arrows to indicate movement of <u>all</u> electrons, write <u>all</u> lone pairs, <u>all</u> formal charges, and <u>all</u> the products for each step.** Remember, I said <u>all</u> the products for each 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.



2 pts In the boxes provided adjacent to the first two sets of arrows, write which of the four basic mechanistic elements are involved (i.e. "Make a bond", "Add a proton", etc.

⇑
NOTICE THIS

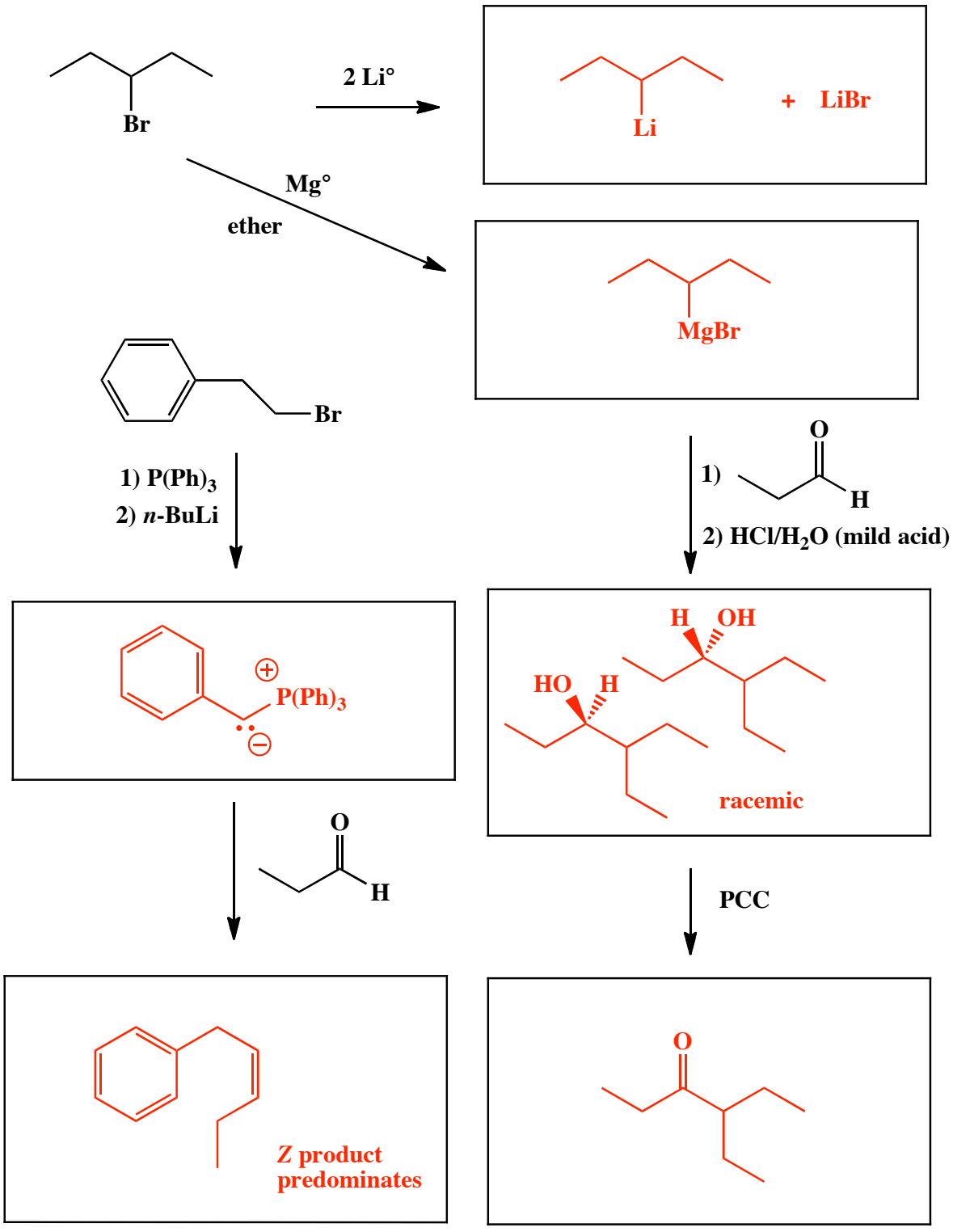
9. (cont.) (18 pts. total) Complete the mechanism for the following Wittig reaction. **Be sure to show arrows to indicate movement of all electrons, write all lone pairs, all formal charges, and all the products for each step.** Remember, I said all the products for each step. **IF A NEW CHIRAL CENTER IS CREATED IN AN INTERMEDIATE, MARK IT WITH AN ASTERISK. IF A CHIRAL CENTER IS CREATED IN THE PRODUCTS YOU NEED TO DRAW BOTH 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.



2 pts In the boxes provided adjacent to the first two sets of arrows, write which of the four basic mechanistic elements are involved (i.e. "Make a bond", "Add a proton", etc.

NOTICE THIS

10. (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 (····ıı) 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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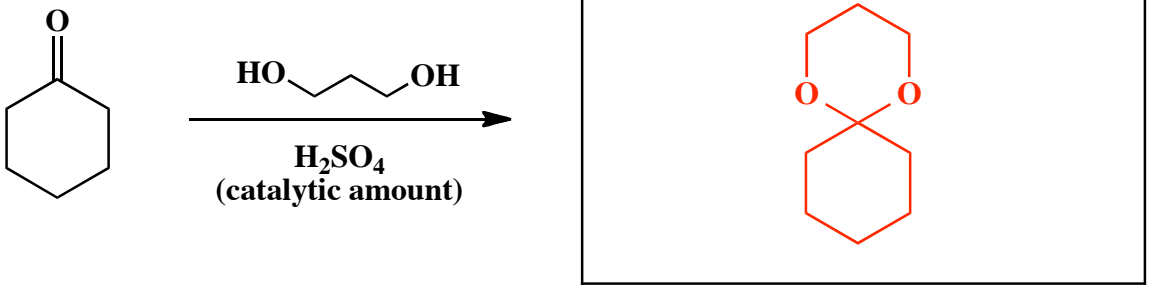
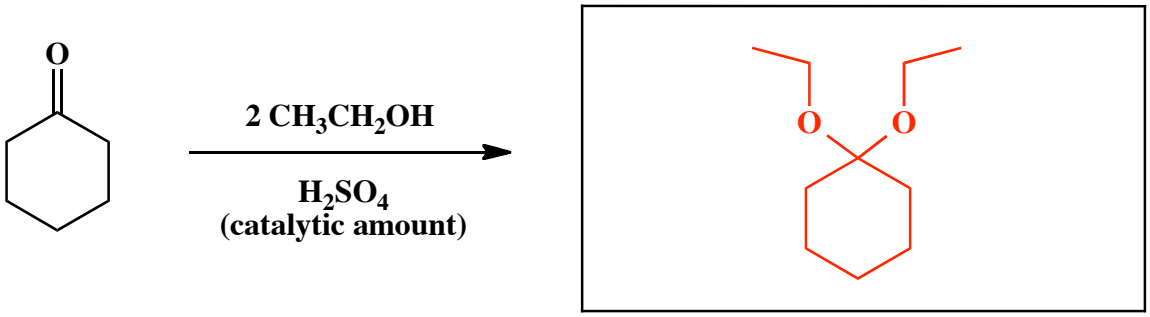
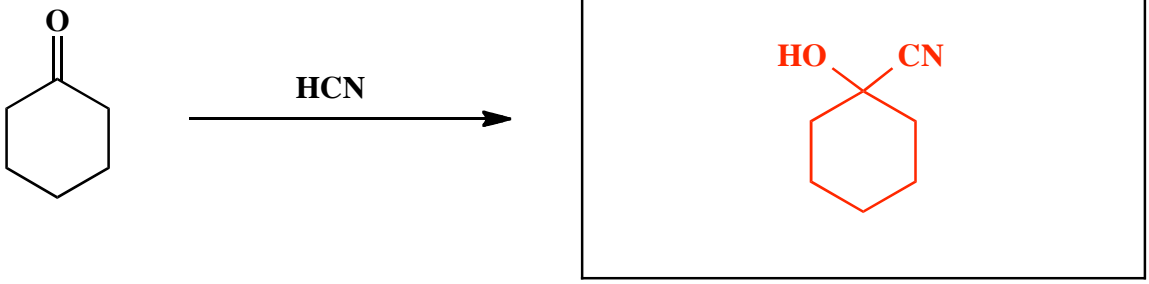
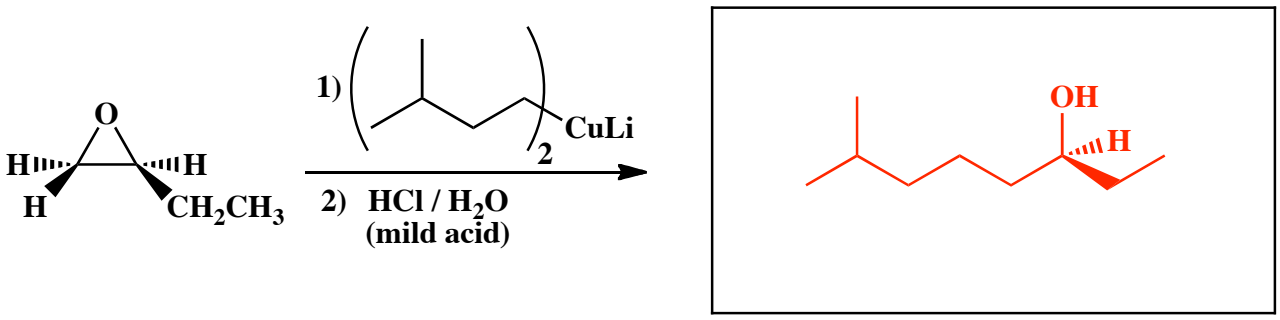
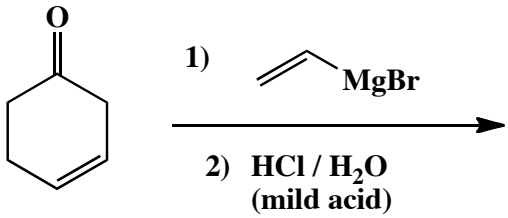


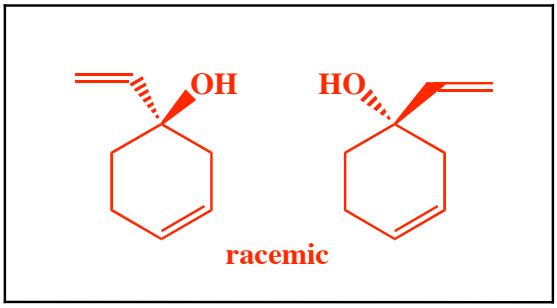


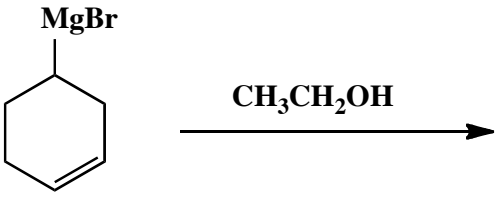


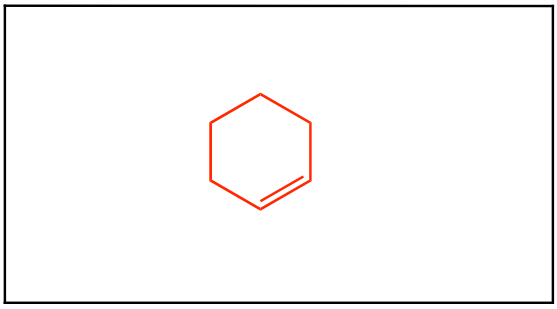


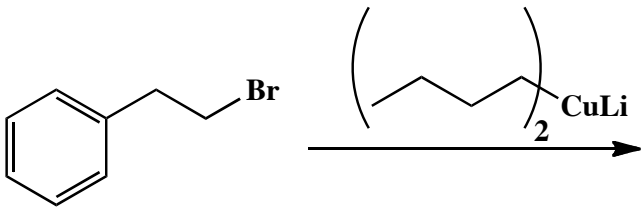
12. (3 or 5 pts.) Write the predominant product or products that will occur for each transformation. **If a new chiral center is created and a racemic mixture is formed, you must draw both enantiomers and write "racemic" under the structure. Use wedges (◄) and dashes (····ıı) to indicate stereochemistry. 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.**

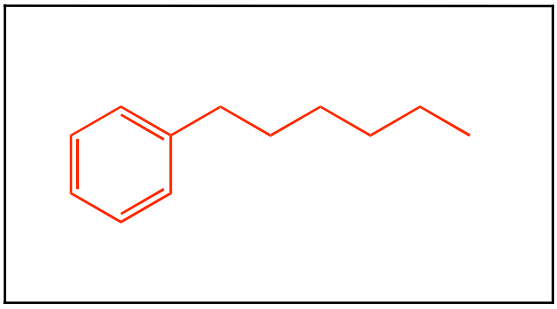


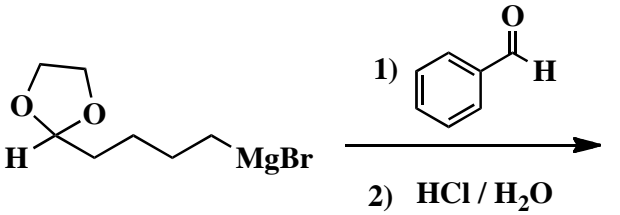


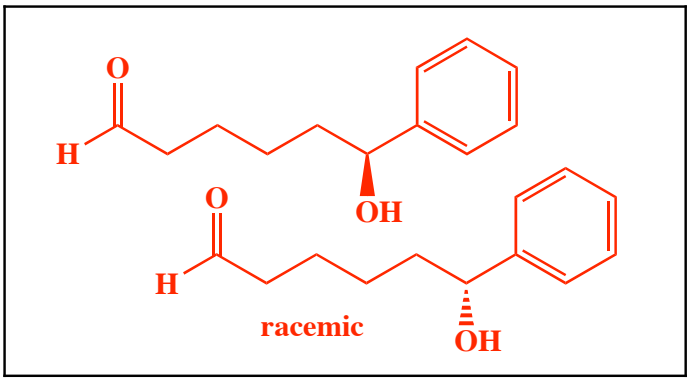






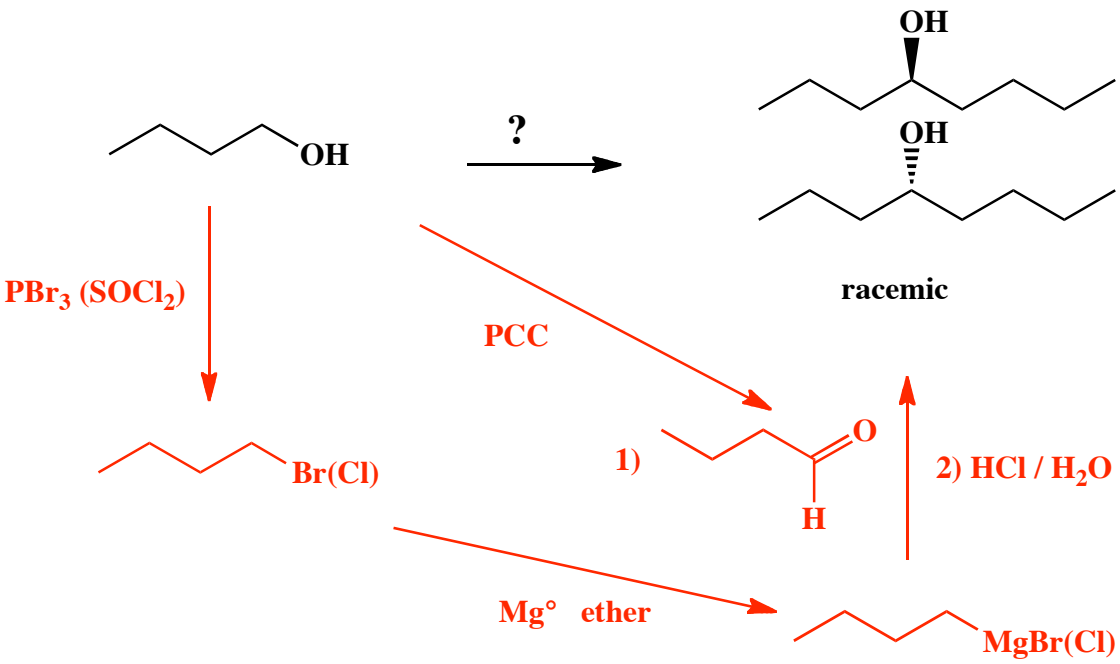






13. These are synthesis questions. You need to show how the starting material can be converted into the product(s) shown. You may use any reactions we have learned. Show all the reagents you need. Show each molecule synthesized along the way and be sure to pay attention to the regiochemistry and stereochemistry preferences for each reaction. If you make a racemic mixture, draw both structures and make sure to write "racemic" next to them.

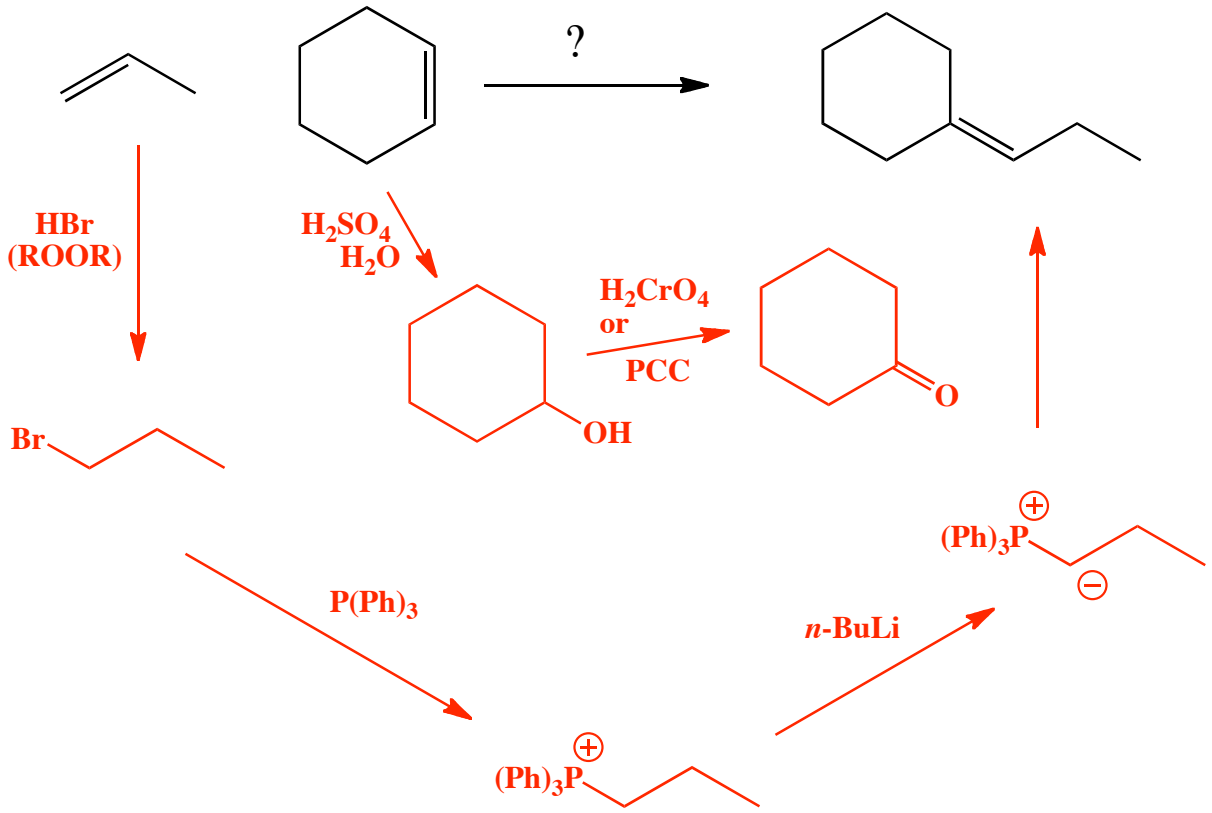
(10 pts) **All of the carbon atoms of the products must come from the starting materials for this one!**



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 betweeen 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 PBr_3 then Mg in ether, respectively. Note that it is perfectly acceptable to use $SOCl_2$ in place of PBr_3, since chloro-Grignard reagents are suitable replacements for bromo-Grignards.

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. If you make a racemic mixture, draw both structures and make sure to write "racemic" next to them.

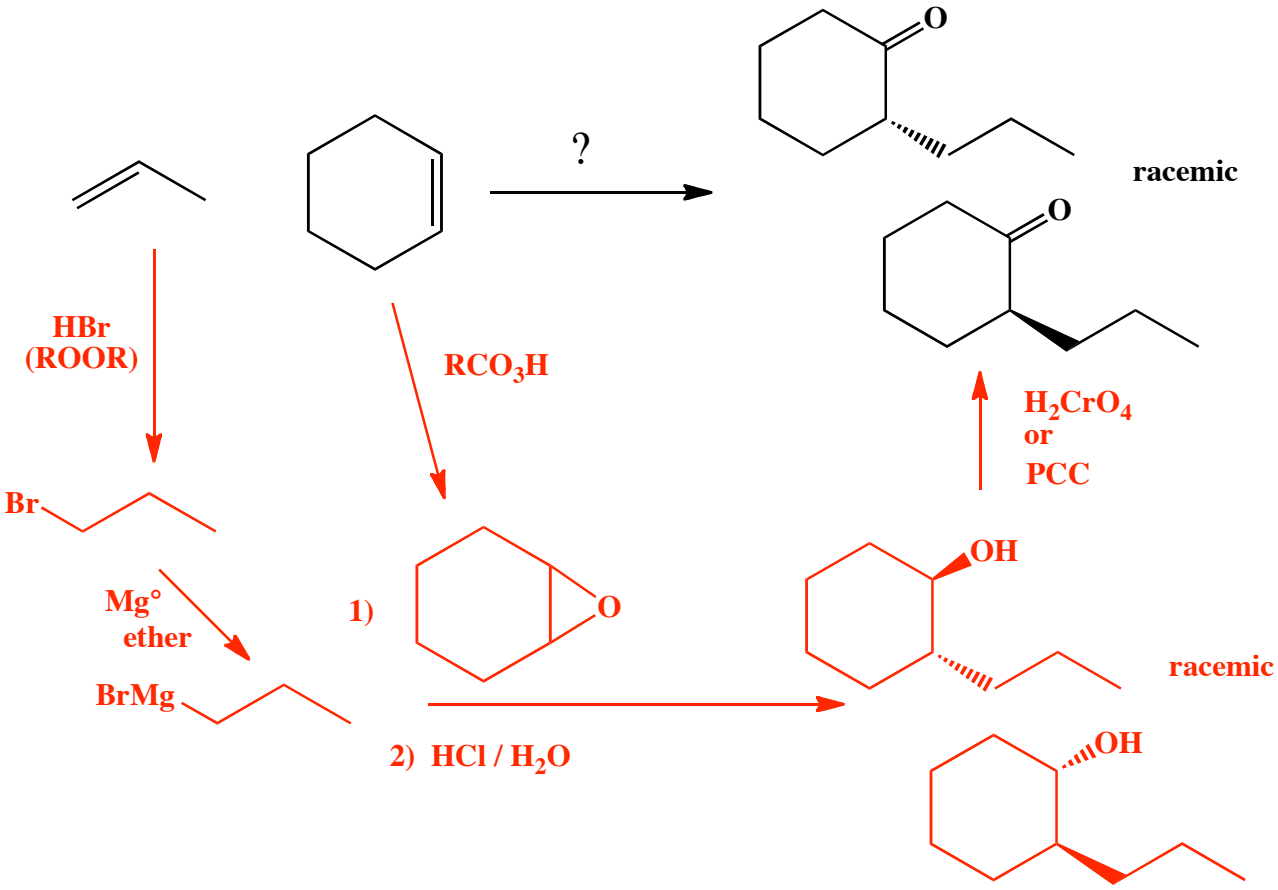
(15 pts) **All of the carbon atoms of the products must come from the starting materials for this one!**



Recognize that the product has nine carbons, exactly the sum of the number of carbons in the two starting materials added together. **Recognize** also that the new carbon-carbon bond is a actually a C=C bond. The only reaction you know that creates this pattern, a new C=C bond, is a Wittig reaction. Hypothesize the last step as a Wittig reaction between cyclohexanone and a propyl Wittig reagent. **Recognize** that the required cyclohexanone comes in two steps from the cyclohexene, namely hydration of the C=C followed by oxidation. The required Wittig reagent comes in two steps from the starting propene. An important consideration is that the HBr must add in a non-Markovnikov fashion, so peroxide must be used in this step. Notice you could have used a Wittig from the cyclohexene and propanal as well.

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. If you make a racemic mixture, draw both structures and make sure to write "racemic" next to them.

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



Recognize that the product has nine carbons, exactly the sum of the number of carbons in the two starting materials added together. **Recognize** also that the new carbon-carbon bond is one carbon away from the oxygen atom on the product. The only reaction you know that creates this pattern, a new C-C bond next to a carbon with an O atom, is an organometallic reagent reacting with an epoxide, which creates an alcohol. Hypothesize the last step as an oxidation, derived from the alcohols shown with *trans* stereochemistry (organometallic reagents add to epoxides from the backside of the C-O bond, leading to *trans* products). **Recognize** that the required epoxide comes in one step from the cyclohexene, and the required organometallic reagent comes in two steps from the starting propene. An important consideration is that the HBr must add in a non-Markovnikov fashion, so peroxide must be used in this step. Notice we used a Grignard reaction, but a Gilman or organolithium would have worked also.

14. (28 pts. total) This is a challenging problem so save it until the end. 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. **YOU HAVE NEVER SEEN THIS BEFORE, BUT WORK THROUGH IT USING THE PATTERNS YOU HAVE SEEN IN CLASS. IN OTHER WORDS, THIS REACTION FOLLOWS ALMOST THE EXACT PATTERN OF STEPS FOR A REACTION YOU HAVE SEEN.**