NAME (Print): ______________________________

SIGNATURE: ______________________________

Chemistry 320N
Dr. Brent Iverson
1st Midterm
Feb. 16, 2017

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 INCIDENTS 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!!!

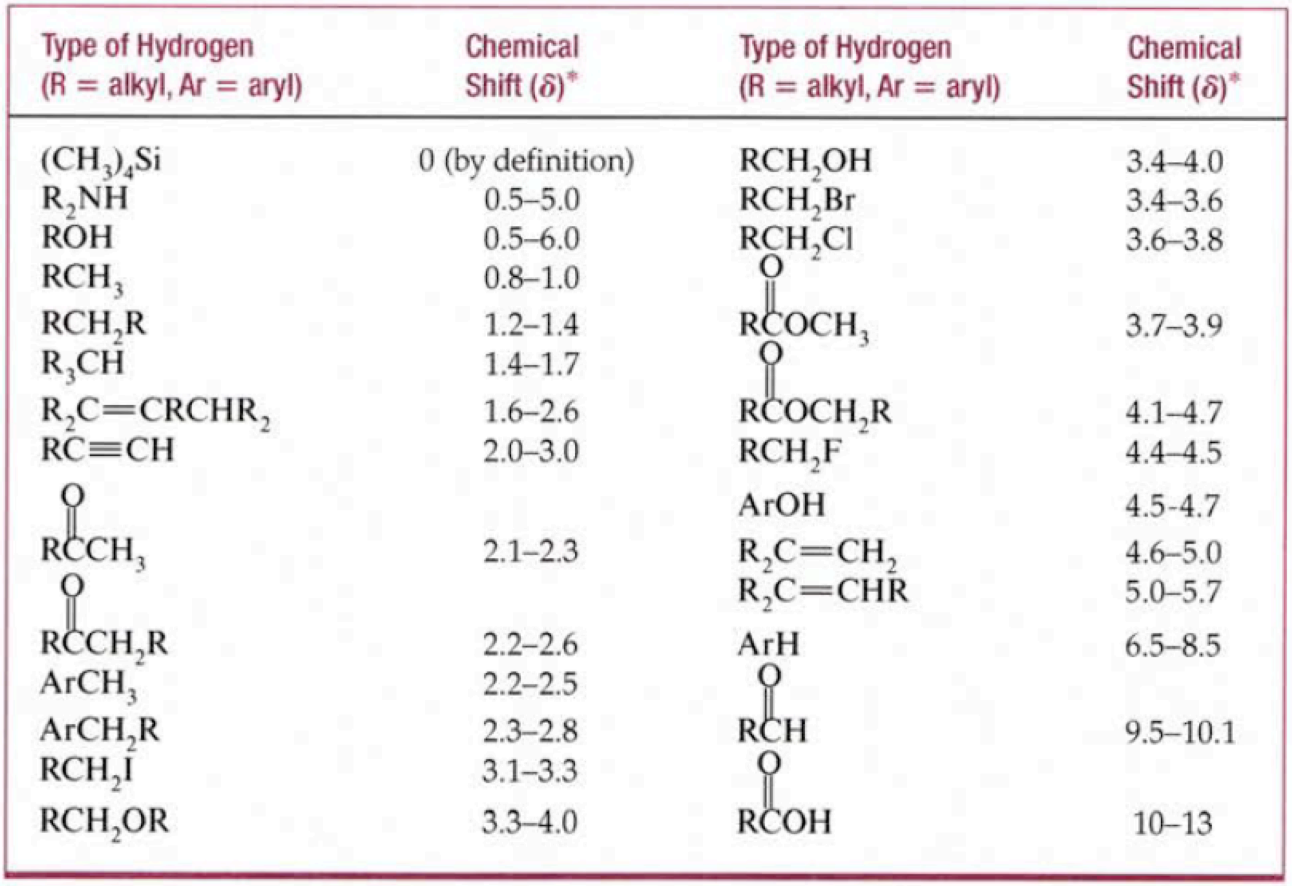
Page	Points	
1		**(18)**
2		**(87)**
9		**(12)**
10		**(40)**
11		**(11)**
12		**(18)**
13		**(26)**
14		**(7)**
15		**(10)**
16		**(19)**
17		**(16)**
18		**(10)**
Total		**(274)**

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."

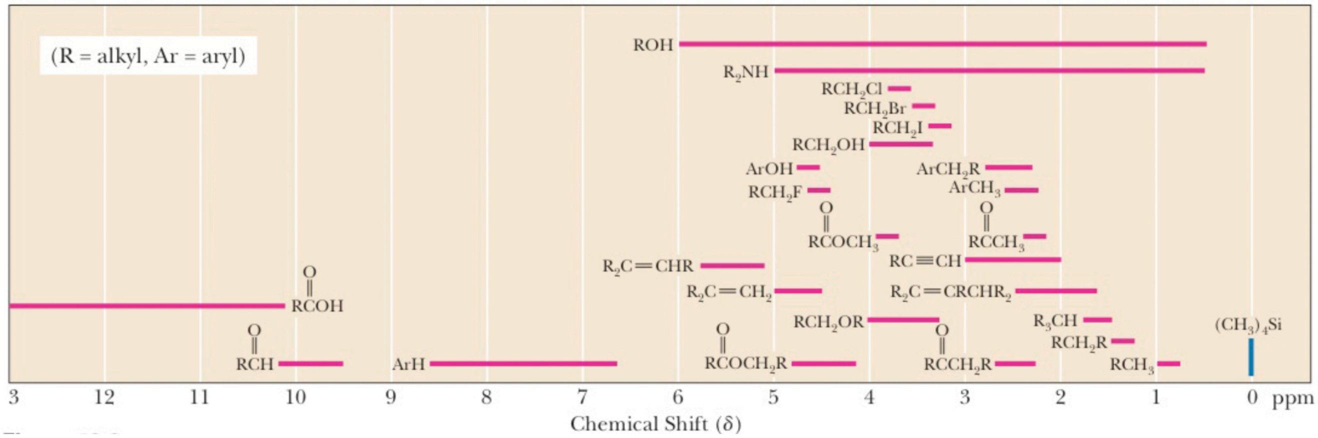
____

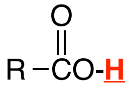
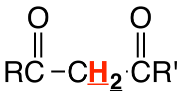
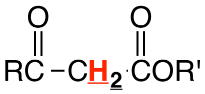
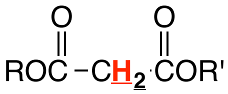
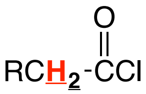
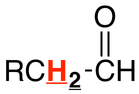
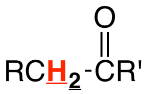
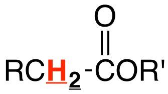
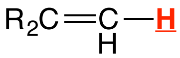
(Your signature)



Type of Hydrogen (R = alkyl, Ar = aryl)	Chemical Shift (δ)*	Type of Hydrogen (R = alkyl, Ar = aryl)	Chemical Shift (δ)*
$(CH_3)_4Si$	0 (by definition)	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	$\mathrm{R\overset{O}{\overset{\|}{C}}OCH_3}$	3.7–3.9
RCH_2R	1.2–1.4	$\mathrm{R\overset{O}{\overset{\|}{C}}OCH_2R}$	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
$\mathrm{R\overset{O}{\overset{\|}{C}}CH_3}$	2.1–2.3	$R_2C{=}CHR$	5.0–5.7
$\mathrm{R\overset{O}{\overset{\|}{C}}CH_2R}$	2.2–2.6	ArH	6.5–8.5
$ArCH_3$	2.2–2.5	$\mathrm{R\overset{O}{\overset{\|}{C}}H}$	9.5–10.1
$ArCH_2R$	2.3–2.8	$\mathrm{R\overset{O}{\overset{\|}{C}}OH}$	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.



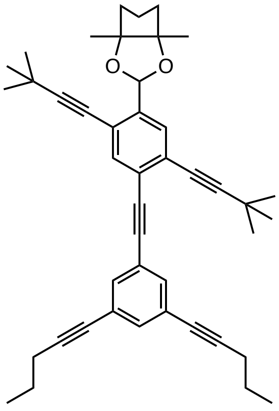
Compound		pKa
Hydrochloric acid	$H-Cl$	-7
Protonated alcohol	$RCH_2OH_2^{+}$	-2
Hydronium ion	H_3O^{+}	-1.7
Carboxylic acids	 $R-\overset{O}{\overset{\parallel}{C}}O-H$	3-5
Ammonium ion	H_4N^{+}	9.2
β-Dicarbonyls	 $R\overset{O}{\overset{\parallel}{C}}-CH_2-\overset{O}{\overset{\parallel}{C}}R'$	10
Primary ammonium	$H_3\overset{+}{N}CH_2CH_3$	10.5
β-Ketoesters	 $R\overset{O}{\overset{\parallel}{C}}-CH_2-\overset{O}{\overset{\parallel}{C}}OR'$	11
β-Diesters	 $RO\overset{O}{\overset{\parallel}{C}}-CH_2-\overset{O}{\overset{\parallel}{C}}OR'$	13
Water	HOH	15.7
Alcohols	RCH_2OH	15-19
Acid chlorides	 $RCH_2-\overset{O}{\overset{\parallel}{C}}Cl$	16
Aldehydes	 $RCH_2-\overset{O}{\overset{\parallel}{C}}H$	18-20
Ketones	 $RCH_2-\overset{O}{\overset{\parallel}{C}}R'$	18-20
Esters	 $RCH_2-\overset{O}{\overset{\parallel}{C}}OR'$	23-25
Terminal alkynes	$RC\equiv C-H$	25
LDA	$H-N(\textit{i}-C_3H_7)_2$	40
Terminal alkenes	 $R_2C=\underset{H}{C}-H$	44
Alkanes	CH_3CH_2-H	51

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 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 H atoms 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 H atoms, especially the H atoms from water and fat, in the different tissues.

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

Where are the electrons?



Johnny Carbon

**Science News Update:
Miniature humans have
just been discovered living
among molecules. Their
species name is:**

(3aR,6aS)-2-(4-((3,5-di(pent-1-yn-1-yl)phenyl)ethynyl)-2,5-bis(3,3-dimethylbut-1-yn-1-yl)phenyl)-3a,6a-dimethyltetrahydro-4H-cyclopenta[d][1,3]dioxole

Signature_________________________

Pg 2 ____________(87)

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 (28 pts) Write the word or words that best completes the sentences.

3.1 resonance

3.2 1/2

3.3 Electron

3.4 magnetic

3.5 shielded

3.6 (two words) chemical shift

3.7 magnetic

3.8 (two words) coupling constant

3.9 Equivalent

3.10 multiply

3.11 n+1

3.12 (two words) four-membered

3.13 (three words) alpha is axial

3.14 chelate

Question 4, page 4 (12 pts) Write the four mechanisitc elements we use to contruct complex mechanisms (3-4 word versions).

4.1 Make a bond

4.2 Break a bond

4.3 Add a proton

4.4 Take a proton away

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 3

5.2 6

5.3 12

5.4 4

5.5 4

5.6 6

(18 pts) These are the NMR spectra questions (pages 5-7). Write the letter of the structure(s) that correspond(s) to the NMR spectrum shown.

6. C

7. A

8. (more than one) A, E, G

Question 9, page 8 (17 pts) For each, circle whether the indicated structure is a nucleophile or an electrophile.

9.1 Nucleophile [✓ Electrophile]

9.2 Nucleophile [✓ Electrophile]

9.3 Nucleophile [✓ Electrophile]

9.4 [✓ Nucleophile] Electrophile

9.5 [✓ Nucleophile] Electrophile

9.6 Nucleophile [✓ Electrophile]

9.7 Nucleophile [✓ Electrophile]

9.8 [✓ Nucleophile] Electrophile

9.9 [✓ Nucleophile] Electrophile

9.10 [✓ Nucleophile] Electrophile

9.11 [✓ Nucleophile] Electrophile

9.12 [✓ Nucleophile] Electrophile

9.13 Nucleophile [✓ Electrophile]

9.14 [✓ Nucleophile] Electrophile

9.15 [✓ Nucleophile] Electrophile

9.16 [✓ Nucleophile] Electrophile

9.17 [✓ Nucleophile] Electrophile

3. (2 pt. each blank) **On page 2, fill in each sentence with the word or words that best complete(s) the following sentences.**

3.1 The “R” in NMR stands for **(3.1)** “**resonance**”.

3.2 Nuclei with spin quantum number **(3.2) 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, 3.4 **(3.3) Electron** density is induced to circulate in a strong external magnetic field, which in turn produces a **(3.4) magnetic** field that opposes the external magnetic field

3.5 The greater the electron density around a nucleus, the more **(3.5) shielded** it is, and the lower the energy (frequency) of electromagnetic radiation required to flip its nuclear spin.

3.6 The location of a given signal with respect to a standard, TMS, is called **(3.6) chemical shift** (two words) (δ) and this has the units ppm (parts per million)

3.7 Adjacent nuclei have **(3.7) magnetic** fields associated with their spins.

3.8 The distance between peaks in a split signal is called the **(3.8) coupling constant** (two words) ("J")

3.9 **(3.9) Equivalent** hydrogen atoms in a molecule give the same NMR signal.

3.10, 3.11 In theory, when there are two sets of adjacent H atoms, the number of peaks **(3.10) multiply**, however for alkyl groups in which the C atoms are freely rotating, the splittings are all about the same for these groups and the peaks overlap. Threfore in practice, for systems with freely rotating C atoms if there are n adjacent H atoms, equivalent or not, you will see only **(3.11) n+1** peaks.

3.12 In the Wittig reaction mechanism, it is important to remember that there is a (**3.12**) **four-membered** (two words) ring intermediate.

3.13 For D-Glucose, it is important to remember that (**3.13**) **alpha is axial** (three words), a phrase intended to remind you which of the two possible anomers is produced when the six-membered ring forms via hemiacetal formation.

3.14 The (**3.14**) **chelate** effect, named after the Latin/Greek word for “claw” explains why cyclic acetals are more stable than normal acetals.

4. (3 pt each) We introduced four mechanistic elements that describe the majority of steps you will encounter in mechanisms this semester. On the four lines provided on Page 2, list the four most common mechanistic elements. We are looking for the short versions, in other words only 3-4 words per line.

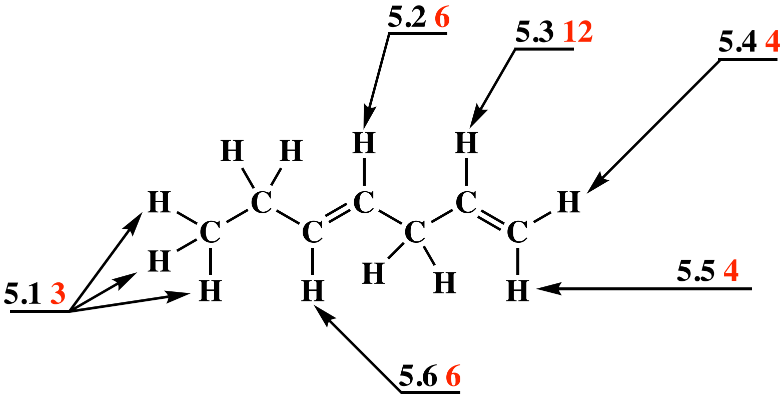
4.1 Make a bond

4.2 Break a bond

4.3 Add a proton

4.4 Take a proton away

5. (2 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. Take your time on this, it may be one of the harder problems on the exam.



5.1 3

5.2 6

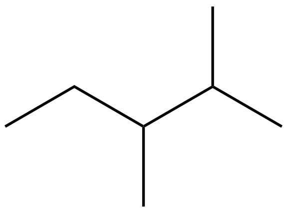
5.3 12

5.4 4

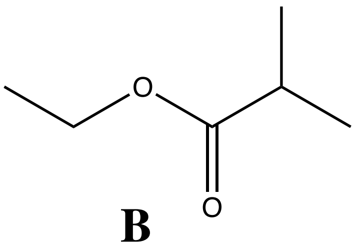
5.5 4

5.6 6

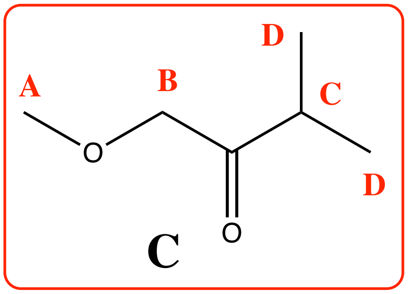
6. (5 pts) On page 2, write the letter of the structure that corresponds to the NMR spectrum below.



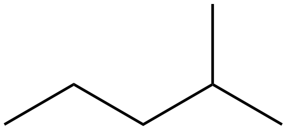
A



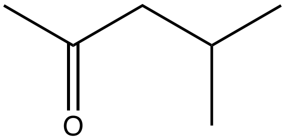
B



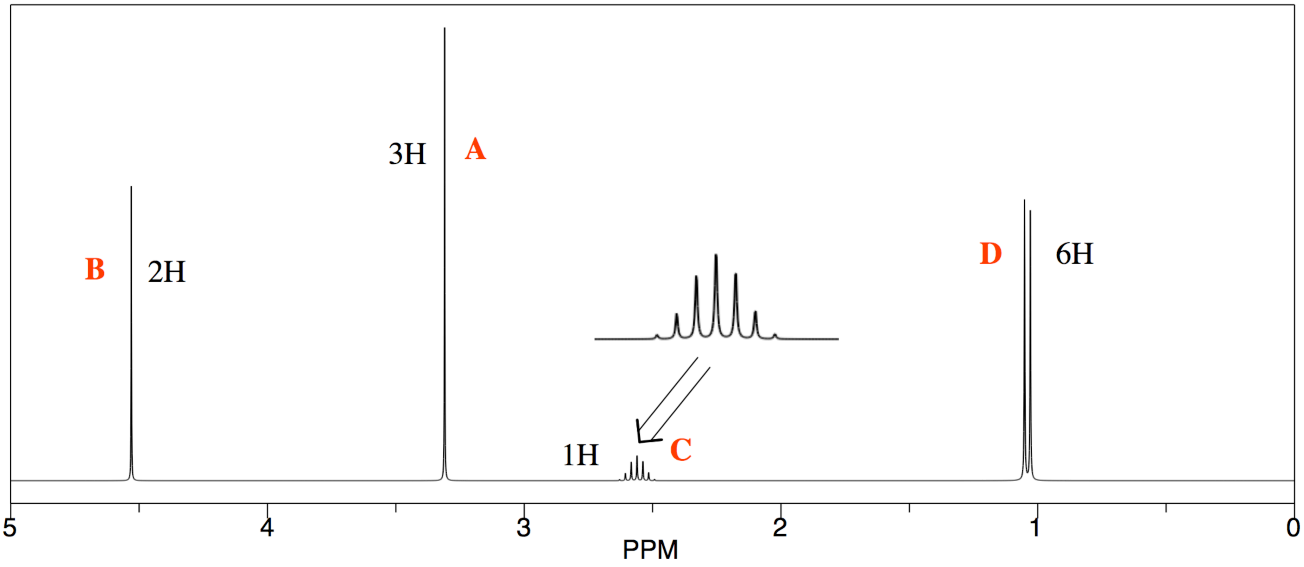
C



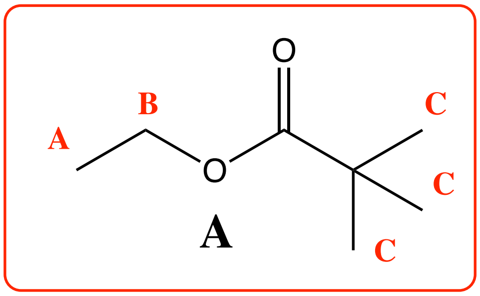
D



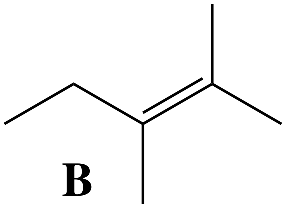
E



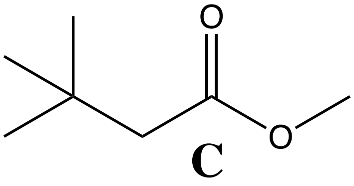
7. (5 pts) On page 2, write the letter of the structure that corresponds to the NMR spectrum below.



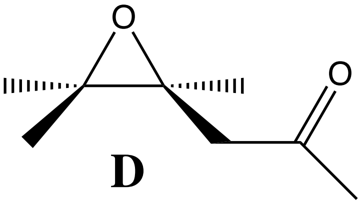
A



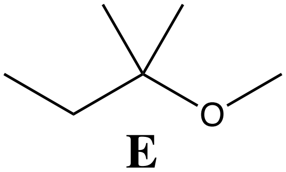
B



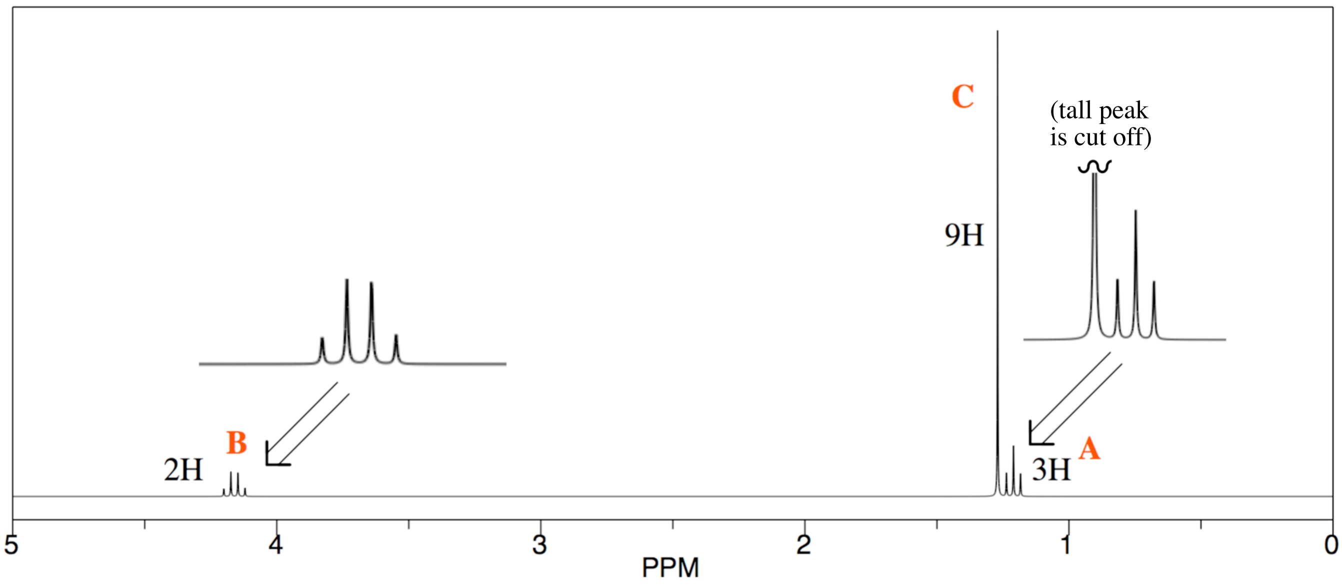
C



D

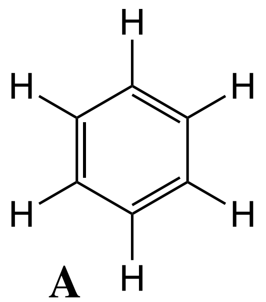


E

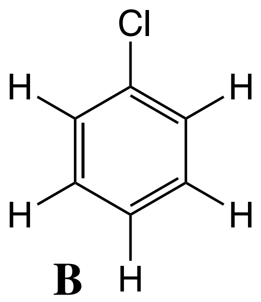


Signature____________________________

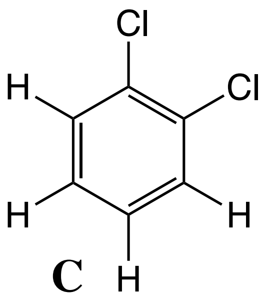
8. (8 pts) Suppose you just carried out a reaction that placed Cl atoms on a benzene ring. You know that somewhere between 1 and 3 Cl atoms ended up on the pure compound that you isolated and analyzed by NMR. To your surpise there is only one signal in the NMR spectum and it is NOT split (the actual spectrum is shown below). On page 2, write the letter of all of the structures from those listed that are consistent with such a simple spectrum. There is more than one correct answer here!



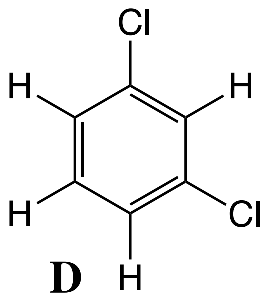
A



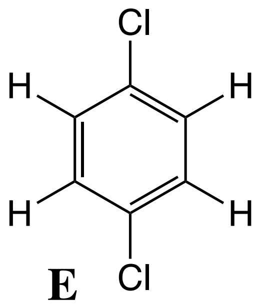
B



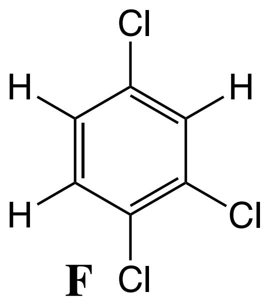
C



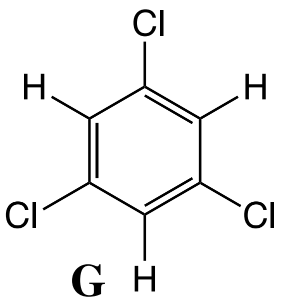
D



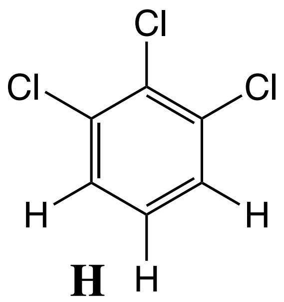
E



F

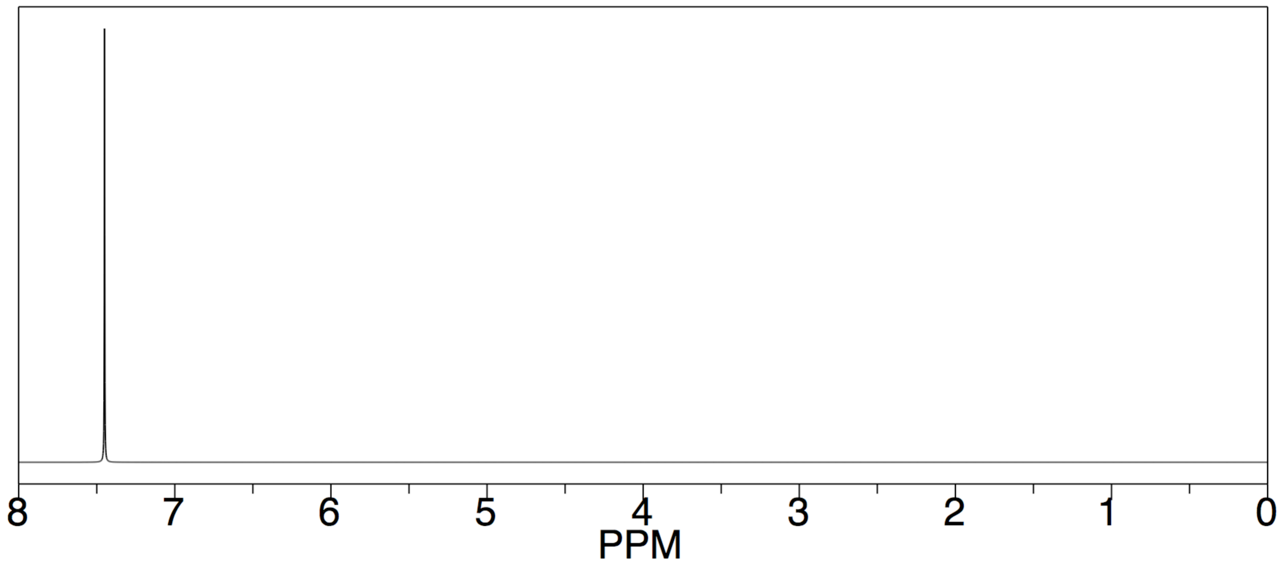


G



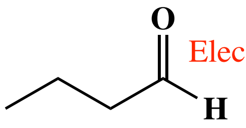
H

Because of symmetry, all of the H atoms in the circled structures are equivalent so predict a single signal with a single peak for each of the three.



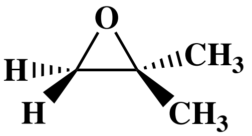
9. (17 pts) Being able to recognize the chemical personality of different species is one of the most important skills you can develop in Organic Chemistry. On page 2 state whether each structure is a nucleophile or electrophile. Note that these species might be acids or bases in certain situations, but we will ignore that for this problem.

9.1



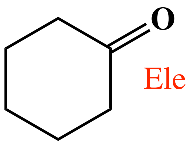
Electrophile

9.2



Electrophile

9.3



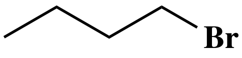
Electrophile

9.4 $^{\ominus}$CN Nucleophile

9.5

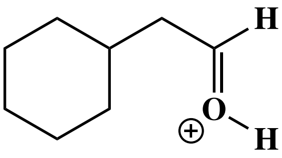
Nucleophile

9.6



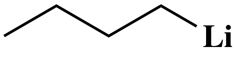
Electrophile

9.7



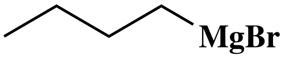
Electrophile

9.8



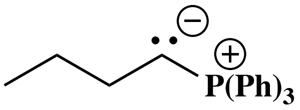
Nucleophile

9.9



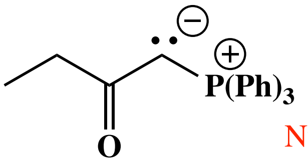
Nucleophile

9.10



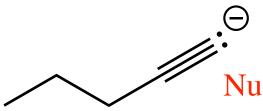
Nucleophile

9.11



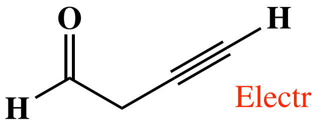
Nucleophile

9.12



Nucleophile

9.13

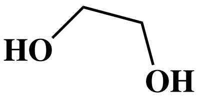


Electrophile

9.14 $NaBH_4$ Nucleophile

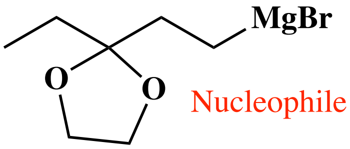
9.15 H_2O Nucleophile

9.16



Nucleophile

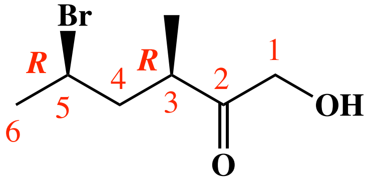
9.17



Nucleophile

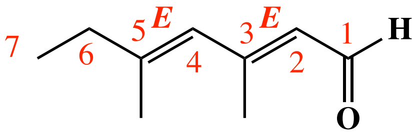
10. (4 pts each) Write an acceptable IUPAC name or draw a structural formula for the following molecules:

A.



(3*R*,5*R*)-5-bromo-1-hydroxy-3-methyl-2-hexanone

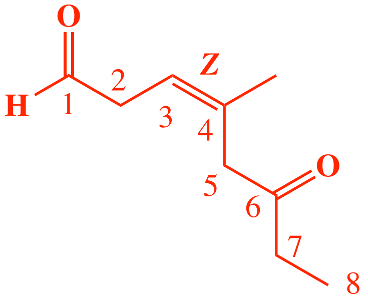
B.



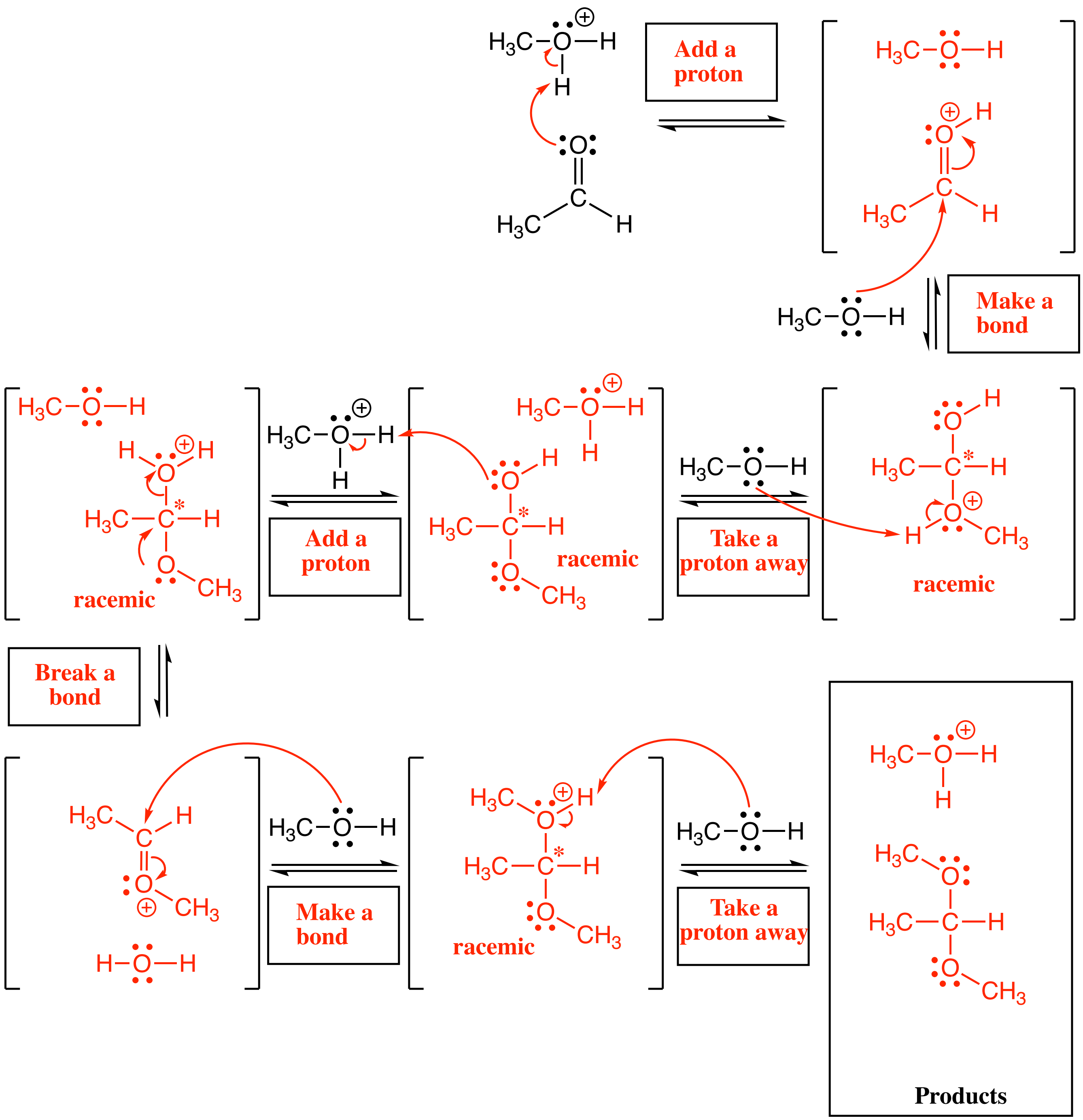
(2*E*,4*E*)-3,5-dimethyl-2,4-heptadienal

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

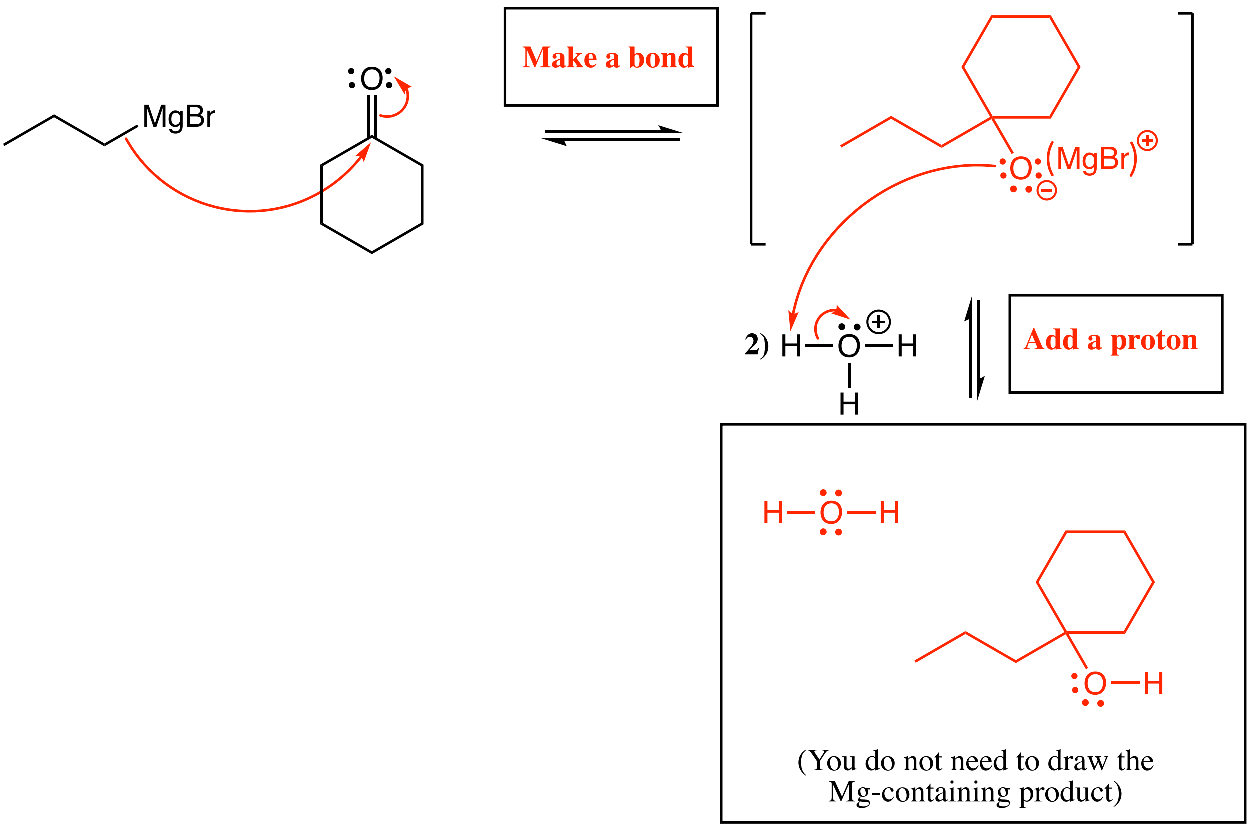
(*Z*)-4-methyl-6-oxo-3-octenal



11. (40 pts. total) Complete the mechanism for the following acetal formation reaction catalyzed by acid (H_2SO_4, not shown) **in the presence of excess methanol**. **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. In the box provided next to each arrow write the mechanistic element used ("Add a proton" etc.)** I realize these directions are complex, so please read them again to make sure you know what we want.

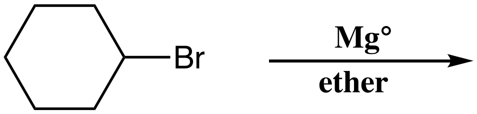


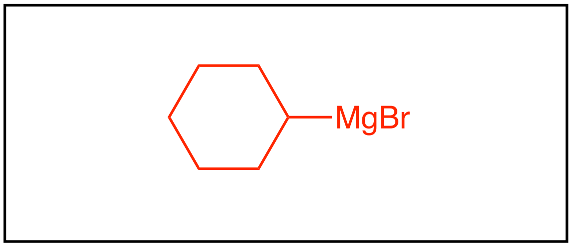
12. (11 pts. total) Complete the mechanism for the following Grignard reaction. **Be sure to show arrows to indicate movement of all electrons, write all lone pairs, all formal charges, and all the products for each step.** Remember, I said all the products for each step. **IF A NEW CHIRAL CENTER IS CREATED MARK IT WITH AN ASTERISK AND WRITE "RACEMIC" IF APPROPRIATE. In the box provided next to each arrow write the mechanistic element used ("Add a proton" etc.)**

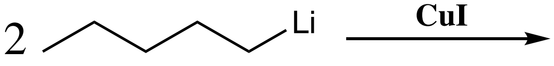


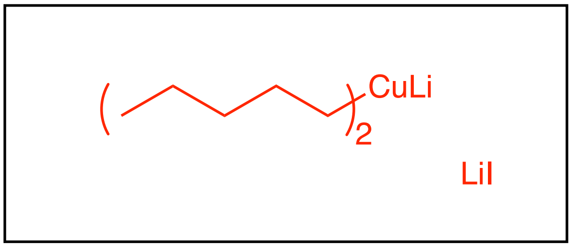
(You do not need to draw the Mg-containing product)

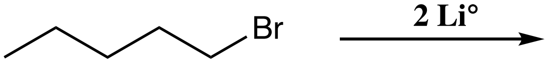
13. (3 or 5 pts.) Write the predominant product or products that will occur for each transformation. **If a new chiral center is created and a racemic mixture is formed, you must draw both enantiomers and write "racemic" under the structure. Use wedges (◀) and dashes (|||||) to indicate stereochemistry. 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.**

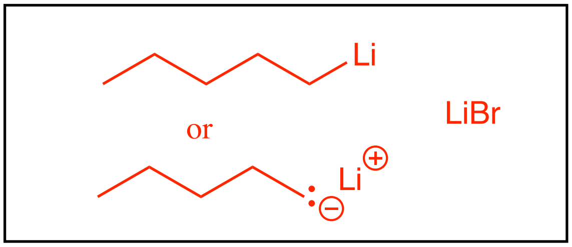


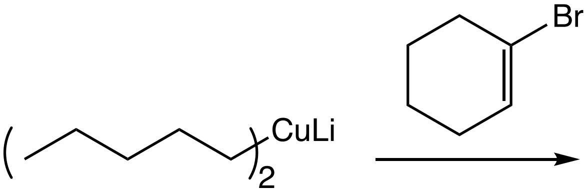


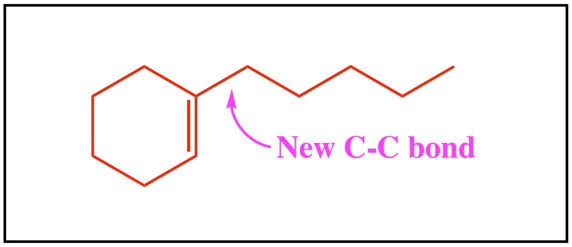


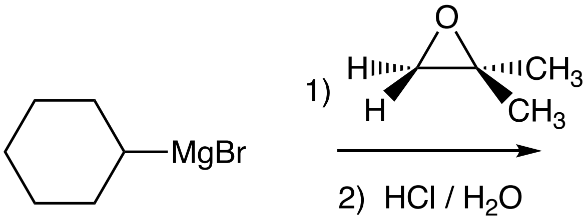


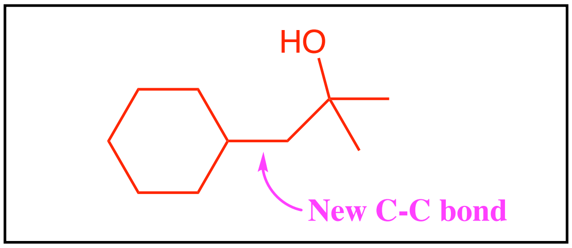


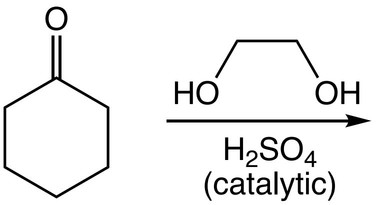


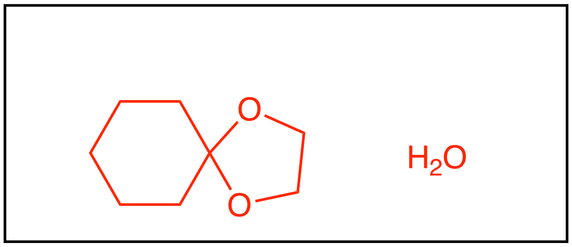




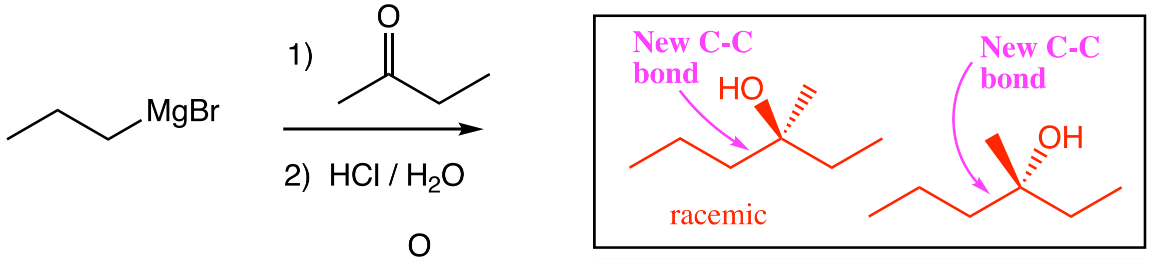


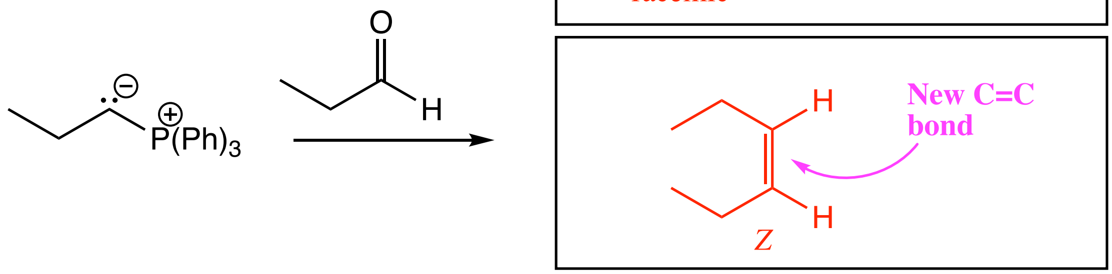


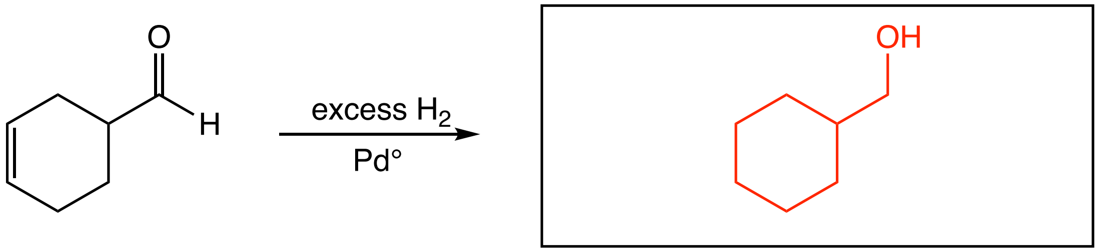


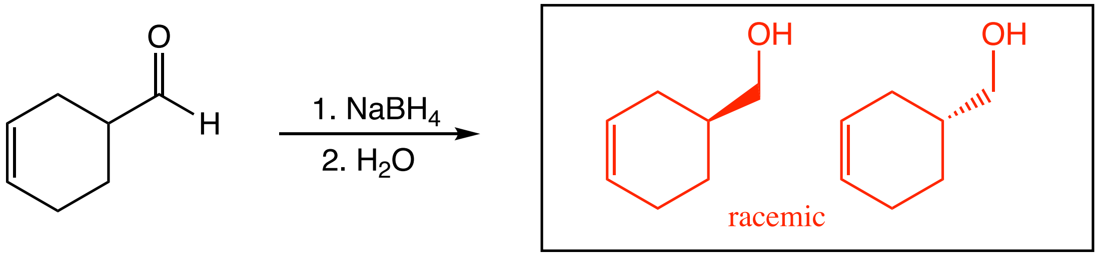


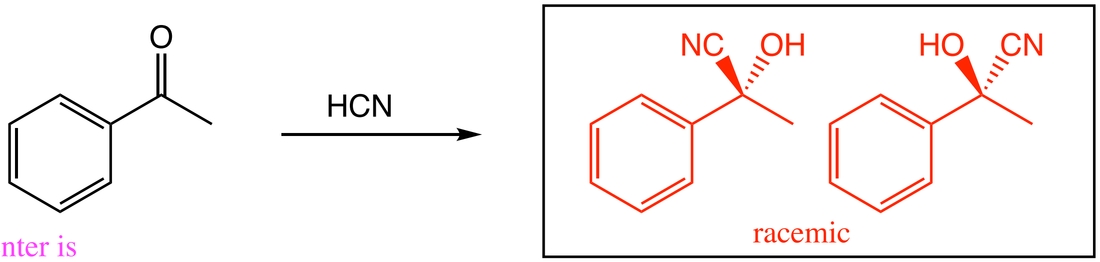
14. (3 or 5 pts.) Write the predominant product or products that will occur for each transformation. **If a new chiral center is created and a racemic mixture is formed, you must draw both enantiomers and write "racemic" under the structure. Use wedges (◀) and dashes (⋯) to indicate stereochemistry. 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.**



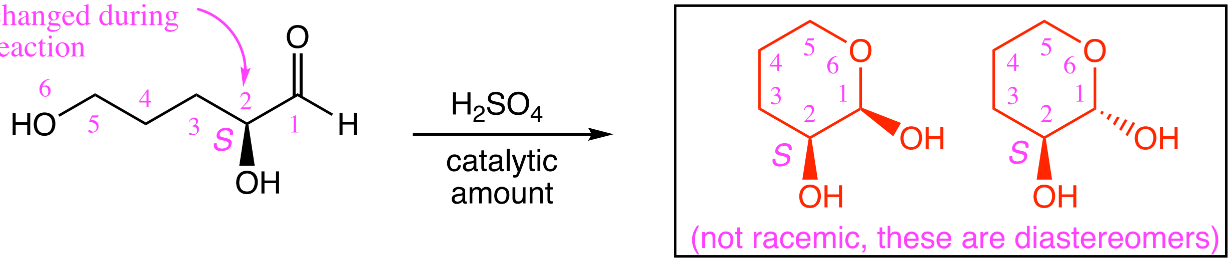




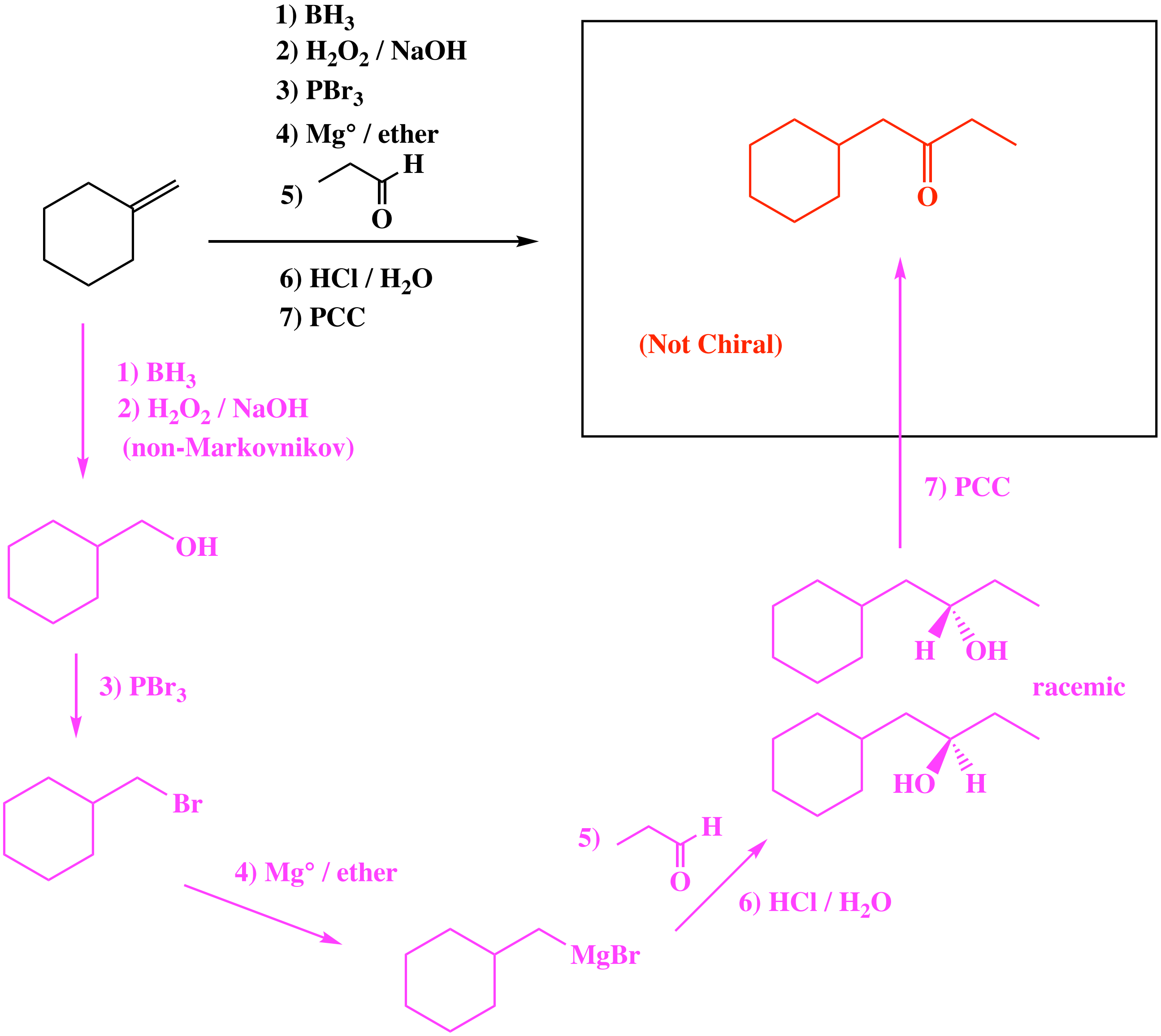




This *S* chiral center is not changed during the reaction

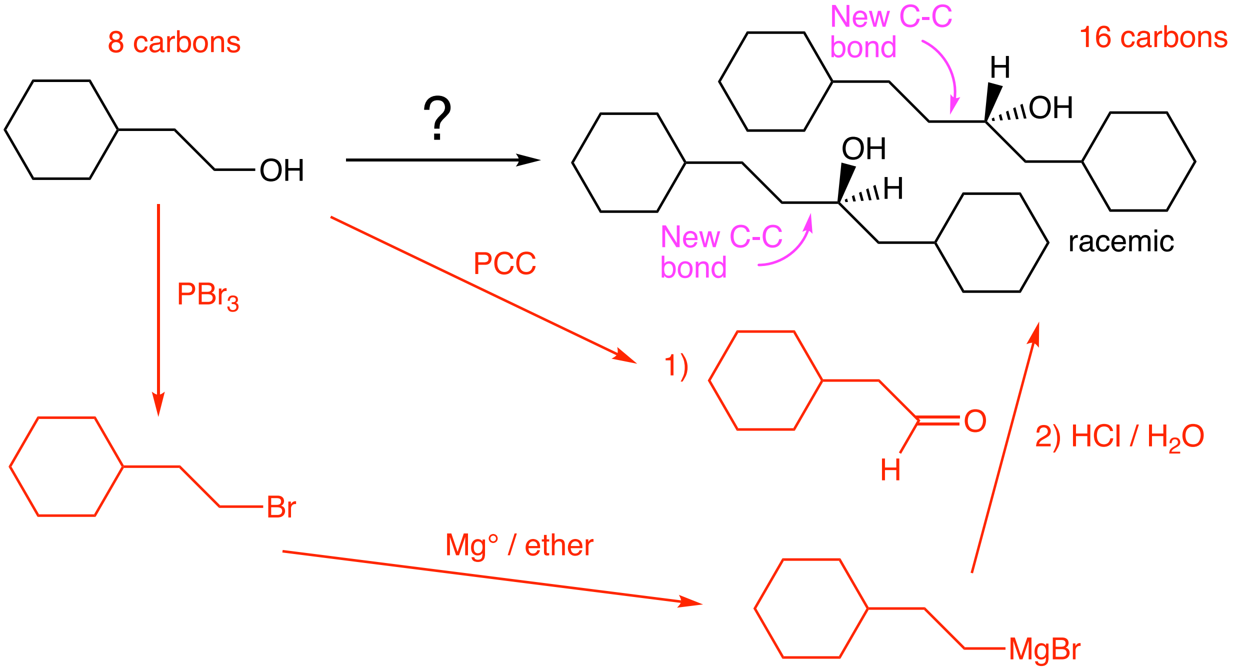


15. (7 pts) Here are a series of syntheticsteps that produce a complex product from simple starting materials. You only need to draw the final product in the box. If a racemic mixture is formed, you need to use wedges and dashes to indicate stereochemistry, making sure to and write "racemic" if appropriate. You can use the bottom of the page for scratch paper. Note we will only grade the final product structure so be careful!



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. 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.

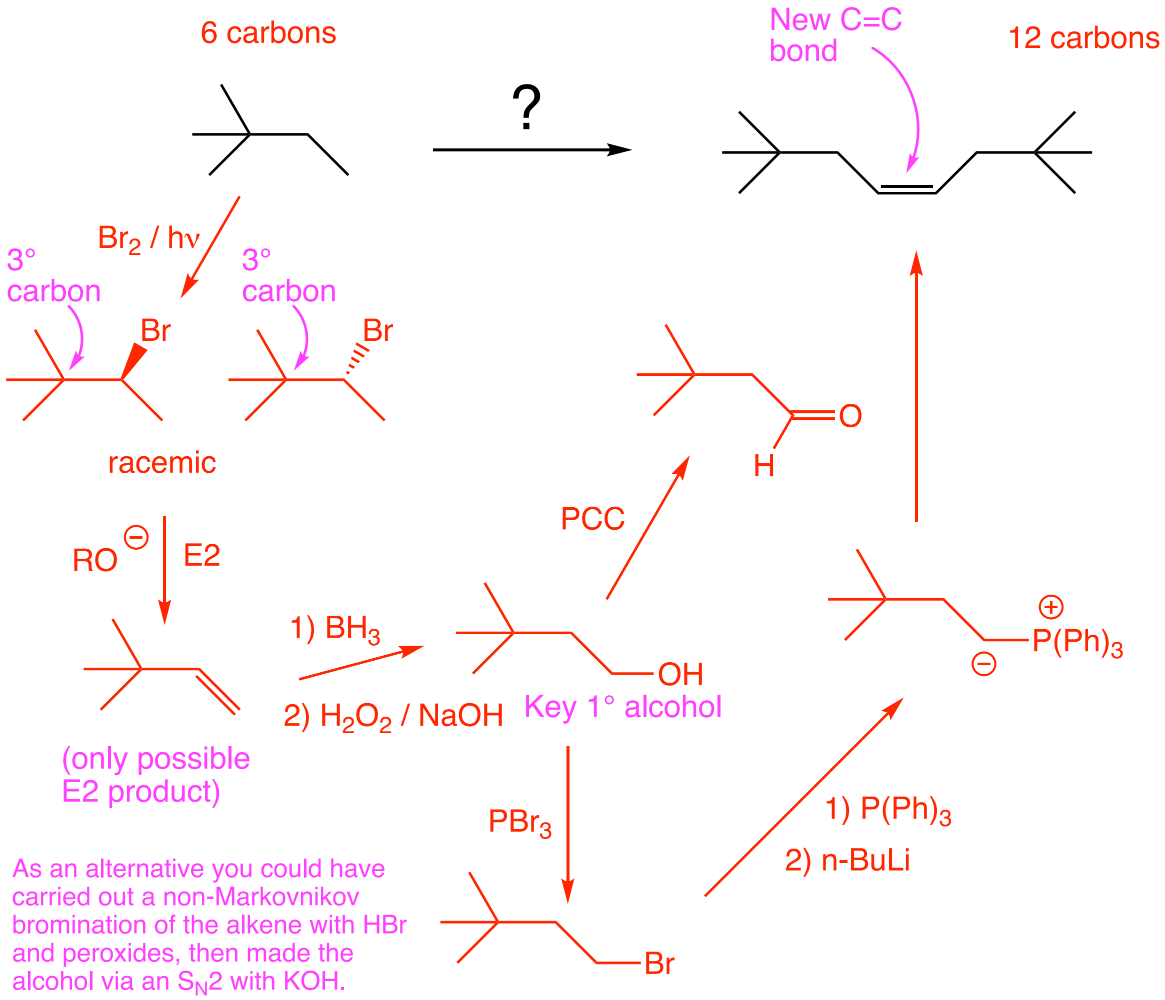
(10 pts) **All of the carbon atoms of the products must come from the starting materials.**



Recognize the product has 16 carbons and the starting material has 8, therefore there must be a new C-C bond created in the middle of the product as indicated. That means the product contains an OH group on the carbon of a new C-C bond, the KRE of a Grignard reagent reacting with an aldehyde. **Recognize** that both the required aldehyde and the required Grignard reagent have 8 carbons, and both can be made from the starting 8 carbon alcohol. The aldehyde can be made via PCC from the starting alcohol, while the Grignard reagent is produced in a two-step process involving conversion of the alcohol to the bromoalkane followed by reaction with Mg° in ether.

17. 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.

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

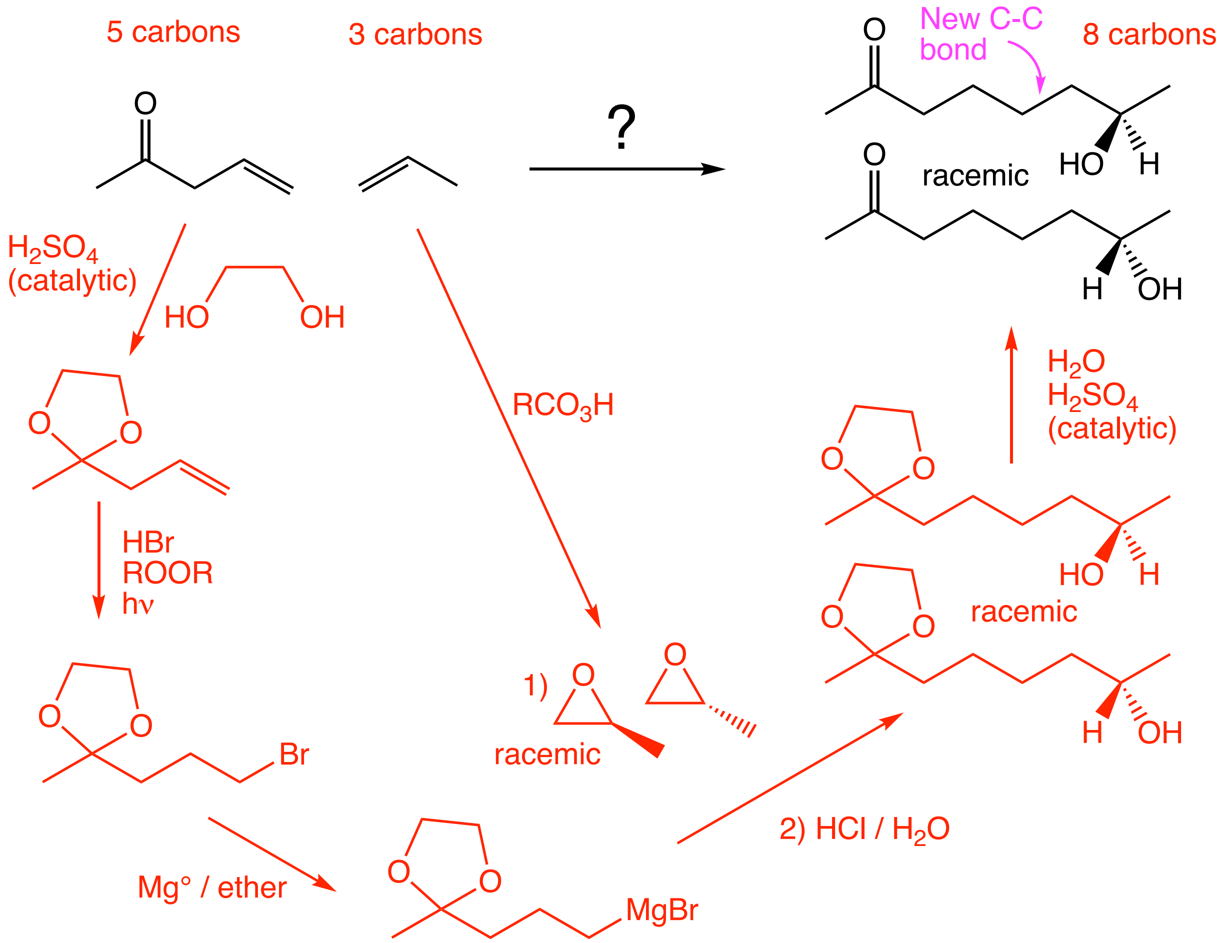


As an alternative you could have carried out a non-Markovnikov bromination of the alkene with HBr and peroxides, then made the alcohol via an S_N2 with KOH.

Recognize that the product has 12 carbons while the starting alkane has 6, therefore the new bond is the central C=C with Z stereochemistry. A new C=C bond with Z stereochemistry is the KRE of an alkyl WIttig reagent reacting with an alldehyde. **Recognize** that the required aldehyde and Wittig reagent can both be derived from the same primary alcohol as shown. A difficult part of this synthesis problem is figuring out how to make the key primary alcohol from the starting alkane. The best approach is to carry out a non-Markovnikov hydroboration - oxidation af an alkene, that itself can be made via the E2 elimination of the racemic bromoalkane that comes from bromination of the starting alkane using UV light. Note that halogenation with UV light is the only reaction that uses an alkane as starting material, so you should always assume this is the first step with an alkane starting material. Note also that in the E2 elmination step, the tertiary carbon center has no H atoms to be removed, so the terminal alkene is the only one that can form from the bromoalkane.

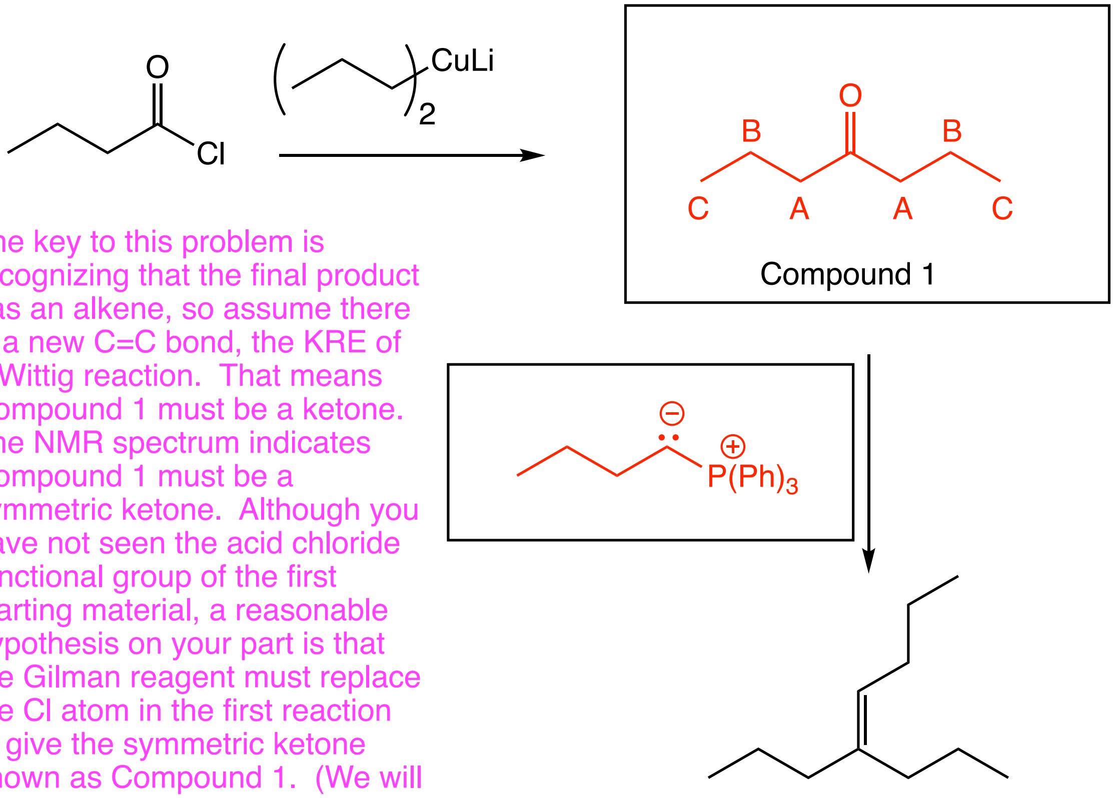
18. These are synthesis questions. You need to show how the starting material can be converted into the product(s) shown. You may use any reactions we have learned. Show all the reagents you need. Show each molecule synthesized along the way and be sure to pay attention to the regiochemistry and stereochemistry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



Recognize that the product has a methyl ketone function and 8 carbons, while the starting materials have 3 and 5 carbons, the five carbon piece being a methyl ketone. Therefore predict the methyl ketone is retained in the product and the new C-C bond must be as shown. **Recognize** the new C-C bond is on the carbon adjacent to the OH group, the KRE of a Grignard reagent reacting with an epoxide. The required epoxide can be made directly from the starting three carbon alkene. Note that the methyl ketone function requires a cyclic acetal protecting group in order to construct the required Grignard reagent as shown.

19. (10 pts) You have not seen the first reaction before, it comes from a much later chapter. The NMR spectrum of the predominant product of the first step (referred to as "Compound 1") is shown. Using your growing intuition about chemical reactivity as well as the NMR, draw the structure of Compound 1, as well as the structure of the reagent that is missing beside the arrow. Hint: the missing reagent next to the arrow will add carbons to the product.



The key to this problem is recognizing that the final product has an alkene, so assume there is a new C=C bond, the KRE of a Wittig reaction. That means Compound 1 must be a ketone. The NMR spectrum indicates Compound 1 must be a symmetric ketone. Although you have not seen the acid chloride functional group of the first starting material, a reasonable hypothesis on your part is that the Gilman reagent must replace the Cl atom in the first reaction to give the symmetric ketone shown as Compound 1. (We will see this reaction in a couple of chapters.)