NAME (Print): _____

SIGNATURE: _____

Chemistry 320N
Dr. Brent Iverson
1st Midterm
Feb. 18, 2016

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 or red 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		(18)
2		(80)
10		(12)
11		(27)
12		(22)
13		(15)
14		(17)
15		(15)
16		(5)
17		(16)
18		(10)
19		(10)
20		(19)
21		(19)
Total		(285)

Student Honor Code

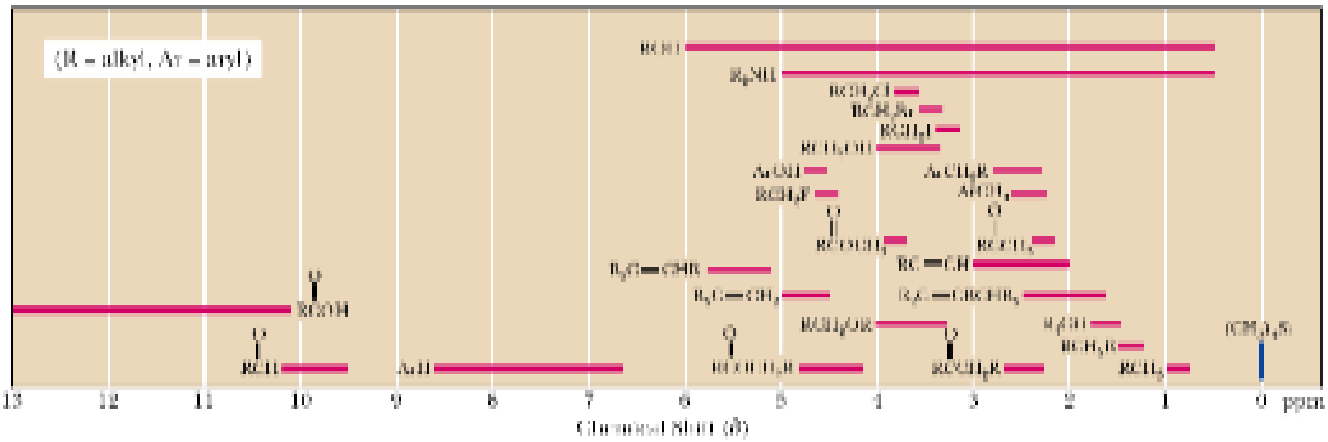
"As a student of The University of Texas at Austin, I shall abide by the core values of the University and uphold academic integrity."

_____

(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		
RCH_2R	1.2–1.4	$RCOCH_3$	3.7–3.9
R_3CH	1.4–1.7		
$R_2C{=}CRCHR_2$	1.6–2.6	$RCOCH_2R$	4.1–4.7
$RC{\equiv}CH$	2.0–3.0	RCH_2F	4.4–4.5
		ArOH	4.5–4.7
$RCCH_3$	2.1–2.3	$R_2C{=}CH_2$	4.6–5.0
		$R_2C{=}CHR$	5.0–5.7
$RCCH_2R$	2.2–2.6		
$ArCH_3$	2.2–2.5	$H_2C{-}CH_2$	3.3–4.0
RCH_2NR_2	2.3–2.8		
RCH_2I	3.1–3.3	RCH	9.5–10.1
RCH_2OR	3.3–4.0		
		RCOH	10–13

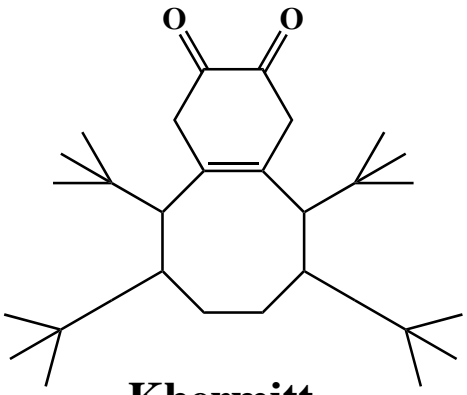
*Values are relative to tetramethylsilane. Other atoms within the molecule may cause the signal to appear outside these ranges.



Signature_____ Pg 1 _____(18)

1. (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.

2. (4 points) What is the most important question in organic chemistry?



Khermitt

A mutant frog species discovered in poluted ponds. Its Latin name is:

5,10-di-*tert*-butyl-6,9-dineopentyl-1,4,5,6,7,8,9,10-octahydrobenzo[8]annulene-2,3-dione

DO NOT TEAR OUT THIS PAGE!!

We do this to improve grading accuracy. You must write the answers for the questions on the next several pages on this single sheet.

Question 3, page 3 (12 pts) True false qustions. As appropriate, circle True or False in each space corresponding to the statements on page 2.

3.1 True False
3.2 True False
3.3 True False
3.4 True False
3.5 True False
3.6 True False
3.7 True False
3.8 True False
3.9 True False
3.10 True False
3.11 True False
3.12 True False
3.13 True False
3.14 True False
3.15 True False
3.16 True False
3.17 True False
3.18 True False
3.19 True False
3.20 True False

Question 4, page 4 (16 pts) Write the word that best completes the sentences.

4.1 _____
4.2 _____
4.3 _____
4.4 (two words) _____
4.5 _____
4.6 (two words) _____

Question 5, page 4 (12 pts) Write the the number of peaks expected for the signals corresponding to the H atoms indicated by the arrows.

5.1 _____ 5.2 _____ 5.3 _____

5.4 _____

(20 pts) These are the NMR spectra questions. Write the letter (A-E) of the structure that corresponds to the NMR structure shown.

6. _____ 7. _____ 8. _____

9. _____

Question 10, page 9 (8 pts) Circle the correct answer.

10.1 Nucleophiles Electrophiles

10.2 Nucleophiles Protons

Question 11, page 9 (12 pts) For each, circle whether the indicated structure is a nucleophile or an electrophile.

11.1 Nucleophile Electrophile
11.2 Nucleophile Electrophile
11.3 Nucleophile Electrophile
11.4 Nucleophile Electrophile
11.5 Nucleophile Electrophile
11.6 Nucleophile Electrophile
11.7 Nucleophile Electrophile
11.8 Nucleophile Electrophile
11.9 Nucleophile Electrophile
11.10 Nucleophile Electrophile
11.11 Nucleophile Electrophile
11.12 Nucleophile Electrophile

3. (1 pt. each) **On page 2, indicate whether the following statements are True or False (we will not grade any writing on this page).**

3.1 The "N" in NMR stands for "nuclear".

3.2 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.

3.3 Energy of exactly the correct frequency (turns out to be radio frequency) can be absorbed by a nucleus and excite it from the lower energy +1/2 spin state to the higher energy -1/2 spin state, a process referred to as resonance.

3.4 The difference in energy between the +1/2 and -1/2 nuclear spin states is proportional to the strength of the magnetic field felt by the nucleus.

3.5 Electron density is induced to circulate in a strong external magnetic field, which in turn produces a magnetic field that reinforces the external magnetic field.

3.6 Electron density is induced to circulate in a strong external magnetic field, which in turn produces a magnetic field that opposes the external magnetic field.

3.7 More electron density around a nucleus is referred to as more shielding.

3.8 More electron density around a nucleus is referred to as less shielding.

3.9 The more shielded the nucleus, the larger the chemical shift.

3.10 The more shielded the nucleus, the smaller the chemical shift.

3.11 The location of a given signal with respect to a standard, TMS, is called chemical shift (δ) and has the units ppm (parts per million).

3.12 On an NMR spectrum, the scale is plotted with larger values of chemical shift toward the left side.

3.13 On an NMR spectrum, the scale is plotted with larger values of chemical shift toward the right side.

3.14 On an NMR spectrum, all things being equal, a more shielded nucleus will give rise to a signal further to the right.

3.15 On an NMR spectrum, all things being equal, a more shielded nucleus will give rise to a signal further to the left.

3.16 The splitting of a $-CH_2-$ group adjacent to a chiral center will usually be a singlet due to exchange, (catalyzed by acid).

3.17 The splitting of a $-CH_2-$ group adjacent to a chiral center is more complex than n + 1.

3.18 The splitting of a $-CH_2-$ group adjacent to a chiral center is always a doublet of triplets

3.19 The H atoms of relatively acidic functional groups (alcohols, carboxylic acids) exchange rapidly, so they often do not split adjacent protons.

3.20 The H atoms of relatively acidic functional groups (alcohols, carboxylic acids) rotate rapidly, so they are always split according to the n+1 rule.

4. (2 pt each) In the appropriate space on page 2, fill in each blank with the word or two words that best completes the following sentences about NMR. We will not grade any writing on this page.

4.1 _____ hydrogens have the same NMR signal

4.2 Electronegative atoms, pi bonds and hybridization state of carbon atoms attached to an H atom influence shielding in predictable ways by removing differing amounts of _____ density around adjacent nuclei

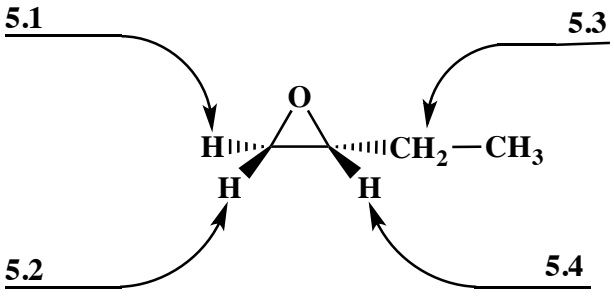
4.3 Non-equivalent H atoms on the same C atom can split each other (called _____ coupling), for example on alkenes or small rings.

4.4 (two words are needed here) For alkyl groups with freely rotating C atoms, complex splittings simplify because _____ _____ ("J") are all about the same.

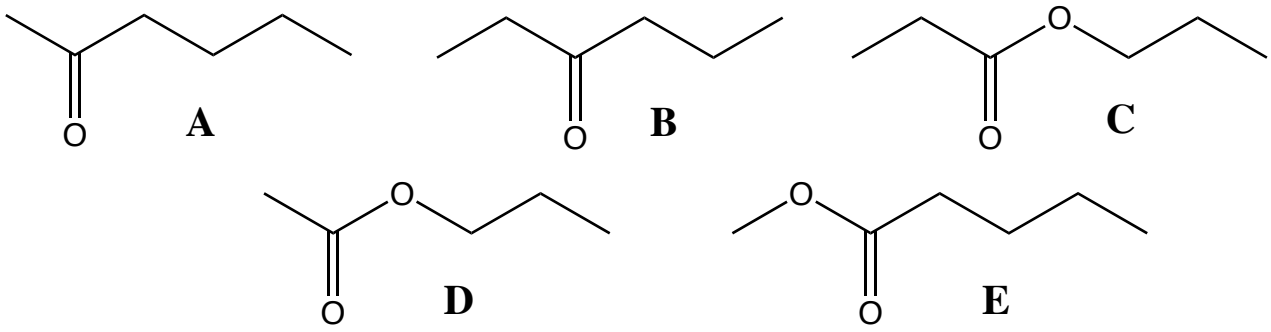
4.5 You can acquire an NMR spectrum by _____ all the nuclear spins instantaneously with a multi-frequency pulse, then monitor the rate at which the spins "relax" back to the +1/2 spin state.

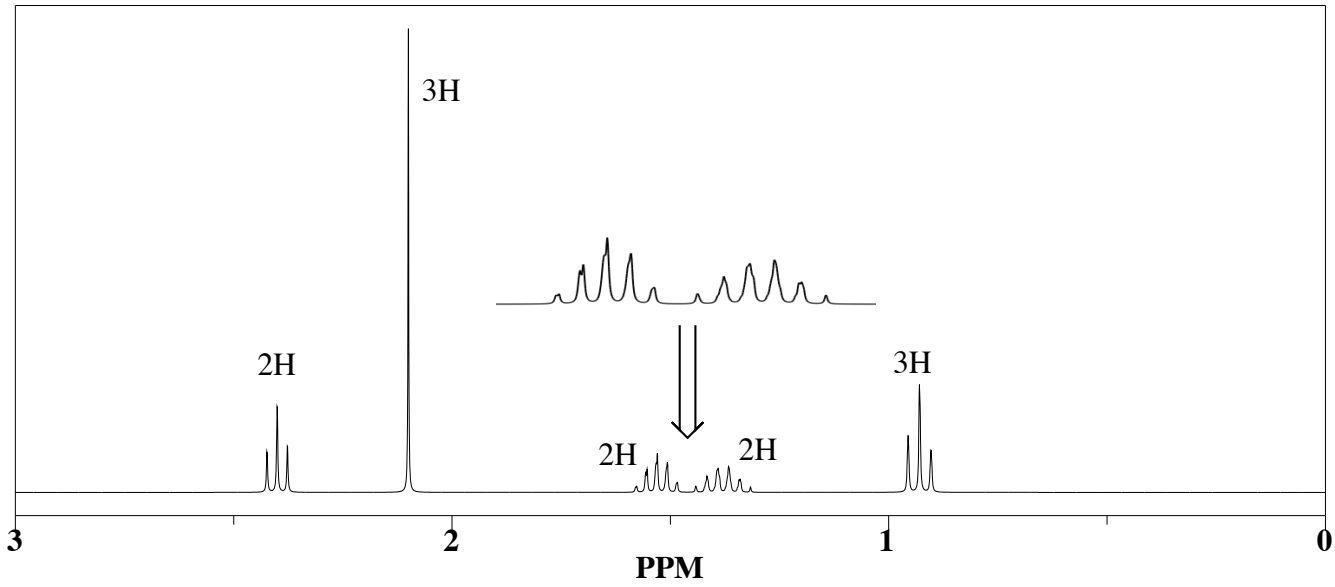
4.6 (two words are needed here) A mathematical algorithm called _____ _____ is used to reconstruct individual resonance frequencies and peak areas for the different equivalent sets of protons so the spectra can be plotted.

5. (3 pts each) In the appropriate space on page 2, fill in each blank with the number of peaks you expect to see for the signals corresponding to the H atom(s) indicated by the arrows.

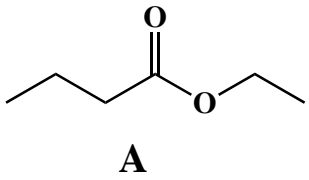


6. (5 pts) On page 2, write the letter of the structure that corresponds to the NMR structure below.

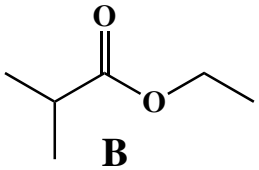




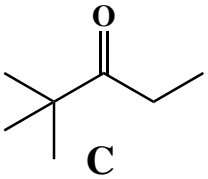
7. (5 pts) On page 2, write the letter of the structure that corresponds to the NMR structure below.



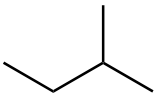
A



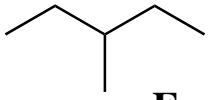
B



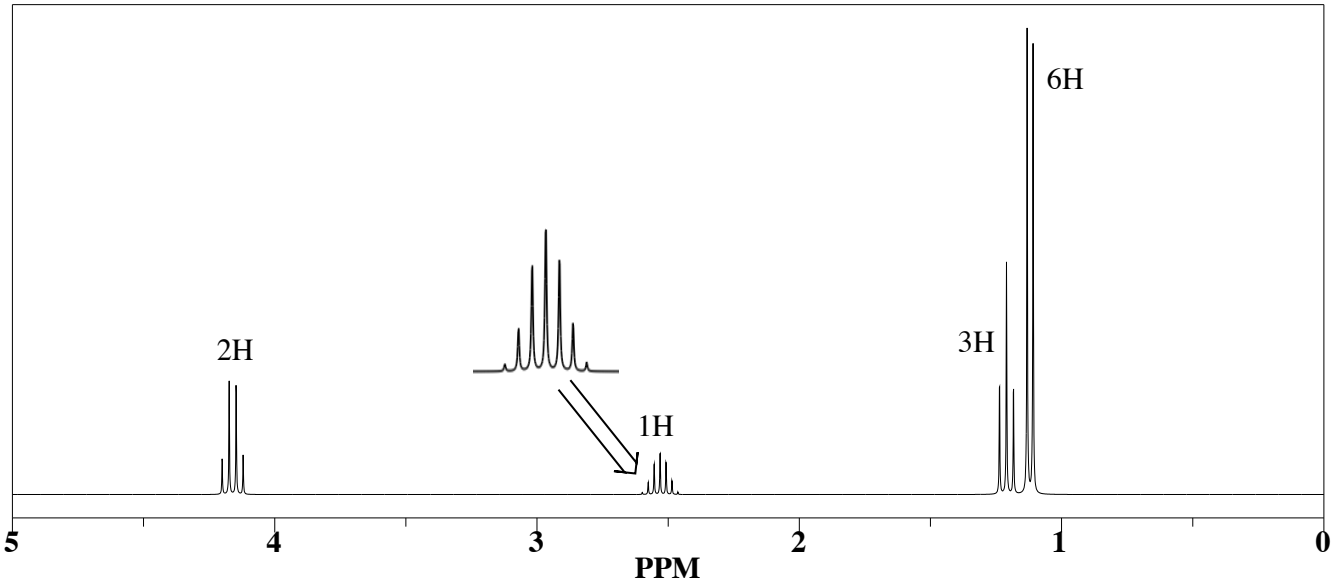
C



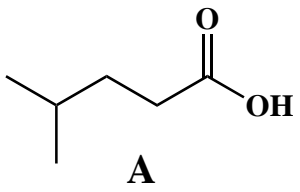
D



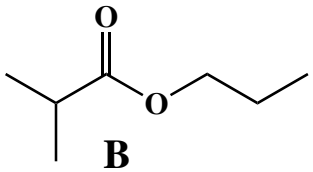
E



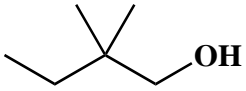
8. (5 pts) On page 2, write the letter of the structure that corresponds to the NMR structure below.



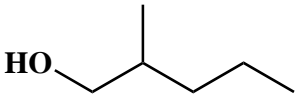
A



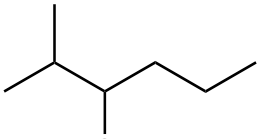
B



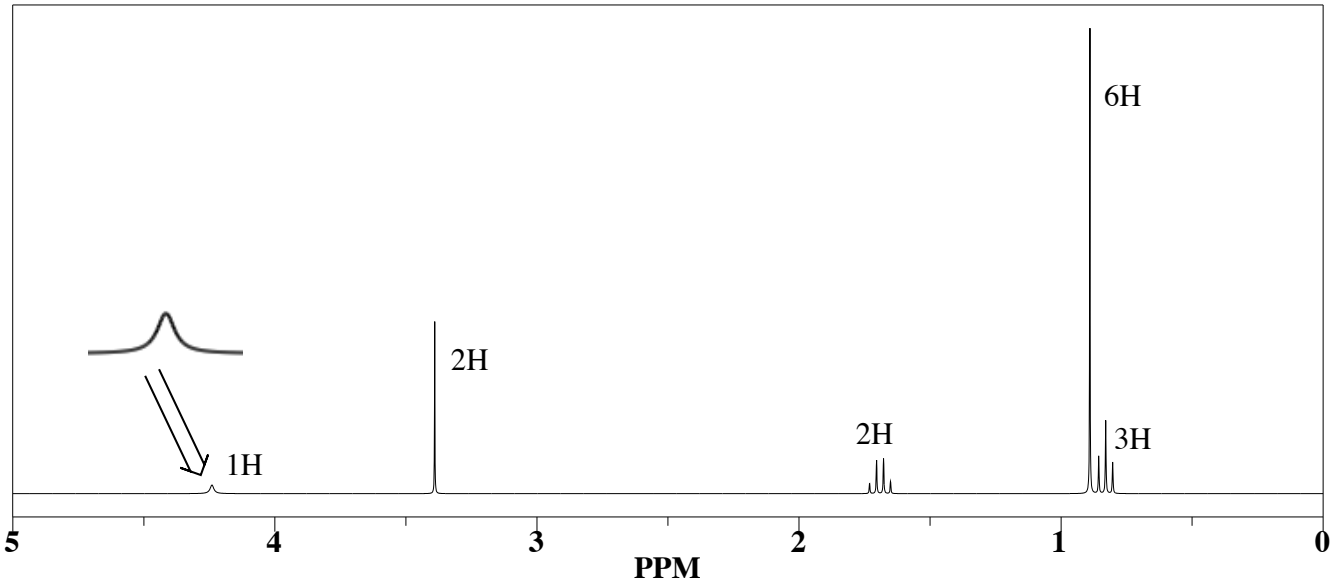
C



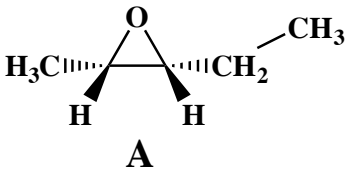
D



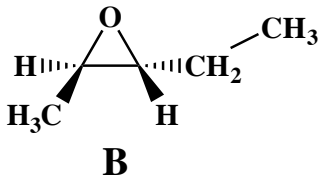
E



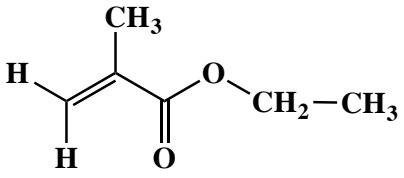
9. (5 pts) This is a very difficult one!! On page 2, write the letter of the structure that corresponds to the NMR structure below.



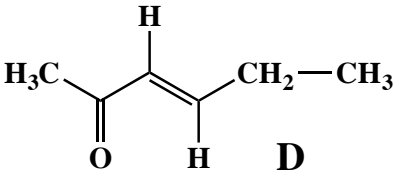
A



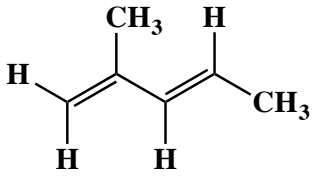
B



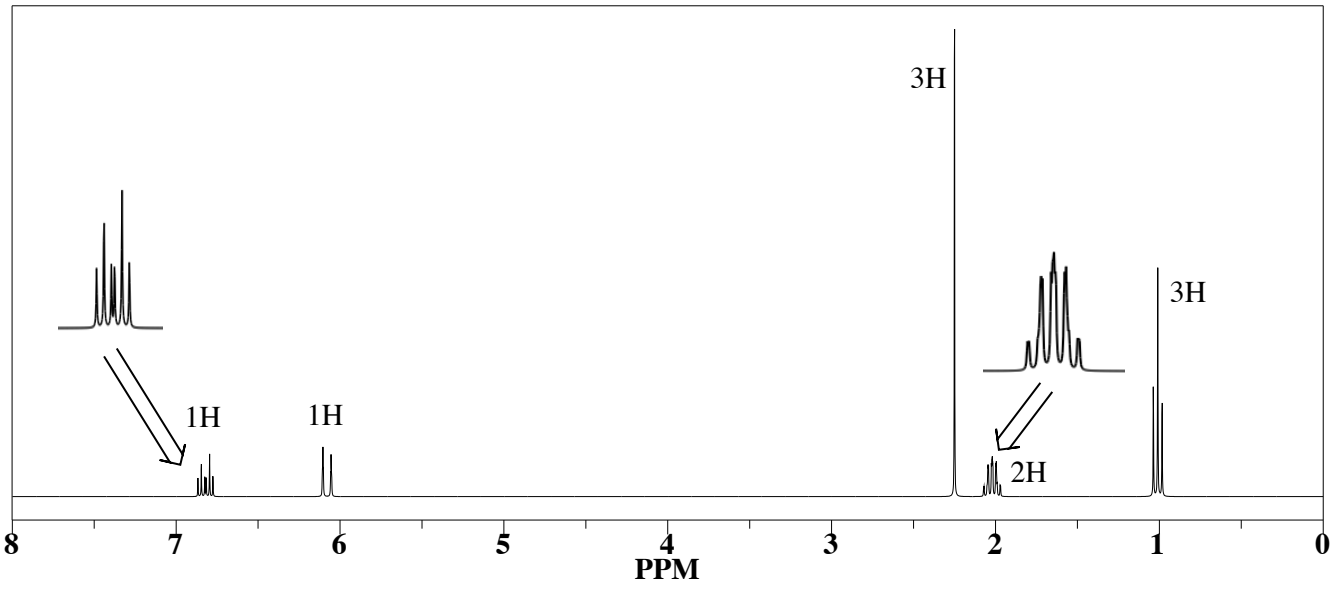
C



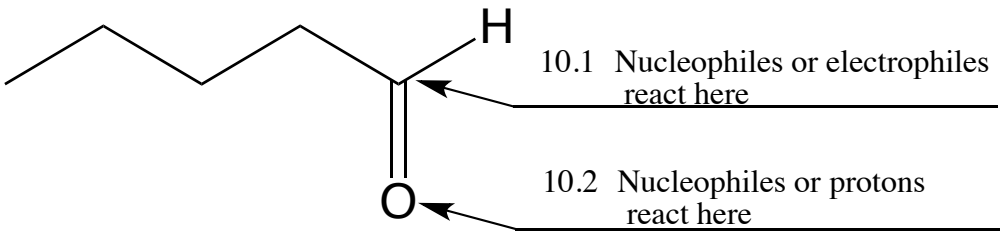
D



E

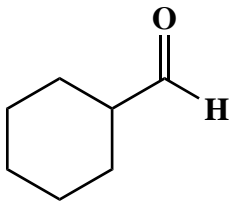


10. (8 pts) Most of carbonyl chemistry can be predicted based on the properties of the C=O group. On page 2, circle the appropriate answer.

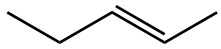


11. (12 pts) Being able to recognize the chemical "personality" of different species is one of the most important skills you can develop in Organic Chemistry. On page 2 indicate the personality of the molecule shown by circling either nucleophile or electrophile. Note that these species might be acids or bases in certain situations, but we will ignore that for this problem.

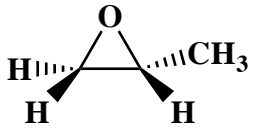
11.1



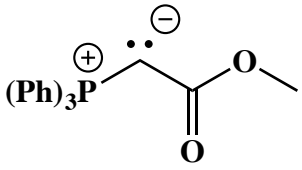
11.2



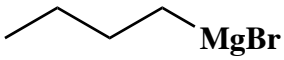
11.3



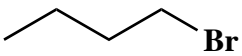
11.4



11.5

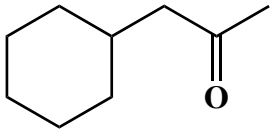


11.6

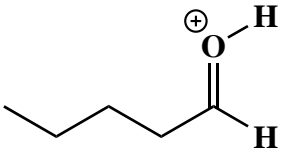


11.7 Br⊖

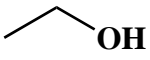
11.8



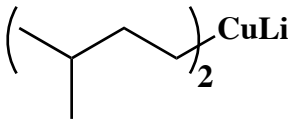
11.9



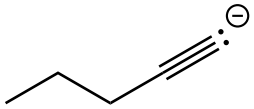
11.10



11.11

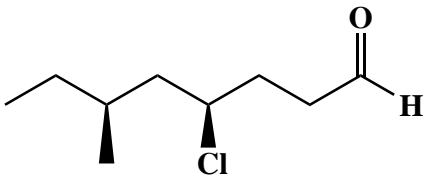


11.12



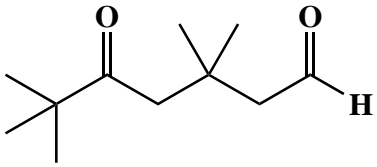
12. (4 pts each) Write an acceptable IUPAC name or draw a structural formula for the following molecules:

A.



_____

B.

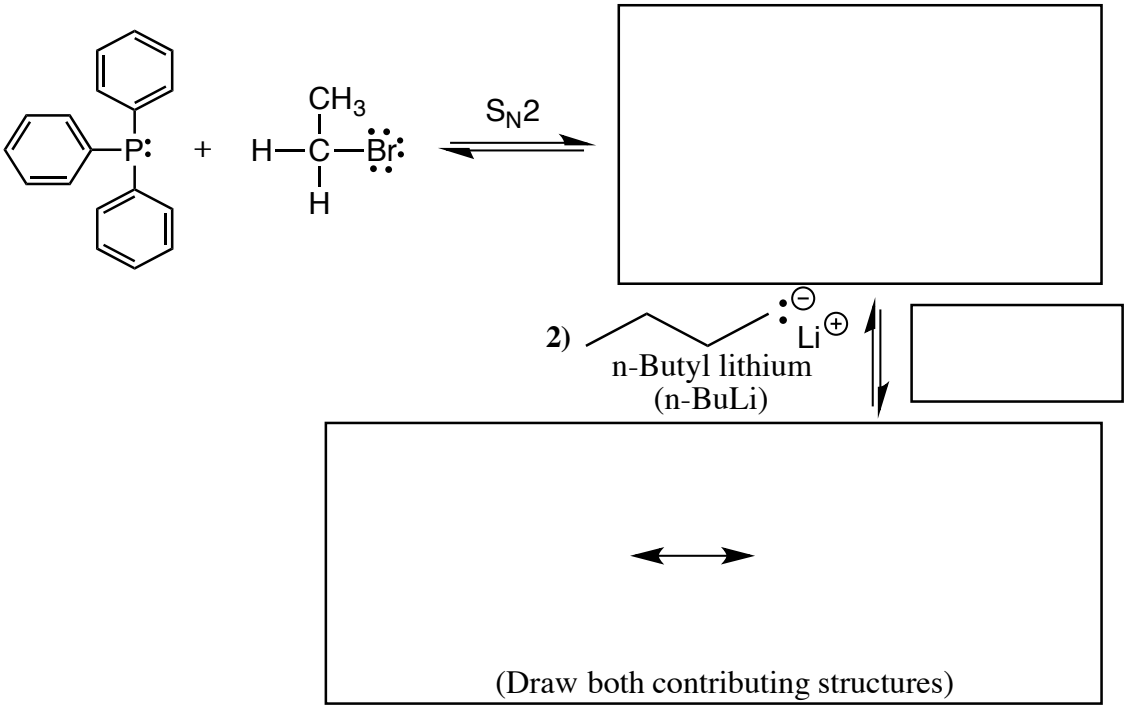


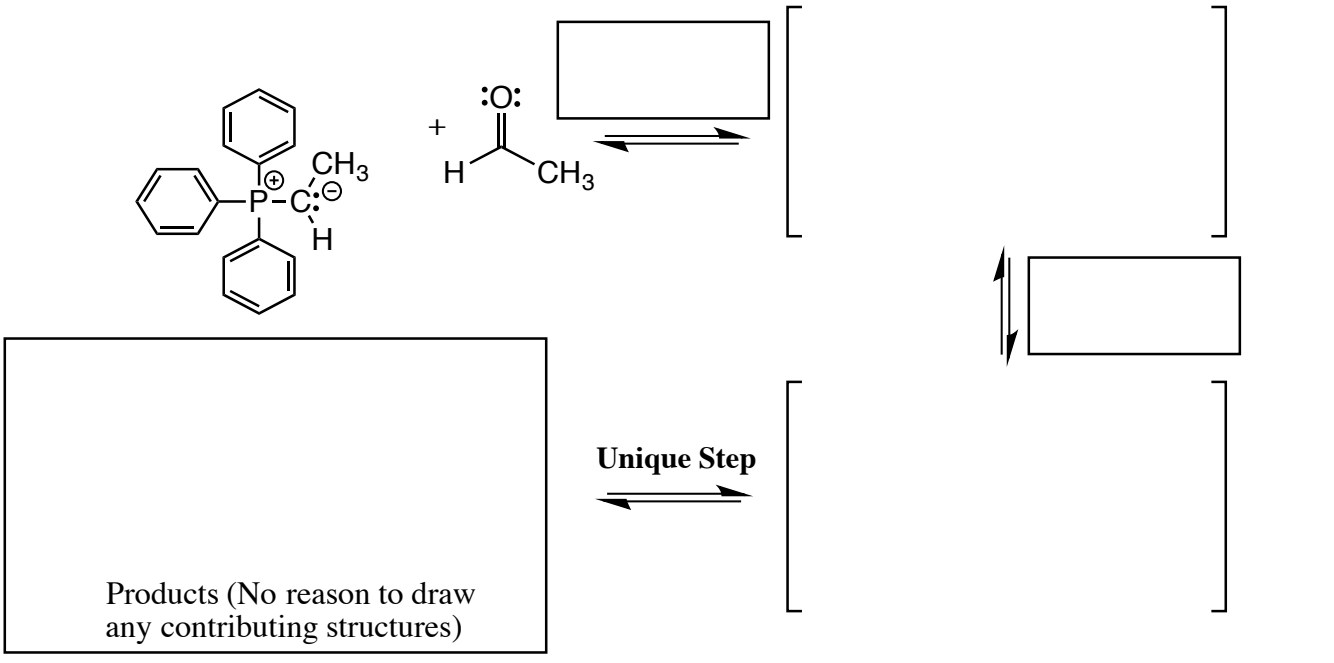
_____

C. In the box, draw the structure corresponding to the following IUPAC name.

(*E*)-5-methyl-4-hepten-3-one

14. (27 pts. total) Complete the mechanism for the following Wittig 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 MARK IT WITH AN ASTERISK AND WRITE "RACEMIC" IF APPROPRIATE.** I realize these directions are complex, so please read them again to make sure you know what we want.





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

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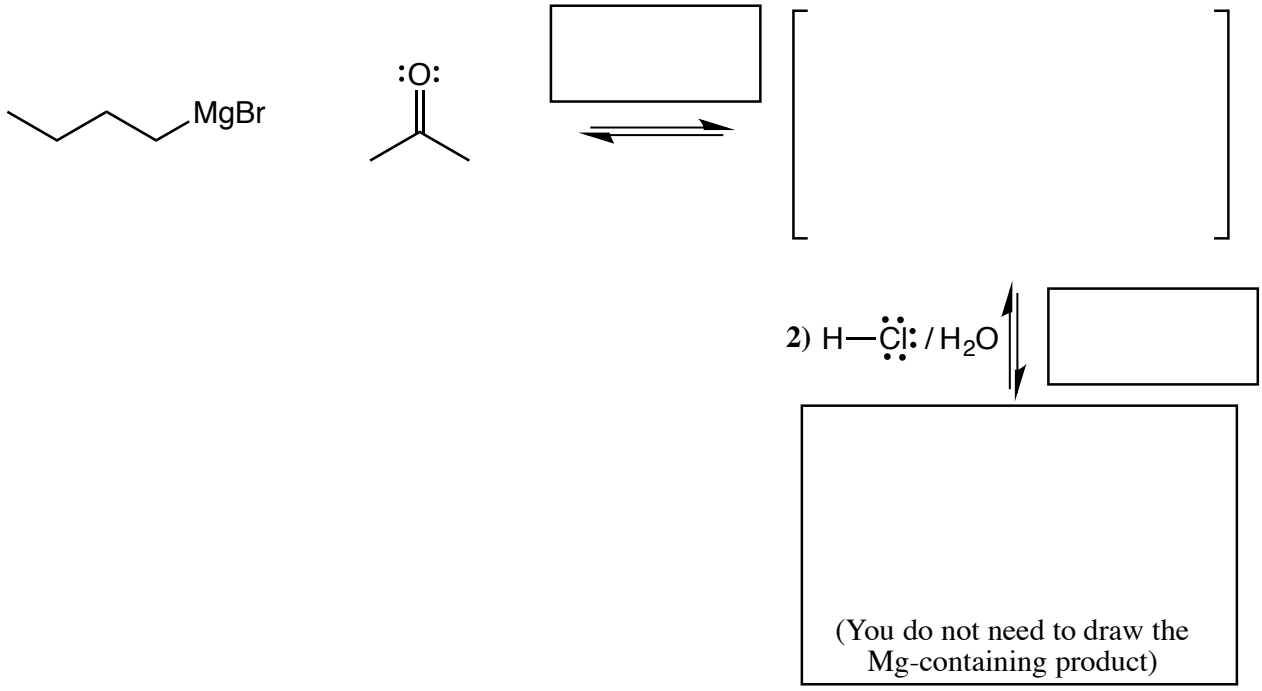
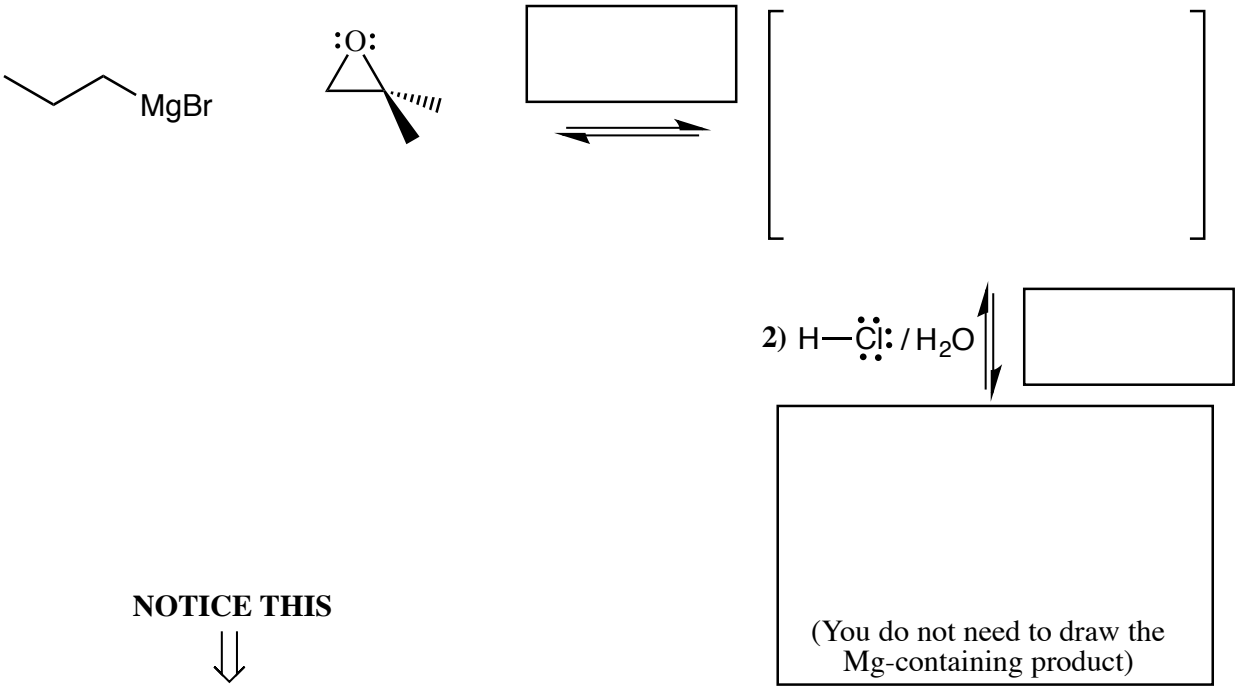
15. (22 pts. total) Complete the mechanism for the following two Grignard reactions. **Be sure to show arrows to indicate movement of all electrons, write all lone pairs, all formal charges, and all the products for each step.** Remember, I said all the products for each step. **IF A NEW CHIRAL CENTER IS CREATED MARK IT WITH AN ASTERISK AND WRITE "RACEMIC" IF APPROPRIATE.** I realize these directions are complex, so please read them again to make sure you know what we want.





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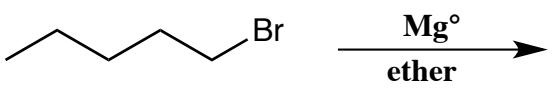
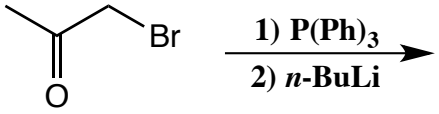
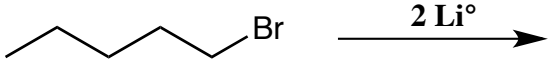
⇓

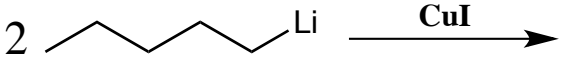
In the boxes provided adjacent to the arrows, write which of the four basic mechanistic elements are involved (i.e. "Make a bond", "Add a proton", etc.)

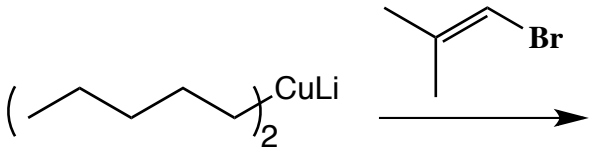
16. (3 or 5 pts.) Write the predominant product or products that will occur for each transformation. **If a new chiral center is created and a racemic mixture is formed, you must draw both enantiomers and write "racemic" under the structure. Use wedges (◄) and dashes (·····) to indicate stereochemistry. 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.**



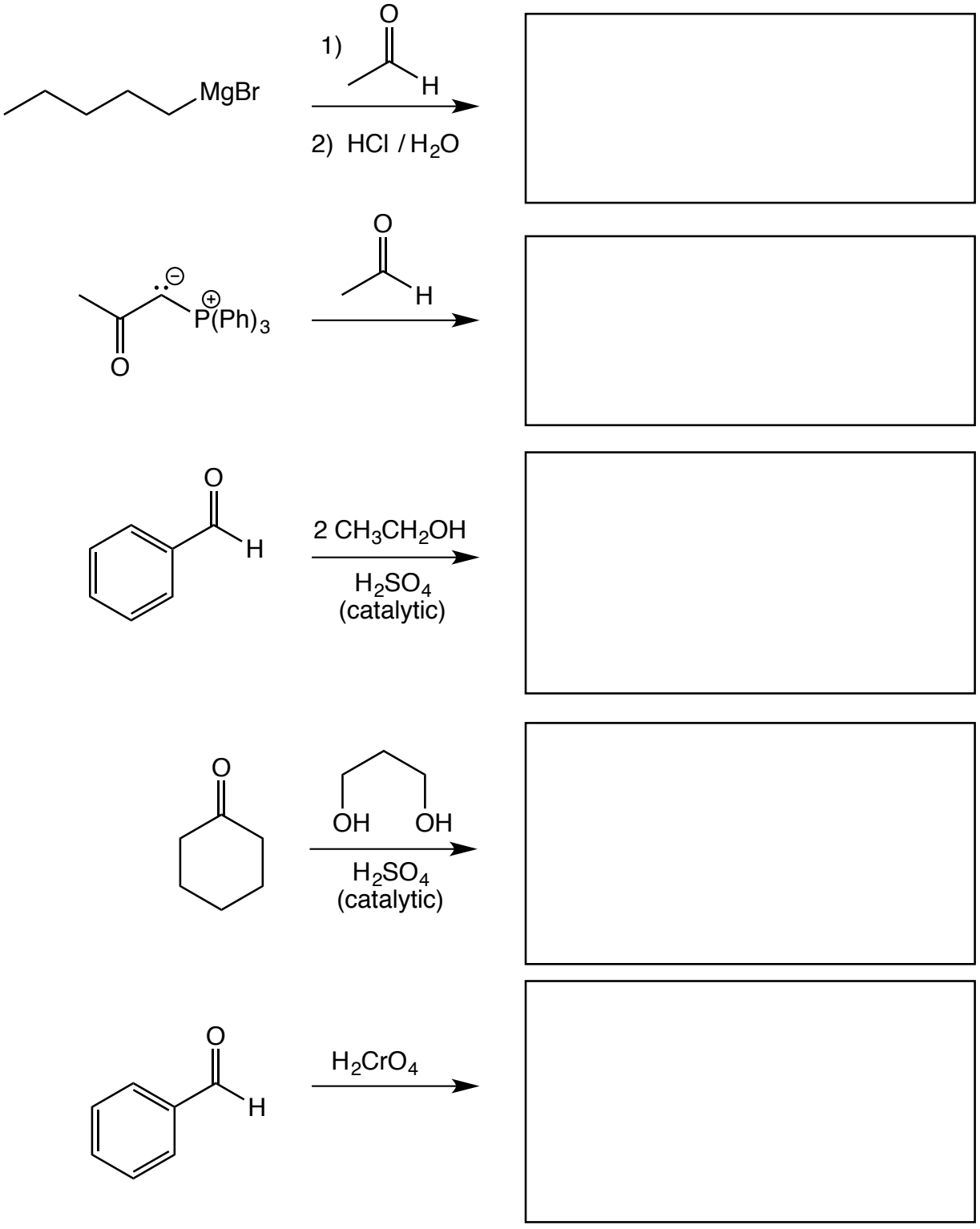




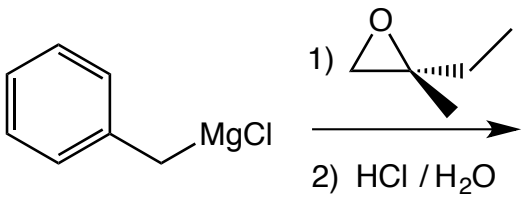


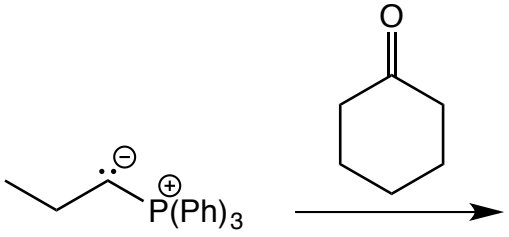


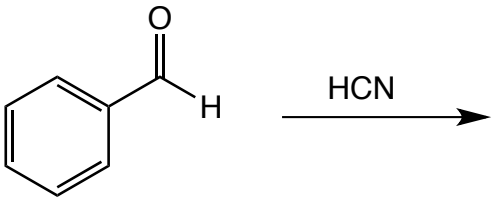
17. (3 or 5 pts.) Write the predominant product or products that will occur for each transformation. **If a new chiral center is created and a racemic mixture is formed, you must draw both enantiomers and write "racemic" under the structure. Use wedges (◄) and dashes (·····) to indicate stereochemistry. 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.**

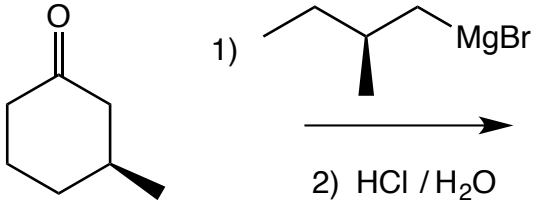


18. (3,4 or 5 pts.) Write the predominant product or products that will occur for each transformation. **If a new chiral center is created and a racemic mixture is formed, you must draw both enantiomers and write "racemic" under the structure. Use wedges (◄) and dashes (·····) to indicate stereochemistry. 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.**

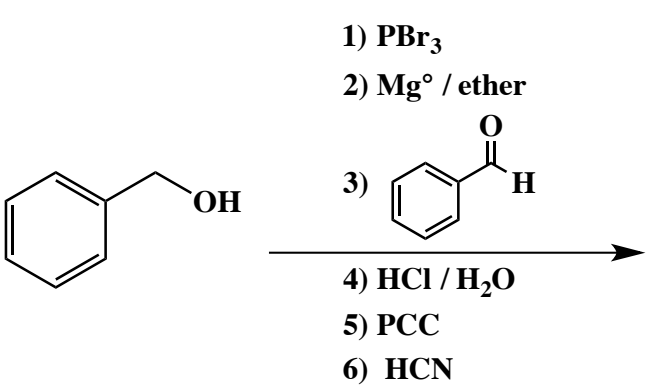






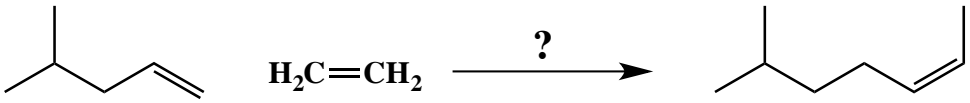


19. (5 pts) Here are a series of syntheticsteps that produce a complex product from simple starting materials. You only need to draw the final product in the box. If a racemic mixture is formed, you need to use wedges and dashes to indicate stereochemistry, making sure to and write "racemic" if appropriate. You can use the bottom of the page for scratch paper. Note that we only grade the final product structure so be careful!



20. 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, you can either draw both enantiomers or simply draw one structure and label all chiral centers with an asterisk (*). Either way, you must write racemic if appropriate.

(16 pts) **All of the carbon atoms of the products must come from the starting materials.**



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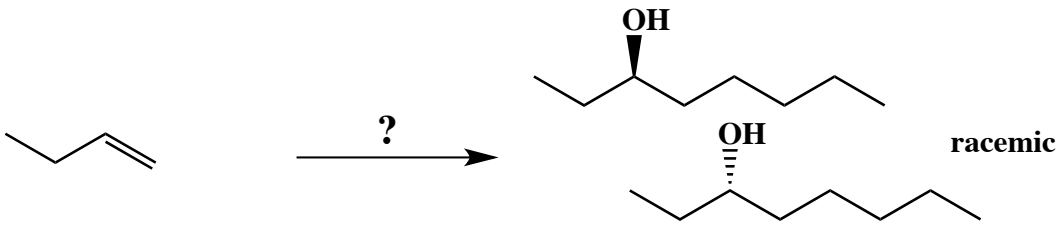
(10 pts) **All of the carbon atoms of the products must come from the starting materials.**



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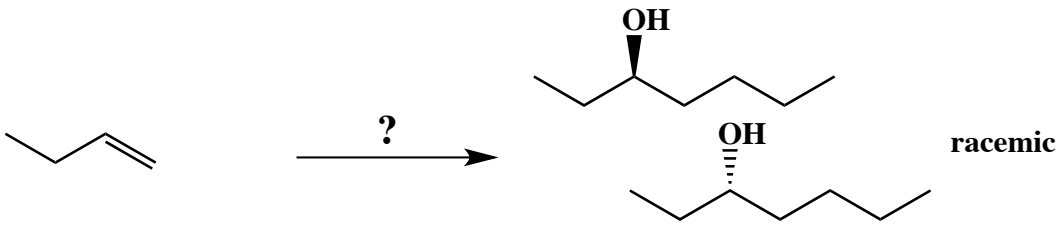

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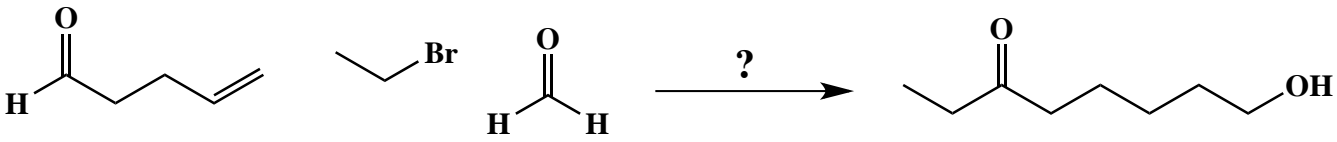
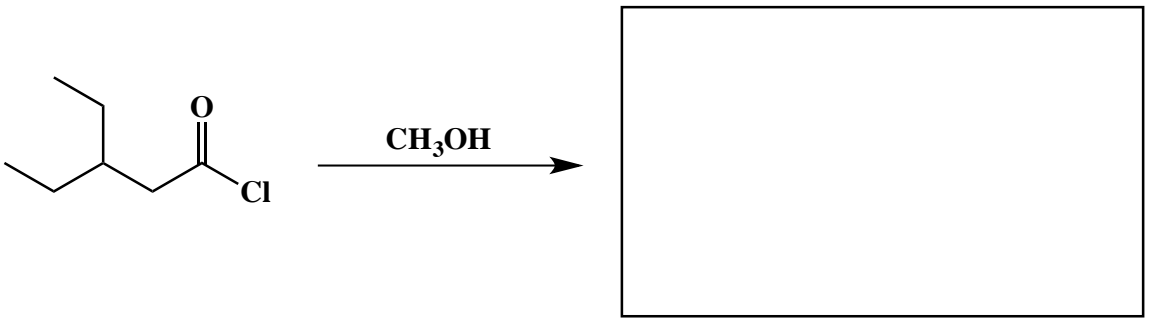
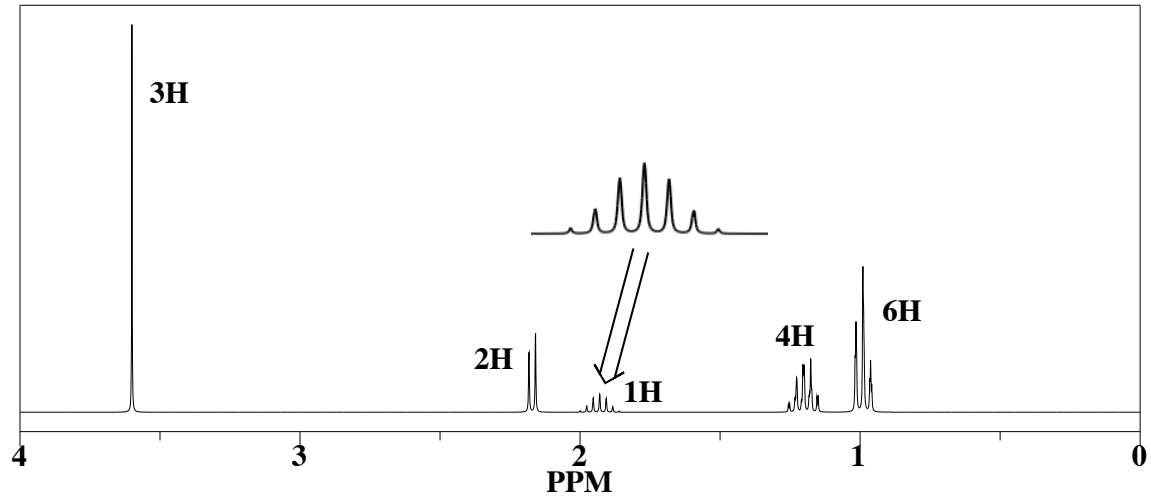
(19 pts) **All of the carbon atoms of the products must come from the starting materials.**

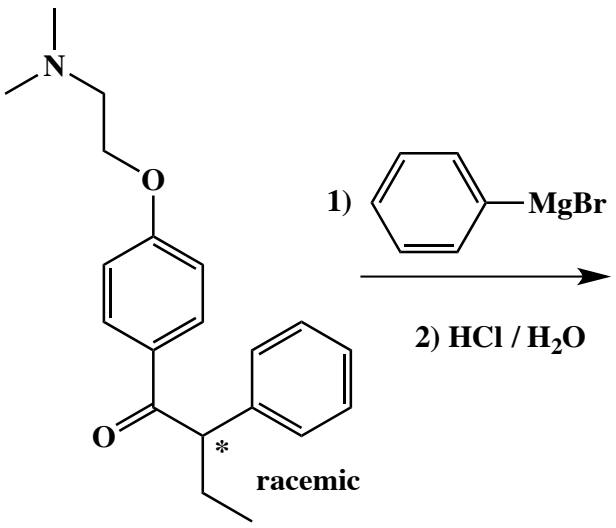


24. (10 pts) You have not seen the following reaction before, it comes from a much later chapter. The NMR spectrum is of the predominant product is shown. Using your growing intuition about chemical reactivity as well as the NMR, draw the structure of the product of this reaction.





25. (9 pts) Reactions in context: Following is the second to the last step in the synthesis of the very important drug Tamoxifen, used to treat breast cancer. Draw the product of the reaction.



NOTICE THIS!! ⇒ **How many product stereoisomers are there?** _____