NAME (Print): _____

SIGNATURE: _____

Chemistry 320N
Dr. Brent Iverson
1st Midterm
Feb. 19, 2015

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		(20)
2		(11)
3		(5)
4		(5)
5		(5)
6		(12)
7		(12)
8		(16)
9		(19)
10		(26)
11		(15)
12		(16)
13		(15)
14		(10)
15		(13)
16		(16)
17		(13)
18		(17)
Total		(246)

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Student Honor Code

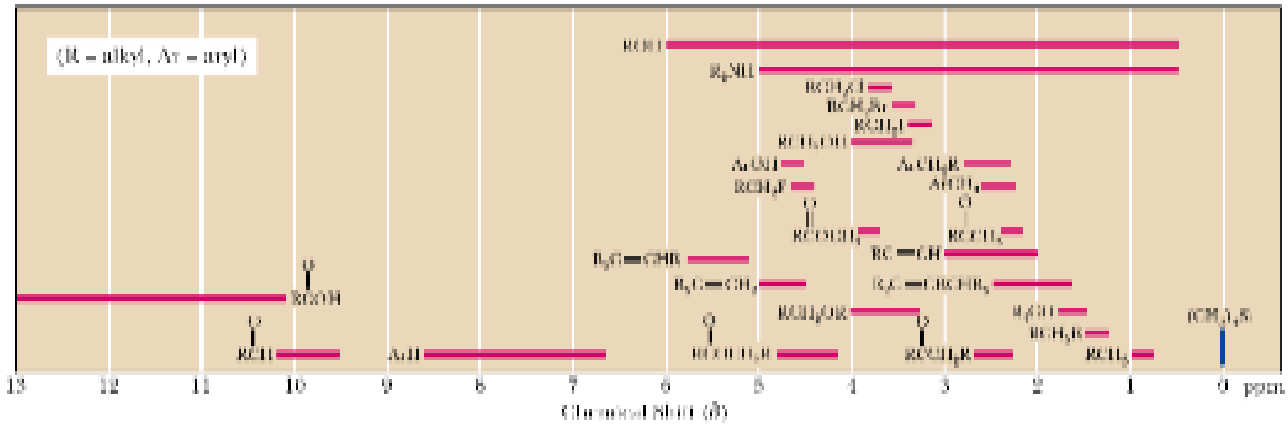
"As a student of The University of Texas at Austin, I shall abide by the core values of the University and uphold academic integrity."

_____

(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	$H_2C{-}CH_2$	3.3-4.0
$ArCH_3$	2.2-2.5		
RCH_2NR_2	2.3-2.8	RCH	9.5-10.1
RCH_2I	3.1-3.3		
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 _____(20)

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.

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**.

2. (1 pt. each) Suppose you place a sample of a molecule in a very strong laboratory magnetic field. Circle the following statements that are true:

"Resonance" in NMR refers to the phenomenon of absorption of energy when a nuclear spin "flips".

A ^{1}H nucleus surrounded by greater electron density feels a stronger net magnetic field (external magnetic field plus the induced magnetic field from the circulating electron density) compared to a ^{1}H nucleus surrounded by less electron density.

A ^{1}H nucleus surrounded by greater electron density is considered to be more shielded.

A ^{1}H nucleus surrounded by greater electron density comes into resonance (absorbs electromgnetic radiation) at a higher frequency (larger ppm).

At room temperature, for a given H atom, slightly more than half of the nuclei are in the +1/2 spin state, while slightly less than have are in the -1/2 spin state.

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

3. (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_____.

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.

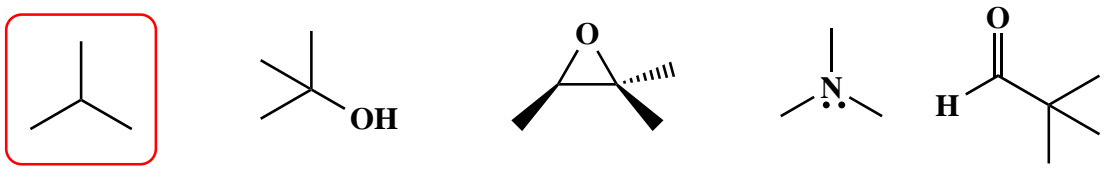
Electron density is induced to move in a strong external magnetic field, and this movement induces a magenetic field that is opposed to the external magnetic field. This has the effect of _____shielding_____ the underlying nuclei from the external magnetic field.

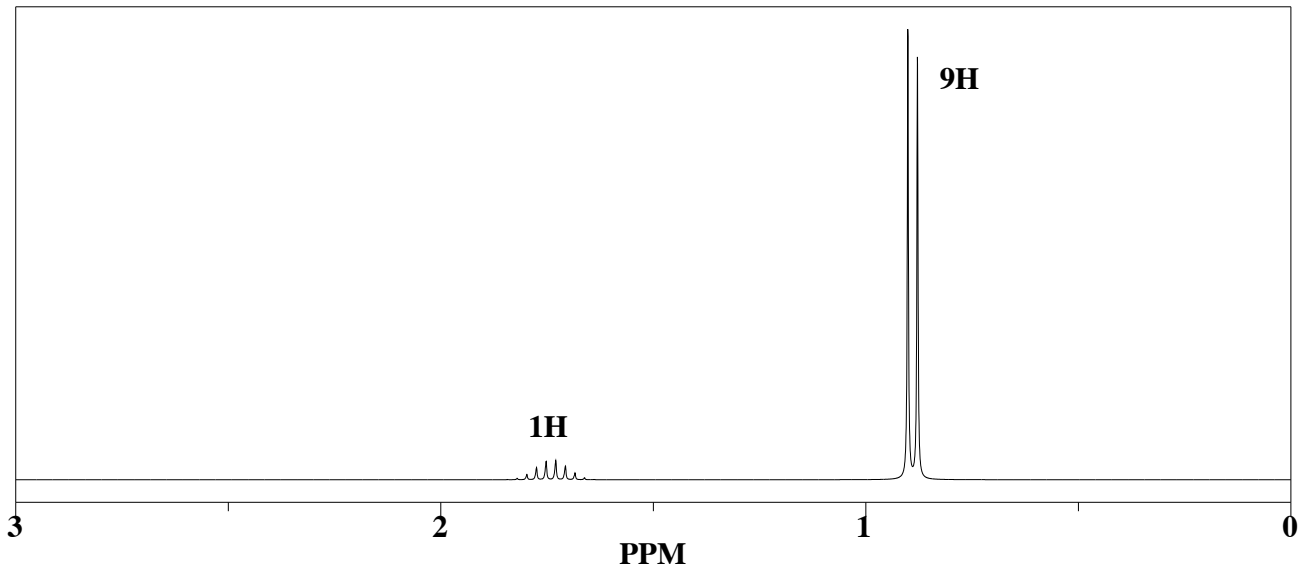
All other factors being the same, the signal for an ^{1}H atom with greater electron density around it will come at _____lower_____ ppm in an NMR spectrum compared to a similar ^{1}H atom with less electron density.

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

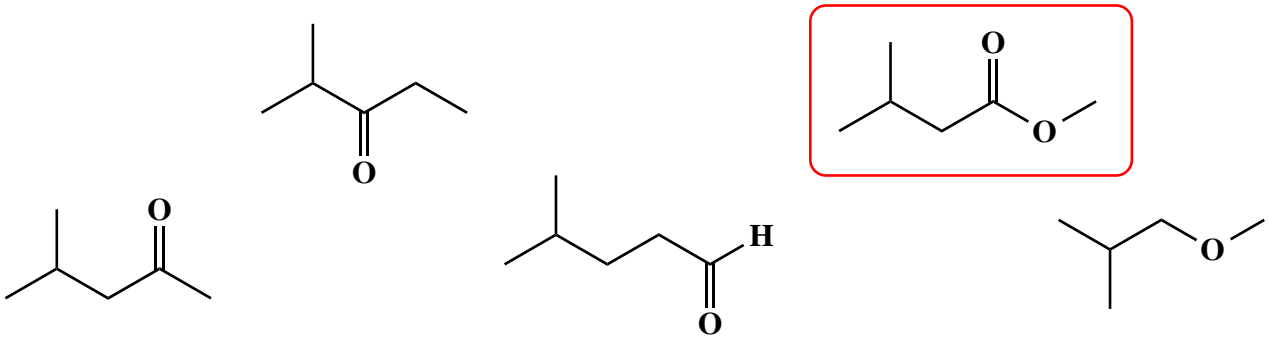
The _____coupling_____ _____constant_____ is the distance between peaks in a ^{1}H NMR signal that has been split due to spin-spin coupling.

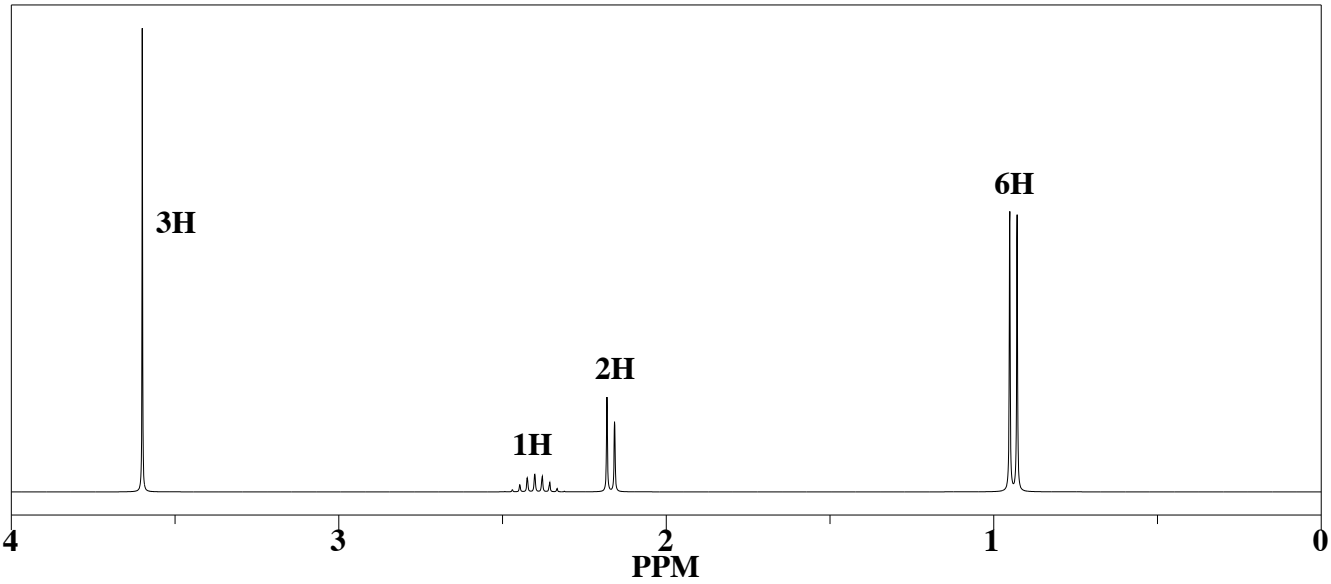
4. (5 pts) Circle the molecule that corresponds to the NMR spectrum shown below.



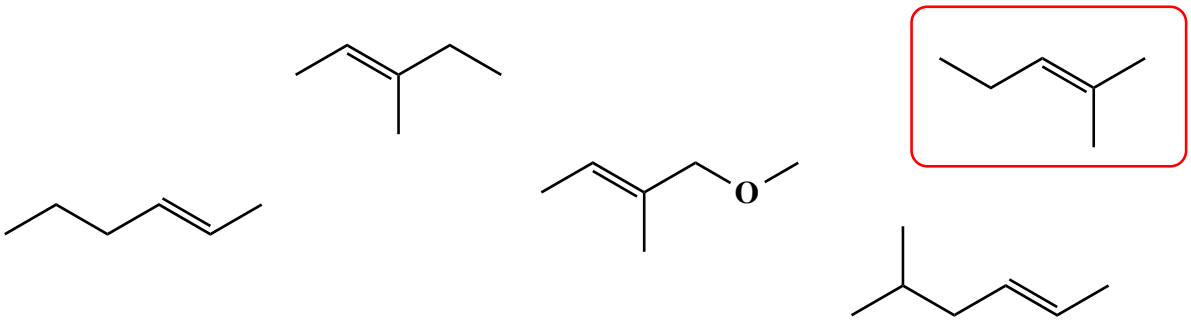


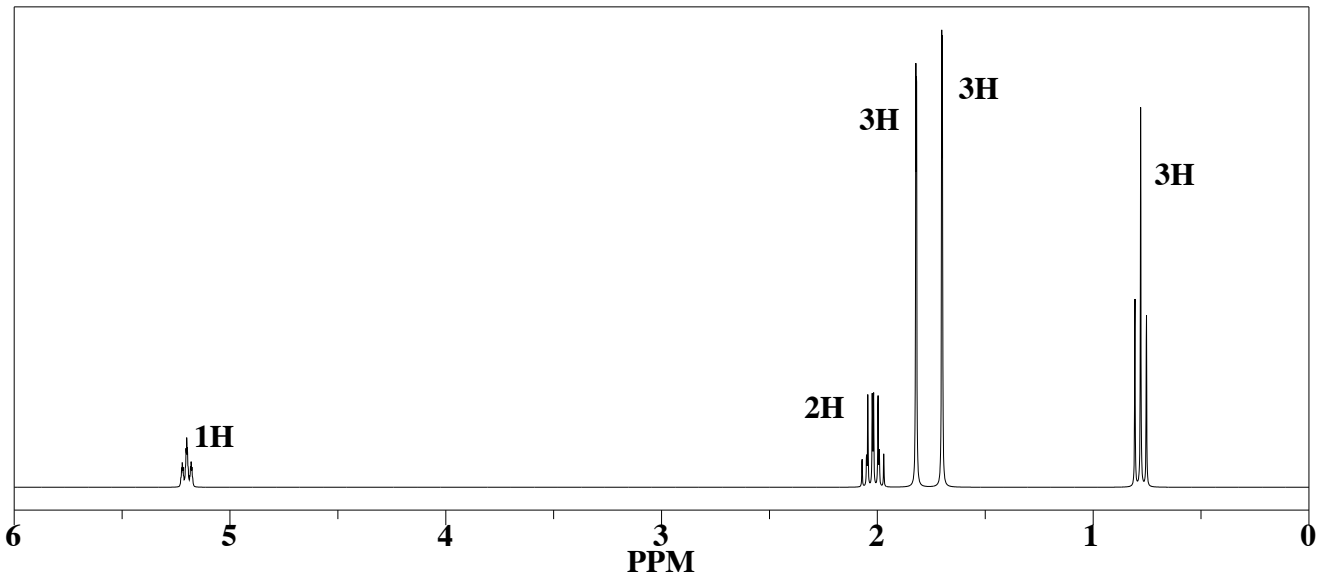
5. (5 pts) Circle the molecule that corresponds to the NMR spectrum shown below.



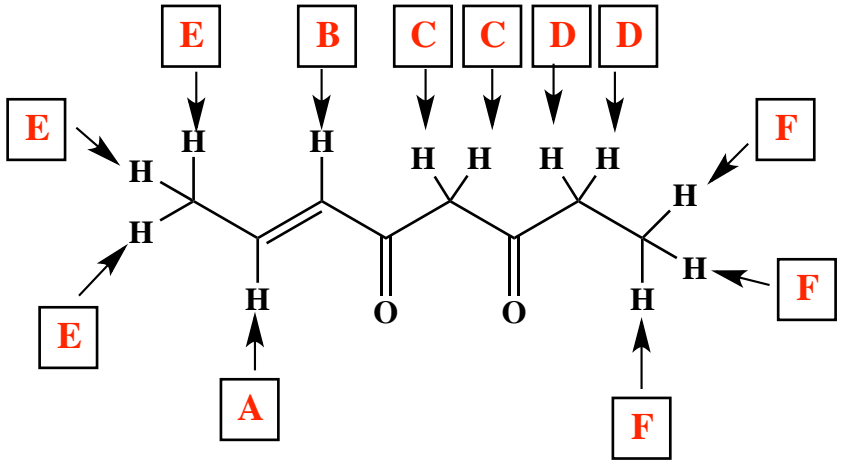


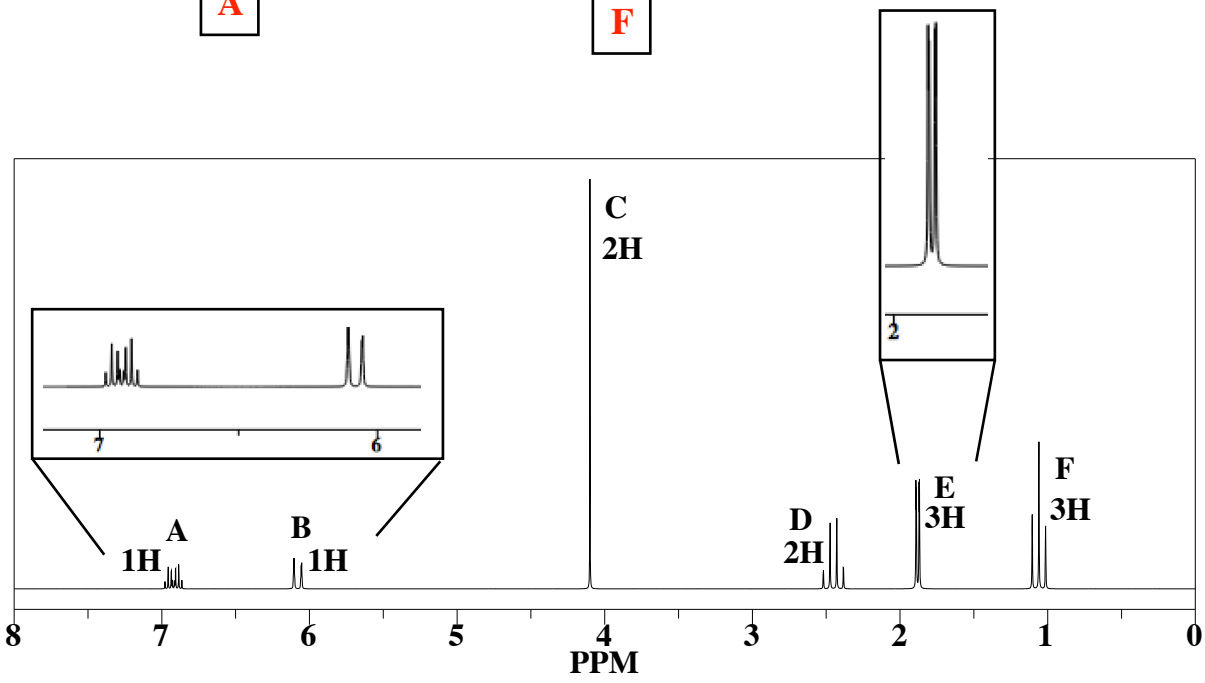
6. (5 pts) Circle the molecule that corresponds to the NMR spectrum shown below.





7. (12 pts) In the boxes provided, place that letter (A, B, C, etc.) that corresponds to the signals in the spectrum provided below.



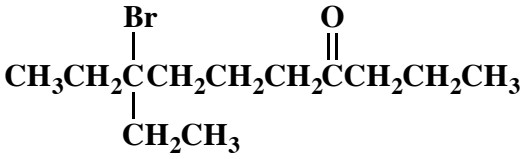


8. (3 pts) The most important question in organic chemistry is:

Where are the electrons?

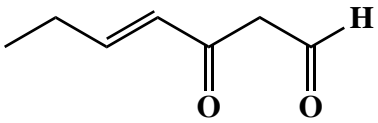
9. (3 pts each) Write an acceptable IUPAC name or draw a structural formula for the following molecules:

A.



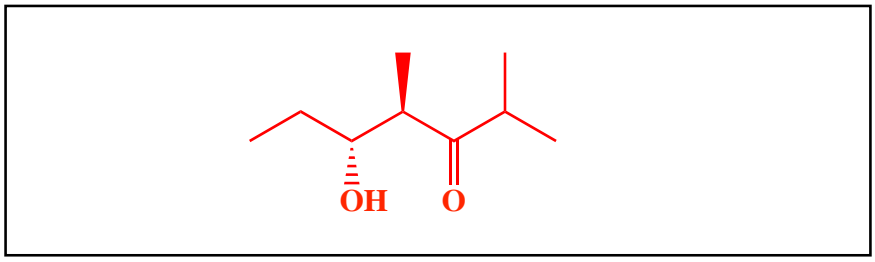
8-Bromo-8-ethyl-4-decanone

B.

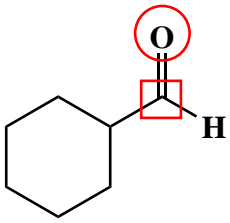


(*E*)-3-oxo-4-heptenal

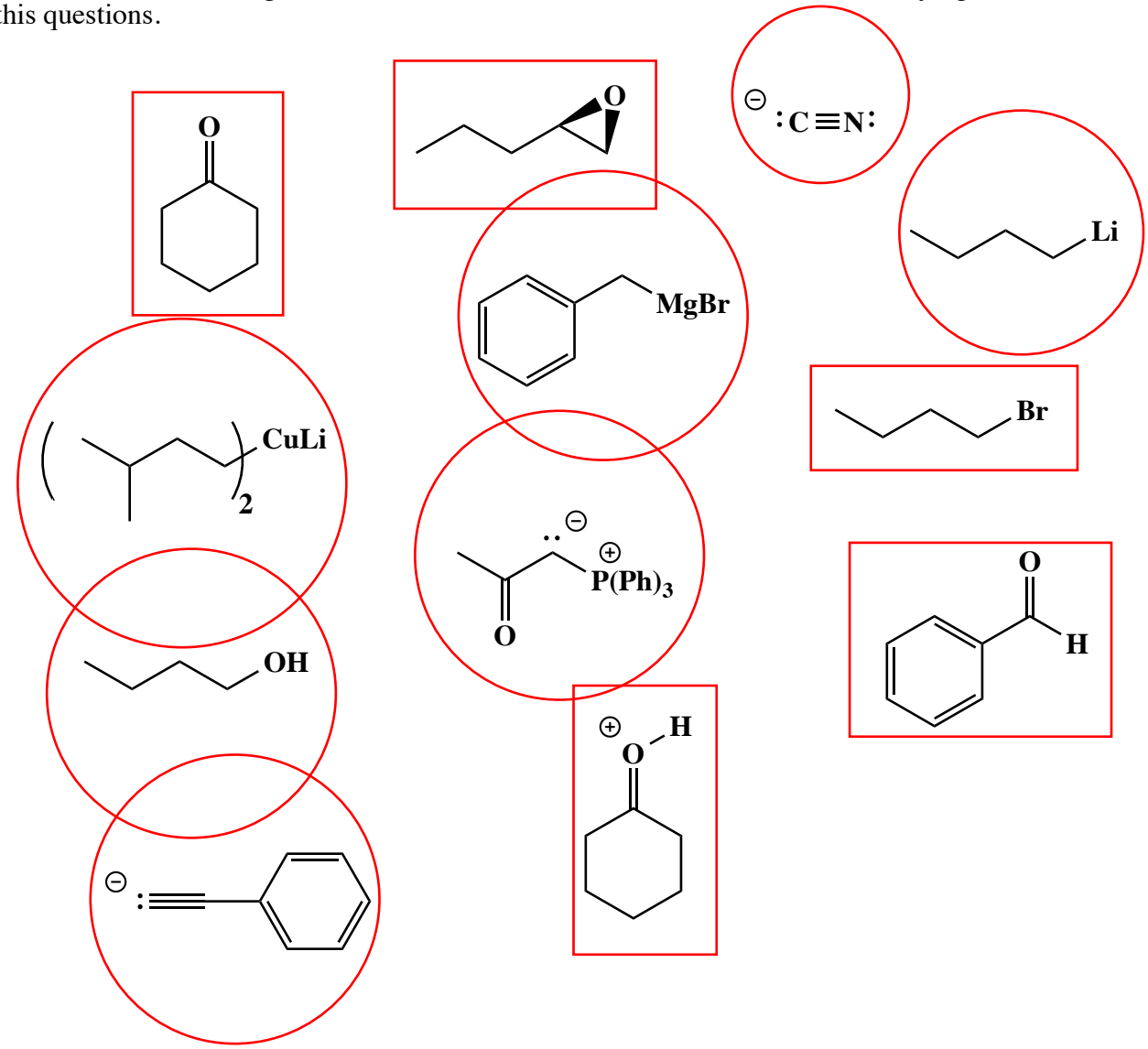
C. **(4*R*,5*R*)-5-hydroxy-2,4-dimethyl-3-heptanone**



10. (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.



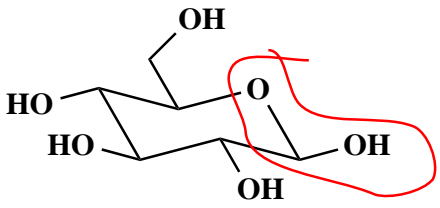
11. (12 pts) Being able to recognize the chemical personality of different species is one of the most important skills you can develop in Organic Chemistry. For the following DRAW A BOX AROUND ANY SPECIES THAT CAN BE CONSIDERED AN ELECTROPHILE, and DRAW A CIRCLE AROUND ANY SPECIES THAT CAN BE CONSIDERED A NUCLEOPHILE. Notice that some of the nucleophiles can also be considered bases, but we are not worrying about that for this questions.



Signature_____

12. (2 pts) The most important question in chemistry is:_____Where are the electrons?_____ ?

13. (7 pts) Shown below is one form of glucose. **Draw a circle around the hemiacetal group (Yep this sweet molecule has a "hemi" in it!)** Then answer the question below the structure.



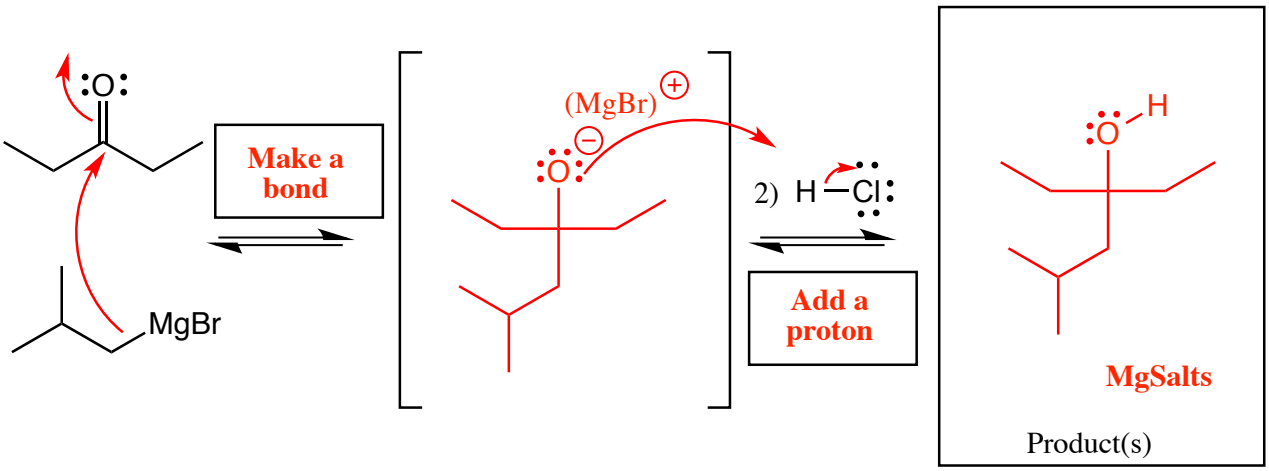
Circle the correct statement:

The structure represents the α form of glucose

The structure represents the β form of glucose

The structure represents the ΔΓ form of glucose

14. (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 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.



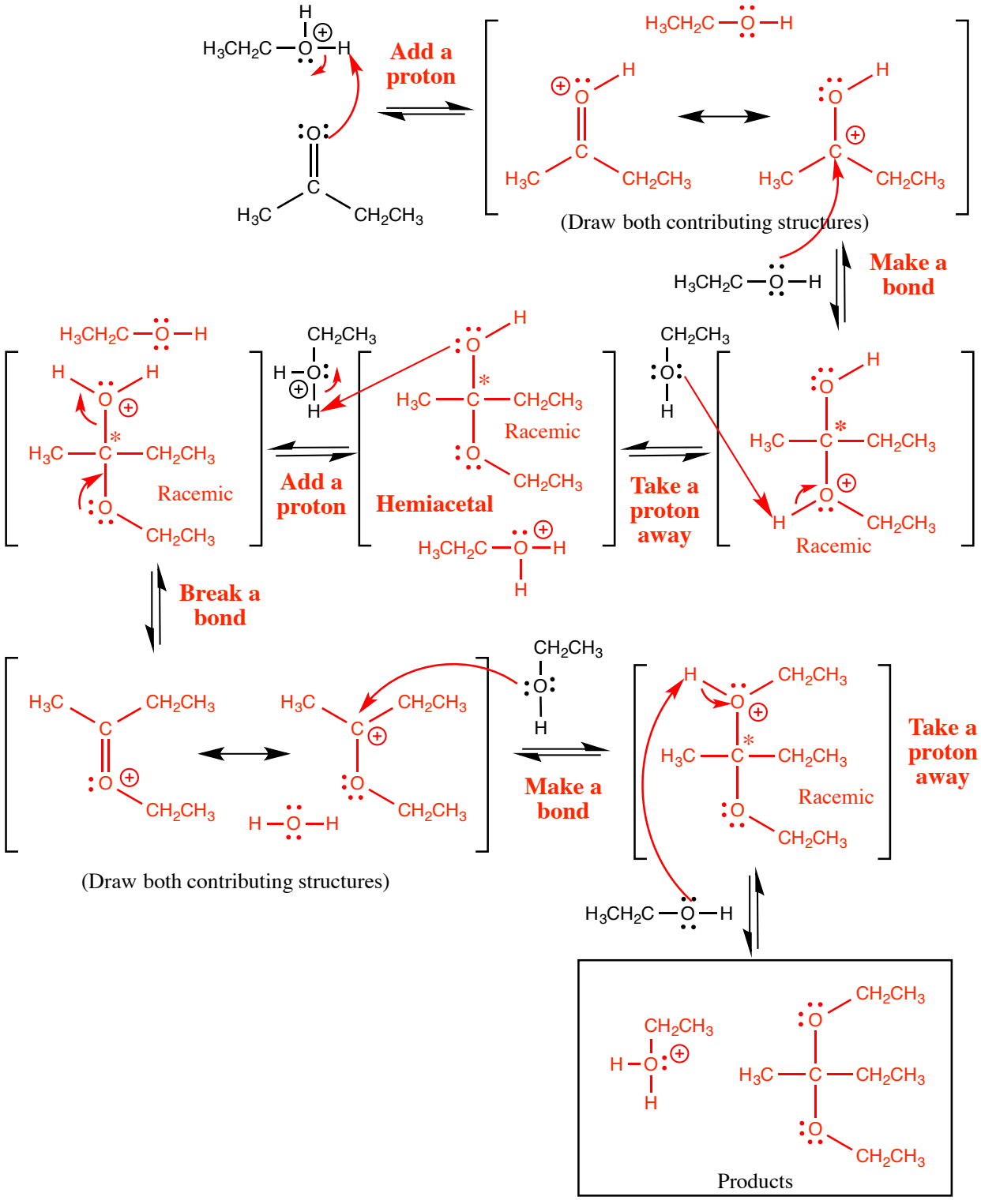
In the boxes provided adjacent to the first two sets of arrows, write which of the four basic mechanistic elements are involved (i.e. "Make a bond", "Add a proton", etc.

⇑

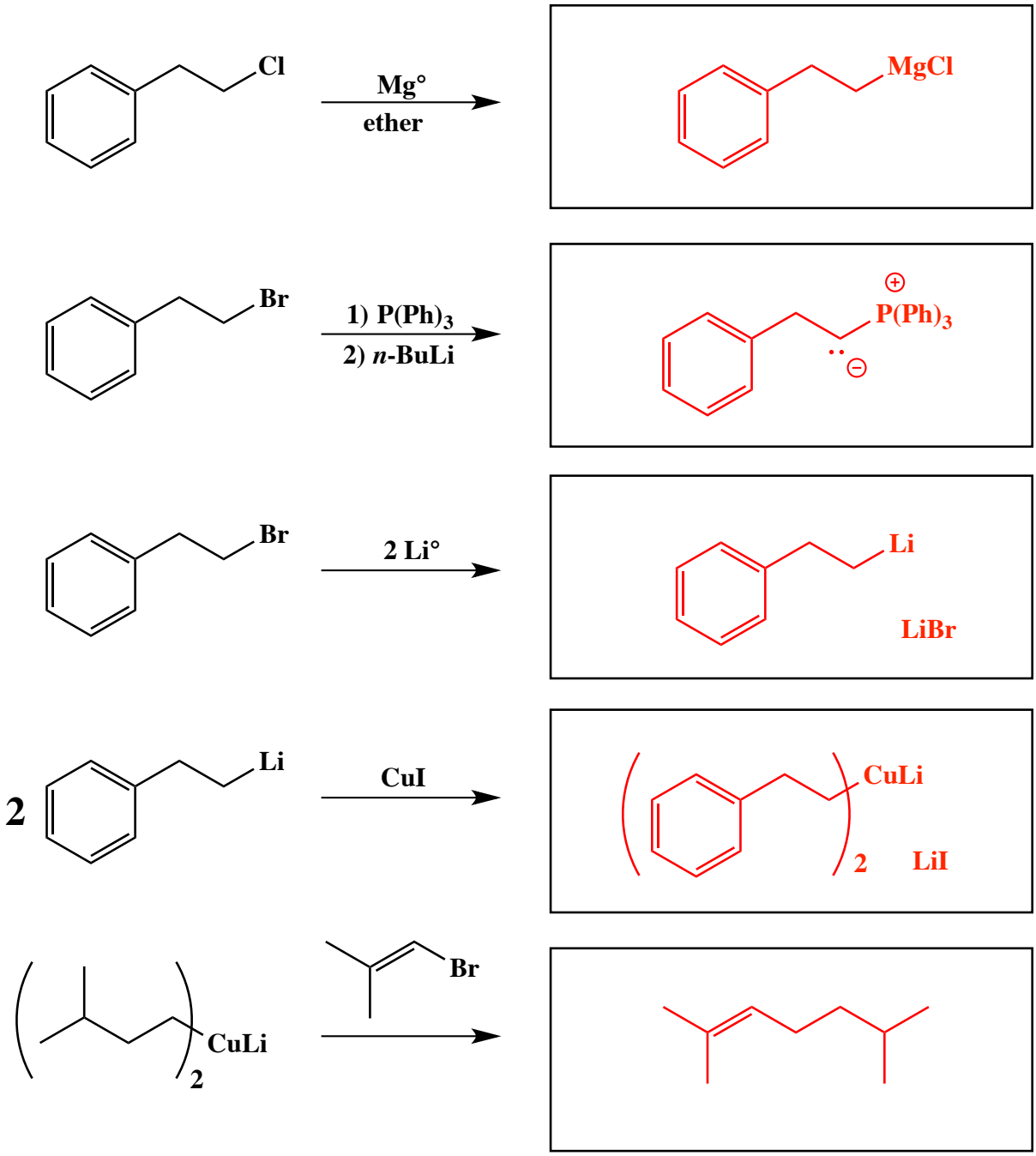
NOTICE THIS

15. (26 pts. total) 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 MARK IT WITH AN ASTERISK AND WRITE RACEMIC IF APPROPRIATE . Do not draw arrows to indicate how one contributing structure relates to the other.**

Acid Catalyzed Acetal Formation from a Ketone



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.**



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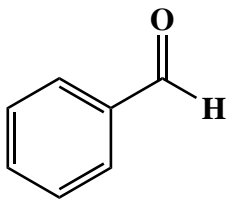
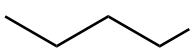
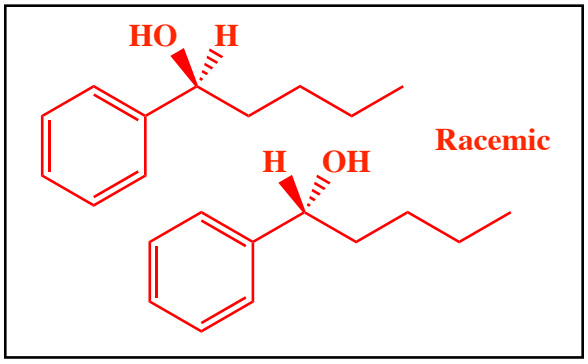
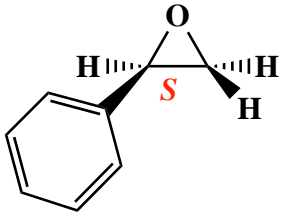
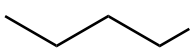


1) 

2) HCl/H_2O (mild)





1) 

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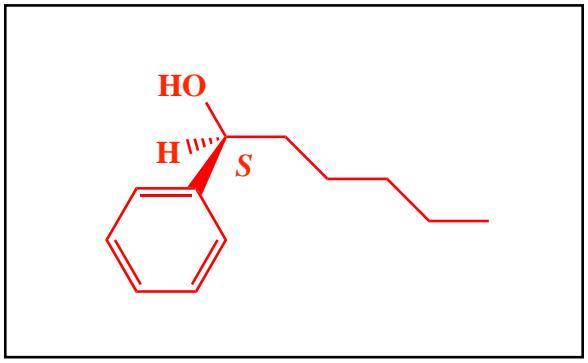
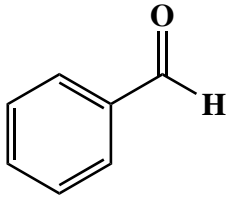
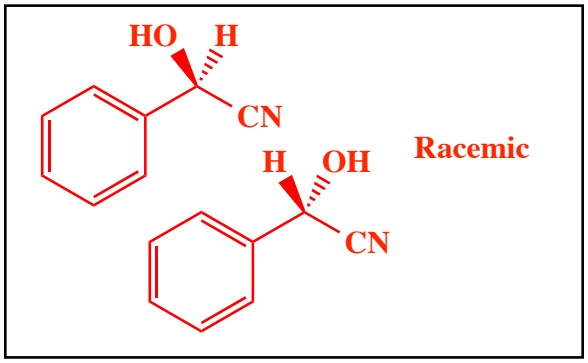
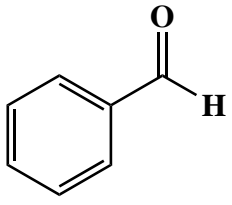
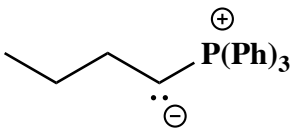




HCN →







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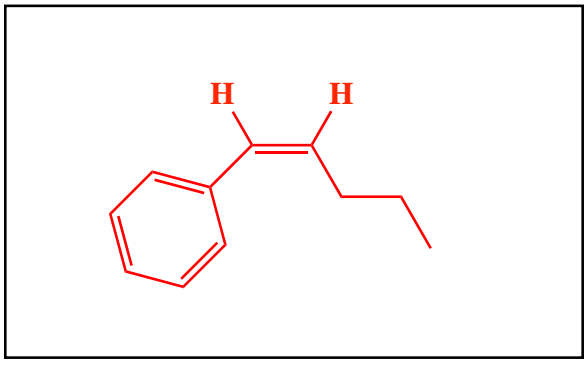
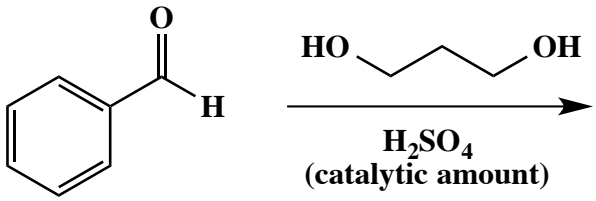
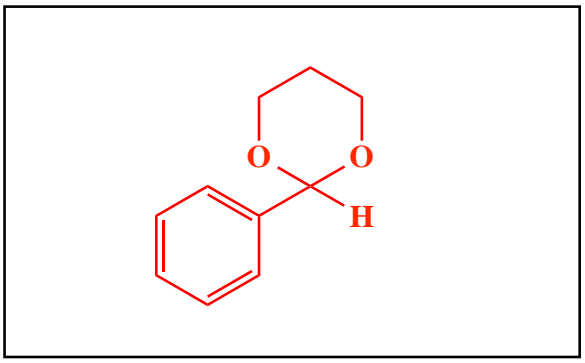
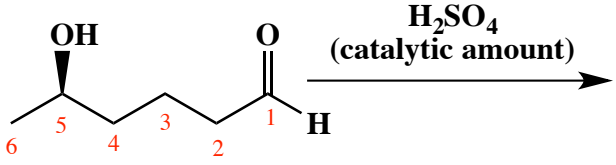
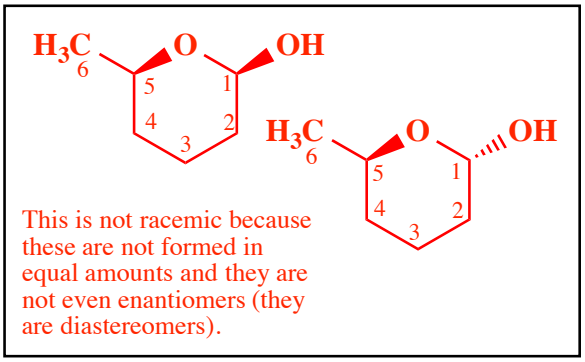


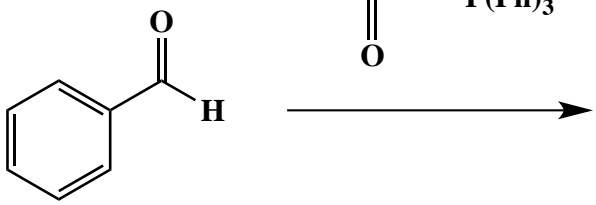
16. (3 or 5 pts.) Write the predominant product or products that will occur for each transformation. **If a new chiral center is created and a racemic mixture is formed, you must draw both enantiomers and write "racemic" under the structure. Use wedges (◄) and dashes (·····) to indicate stereochemistry.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

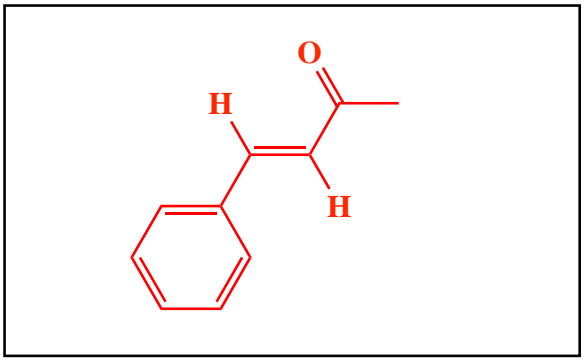


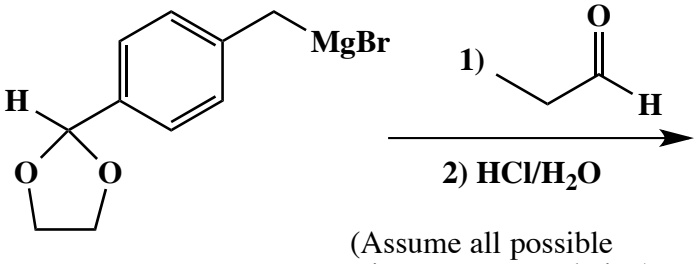




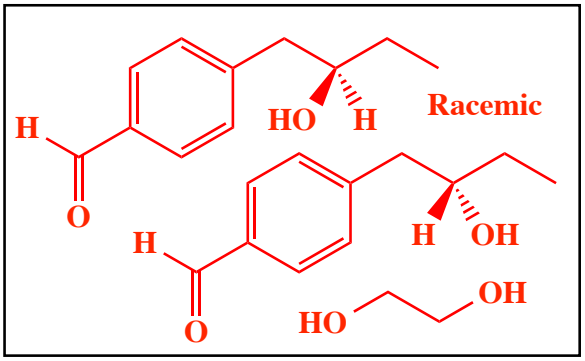








(Assume all possible reactions go to completion)

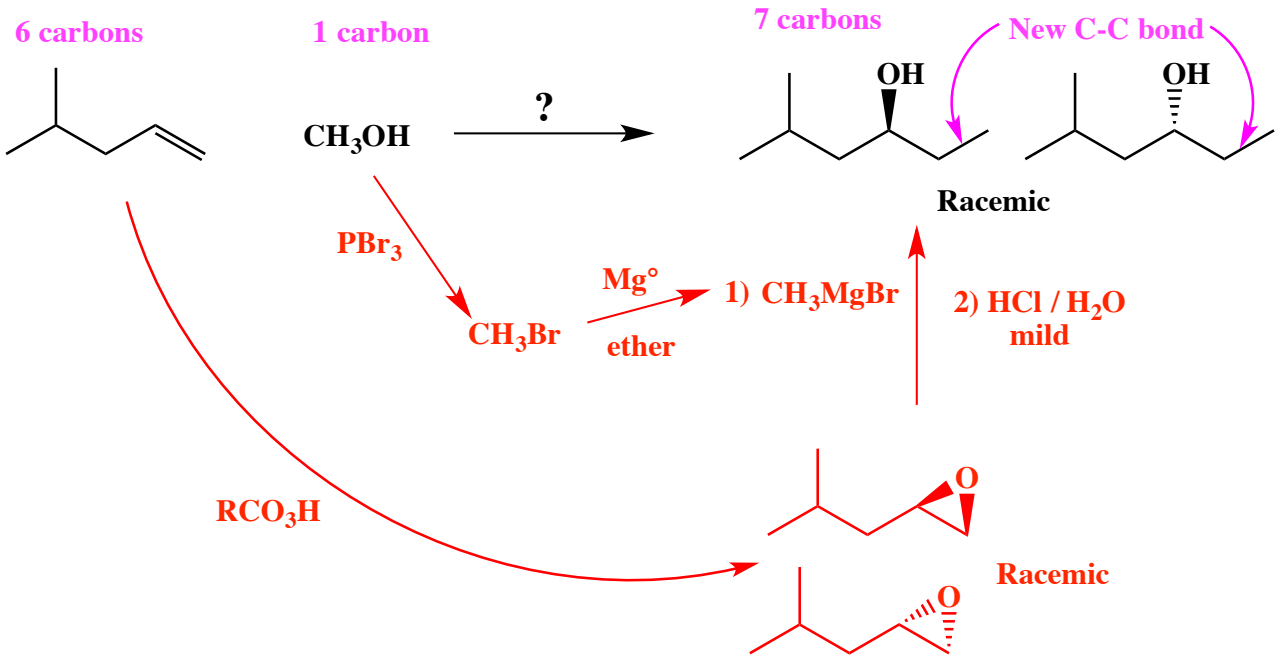


x

Signature_____ Pg 14_____(10)

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.

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



Recognize that the product has 7 carbons, and the starting materials have 6 and 1, respectively. Therefore they must combine implying a new C-C bond as indicated. Notice also, that the OH group of the product is two bonds away from the new C-C bond, the KRE of an epoxide reacting with a Grignard reagent. Predict the last step to be the reaction between the racemic epoxide shown with methylGrignard. **Recognize** the methylGrignard coming from methanol via reaction with PBr_3 followed by Mg° in the presence of ether. **Recognize** the epoxide comes from reaction of the starting alkene with a peracid.

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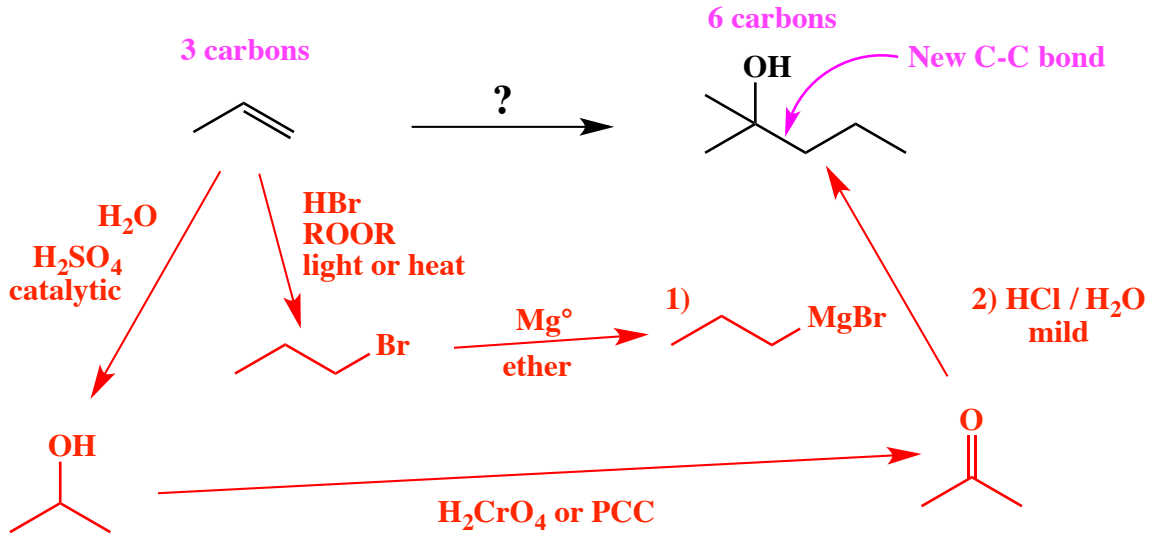
(13 pts) **All of the carbon atoms of the products must come from the starting materials.**



Recognize that the product has 6 carbons, and the starting material has 3. Therefore there must be a new C-C bond linking two three carbon units as indicated. Notice also, that the OH group of the product is on a carbon making the new C-C bond, the KRE of an ketone reacting with a Grignard reagent. Predict the last step to be the reaction between actone with propylGrignard. **Recognize** the propylGrignard as coming from propene via reaction with HBr in the presence of ROOR and hear or light. **Recognize** that acetone can be made from propene via reaction with H_2O in the presence of catalytic H_2SO_4 followed by oxidation with H_2CrO_4 or PCC

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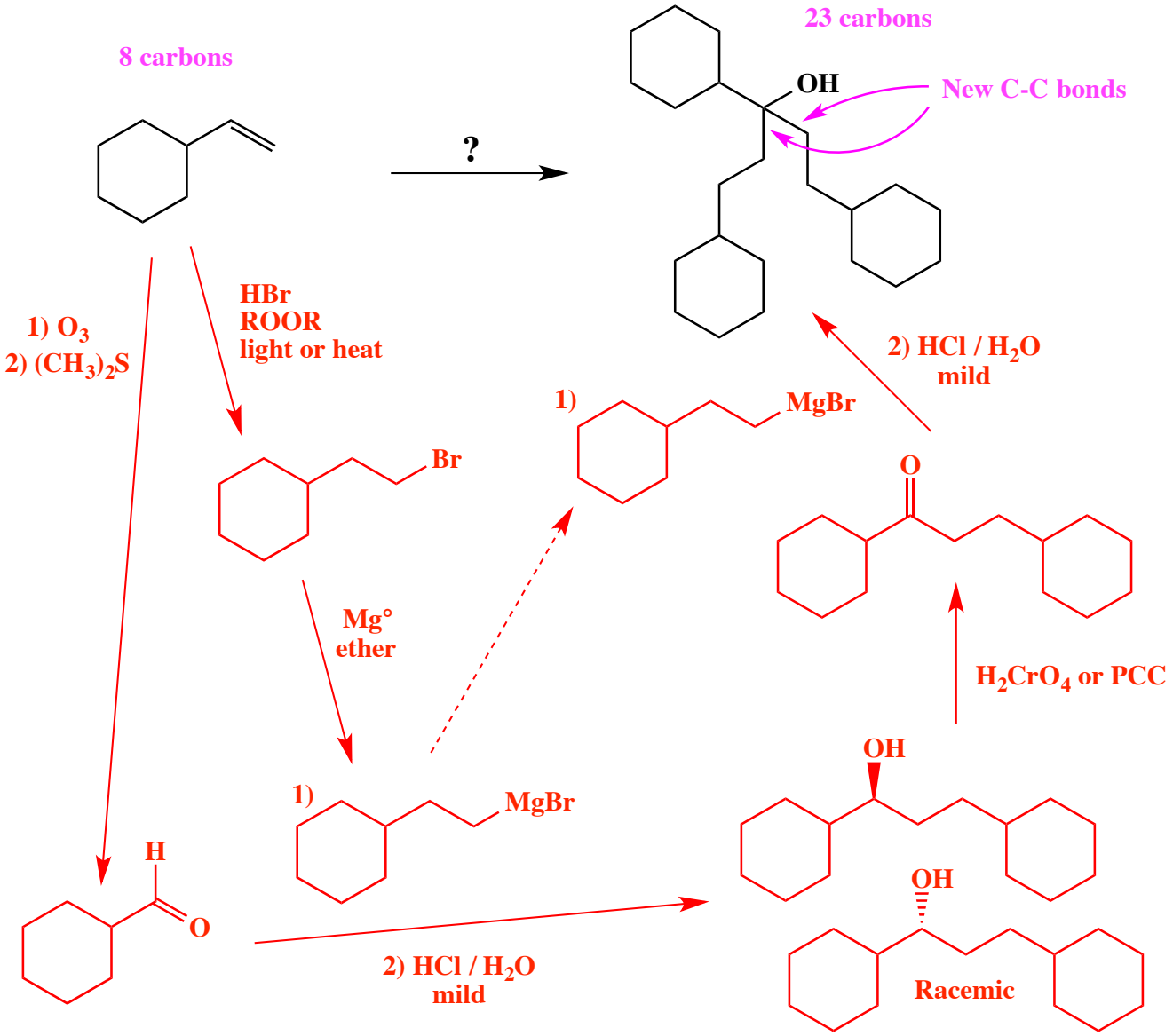
(16 pts) **All of the carbon atoms of the products must come from the starting materials.**



Recognize that the product has 23 carbons (not 24!), and the starting material has 8. Therefore there must be two new C-C bonds linking two 8 carbon units and one 7 carbon unit as indicated. Notice also, that the OH group of the product is on a carbon making the new C-C bonds, the KRE of a ketone reacting with a Grignard reagent. Predict the last step to be the reaction between the ketone shown with an 8 carbon Grignard. **Recognize** the required ketone as being the result of oxidation of the corresponding racemic alcohol, which itself is the product of a 7 carbon aldehyde reacting with the same 8 carbon Grignard. The 7 carbon aldehyde comes from ozonolysis of the 8 carbon starting material, and the 8 carbon Grignard comes from the standard non-Markovnikov brominatin followed by Mg° in ether.

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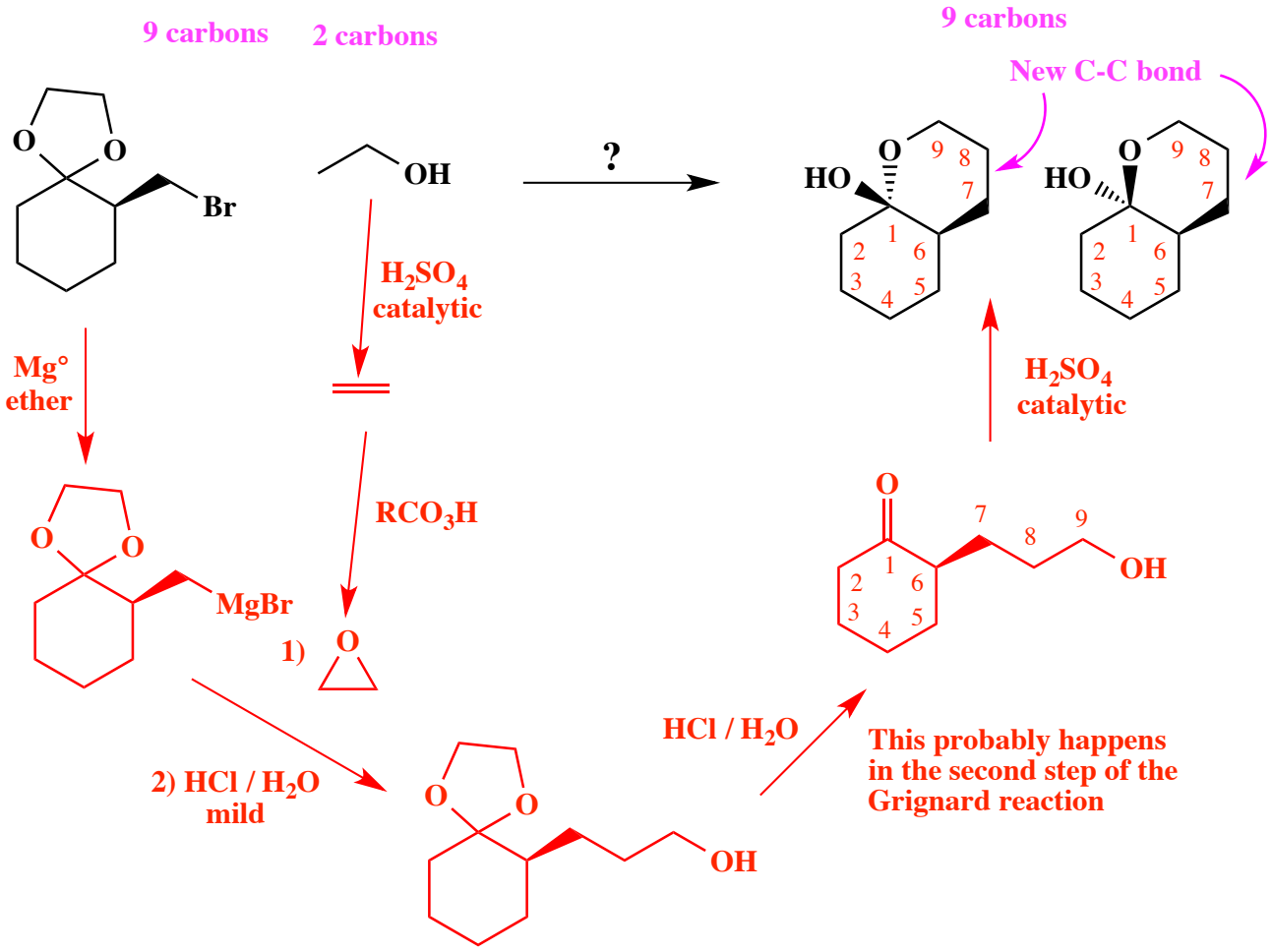
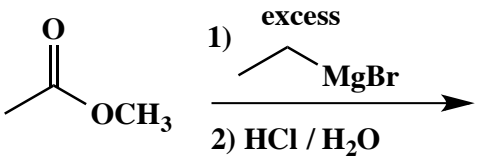
(13 pts) **All of the carbon atoms of the products must come from the starting materials.**



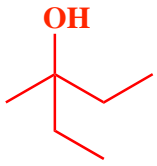
Recognize the product as a cyclic acetal derived from the 9 carbon chiral keto alcohol shown. Notice further where the new C-C bond had to be formed to create the chain long enough to make a new 6-membered ring cyclic hemiacetal. **Recognize** that the 2 carbons required can be put on via reaction of ethylene oxide with the protected Grignard ketone, followed by removal of the protecting group. Ethylene oxice is made from ethanol by first eliminating the OH with catalytic H_2SO_4 to give ethylene followed by reaction with RCO_3H. We already added the cyclic acetal protecting group to the starting bromide derivative for you, so the required Grignard reagent can be made from the starting material plus Mg° in ether. If you got this right, congratulations. You officially rock synthesis!!

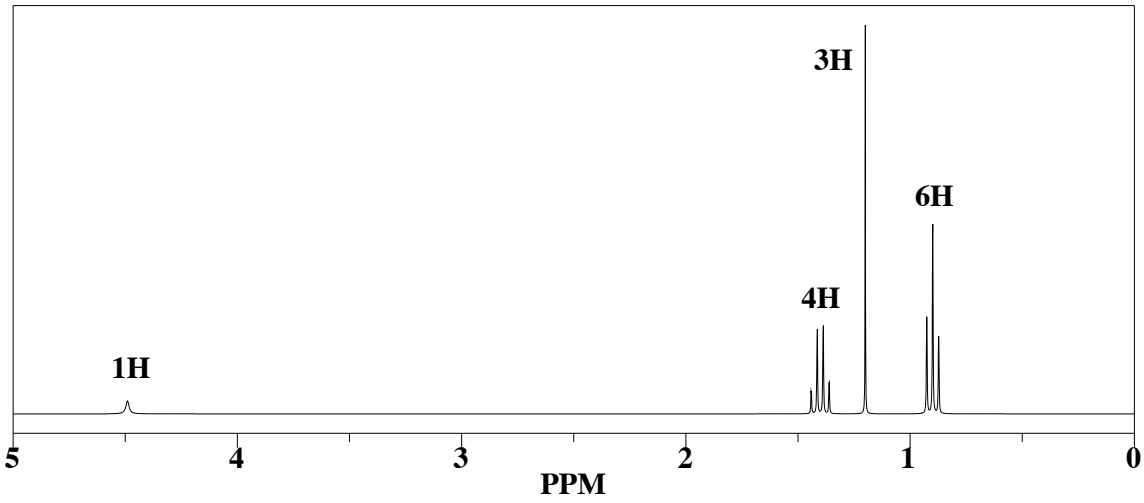
18. (10 pts) You have not seen the following reaction before, it comes from chapter 18. You might find it useful to know that $RO^{\ominus}$ groups can serve as a leaving group. The NMR spectrum is of the predominant product. Using your growing intuition about chemical reactivity as well as the NMR, draw the structure of the product of this reaction.



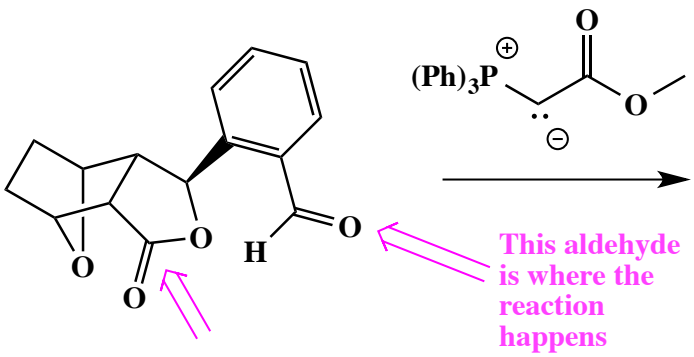
This is mechansim B followed by mechanism A!!

The Grignard adds to the ester carbonyl then the OCH_3 departs leaving a ketone, that reacts with a second Grigard reagent to give the product tertiary alcohol shown





19. (7 pts) Reactions in context: Following is a Wittig reaction used in the published synthesis of a pharmaceutical called Ifetroban used to treat hypertension. Draw the product of the reaction.



This aldehyde is where the reaction happens

This is an ester and esters do not react with Wittig reagents (notice the ester function on the Wittig ylide!