NAME (Print): _____

SIGNATURE: _____

Chemistry 320N
Dr. Brent Iverson
1st Midterm
Feb. 14, 2013
(Sorry about the Valentine's day exam!)

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!!!

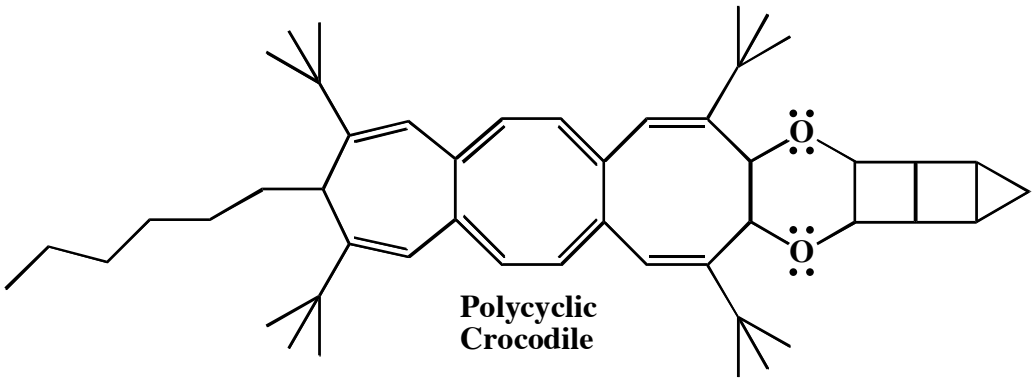
Page	Points	
1		(17)
2		(25)
3		(15)
4		(16)
5		(32)
6		(17)
7		(12)
8		(23)
9		(18)
10		(10)
11		(10)
12		(13)
13		(21)
Total		(229)

Honor Code

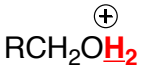
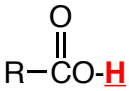
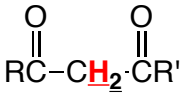
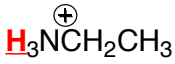
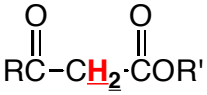
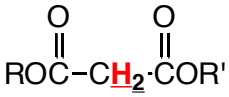
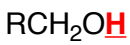
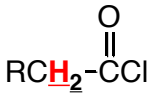
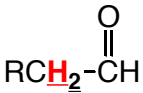
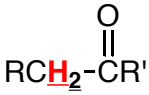
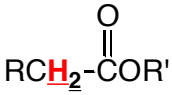
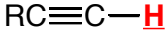
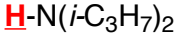
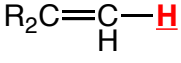
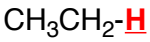
The core values of the University of Texas at Austin are learning, discovery, freedom, leadership, individual opportunity, and responsibility. Each member of the University is expected to uphold these values through integrity, honesty, trust, fairness, and respect toward peers and community.

_____

(Your signature)



Polycyclic Crocodile

Compound		pK_a
Hydrochloric acid		-7
Protonated alcohol		-2
Hydronium ion		-1.7
Carboxylic acids		3-5
Ammonium ion		9.2
β-Dicarbonyls		10
Primary ammonium		10.5
β-Ketoesters		11
β-Diesters		13
Water		15.7
Alcohols		15-19
Acid chlorides		16
Aldehydes		18-20
Ketones		18-20
Esters		23-25
Terminal alkynes		25
LDA		40
Terminal alkenes		44
Alkanes		51

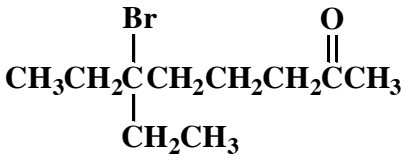
Signature_____ Pg 1 _____(17)

1. (3 pts) The most important question in organic chemistry is:

Where are the electrons?

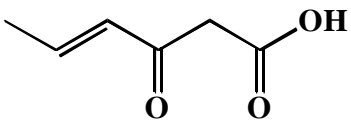
2. (3 or 4 pts each) Write an acceptable IUPAC name or draw a structural formula for the following molecules:

A.



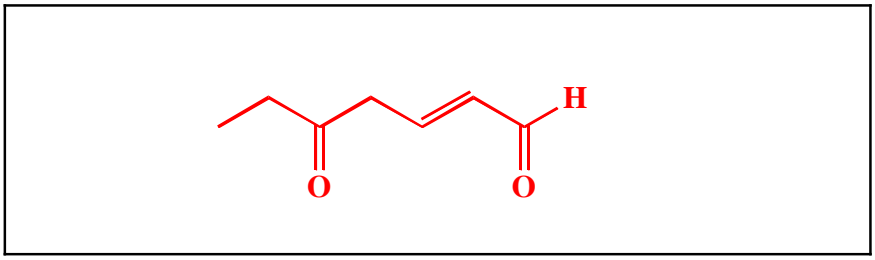
6-Bromo-6-ethyl-2-octanone

B.

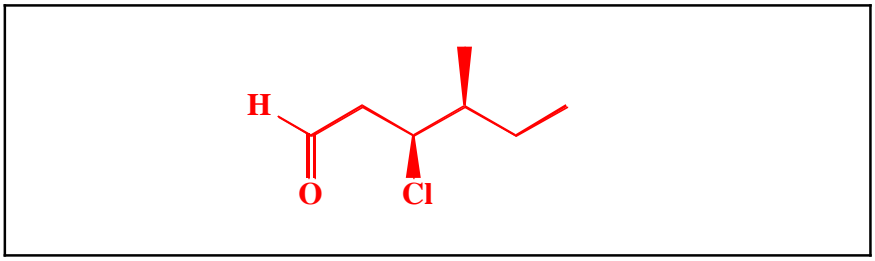


(*E*)-3-oxo-4-hexenoic acid

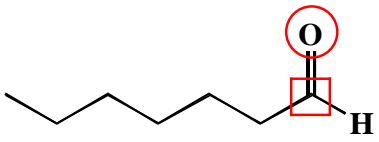
C. **(*E*)-5-oxo-2-haptenal**



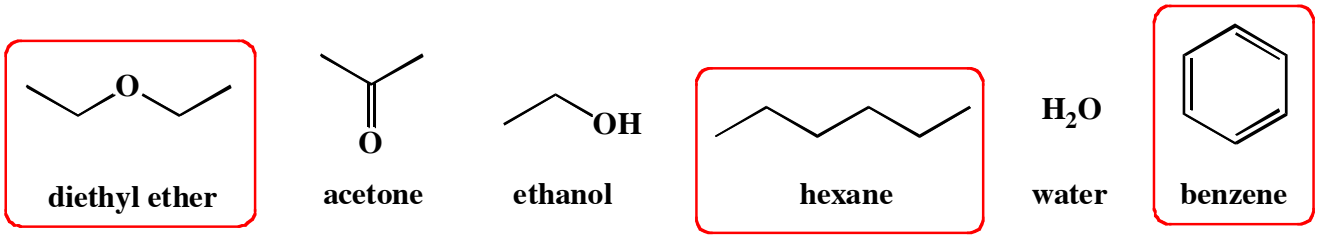
D. **(*3S*,*4S*)-3-Chloro-4-methylhexanal**



3. (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.

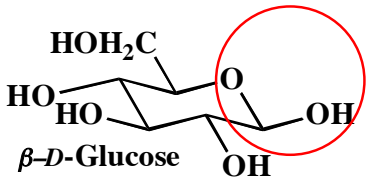


4. (6 pts) It is important to remember that organometallic reagents are bases as well as nucleophiles. These are important considerations when choosing a solvent. From the following list of common solvents, circle any that would be compatible with using an organolithium reagent.

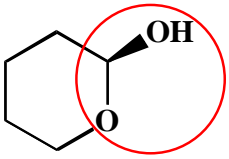


5. (3 pts each) Some functional groups are hard to recognize. Under each molecule, indicate the best description of the functional group present (acetal, cyclic hemiacetal, cyclic acetal, or lactone).

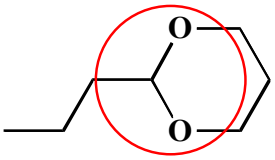
Note the circles are not necessary, I just added them to help you identify the fuctional groups.



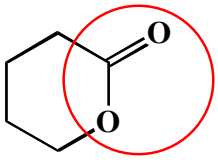
Cyclic hemiacetal



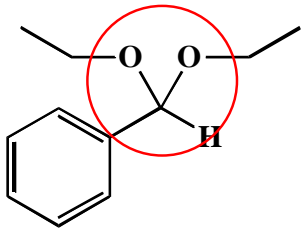
Cyclic hemiacetal



Cyclic acetal

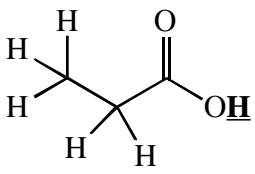


Lactone

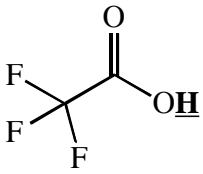


Acetal

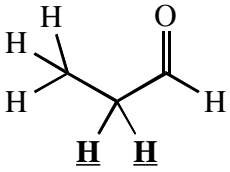
6. (4 pts) Rank all of the following with respect to relative acidity. The acidic H atom in question is indicated in bold and with an underline for each molecule. **Place a 1 under the most acidic molecule, and a 4 under the least acidic molecule.**



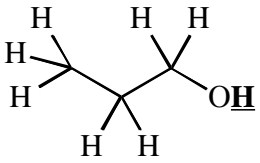
2



1

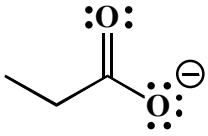


4

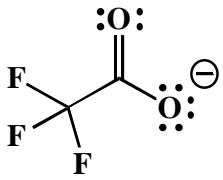


3

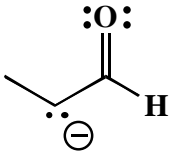
7. (4 pts.) Rank the following in terms of anion stability, with a **1 under the anion that is the most stable** and a **4 under the anion that is least stable.**



2



1



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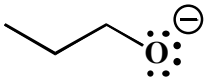

3

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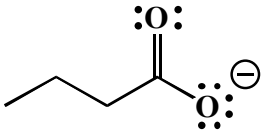
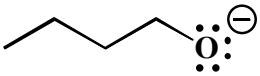


2

1



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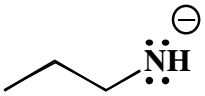
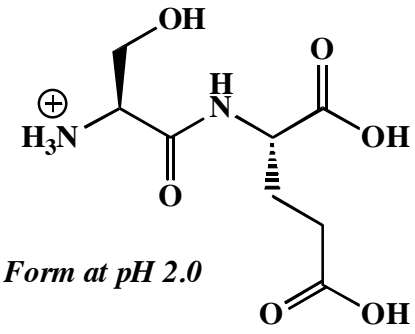


4

Please reread the directions to make sure you did not rank backwards!

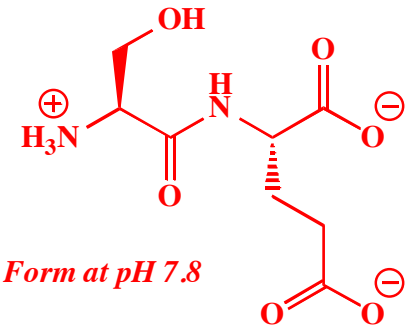
9. (3 pts.) Following is a peptide (small chain of amino acids), written in the form it would be found at pH 2.0. **In the box provided, state the total charge expected for this peptide at pH 7.8, a common pH found in biological fluids.**



Form at pH 2.0

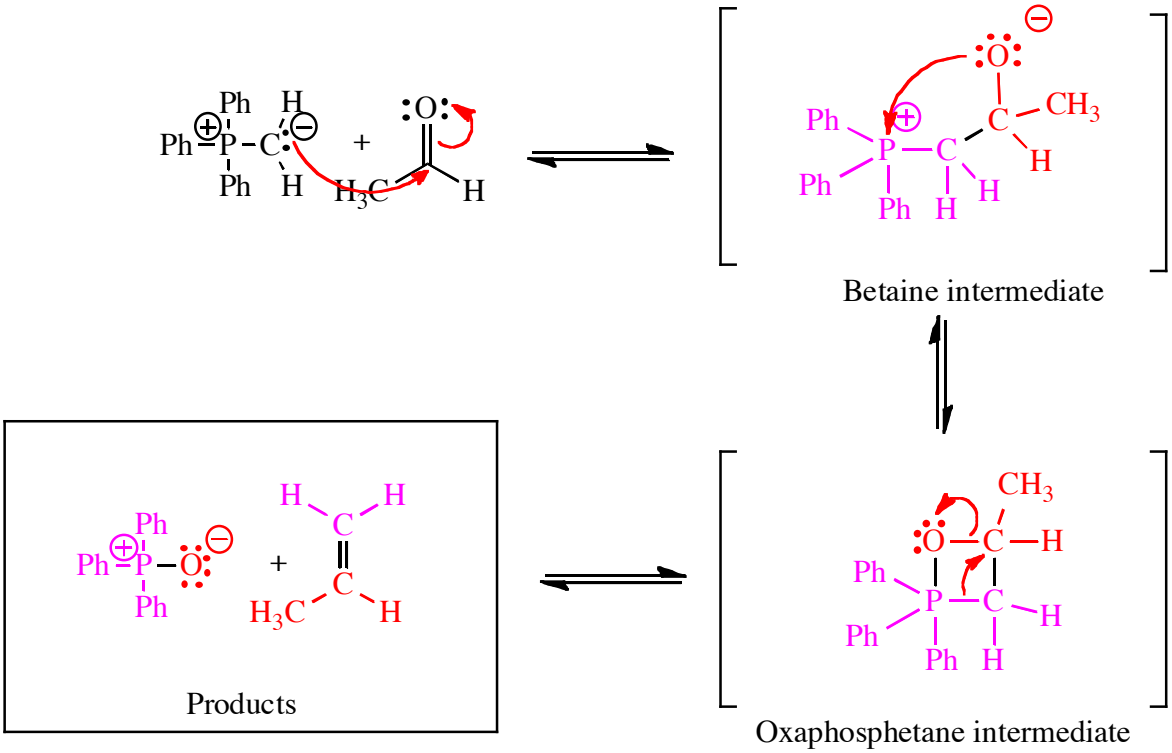
-1

The total charge on the peptide at pH 7.8



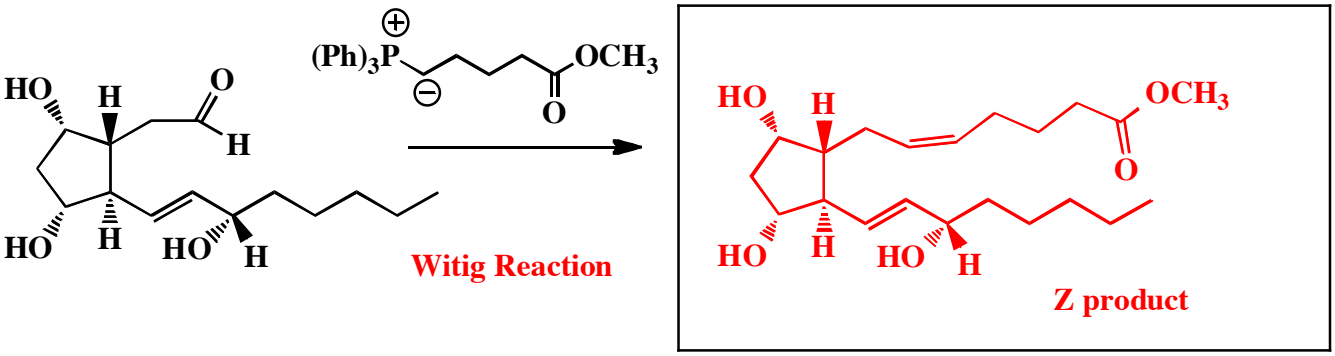
Form at pH 7.8

10. (13 pts.) Complete the mechanism for the following 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.

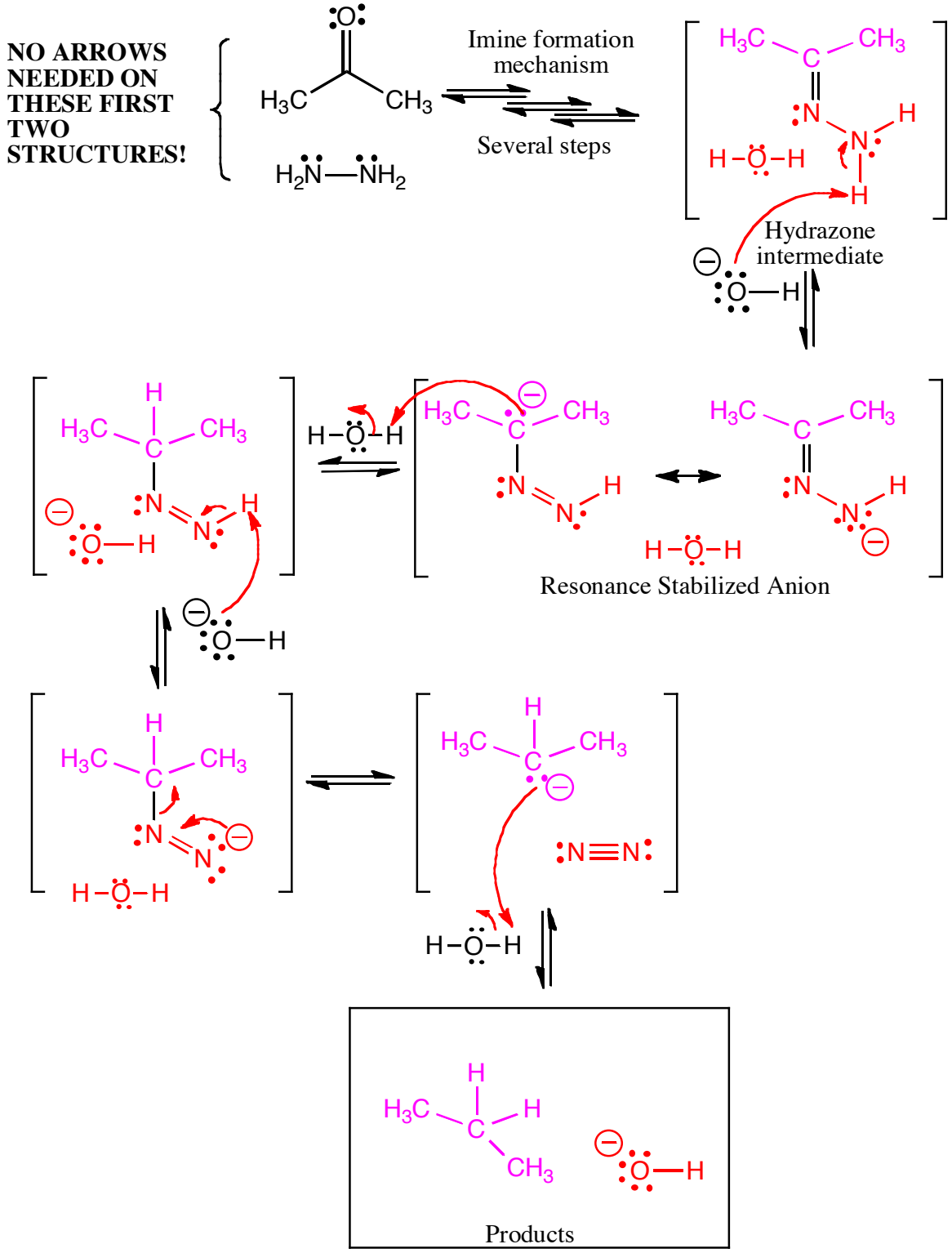


Note: It would be perfectly acceptable to draw the phosphine oxide product with a P=O. In that case the arrows on the oxaphosphatane intermediate would have to match.

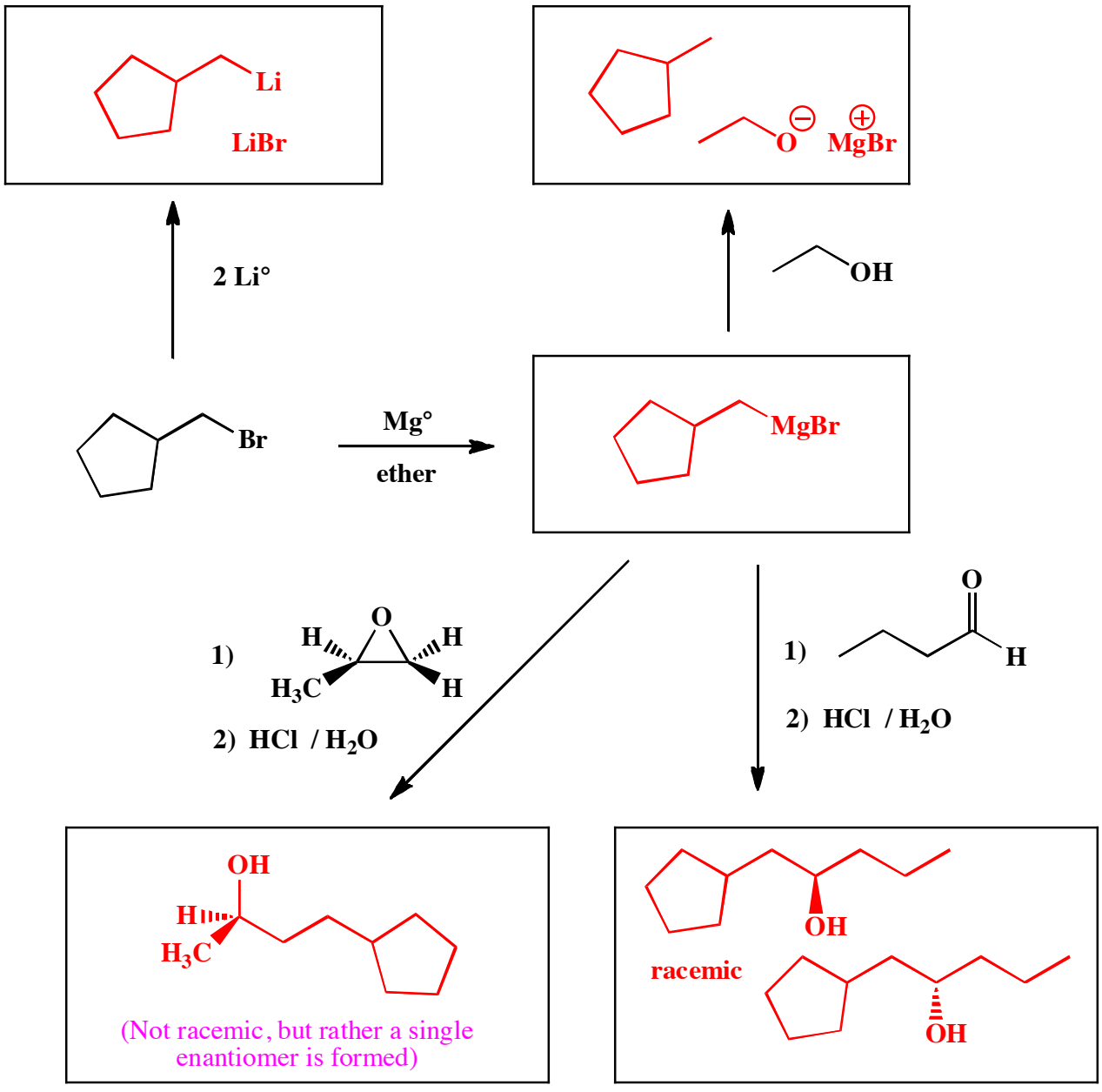
(4 pts) It is important that you are able to recognize reactive functional groups even in the context of complex molecules. You understand the chemistry important for the following reaction. In the space provided, draw the predominant product (including stereochemistry) of the following reaction (that was used in the actual synthesis of an important natural molecule, a prostaglandin).



11. (32 pts.) 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. **In the box with the resonance arrow, you need to draw both resonance contributing structures.** You only need to indicate the flow of electrons on one structure (i.e. contributing structure) per intermediate.



12. (3 or 5 pts.) Write the predominant product or products that will occur for each transformation. **If a new chiral center is created and a racemic mixture is formed, you must draw both enantiomers and write "racemic" under the structure. Use wedges (◄) and dashes (┈┈) to indicate stereochemistry. To get full credit, you only need to write the the major organic product for these. You do not have to worry about the other products.**



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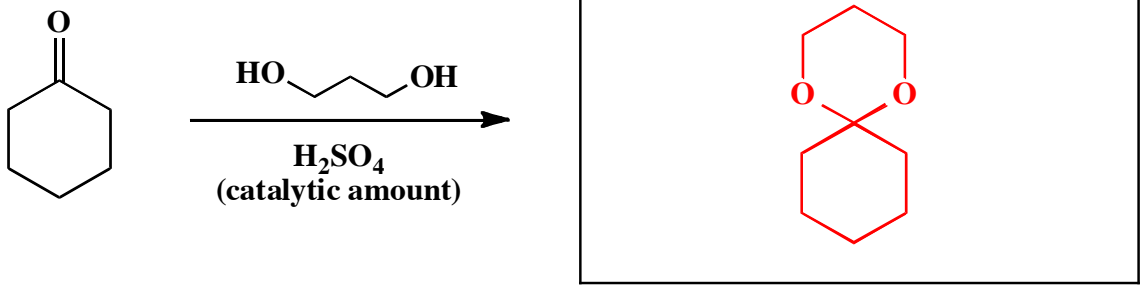
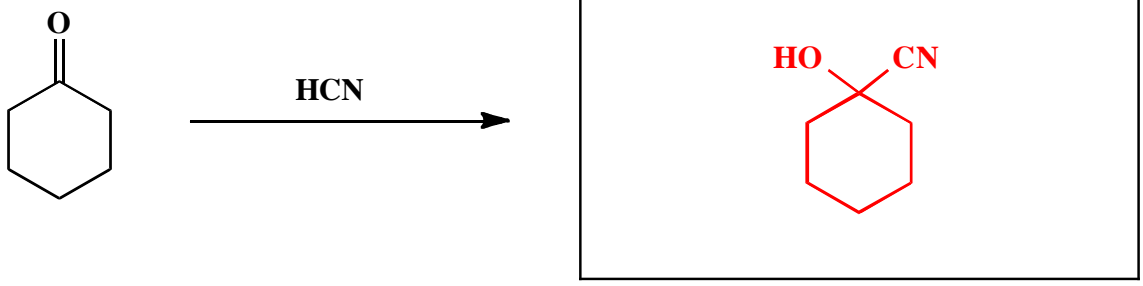
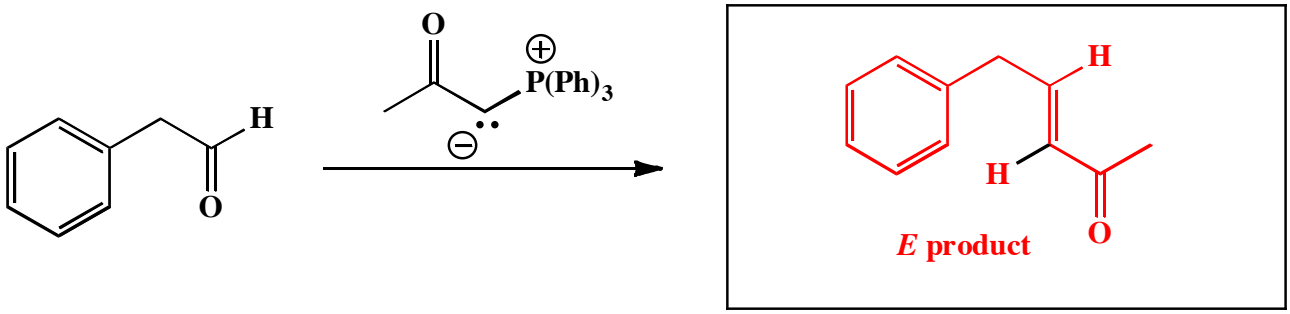
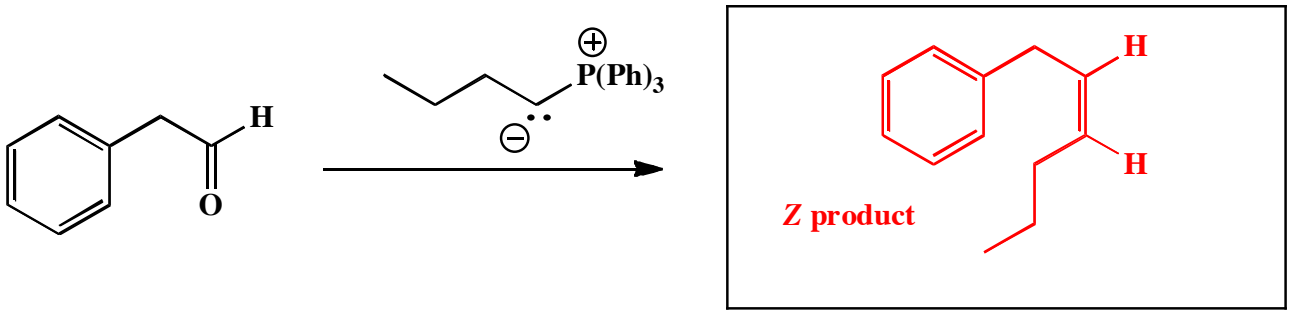
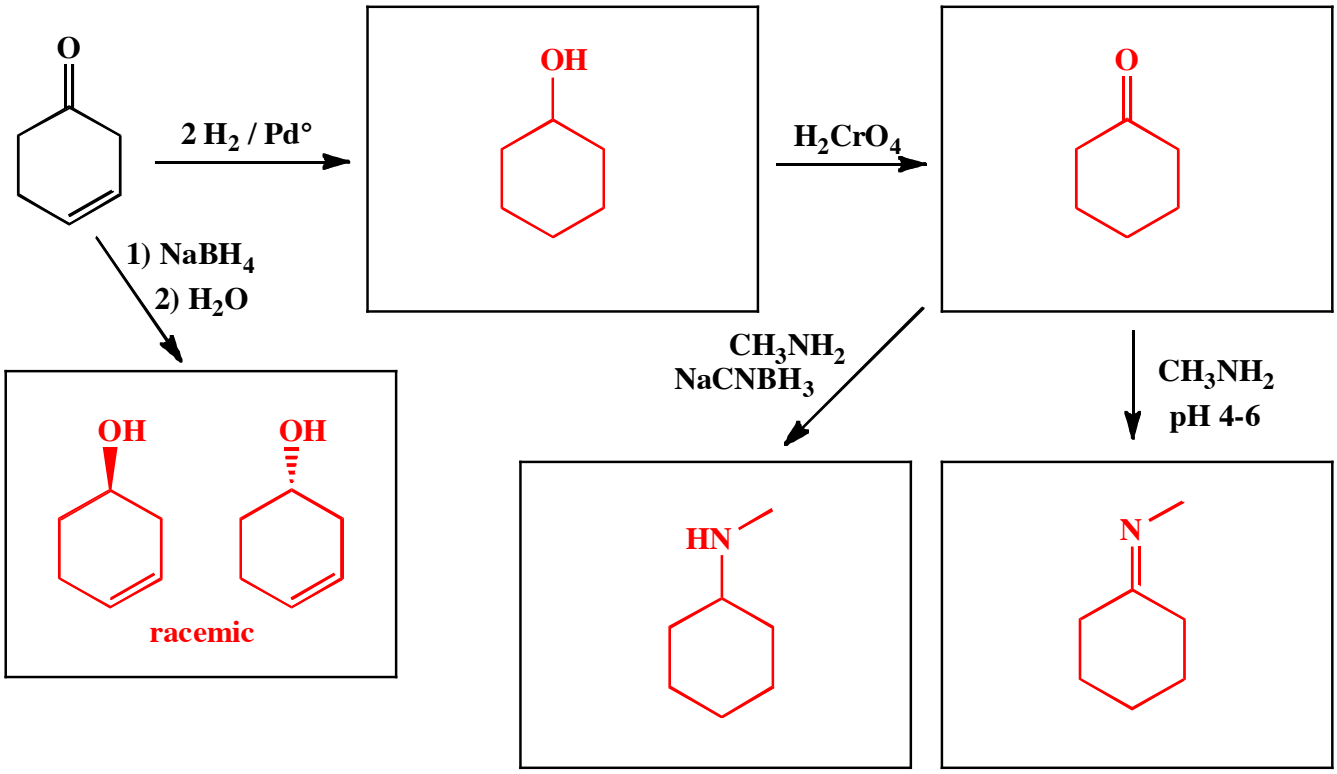


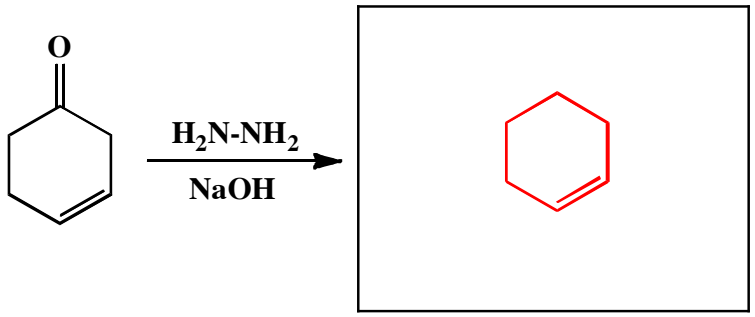


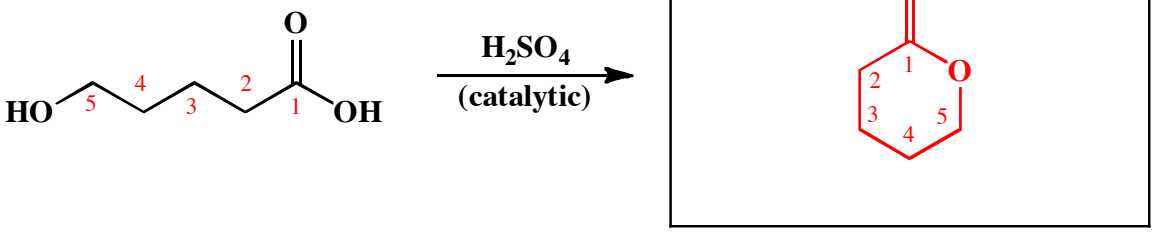




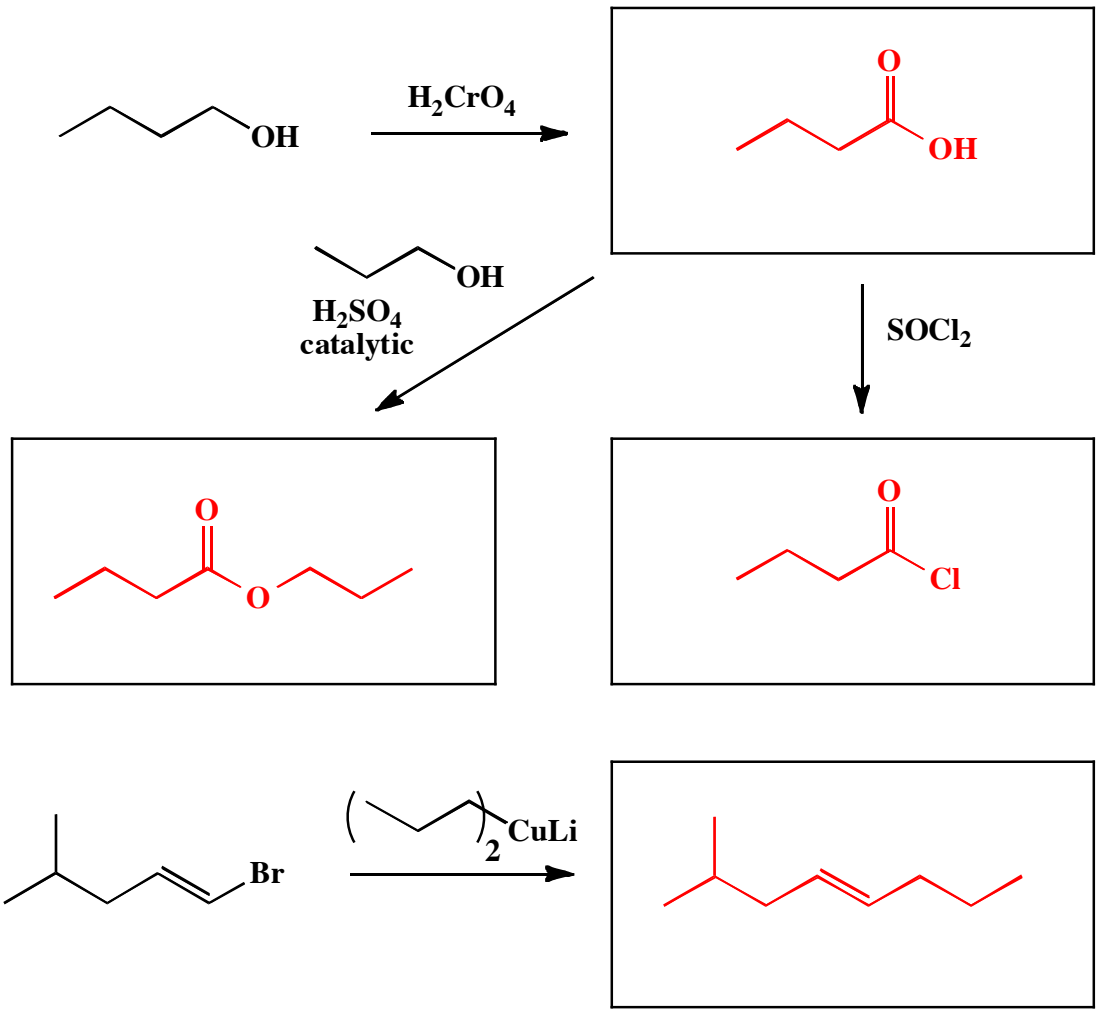
14. (3 or 5 pts.) Write the predominant product or products that will occur for each transformation. **If a new chiral center is created and a racemic mixture is formed, you must draw both enantiomers and write "racemic" under the structure. Use wedges (◄) and dashes (┈┈) to indicate stereochemistry.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



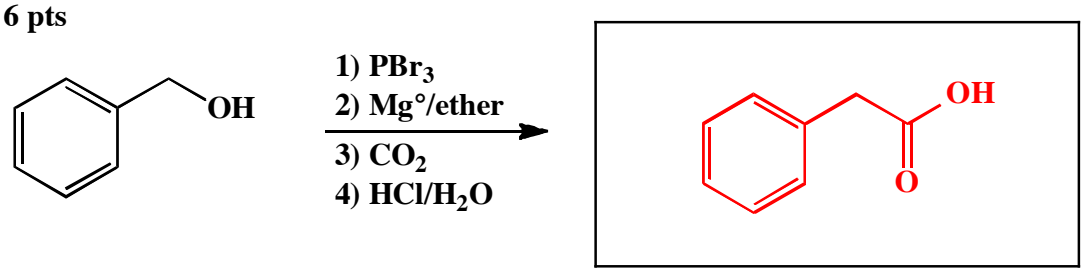




15. (3 or 5 pts.) Write the predominant product or products that will occur for each transformation. **If a new chiral center is created and a racemic mixture is formed, you must draw both enantiomers and write "racemic" under the structure. Use wedges (◄) and dashes (┈┈) to indicate stereochemistry. 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.**

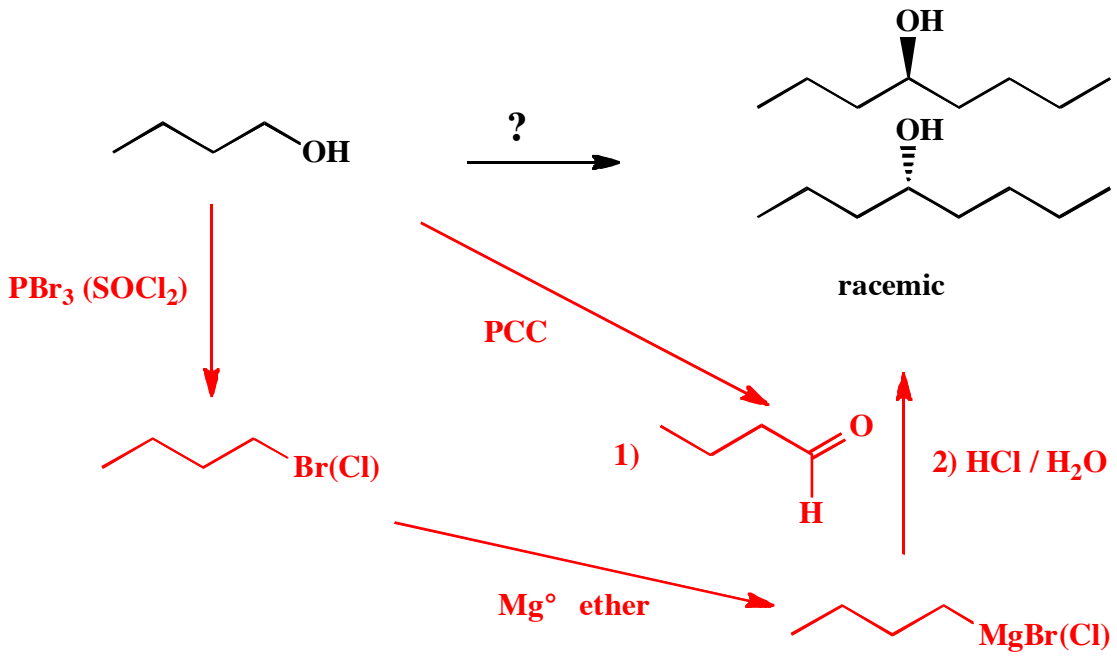


6 pts



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. If a racemic mixture is made, draw both enantiomers using wedges and dashes and make sure to write "racemic".

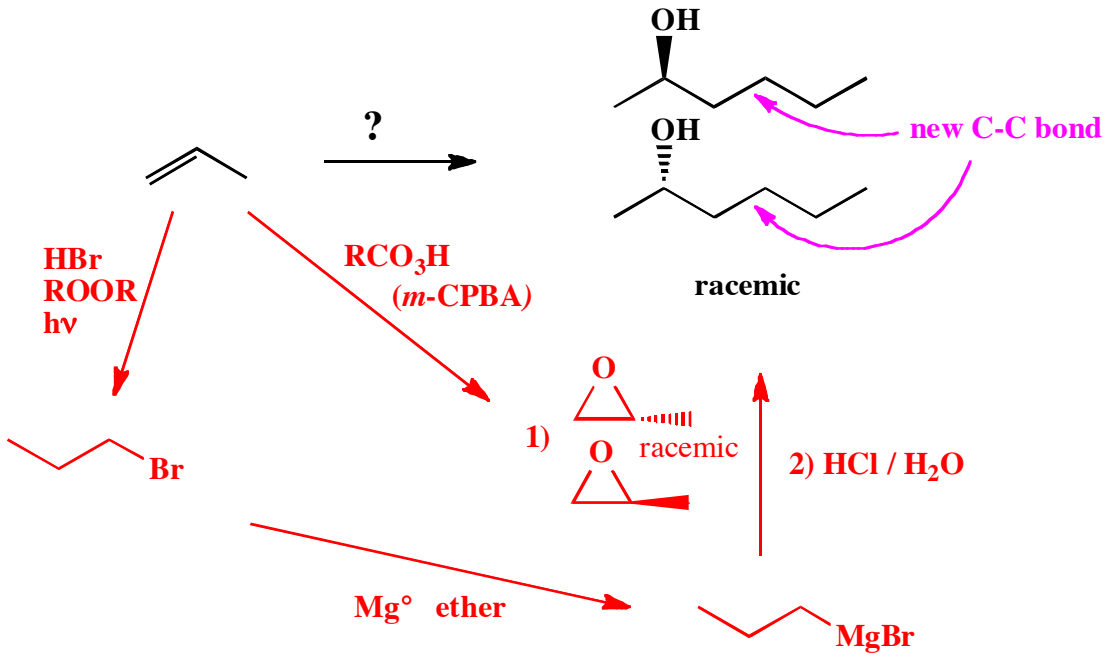
(10 pts) **All of the carbon atoms of the products must come from the starting materials for this one!**



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.

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. If a racemic mixture is made, draw both enantiomers using wedges and dashes and make sure to write "racemic".

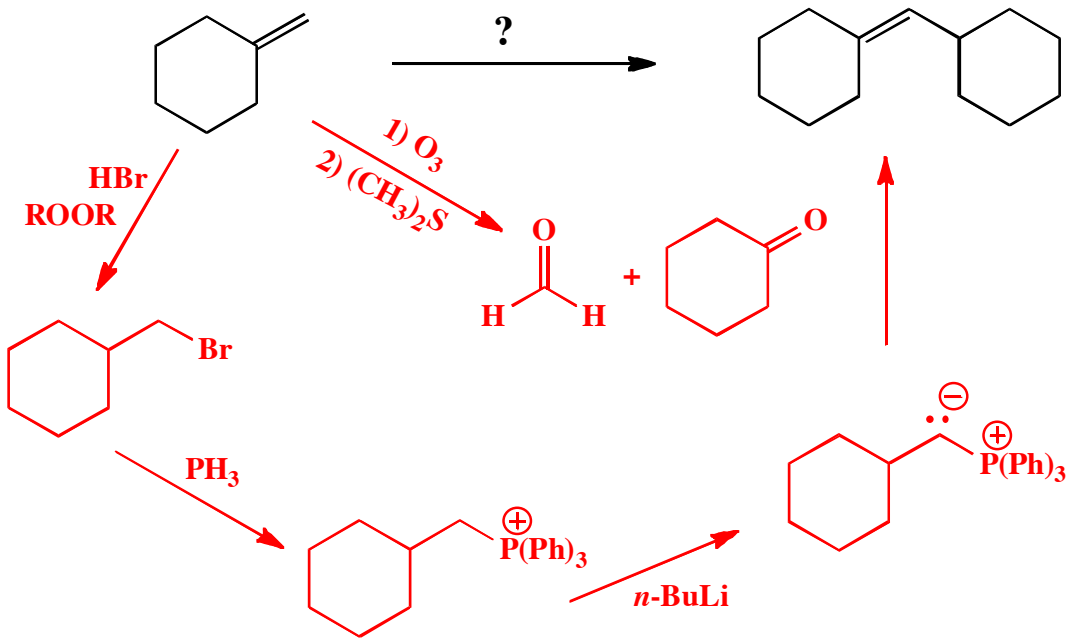
(10 pts) **All of the carbon atoms of the products must come from the starting materials for this one!**



Recognize that the product has six carbons, exactly twice that of the starting propene so assume to molecules of starting material must be connected. **Recognize** also that the product is an alcohol with an OH group one carbon away from the new C-C bond, the Key Recognition Element of a Grignard reaction with an epoxide. In this case, the reaction must be betweeen racemic epoxide derived from propene and the Grignard made from the 1-bromopropane. The 1-bromopropane must come from the non-Markovnikov addition of HBr to propene in the presence of peroxide.

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. If a racemic mixture is made, draw both enantiomers using wedges and dashes and make sure to write "racemic".

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

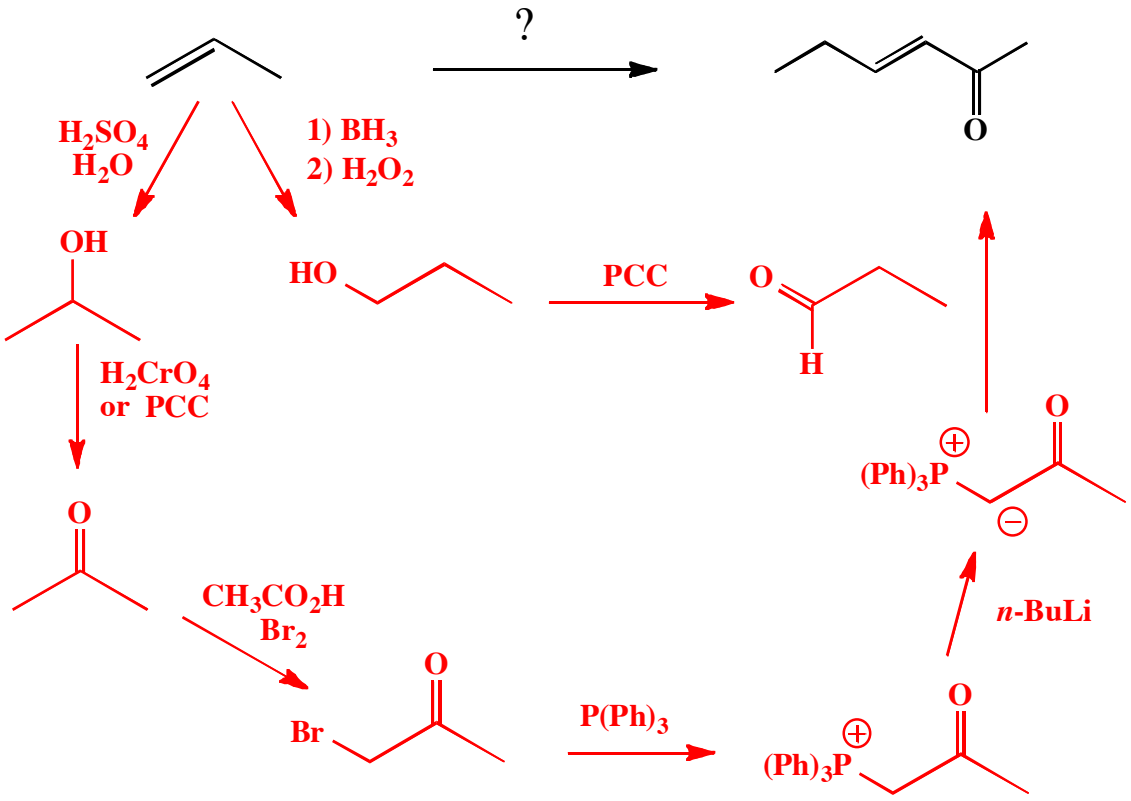


Recognize that the product has thirteen carbons, exactly twice that of the starting alkene **MINUS 1**, so assume two molecules of starting material must be connected, although ONE carbon must be removed (i.e. a seven carbon piece must react with a six carbon piece). **Recognize** also that the product has an alkene for a new C-C bond, the Key Recognition Element of a Wittig reaction. In this case, the reaction must be betweeen cyclohexanone and the Wittig (phosphonium ylide) made from 1-bromomethylcyclohexane. Cyclohexanone, in turn, is made from ozonolysis of the starting alkene, and this nicely removes the single carbon atom as required. The bromomethylcyclohexane comes from reaction of the starting alkene with HBr in the presence of peroxides to give the non-Markovnikov addition regiochemistry resulting in the desired placement of -Br at the less substituted side of the alkene.

Note that it would also be possible to carry out the reverse Wittig reaction between the cyclohexyl aldehyde and a Wittig reagent made from bromocyclohexaine.

19. 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. If a racemic mixture is made, draw both enantiomers using wedges and dashes and make sure to write "racemic".

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



Recognize that the product has six carbons, so two of the three carbon strating molecules need to come together. **Recognize** also that the new carbon-carbon bond is a actually a C=C bond, that it is *E* and that it is next to a carbonyl. The only reaction you know that creates this pattern, a new C=C bond, is a Wittig reaction with a carbonyl next to the negative charge of the Wittig reagent. Hypothesize the last step as a Wittig reaction between propanal and the acyl Wittig reagent. **Recognize** that the required 1-propanal comes in two steps from the propene, namely non-Markaovnikov hydroboration hydration followed by oxidation with PCC. The required Wittig reagent comes in four steps from the starting propene. The key is rocognizing that α-halogenation of acetone is required. The required acetone is available in two steps from propene through the sequence of Markovnikov hydration followed by oxidation.